Long-term storage stability studies of vinyl ester resins using commercial antioxidant polymerisation inhibitors

Long Term Storage Stability Studies of Vinyl Ester Resins Using Commercial Antioxidant Polymerisation Inhibitors

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A Doctoral Thesis

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Abstract

The use of resins with carbon-carbon terminal functional groups, often referred to as vinyl ester resins, have found a wide commercial use, and their production is in the millions of tonnes per year, as either unsaturated polyesters (estimated 3.0 million tonnes in 2018), acrylate or methacrylate monomers and oligomers (estimated 150 thousand tonnes in 2018). In all cases the resins are synthesised, stored and transported for further processing into the finished article, either as a coating or a resin often at a second site. The use of antioxidants as polymerisation inhibitors is widely known and understood, but the relative efficiency of each of these compounds in different resin types is not widely published. This study has looked at a range of amine, epoxy and urethane acrylate and methacrylate oligomers. These oligomers were synthesised to control the antioxidant concentrations and comparative stability testing was undertaken to obtain representative data in terms of long term stability at various temperatures and concentrations (100 to 1000ppm), with testing at 20°C taking between 3 to 5 years to complete for each sample set. The resins were evaluated in glass vials so that the head space conditions (air and nitrogen) could be controlled and to mimic industrial practice. The stability data showed that for a given concentration, the stable radical compound (4-hydroxy-2,2,6,6-tetramethyl-1-piperdinyloxy) was the most efficient, although it was the most expensive and discoloured the resin.

The antioxidants evaluated were a mixture of commercially available compounds and which have use within various segments of the polymer industry, with both phenolic antioxidants and stable radical compounds examined. Rheology was used to evaluate the degree of polymerisation and resultant gel formation due to free radicals formed by peroxides. The measurement of the dissolved oxygen content of monomers was investigated to determine the amount of oxygen present. A number of antioxidants were used to create blocked isocyanates to evaluate their potential for use in high temperature resin systems with limited success due to their high unblocking temperatures.

Since the bulk of resins supplied are subsequently cured to form coatings or resins, work was also undertaken to see what effect the addition of antioxidants have upon the curing by free radical sources either peroxide or Ultra-Violet active initiators at 1% loading, with resins both fresh and 12 months old. It was found that at these concentrations of free radical sources, the rate of polymerisation was not significantly affected at the highest concentrations of the antioxidants used.

Abstract

The use of resins with carbon-carbon terminal functional groups, often referred to as vinyl ester resins, have found a wide commercial use, and their production is in the millions of tonnes per year, as either unsaturated polyesters (estimated 3.0 million tonnes in 2018, world-wide), acrylate or methacrylate monomers and oligomers (estimated 150 thousand tonnes in 2018, world-wide). In all cases the resins are synthesised, stored and transported for further processing into the finished article, either as a coating or a resin often at a second site. The use of antioxidants as polymerisation inhibitors is widely known and understood, but the relative efficiency of each of these compounds in different resin types is not widely published. This study has looked at a range of amine, epoxy and urethane acrylate and methacrylate oligomers. These oligomers were synthesised to control the antioxidant concentrations and comparative stability testing was undertaken to obtain representative data in terms of long term stability at various temperatures and concentrations (100 to 1000ppm), with testing at 20°C taking between 3 to 5 years to complete for each sample set. The resins were evaluated in glass vials so that the head space conditions (air or nitrogen) could be controlled and to mimic industrial practice. The stability data showed that for a given concentration, the stable radical compound (4-hydroxy-2,2,6,6-tetramethyl-1-piperdinyloxy) was the most efficient, although it was the most expensive and discoloured the resin.

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Glossary

4H-TEMPO – 4-Hydroxy-2,2,6,6-tetramethyl-1-piperdinyloxy

AA - Ascorbic acid

Ac – Acetyl

ASTM – American Society for Testing and Materials

ATR – Attenuated total reflectance

BADGE – Bisphenol A diglycidyl ether (Bisphenol A epoxy)

BADGEDA – Bisphenol A epoxy diacrylate

BADGEDMA – Bisphenol A epoxy dimethacrylate

BAPO – bis(2,4,6-Trimethylbenzoyl)-phenylphosphine oxide

BASF – Bayerisch Analine und Soda Fabrik SE, Lugwigshafen, Germany

BFDGE – Bisphenol F diglycidyl ether

BFDGEDA – Bisphenol F epoxy diacrylate

BFDGEDMA – Bisphenol F epoxy dimethacrylate

BHT – 2,6-di-*tert*-Butyl-4-methylphenol

BP – Benzophenone

BPO – Dibenzoyl peroxide

BS – British Standard

BTC- 4-*tert*-Butylcatechol

°C – Degrees Celsius

CLP – Classification and Labelling of Products Regulations

CoRAP – Community Rolling Action Plan

DABCO – Trade name for polyurethane catalysts produced by Evonik AG, Germany

DBTDL – Dibutyltin dilaurate

DMAP – 4-Dimethylaminopyridine

DMHA – 2,2-Dimethyl-2-hydroxyacetone

DMSO – Dimethyl sulfoxide

DSC – Differential Scanning Calorimetry

DTBP – 2,6-di-*tert*-Butylphenol

ECHA – European Chemicals Agency

EN – European Norm

EPA – Environmental Protection Agency

FID – Flame Ionisation detector

FT-IR – Fourier transform infrared spectroscopy

GAA – Glacial acrylic acid

GMA – Glacial methacrylic acid

GPC – Gel permeation chromatography

HDDA – 1,6-Hexanediol diacrylate

HDDGE – 1,6-Hexanediol diglycidyl ether

HDDGEDA – 1,6-Hexanediol epoxy diacrylate

HDDGEDMA – 1,6-Hexanediol epoxy dimethacrylate

HDDMA – 1,6-Hexanediol dimethacrylate

HDI – Hexamethylene-1,6-diisocyanate

HDT – Hexamethylene-1,6-diisocyanate trimer

HDPE – High density polyethylene

HEA – 2-Hydroxyethyl acrylate

HEMA – 2-Hydroxyethyl methacrylate

HMDI – Dicyclohexylmethane-4,4’-diisocyanate

HPA – Hydroxypropyl acrylate

HPMA – Hydroxypropyl methacrylate

HQ - Hydroquinone

IPDI – Isophorone diisocyanate

K - Kelvin

Kg - Kilogram

LED – Light emitting diode

lt – Litre

MEA – Monoethanol amine

MDI – Diphenylmethane-4,4’-diisocyanate

MeHQ – Methyl hydroquinone

mg – Milligram

ml – Millilitre

μm - Micrometer

mPas – Millipascal second

MW – Molecular weight

nm - Nanometer

PCB – Printed circuit board

PDI – Polydispersity index

PEA – Polyethylene glycol acrylate (6 monomer repeat units)

PEG – Polyethylene glycol

PEM – Polyethylene glycol methacrylate (6 monomer repeat units)

Ph - Phenol

PMP – 4-Methoxyphenol

PP - Polypropylene

ppm – Parts per million

PTFE - Polytetrafluoroethyelene

PTZ – Phenothiazine

Py - Pyridine

R – Can be an alkyl or aryl substituent

REACH – Registration, Evaluation and Authorisation of Chemicals Regulations

tBu – *tert*-Butyl

TDI – Toluene diisocyanate

TEGDA – Triethylene glycol diacrylate

TEGDMA – Triethylene glycol dimethacrylate

TEMPO – 2,2,6,6-Tetramethyl-1-piperdinyloxy

TMPTA – Trimethylolpropane triacrylate

TPGDA – Tripropylene glycol diacrylate

TPO – 2,4,6-Trimethylbenzoyldiphenylphosphine oxide

TPP – Triphenyl phosphine

TSCA – Toxic Substances Control Act

UPE – Unsaturated polyester

UV-A – Ultra-violet spectral region (315-400nm)

UV-B – Ultra-violet spectral region (280-315nm)

UV-C – Ultra-violet spectral region (100-280nm)

UV-V – Ultra-violet/visible spectral region (400-760nm)

VOC – Volatile organic compound

1 Introduction

Vinyl ester resin is a description that covers a broad range of substances that contain terminal carbon-carbon double bonds. It is the presence of the double bond that allows the resins to be cured via free radicals into the final desired polymer. Without the presence of inhibitors in the resin systems, the resins will invariably over time increase in viscosity due to self polymerisation taking place. The ultimate conclusion of this process is that the resin will turn into a solid block of polymer. The self polymerisation needs to be prevented because this results in a poor quality product, the resin is unusable as it is either too viscous to handle, or solidified, and uncontrolled polymerisation is unsafe due to potentially high exotherms.

The amount and type of inhibitors, typically alkylphenols, added is critical to ensure that the resin has a good shelf life, yet is still able to be processed when required. If the concentration of the inhibitor is too low, then the shelf life may be too short and the resin will begin to self polymerise, however if the concentration is too high, then the resin may have a long shelf life, but the amount of initiator and activators required to start the polymerisation may be excessive. Commercially unsaturated polyester resins are often grouped together with vinyl esters because the carbon-carbon double bonds which are present in their structure, and not just in the terminal positions, give rise to similar curing characteristics when peroxides are used.

There are a number of different inhibitors used commercially, but there is very little published data available concerning the inhibitors used and the concentrations used. Commercially the use of vinyl ester resins in their various guises is quite significant. It was estimated that in 2010 that the annual global demand for radiation curable (rad-cure) resins[1,2] was approximately 100,000 tonnes with a predicted 4.5% per annum growth rate. The market for radiation curable resins was estimated to be worth US$ 4,900 million in 2012 with a predicted 7% per annum growth rate. A realistic estimate for the manufacture and consumption of acrylate and methacrylate resins in 2015 would be in the order of 120,000 tonnes. In 2014 it was predicted that the global unsaturated polyester (UPE) market[3] would reach a value of US$ 10,480 million by 2019, while in 2015 it was predicted that the global radiation curable market[4] would reach a value of US$ 7,900 million also by 2019. Allowing for an average price of US$3.50/Kg (approximately €3.25/Kg) for UPE resins, this would equate to approximately 3,000,000 tonnes of UPE resins, while for radiation curable resins an average price of US$6.00/kg (€5.50/kg) can be expected. This would give an estimated total market of approximately 3,150,000

tonnes of resin manufactured in 2018. All of the resin produced will require some inhibitor to be added, and allowing for a conservative 100-250ppm addition level, this would require between 275 and 700 tonnes. The price of inhibitors does vary considerably, but €10.00/Kg is not unrealistic as a global average. This would equate to a global annual market of €3 to 7 million.

There are various pieces of legislation and regulations throughout the world which are increasingly controlling and restricting the chemicals that may be used. Within the European Union (EU) there is the Registration, Evaluation and Authorisation of Chemicals Regulations (REACH)[5] and the Classification, Labelling and Packaging Regulations (CLP)[6] that affect all chemicals manufactured and sold within the EU. Additionally there are other directives and regulations that impact upon chemicals used within certain defined industries, such as cosmetics.[7] The use of the terminology of monomers, oligomers and polymers follows the guidance notes issued by the European Chemicals Agency (ECHA).[8] In the United States the Toxic Substances Control Act (TSCA) was amended in June 2016 by the Frank R. Lautenberg Chemical Safety for the 21st Century Act, which has empowered the Environmental Protection Agency (EPA) to investigate and regulate all chemical substances used in the United States of America.

The regulatory pressures and associated costs, and the increasing costs of raw materials combined with increasing consumer/customer awareness of chemicals, particularly the "hidden" additives, has caused many companies to look carefully at the additive packages that they use to meet these concerns. Although the inhibitor is often only one component in these packages it is in many respects the least understood.

The aim of this project is to evaluate and quantify which inhibitors are effective at various concentrations in differing resins, and the conditions to which they would be exposed to during storage.

1.1 References

1 Frost and Sullivan, *European Markets for Radiation Curable Coatings*, London 2006.

2 Frost and Sullivan, *Asian Radiation Cured Formulations Market*, Singapore, 2007.

3 Transparency Market Research, *Unsaturated Polyester Resin Market by Product Segment*, Albany, 2014.

4 Transparency Market Research, *Radiation Cured Products Market – Global Industry Analysis, Size, Share, Growth, Trends and Forecast*, 2013-19, Albany 2015.

5 EC-1907/2006, Regulation Concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals, *Off. J. Eur. Union*, 2006, **L 396**.

6 EC-1272/2008, Regulation on the Classification, Labelling and Packaging of Substances and Mixtures, *Off. J. Eur. Union*, 2008, **L 353**, 1.

7 EC-1223/2009, Regulation on Cosmetic Products, *Off. J. Eur. Union*, 2009, **L 342**, 1.

8 ECHA, *Guidance for Monomers and Polymers*, Helsinki, 2012.

2 Vinyl Ester Resins and Inhibitors

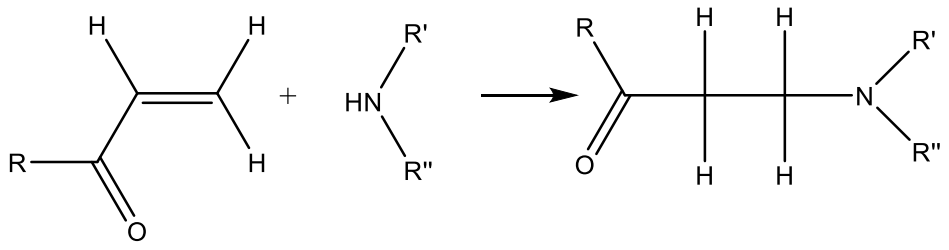
2.1 Vinyl Ester Resins

The term vinyl ester resins covers a wide variety of different types of resins that are produced on a commercial basis, as well as those studied both in academia and industry. For the purposes of this project the resins of primary interest are those which have terminal carbon-carbon double bonds available to enable crosslinking. Unsaturated polyesters are not examined, although they do also often contain such terminal groups, they also include carbon-carbon double bonds throughout the structure, with varying degrees of suitability for crosslinking due to location, polymer molecular weight, steric hindrance and conformity. This chapter looks at acrylate and methacrylate resins, in particular amine, epoxy and polyurethane (meth)acrylates, with a brief mention of polyester (meth)acrylates which are a type of unsaturated polyester.

The normal method of initiating the crosslinking reaction to cure the (meth)acrylate resins is to introduce a free radical source. This is normally either by adding peroxide or photoinitiator, and occasionally the use of electron beam curing equipment. Peroxides are widely used to cure large amounts of resins, particularly for composite applications, while photoinitiators are widely used in the coatings industry for thin film (<250μm) applications. Electron beam equipment has a significant advantage in not requiring the use of any initiator, but a couple of major disadvantages, namely the cost of the equipment and limitations concerning the size of the equipment and the resultant power output.

2.1.1 Amine Acrylate

Amine acrylates, also called amine modified acrylates or amine synergists, are formed by the reaction of a primary or secondary amine to an unsaturated carbon – carbon double bond in a terminal position. This is done via the Michael addition reaction (see Scheme 2.1).[1]



Scheme 2.1

The normal practice is to use low molecular weight polyester (meth)acrylates as the source of the unsaturation. It is not possible to use tertiary amines due to a lack of a hydrogen to be abstracted during the addition reaction. If a monofunctional polyester (meth)acrylate is used, the resultant compound cannot be cured as the vinyl group has been utilised during the addition reaction. By controlling the ratio of reactants it is possible to determine the molecular weight and functionality of the final molecule. In general the products exhibit low viscosity and high reactivity.

Amine acrylates are used to improve the cure of the polymer film when cured by UV radiation, particularly the surface cure. Work done by Decker *et al*[2] and Studer *et al*[3,4] has shown that for certain applications use of amine acrylates eliminates the need for inert atmospheres due to oxygen inhibition at the surface of the coating. This is a problem that had limited the use of UV curable coatings in the past, and is still a problem in North America and parts of the Far East as amine (meth)acrylates have not gained a wide acceptance. There has been very little reported activities concerning any advances in amine (meth)acrylate technology since 2012, except for some work by González *et al*[5] which concerned the polymerisation of amine acrylates to produce thermosets in a two stage or dual cure process.

Industrial manufacture of amine (meth)acrylates has mainly concentrated on the production of the acrylate variants, rather than the methacrylate. This is due to the difference in reactivity between two functional groups, with the methacrylate exhibiting a lower rate or reaction compared to the acrylate. Freidig, Verhaar and Hermens[6] looked at the structure of a number of different acrylates and methacrylates and the affect upon the reactivity of the substance. When the rate constants were calculated for the hydrolysis of the substance under basic conditions, the reactivity of the methacrylate was between 2 to 10 times lower compared to its acrylate analogue. The most likely explanation for this is that an inductive effect takes place due to the presence of the methyl group. It is not likely to be due to steric hindrance as the methyl group is not shielding the carbon-carbon double bond from attack. Mather *et al*[7] discuss how the steric environment of the amine will play a significant effect upon the rates of reaction observed. Also a secondary amine is more nucleophilic than a primary amine, hence more reactive.

Normally primary and secondary amines are reacted with di- and trifunctional polyester acrylates (often referred to as acrylate monomers) under controlled conditions to minimise the potential exotherm and resultant runaway reaction. With the increased use of waterbased acrylate formulations, a hydroxy terminated amine is often used to improve the solubility of the resultant substance.

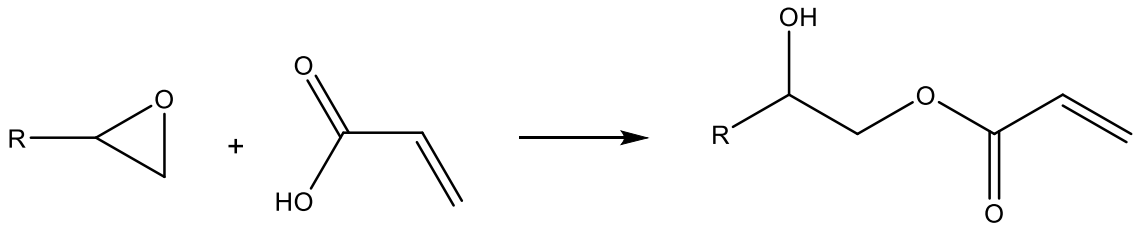
The first reported industrial use of amine acrylates was the issuing of a patent to Hube[8] in 1956 describing a process of synthesising amine acrylates for use in the manufacture of paper and associated coatings (printing inks and clear coats), while Gaske[9] was issued a patent in 1974 covering the synthesis and use of amine acrylates in UV curable resins for the use reducing oxygen inhibition at a coatings surface.

The addition of 5-10% of an amine acrylate into a UV resin formulation does almost eliminate the problem of oxygen inhibition, particularly for thin coatings. This has meant that it has found wide application in the printing ink sector as it can permit faster curing speeds to be obtained, and allow the coated materials to be stacked safely.[10] This is despite the tendency to yellow with age and/or further exposure to UV light. The problem concerning the slight amine odour that was present in older generations of coatings has been overcome by ensuring that any residual free amine in the resin is minimised due to a combination of careful formulation and processing. In order to maximise the application potential the industry has been developing products which have lower colour, in which the role of the inhibitor package is also to prevent the product yellowing over time in storage, as well as inhibiting further polymerisation.

When amine acrylates are cured, the resultant polymer is generally rigid and has poor abrasion resistance, but with reasonable chemical and water resistance. They do have good adhesion to paper and wood substrates.

2.1.2 Epoxy Acrylate

The term epoxy acrylate is a bit of a misnomer, as in the majority of cases there no epoxy groups present. The epoxy ring is opened in the presence of a catalyst, normally either an organometallic or an amine, which then allows the acrylic or methacrylic acid to react via an addition reaction (see Scheme 2.2).[11]



Scheme 2.2

Due to their good cured properties in terms of strength, toughness, electrical insulation and chemical resistance properties, epoxy (meth)acrylates are used in a wide variety of applications, either UV or peroxide cured. The bulk of printed circuit board manufacture (PCB) utilise epoxy (meth)acrylates and in the past few years there has been an increasing demand for their use in structural and dental composites, as well as for tough and chemical resistant coatings.

2.1.2.1 Epoxy Resins

There has been increasing interest in the development of new epoxies over the past few years, with interesting reviews of the current state of technology, with Jin *et al*[12] looking at the synthesis methods used, Nagarjuna *et al*[13] looked at synthesis of resin composites, Vidil *et al*[14] looking at epoxy thermoset curing and Pagyan *et al*[15] as a general review. Two main areas of development have come to the fore, namely the development of bio-based epoxies and processes, and the development of cycloaliphatic epoxies. The need to look at alternative sources for the production of epoxies has long been acknowledged and a lot of effort has been expended in this direction over the years both in academia and industry. These have generally followed one of two routes;

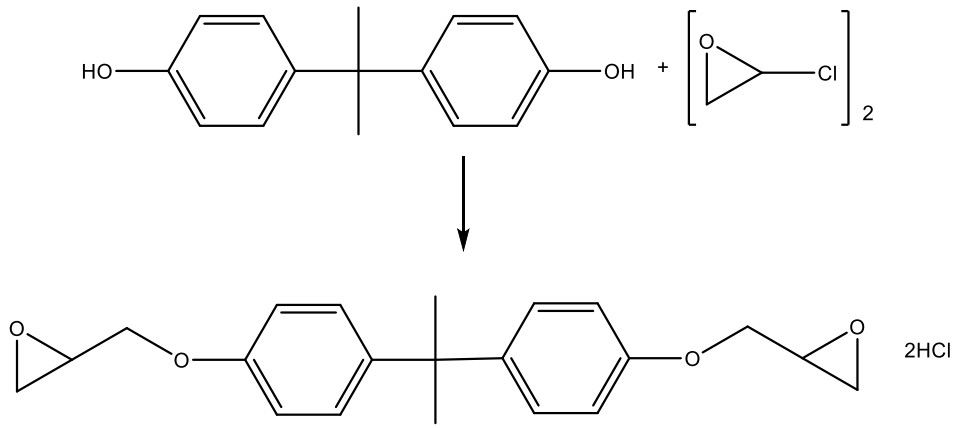
i. Environmentally benign processes for existing chemistries,

ii. Use of natural/bio-sourced raw materials

The use of natural oils to produce epoxies via the reaction with peracetic acid or acetic acid and hydrogen peroxide has long been known, with a number of different fatty acid oils. The most commonly used are castor, linseed, palm, rapeseed and soybean oils. Also coconut fatty acid is widely used to modify epoxies to improve the wetting characteristics of the liquid resin to ensure better binding in of fillers, particularly pigments, due to the long chains present with varying degrees of unsaturation which allow the fatty acids to envelop the pigment particles.

Cycloaliphatic epoxies have been known for a long time, having been developed in the 1950's, but have only attracted the interest of industry over the past ten years.[12] The main problem is that unlike most other epoxies that are available they cannot be cured using amines, which is the main curing agent of choice for most epoxy formulators due to their ready availability and the wide variety. Cycloaliphatic epoxies can be cured using anhydrides, but recently the availability of sulphonium and iodonium salts of hexafluorophosphoric and hexafluoroantimonic acids have allowed the development of cationic curing using conventional UV curing equipment which has increased interest. The epoxidation reaction is similar to that used for natural oils, in that peracetic acid is used. This has meant that since no chlorine or chloride containing substances are used in the process, it has attracted the attention of the electronics industry, since even low levels of free chlorine (10-50ppm) can over time result in the corrosion of copper contacts. This is of a particular concern where components/units are exposed to either high humidity atmospheres, or expected to perform continuously for 20+ years.

The normal method of producing epoxies, is by reacting a hydroxy terminated compound with epichlorohydrin (see Scheme 2.3). This was commercialised independently by De Trey Frères, Switzerland, in 1936 following the work done by Castan[16], and by Devoe-Raynolds, USA, in 1939 following the work done by Greenlee[17], all based on the reaction of bisphenol A with epichlorohydrin. However the first reported work done on the reaction of phenols and epichlorohydrin goes back to 1920 with McIntosh & Wolford[18] producing plastics made from the reaction products of phenol and cresol with epichlorohydrin in the presence of suitable catalysts, and in 1933 Schlack[19] produced a bisphenol A epoxy with 5:1 molar excess of epichlorohydrin.



Scheme 2.3

The standard process for the manufacture of epoxy resin with epichlorohydrin, requires the use of sodium hydroxide as a basic catalyst, and epichlorohydrin to be in excess (about 10% excess has been found sufficient to drive the reaction forward). When the reaction takes place between the phenol (or hydroxy terminated compound of choice) and the epichlorohydrin, the hydrogen and chlorine are released, this then is conventionally believed to form hydrochloric acid, which then goes on to react with the sodium hydroxide to form water and sodium chloride. This requires that the pH of the reaction mixture has to be monitored to keep the reaction conditions basic enough to keep the reaction moving, also azeotropic distillation is used to remove the water, and return the epichlorohydrin back to the reaction mixture. At the end of the process, the excess epichlorohydrin is stripped off under vacuum and the resultant resin is washed with aqueous sodium hydroxide to remove any unreacted hydrochloric acid, then at least two water washes to remove any sodium chloride. The aim is to have a maximum of 50ppm of free chlorine in the final resin, although many manufacturers will routinely report free chlorine levels of <5ppm. As can be seen, although from a chemical reaction and mechanism perspective the reaction is quite simple, the process is time consuming, and more importantly generates a large amount of waste products which have to be further treated to make safe for disposal.

To reduce the dependency upon crude oil based raw materials an alternative process has been developed to produce epichlorohydrin from glycerine, which can be sourced from the by-products from the production of bio-diesel, and chlorine. (Combined with improvements in recovering the sodium chloride from the waste wash water and converting back to sodium hydroxide and chlorine gas, has meant that it has become

feasible to devise a commercially viable process.) This process has been implemented at 2 plants in Europe, one in the Czech Republic (Spolchemie) and the other in Germany (Leuna Harze), thereby reducing the environmental impact of the plants.

2.1.2.2 Applications for Epoxy Resins

The most common use for epoxies is for coating applications, but they are also used in composites, which is a logical extension as the epoxy is just coating and adhering the fillers used in the composite system. Epoxies have been widely used in composite applications from the very beginning as adding filler to any resin will create a composite material. True composites (where the combination of resin and filler result in a material that has better combined tensile, flexural and compressive properties, than either the resin or filler on their own) for structural applications really took off in the 1960's for aerospace and marine applications, where the fillers used were mainly glass fibre and boron nitride. Boron nitride was replaced by carbon fibre due to the ease of handling carbon fibre compared to boron nitride. In the 1960's it was understood that unsaturated polyesters would suffer from hydrolysis when in service, hence epoxies were selected despite the significant increase in cost. Although polyesters can undergo hydrolysis under certain conditions, this can be minimised by raw material selection. Also the ability to be hydrolysed allows the potential for polyester resins and composites to be recycled, while there is not the same opportunity of epoxy composites, resulting in mounds of composite structures left in scrap heaps and corners of ship yards with no environmentally benign method of disposal. At the moment the only economic option for used epoxy composites is to be used as fuel for incinerators, and for the fibre to be recovered from the ash waste stream.

Normally epoxy composite structures are either formed via infusion or pre-impregnated sheet (pre-preg) methods of construction. Infusion is by far the most common and the cheaper of the two methods. A mould of the structure is fabricated and a layer of release agent (normally silicone based) applied to the side being used to form the structure. A release fabric is laid down, followed by the required reinforcement laid down to the required depth, this is then finished off with a vacuum bag which is secured around the edge of the mould with tape. Depending on the size of the moulding two or more outlets are inserted at the end of the film, one or more for a vacuum line, and the others for the mixed epoxy system. The vacuum is applied and the epoxy mixture is drawn through

the reinforcement to create a single mass. Care has to be taken to ensure that the epoxy mixture reaches all of the required moulding and that the epoxy mixture does not cure too quickly. In large mouldings there is a real danger of too much heat being generated due to the exotherm and there being a fire risk as the heat generated cannot be dissipated quickly enough. To minimise the risk a slow cure time epoxy system is often used as the heat generated during the exotherm is spread out over a longer time scale, this is way most epoxy systems sold for composite applications come in a range of cure speeds to offer the user a degree of flexibility in handling and use, and to provide a safe cure regime.

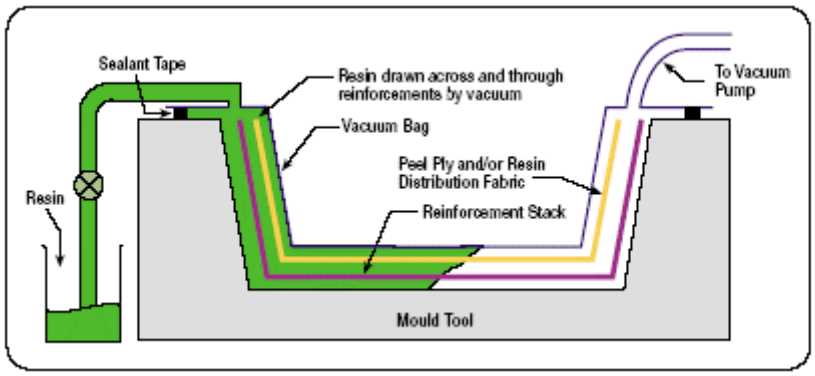


Figure 2.1 – Typical Composite Epoxy Resin Infusion Process Setup. Taken from Gurit Application Guide © 2013

In the case of using pre-preg materials, a layer of epoxy has been laid on top of a layer of reinforcement and then rolled under heat and pressure to force the resin in between the fibres. The epoxy is premixed with a suitable latent catalyst, normally either dicyandiamide or blocked amine catalysts (boron trifluoride amine complexes), and are then stored at -18°C to give a shelf life of 12 months. If left at room temperature then the material become unusable after 7 days, but does not fully cure. Again the mould is prepared as for the infusion method, and the required number of layers of pre-preg laid down. Again a vacuum bag is laid down and taped down around the edge of the mould. Outlets are required for the vacuum to be applied to allow all the layers to be consolidated and for any air pockets to be removed, before going into an oven to cure the epoxy up. One advantage of the pre-preg method is that it is possible to obtain far greater control of the distribution of the resin within the structure, as well as a higher fibre volume fraction (ratio of fibre to resin) than is possible by the infusion method. By infusion normally 65% fibre volume is achieved, up to 70% with care and experience,

while with pre-preg 75% is possible. The main disadvantages are the fact that an oven and freezer are required and that pre-preg materials are about twice the price of the equivalent reinforcement and epoxy raw materials. There are also polyester on the market, but they require careful storage depending upon the type of peroxide catalyst used in the formulation. They have not been as widely adopted as the epoxy pre-pregs.

2.1.2.3 Applications of Epoxy (Meth)Acrylates

There are also cases where epoxy (meth)acrylates have been looked at for composite applications, in the case of structural composites and adhesives peroxides are used and have to be mixed together prior to application. The cure conditions are dependent upon the type of peroxide used, but in the case of adhesives the rapid cure time achievable with the epoxy (meth)acrylate/peroxide combination is significantly quicker than that obtained using amine based chemistries, also the structural modification of the epoxy gives many the desired mix of adhesion, chemical resistance and flexibility. A couple of epoxy (meth)acrylate pre-pregs have been developed, but these have not been well received by the industry and are only used for specialised repair applications. The desire for decreasing production cycle times and/or faster throughput has led to the demand for what has been called "on demand curing" methods, meaning fast curing times, reduced floor space for equipment and the ability to handle the material after curing.[20]

There has been a significant amount of interest in the use of epoxy acrylates and methacrylates for dental applications, this is in some respects analogous of the work done on epoxy resins by Castan[16] which was primarily driven to find an alternative to mercury amalgam for fillings. The first generation of UV curable resins for dental applications used mercury lamps and had problems with getting deep sections fully cured, hence required the use of multiple layers to ensure an adequate degree of cure. With the development and commercialisation of LED's that emit in the UV-C region of the spectrum, and the associated photoinitiatiors, it has become possible to cure vinyl terminated resins to significantly greater depths and with less harm to the operator and patient than was ever possible using mercury based lamp systems. For the majority of medical applications the methacrylate analogue is preferred on the grounds of toxicity, although the cure speeds are significantly lower. It has been found that the shrinkage experienced during curing with all acrylate resins is lower with their methacrylate

analogues, most likely due to the differences in molecular weight between the reactive groups.

Industrial production of epoxy (meth)acrylates is mainly concentrated on the production of bisphenol A epoxy acrylate for the coatings industry, and phenol novolac epoxy acrylates for the production of PCB's. It is estimated that 75-80% of all the epoxy used worldwide is of the bisphenol A type, with 10-15% of the bisphenol F and phenol novolac type, with the remainder made up of aliphatic, cycloaliphatic and natural oil types. In the case of (meth)acrylate production the estimated ratio of epoxy usage is slightly different, with about 70-75% bisphenol A epoxy, 10-20% bisphenol F/phenol and cresol novolac epoxies, 5-10% aliphatic epoxies and the remainder natural oil epoxies. It is a historic anachronism that high molecular weight bisphenol F epoxies are called novolac epoxies, as they were made from novolac (phenol-formaldehyde) resins. Bisphenol F is just a low molecular novolac resin, being the reaction product of 2 moles of phenol to 1 mole of formaldehyde.[21,22]

The most common epoxy curing agents are either primary or secondary amines, which react with most epoxy types without the need of any additional catalyst, however tertiary amines, although they do not react with the epoxy group, are able to act as a catalyst to help other functional groups to react with the epoxy ring. Mercaptans and other thio complexes also readily react with the epoxy ring. In the case of performing synthesis work at high temperatures (>60°C) a number of other catalysts are industrially important as a route to opening the epoxy ring, the most common being triphenyl phosphine which was first reported by Wittig and Haag in 1955 and commercialised by Degussa.[23] Other common industrial epoxy catalysts are 4-methyl morpholine and 2,4,6-tris(dimethylaminomethyl)phenol.

The most common method to produce commercially available epoxy (meth)acrylates is the reaction of the epoxy of choice with (meth)acrylic acid. There is a long history within the patent literature concerning the reactions between acid and epoxy functional groups. The first recorded commercial synthesis of an epoxy acrylate was between a bisphenol A diglycidyl ether and peracetic acid, issued to Payne and Smith[24] in 1957. The now common synthesis route of bisphenol A diglycidyl ether and acrylic acid was reported in a patent issued to Hall[25] the following year, using a tertiary amine (trimethylamine) as the catalyst. In 1959 a patent was issued to Parker for the synthesis

of an epoxy methacrylate by the reaction between polymeric bisphenol A diglycidyl ether and methacryl chloride.[26] The use of the methacryl chloride caused a number of processing difficulties as regards to the generation of hydrochloric acid, and its subsequent removal. While not a problem for epoxy producers who have water wash and neutralisation processes in place to handle epoxy production using epichlorohydrin, it was a major hurdle for downstream epoxy methacrylate producers. It was quickly realised that the simple substitution of methacrylic acid for acrylic resulted in a clean addition reaction without any by products to deal with.

It is possible for all types of epoxies to be used as the starting point for the manufacture of epoxy (meth)acrylates. These can be broken down in to six main types;[27]

i. Bisphenol A epoxy (BADGE) (**1**)

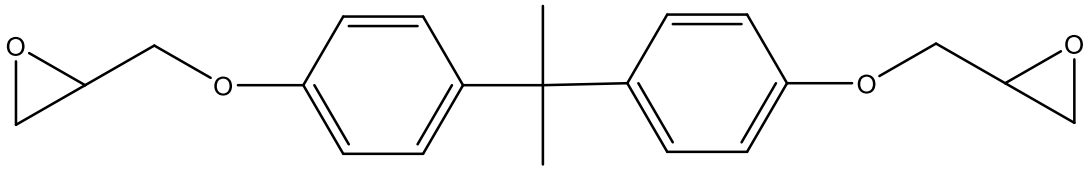
ii. Cresol and phenol novolac epoxies, eg. bisphenol F epoxy (BFDGE) (**2**)

iii. Aliphatic epoxies, eg. 1,6-hexanediol epoxy (HDDGE) (**3**)

iv. Natural oil based epoxies

v. Cycloaliphatic epoxies

vi. Other epoxies



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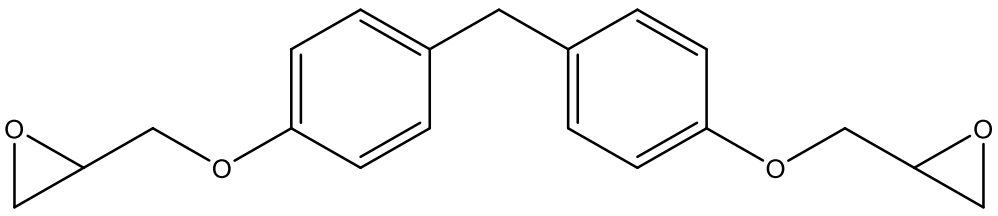

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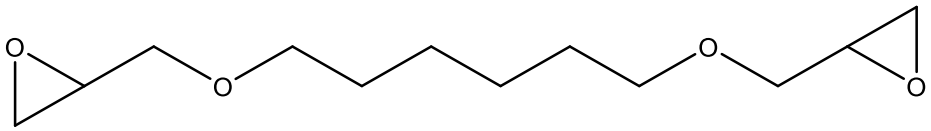


3

When processing bisphenol A, bisphenol F and aliphatic epoxies, the normal industrial practice is to add the epoxy in aliquots to the (meth)acrylic acid. The resin is then processed so that there is a slight excess of epoxy present to minimise polymerisation occurring during the reaction and subsequent storage. With higher molecular weight epoxies the acid is normally added to the epoxy in aliquots to reduce the potential exotherm. If the temperature exceeds 120°C, then once all the inhibitor is consumed/deactivated, the acrylic acid begins to exothermically self polymerise, and the same with methacrylic acid.[28] Each 1mg KOH difference between the acid value and the epoxy value of the reaction mixture has a potential exotherm (ΔT) of 0.6°C.

It is possible to acidify the epoxy acrylate by reacting an anhydride to the hydroxy group that is formed when the epoxy is opened during the addition reaction with the acid. The hydroxy-anhydride reaction opens up the anhydride ring to form an acid group. Since anhydrides are also very good at opening up epoxide rings as well, the initial addition reaction with the (meth)acrylic acid is run with a slight excess of acid present.

Acidifying the epoxy acrylate both improves the adhesion of the cured resin to metal substrates, but also improves the solubility of the uncured resin. This is of particular benefit for resins used for etch resist applications, as the uncured resin can be quickly and cleanly stripped off printed circuit boards (PCB) prior to the acid etch process to remove the unwanted metal.

All of the bisphenol A, cresol and phenol epoxy acrylates suffer from the disadvantage of being prone to yellowing and having a very high viscosity, hence are generally supplied diluted in either reactive monomers (polyester (meth)acrylates) or solvents dependent upon the application and the end use. The advantage of using reactive monomers is that the formulated system can be classified as 100% solids and, according to some definitions, free of volatile organic compounds (VOC) as all the component parts will react together to form the polymer film.[28]

Aliphatic epoxies are more expensive than standard bisphenol A epoxy due to a combination of lower volumes and higher raw material costs, but due to their superior resistance to photo-oxidation and yellowing they are gaining acceptance in industry. They generally exhibit a lower viscosity, and greater flexibility for their molecular weight compared to aromatic based epoxy acrylates. The mono and difunctional epoxies are often used as reactive diluents for bisphenol A epoxy acrylates.

Natural oil epoxy acrylates were more of a European product based on castor, linseed, rapeseed and soybean oils.[27] However these have become more accepted in North America due to increasing interest and demand for materials derived from bio sources. In Asia castor, cashew nut shell, palm and soybean oils are widely used as the starting points. These are primarily used in ink formulations to improve the pigment wetting, to help incorporate and stabilise the pigments in the ink. Due to their compatibility with other natural oils they are increasingly used in the formulation of wooden furniture coatings. They are low in viscosity and reasonably cheap, however they suffer from generally being yellow in colour, oxidation and low reactivity due to steric hindrance.

There are various other more exotic epoxies slowly coming onto the market, as well as different possible modifications to standard epoxies, the most common commercial modification is the addition of a fatty acid to improve the wetability of a polymer formulation.

It is of note that the present consumer concern over bisphenol A has become a political as well as environmental issue, with Denmark and France having introduced national legislation in Europe and California in the USA. It is possible that resin systems that are associated with Bisphenol A will be stigmatised by association and either be phased out by commercial or legislative pressures. This is despite the fact that amount of free bisphenol A in bisphenol A epoxy resin is very low (<100 ppm), and similarly for polycarbonate. Bisphenol A has been added to the CoRAP list by the European Union for further investigation.

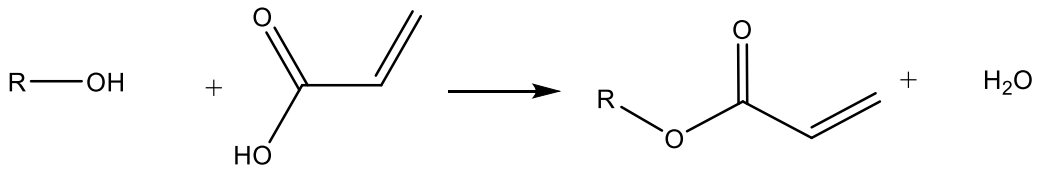
2.1.3 Polyester Acrylate

Polyester acrylates are the most commonly encountered acrylate by the general public, as they are used in the printing industry as the basics of pigmented inks and the clear top

coats and also used in wood coatings for both flooring and furniture. The primary reason is due to the comparative cheapness of the raw materials used.

The reaction of an acid group with an alcohol is well known in many text books, Braun *et al*[29] and Sorenson *et al*[30] give good examples of different experiment synthesis routes. Industrially it is a long and well establish process to produce polyesters. In 1954 Necker *et al*[31] were issued a patent to cover a process for synthesising acrylic esters from alcohols and polyols with acrylic acid. It was not until 1979 when Vrancken *et al*[32] was issued a patent to cover the synthesis of polyols with acrylic acid, that a radiation source mentioned as a method of curing the resultant polyester acrylate resins. Previous to this patent the use of peroxides as the curing agent was either mentioned or assumed.

The esterification process is well established, but due to the tendency of acrylic and methacrylic acid to self polymerise at temperatures above 120°C, the process is necessarily a low temperature one.[16] This requires the use of vacuum to strip the water out, via azeotropic distillation, during the reaction to stop the esterification reaction running in reverse and reverting back to the original raw materials (see Scheme 2.4). Standard practice is to use methane sulphonic acid as the catalyst, but the use of acid activated resin bead beds, such as Amberlite or Amberlyst from Dow, has become increasingly used on a commercial scale.



Scheme 2.4

The use of an azeotrope to remove the water means that solvent is added to the system, which then has to be removed at the end the polymer synthesis, together with any unreacted raw materials as the reaction is run with a slight excess of either acid or hydroxy groups to push the reaction kinetics forward. The variations possible in modifying the polyester backbone are almost limitless and allow for a great variety of products to be formulated. In many cases the reaction is done in two stages, with the core polymer reacted at a higher temperature to improve the reaction cycle time, followed by the acrylic acid esterification taking place at the lower temperature.

Due to the low temperatures used, the process time of a batch reaction can be over 24 hours. This long processing time leads to issues concerning the stabilisation of the acid, as the inhibitors to stabilise the acid are exhausted. Also undesirable polymerisation can take place in the distillation columns due acid in the water vapour. This is due to the low concentration of inhibitors found in the water, because of poor solubility in water. Some solutions to these problems have been outlined in the patent literature, but these only strictly apply to commercial scale operations. It is reported in the patent literature the use of hydroxy terminated acrylates (eg. hydroxy ethyl acrylate) instead of acrylic acid. The main disadvantage is cost, acrylic acid is considerably cheaper than the hydroxy acrylates.

2.1.4 Urethane Acrylate

There has been a great deal of research and development activity into polyurethanes in general, and polyurethane (meth)acrylate resins. The main driver for the research into polyurethanes is the desire to find a method of producing a non-isocyanate derived urethane. This has been brought about by the regulatory activities instigated by the ECHA in regards to REACH. The bulk of the isocyanates used to produce urethanes have had their health and safety classifications increased in severity and as a consequence restrictions placed upon their use. This has effectively prohibiting their use by the general public, and restrictions within industry.

Polyurethane chemistry was first described by Bayer in 1937, based on the reaction of various glycols, with difunctional isocyanates.[33,34] It was not until the 1950's that polyurethane chemistry became industrially significant, primarily with the development of suitable equipment for handling and mixing the constituents.

Initially aromatic diisocyanates were commercially used, but resulted in UV unstable polymers. This in turn led to development of aliphatic isocyanates which resulted in more UV stable polymers. It was the development of polyurethane foams that lead to the massive expansion in the use and application of polyurethanes. As more work was done looking at these systems it became apparent that the first generation of diisocyanates, which were very reactive, posed considerable health risks. This drove the search for safer alternatives, which were generally lower in their inherent reactivity, hence also required the use of catalysts. At the same time there was also the drive towards developing new hydroxy terminated polymers, these included linear and branch

hydroxy terminated polyesters, polyethers and caprolactones. Polyurethanes have become widely used in a variety of different applications ranging from rigid and flexible foams to flexible coatings. As more data has been accumulated over the years through the industrial use of polyurethanes and polyureas, which also use isocyanates, it has been found that there are a number of serious health risks associated with isocyanates. This has driven research into alternatives.

The desire to find a route to produce polyurethanes without the use of isocyanates has been going on since the 1950's but has only really gathered momentum in the past 10 years due to the increase in research funding, from both government and industrial sources. In turn this has generated a large number of papers and patents covering the subject. Rokicki *et al* have reviewed the state of the art concerning the developments in isocyanate free polyurethanes[35] dividing the main synthesis routes into, polyaddition, polycondensation and ring opening polymerisation.

Generally there are two reaction pathways that have attracted the attention of researchers, the reaction between a cyclic carbonate and an amine, and the reaction of a carbamate with either dicarboxylic acids or diols.[36,37] Researchers have utilised the routes above for both pathways in order to fully explore the various possibilities to form the urethane bond. The main problem with many of these synthetic routes is that either high temperatures or long reaction times are involved. When this is compared to the current state of isocyanate based chemistry, this is a significant disadvantage. Particularly since many urethane reactions can take place at room temperature with no additional heat requirement, the speed of reaction can adjusted with the use of catalysts.

The carbonate-amine synthesis route is seen by many as the most likely by many research groups and has the advantage of a large number of amines available, either in commercial quantities or on lab scale. The major hurdle is the availability of suitable difunctional cyclic carbonates, virtually all the studies reported to date have to first synthesise a suitable starting cyclic carbonate. The use of carbon dioxide as a raw material for the synthesis of these cyclic carbonates is a matter of great interest, particularly for the environmental benefits that would accrue. There are also projects looking the use of natural oil based epoxies to create various cyclic carbonates via the reaction of the epoxide group with carbon dioxide via a suitable catalyst.

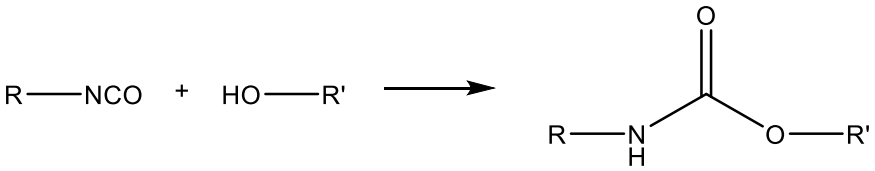
In many cases the reaction of the cyclic carbonate and the amine require both a catalyst and heat to drive the reaction forward. The resultant resin intermediates are often significantly higher in viscosity than the isocyanate-polyol equivalents. Major companies such as Arkema (Bostik) have published a lot of data showing comparisons between carbonate-amine and isocyanate-polyol systems, where the carbonate-amine systems generally performed better, but could only be processed at high temperatures to ensure the same degree of cross-linking as the isocyanate-polyol analogues.[38]

The reaction between carbamates and either dicarboxylic acids or diols has attracted less attention, but still has many possibilities. One aspect is the environmentally sensitive/benign processes to synthesise suitable carbamate starting compounds, compared to the phosgene starting point for isocyanates. Again the major stumbling block for these routes is the requirement for heat to drive the reaction forward.

A variation to the carbamate-dicarboxylic acid route, is the carbamate-dialdehyde developed, patented and marketed by Dow Chemicals as the Paraloid Edge system.[39] The system uses a dialdehyde acid to act as a cross-linker between polymers with carbamate functional groups, which are claimed to have reasonable processing time at room temperature.

Although very attractive from a health and safety perspective, it has not been taken up commercially as the properties of the resultant resins are very limited compared to what is available with the existing technology. Also there is a significant cost differential between conventional isocyanate based polyurethanes and the isocyanate free systems, assuming that the starting raw materials are available in commercial quantities.

Urethane acrylates are the most expensive of the various (meth)acrylate resins produced due to the cost of the raw materials, but the reaction is well understood and does not require any complicated processes or equipment. Like the polyester acrylates, a wide range of polymer backbones is possible. The reaction between an isocyanate group and a hydroxyl group to form a urethane group is well known (see Scheme 2.5).[40]



Scheme 2.5

Due to the wide range of diols, triols and polyols available, this gives rise to the large number of different oligomers and polymers that are on the market. The use of hydroxy terminated (meth)acrylates allows for the production of urethane (meth)acrylates, the most common being;

i. 2-Hydroxyethyl acrylate (HEA) (**4**)

ii. 2-Hydroxyethyl methacrylate (HEMA) (**5**)

iii. 2-Hydroxypropyl acrylate (HPA) (**6**)

iv. 2-Hydroxypropyl methacrylate (HPMA) (**7**)

A number of different isocyanates are regularly used on a commercial basis;

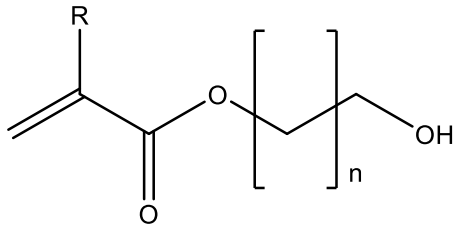
i. Toluene diisocyanate (both 2,4 and 2,6 isomers) (TDI) (**8**)

ii. Diphenylmethane-4,4'-diisocyanate (and 2,4' isomer) (MDI) (**9**)

iii. Isophorone diisocyanate (IPDI) (**10**)

iv. Hexamethylene diisocyanate (HDI) (**11**)

v. 4,4'-Disocyanatodicyclohexylmethane and isomers (HMDI)[41] (**12**)

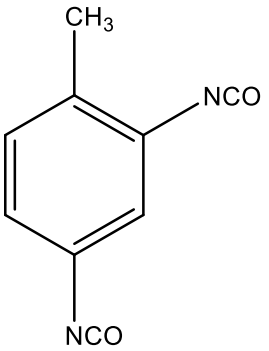


Where: n = 1 and R = H **4**

n = 1 and R = CH_3 **5**

n = 2 and R = H **6**

n = 2 and R = CH_3 **7**



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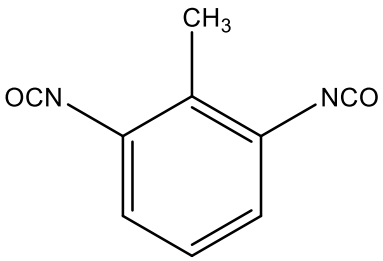

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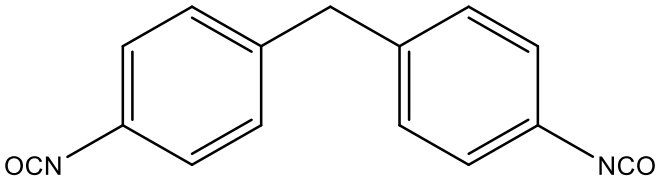

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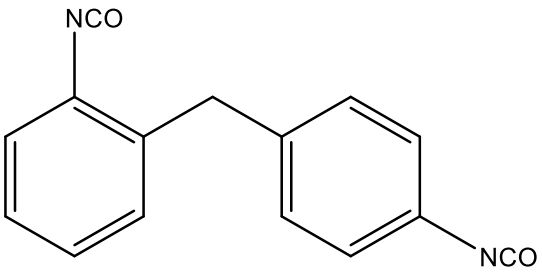

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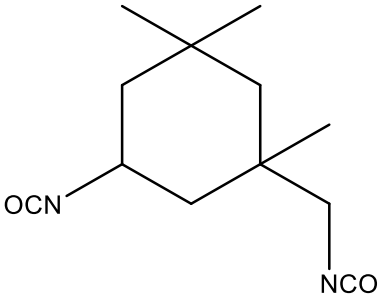

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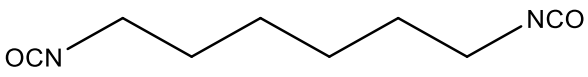

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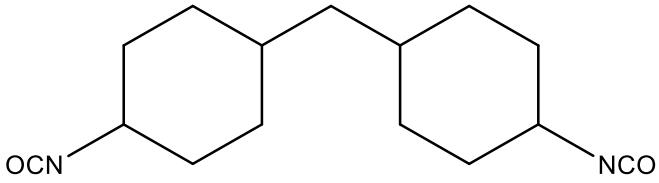

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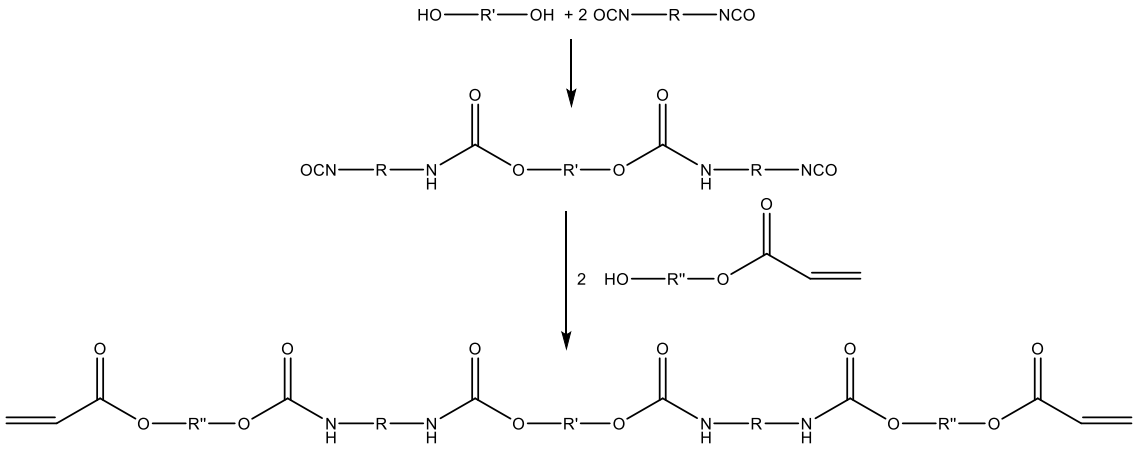
The first two isocyanates mentioned are aromatic, and also the most commonly used. This is due to the cost, availability and reactivity. The last three mentioned are all aliphatic, but generally cost more. Although aliphatic isocyanates are becoming more widely used, they still only represent 10% of the isocyanates produced generally, and 25% of the urethane (meth)acrylates produced, MDI represents the largest volume consumed with 75% of all isocyanates and ~70% of urethane (meth)acrylates.

TDI is classified under CLP as very toxic, but the resultant polymers have interesting properties due to the 2,4 and 2,6 positioning of the isocyanate groups. MDI is classified as harmful. The 4,4’ positioning of the isocyanate groups gives rise to linear polymers, these generally have very good flexibility and elongation properties. There are 2 other isomers available for MDI, 2,2’ and 2,4’. Generally these are not as commonly used as the 4,4’ isomer.

IPDI is classified as toxic, but it is the most widely used aliphatic isocyanate. Its structure is such, that it is the only asymmetric diisocyanate in common use. HDI is also

classified as toxic, but is becoming more commonly used, particularly with water based systems. HDI has the advantage of being linear, which, like 4,4' MDI, results in polymers with very good flexibility and elongation properties. In order to get around the problems associated with the toxicity of HDI, there are now a number of polymeric HDI products available, these are unfortunately considerably higher in viscosity and normally trifunctional, but are classified as polymers under REACH and have a low hazard rating. HMDI is a hydrogenated form of MDI. Although it does produce aliphatic variants of MDI based systems, the resultant polymers are significantly higher in viscosity than their aromatic counterparts, most probably due to van der Waals effects. Also HMDI has very poor reaction kinetics compared to all the other isocyanates considered.[41]

The normal method of producing a urethane (meth)acrylate is to undertake the polymer building in the first stage, by reacting the desired polyol(s) with the isocyanates, then in the second stage cap the remaining free isocyanate with the desired hydroxy terminated monomer. Since there is a large number of different potential polyols to choose from to obtain the required properties and/or structure, it is not surprising that there are a large number of urethane (meth)acrylates available on the market today.



Scheme 2.6

MDI and TDI isocyanates are often used to produce clear, colourless resins, however the aromatic ring does act as a chromophore when attacked by UV radiation over a period of time. Applications that require colour stability aliphatic isocyanates are preferred, despite the cost. In 2010-14 there was a global shortage in the supply of aliphatic isocyanates due to the diamine feedstocks being allocated to the manufacture

of epoxy hardeners. This was due to the demand for wind turbines, and their blades, the consequent demand for epoxy resin and hardeners. Since 2014 the wind turbine market in Asia has collapsed and demand in Europe and North America has remained static, which along with increased amine production capacity, has stabilised the market and increased the quantity of isocyanates produced and available on the open market.

The viscosity of urethane acrylates can vary widely and is very dependent upon the molecular weight and the functionality of the polymer used. Generally difunctional materials have the lowest viscosity and best flexibility when cured, while the hexafunctional materials have high viscosities, but very good chemical and abrasion resistance. The use of hydroxy terminated pendant groups has led to the development of true water soluble urethane acrylates in the past five years.

Recently two groups have reported on the synthesis of an isocyanate free urethane methacrylate, El Fray *et al*[42] used a 6 membered cyclic carbonate reacted with a fatty acid based diamine, while Ochiai and Utsuno produced a resin via the polycondensation of a dihydroxyurethane formed from the reaction between diamines and ethylene carbonate.[43] The viscosity of these resins is higher than would be expected for a comparable isocyanate based urethane methacrylate of similar molecular weight and structure.

2.2 Free Radical Chemistry and Mechanisms

It is known that the presence of free radicals in vinyl ester resins is the reason that polymerisation occurs in storage. Below is a brief overview of what is the current state of knowledge concerning free radical formation and propagation, together with the mechanisms and chemistry of the most commonly used inhibitors.

2.2.1 Oxidation and Peroxide Formation

In free-radical polymerisation there are the three classical stages;

1. Initiation,

$$\text{R-H} \rightarrow \text{R}^{\bullet} + \text{H}^{\bullet}$$
$$\text{R-R} \rightarrow \text{R}^{\bullet} + \text{R}^{\bullet}$$

2. Propagation,

$$\text{R}^{\bullet} + \text{O}_2 \rightarrow \text{ROO}^{\bullet}$$
$$\text{ROO}^{\bullet} + \text{RH} \rightarrow \text{ROOH} + \text{R}^{\bullet}$$
$$\text{ROOH} \rightarrow \text{RO}^{\bullet} + {}^{\bullet}\text{OH}$$
$$2\text{ROOH} \rightarrow \text{RO}^{\bullet} + \text{ROO}^{\bullet} + \text{H}_2\text{O}$$
$$\text{RO}^{\bullet} + \text{RH} \rightarrow \text{ROH} + \text{R}^{\bullet}$$

3. Termination.

$$\text{R}^{\bullet} + \text{ROO}^{\bullet} \rightarrow \text{ROOR}$$
$$\text{R}^{\bullet} + \text{R}^{\bullet} \rightarrow \text{R-R}$$
$$\text{R}^{\bullet} + \text{RO}^{\bullet} \rightarrow \text{ROR}$$

If there is oxygen present in the system, then the oxygen molecule is available to participate in the propagation and termination stages if there are free-radical species present. The process by which the initial primary alkyl radical is formed is not fully understood. The direct reaction of oxygen with a suitable hydrocarbon group is thermodynamically and kinetically unfavourable. The most likely explanation is that during the polymerisation reaction various catalysts (transition metals, radical initiators, impurities in the raw materials, etc) and low concentration of oxygen react to form peroxy radicals ($\text{ROO}^{\bullet}$). These in turn are able to abstract hydrogen from the polymer to form the alkyl radical.[44-46]

Since it is not technically possible to produce a pure oligomer or polymer, various impurities, unreacted monomers and isomers will be present, offering opportunities for radicals to be formed during the polymerisation reaction. The geometry of the reaction

vessel and the stirrer will mean that some mechanical shearing of the product will have taken place, particularly in high solids and viscosity processes, which again will offer opportunities for radical formation.

The peroxy radicals thus formed can abstract a further hydrogen atom to form hydroperoxides (ROOH). The decomposition of the hydroperoxide to alkoxy and hydroxy radicals is a reaction with considerable activation energy, hence as the temperature increases, the rate of decomposition increases. This reaction can be catalysed by metal ions and UV and visible radiation.

The activation energy required for oxygen to react with an alkyl radical is very low, and is effectively temperature independent. However since the abstraction of hydrogen by a peroxy radical involve the breaking of a carbon-hydrogen bond, this requires considerable energy and becomes the rate determining step as to the formation of the hydroperoxides. The rate of abstraction is also determined by the structural location of the potential hydrogen within the donor. This is due to inductive effects. It has been found that the rate of reaction decreases in the following manner;

α H to a C=C > aromatic H or tertiary H > secondary H > primary H

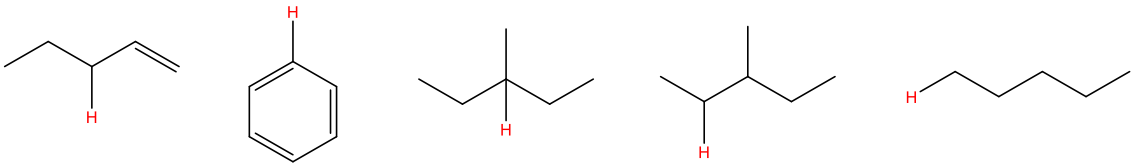


Figure 2.2 – Location of hydrogen suitable for abstraction

If there is sufficient oxygen present in the system, and the radical formation temperature is not too high, then chain termination occurs, with the peroxy radicals recombining. Conversely if the system is oxygen deficient, and the concentration of $R^{\bullet}$ is greater than the concentration of $ROO^{\bullet}$, chain termination occurs with the recombination with other radical species available.

2.2.2 Antioxidant

As seen above, the role that oxygen plays in the formation of free radicals is critical, hence antioxidants can play a critical role in the stabilisation of the resin system. There are 2 types of antioxidants that are of interest, primary and secondary.

2.2.2.1 Primary Antioxidants

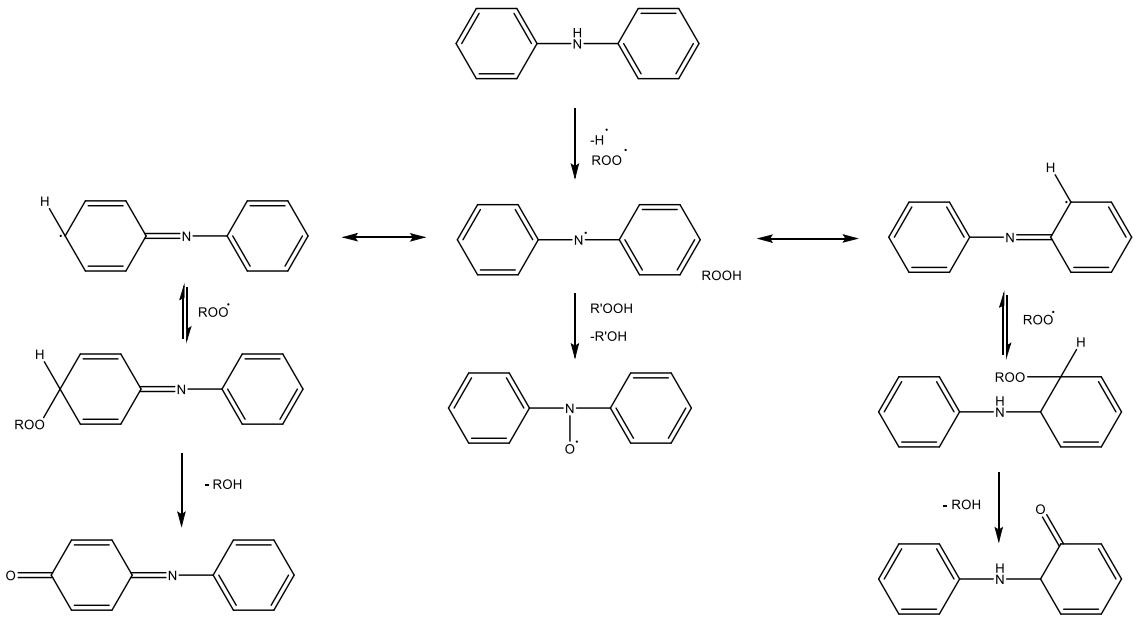
Primary antioxidants are free-radical scavengers, which react with propagating radicals to terminate them. This is achieved by donation of a hydrogen to terminate the radical species, typically peroxy, alkoxy and hydroxy radicals. It is for this reason that primary antioxidants are also known as hydrogen donors.

The rate determining step in the autoxidation cycle is the hydrogen abstraction of the peroxy radical from the polymer backbone, to form the relatively stable polymer bound hydroperoxide. If the peroxy radical is offered a more easily abstractable hydrogen from an intentionally added hydrogen donor, then effectively the abstraction from the polymer will not take place until the hydrogen donor is consumed.[47] Substances are determined to be suitable hydrogen donors by the fact that they do not react further by abstracting hydrogen from the polymer backbone. The main groups of substances used to act as hydrogen donors, hence acting as antioxidants are:

i. Aromatic amines (e.g. benzylamine), and
ii. Phenols (e.g. 2,6-di-tert-butyl-4-methylphenol).

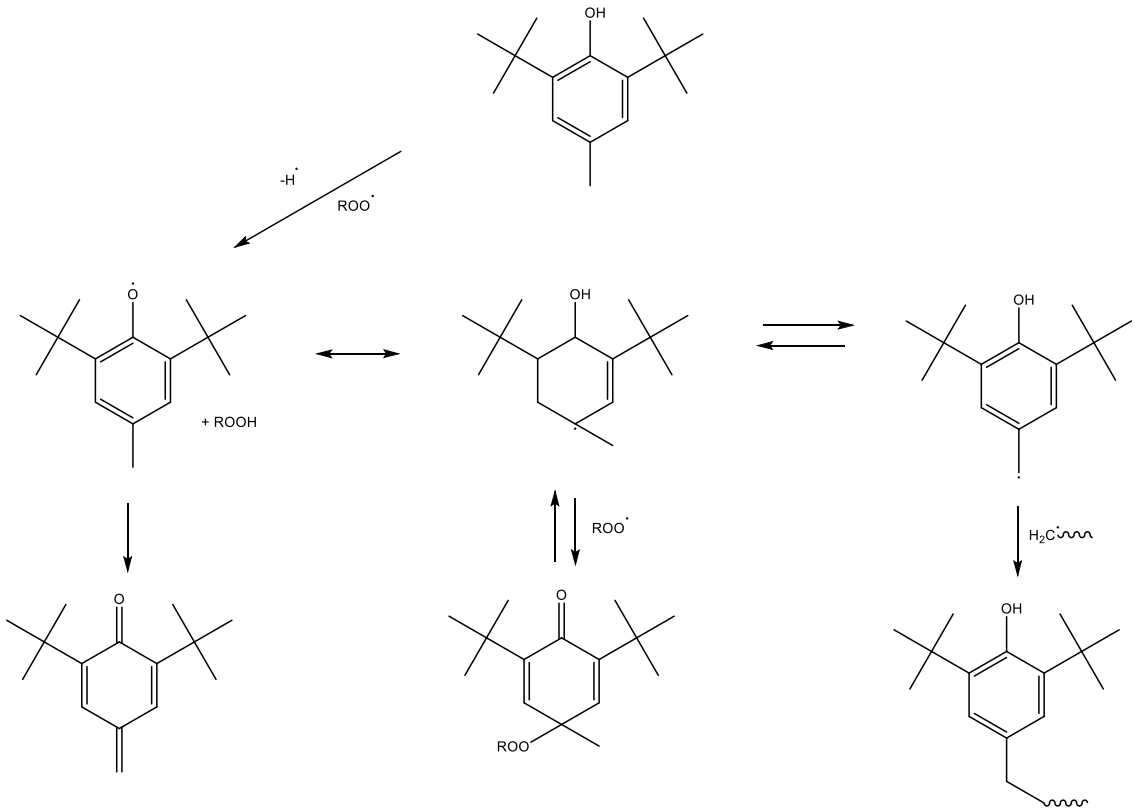
Secondary amines and diamines have long been recognised and used as antioxidants. However their main disadvantages are that they are prone to discolouration and can leach out of cured polymers over time. If the polymer has a food contact requirement, very few amines are approved for use in either Europe or North America.

The abstraction of hydrogen by the amine leads to the formation of aminyl and other related mesomeric radicals, see Scheme 2.7.



Scheme 2.7

Phenolic compounds acting as hydrogen donors are widely known and used commercially to stabilise polymers. These vary from naturally occurring compounds (α-δ tocophenols, Vitamin E) to complex synthetic compounds. The main reaction is the formation of hydroperoxides by hydrogen abstraction from the phenolic group to form the phenoxy radical. The stability of the resultant phenoxy group is determined by the steric hindrance of the substituents in the 2,6 position. At ambient temperatures phenoxy radicals do not abstract hydrogen from the polymer backbone.[48]



Scheme 2.8

The substituent groups found present on sterically hindered phenolic antioxidants have a considerable effect upon the efficiency of the compound, particularly when used for long term stability at elevated temperatures (120-150°C). It has been found that relative efficiency decreases in the order, 2,6-di-tert-butyl > 2-tert-butyl-6-methyl > 2,6-dimethyl. This could be due to the increased exposure of the hydroxyl group leading to greater reactivity and decomposition rate, or the reduction in size of the substituent groups reduced the inductive effects that can be created by the presence of the free radicals.

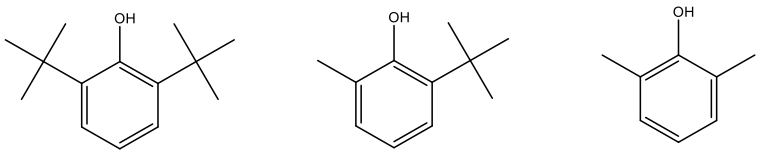


Figure 2.3 – Reduction of steric hindrance around the hydroxyl group on different alkyl phenols

Further reactions of phenoxy radicals play an integral part in the stabilisation mechanisms of phenolic antioxidants. Alkyl phenols with one or more hydrogens in the

vicinity of the phenyl group can undergo a disproportionation reaction to the initial phenol and a quinone methide. Quinone methides react further with alkyl, alkoxy and peroxy radicals. Quinone methides are not considered to be acting as inhibitors to autoxidation, but as retardants of the oxidation mechanism.

Due to the structural changes that the phenolic antioxidants undergo, some of the resultant phenolic compounds act as chromophores, leading to the polymer system becoming discoloured. Generally though the majority of phenolic antioxidants are reasonably colour stable throughout the life time of the polymer, which is the reason why phenolic antioxidants are preferred over the secondary aromatic amines.

2.2.2.2 Secondary Antioxdants

Secondary antioxidants act as peroxide scavengers and decompose peroxides. The most common compounds used are trivalent phosphorus complexes. Phosphites and/or phosphonites are oxidised in a stoichiometric way to the phosphates. Further $ROO^{\bullet}$ and $RO^{\bullet}$ radicals are also reduced by the reaction with trivalent phosphorous compounds. The alkyl radicals ($R^{\bullet}$) can undergo disproportionation or fragmentation in oxygen deficient conditions. Commercially the use of hydroperoxide decomposers is usually combined with a primary antioxidant to ensure the stability of the polymer system through synergistic effects. However due to the stoichiometric nature of the reaction, the under elevated temperatures the secondary antioxidant can be exhausted more rapidly than predicted.

Phosphites normally oxidise to phosphates, however they can be hydrolysed to produce acidic species. These can cause problems with stability and potential corrosion problems, particularly if unlined or poor quality lined metal containers are used.

Sterically hindered amines are widely used to improve the stability and appearance of polymer resin systems. Those based on tetramethyl piperidine derivatives are readily oxidised to nitroxyls with peroxy radicals, and to hydroxylamines with peracids. This means that the initial oxidation of the polymer is the prerequisite for the formation of the nitroxyl species.

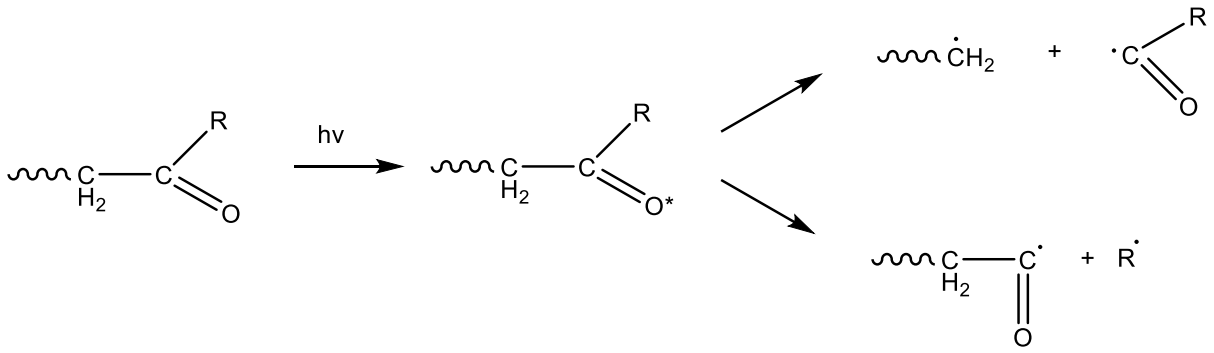
The mechanism of hindered amines has been explained by the reaction of alkyl radicals with nitroxyl radicals. The reaction rate between the nitroxyl and alkyl radicals appears

to be only slightly lower than that between alkyl radicals and oxygen. This is a cyclic reaction and the nitroxyl radical is reformed until it is destroyed via a side reaction. Nitroxyl radicals also react with peroxy and acylperoxy radicals, thereby increasing the efficiency of the compound. The mechanisms are not fully understood.

2.2.3 Photolysis

Light is an energy source that can initiate free radical production. If plastic containers, particularly clear, translucent or with low filler contents, are used to store vinyl ester resins, then there is a high probability that photolysis will occur. There are two main routes for the photolysis of compounds,

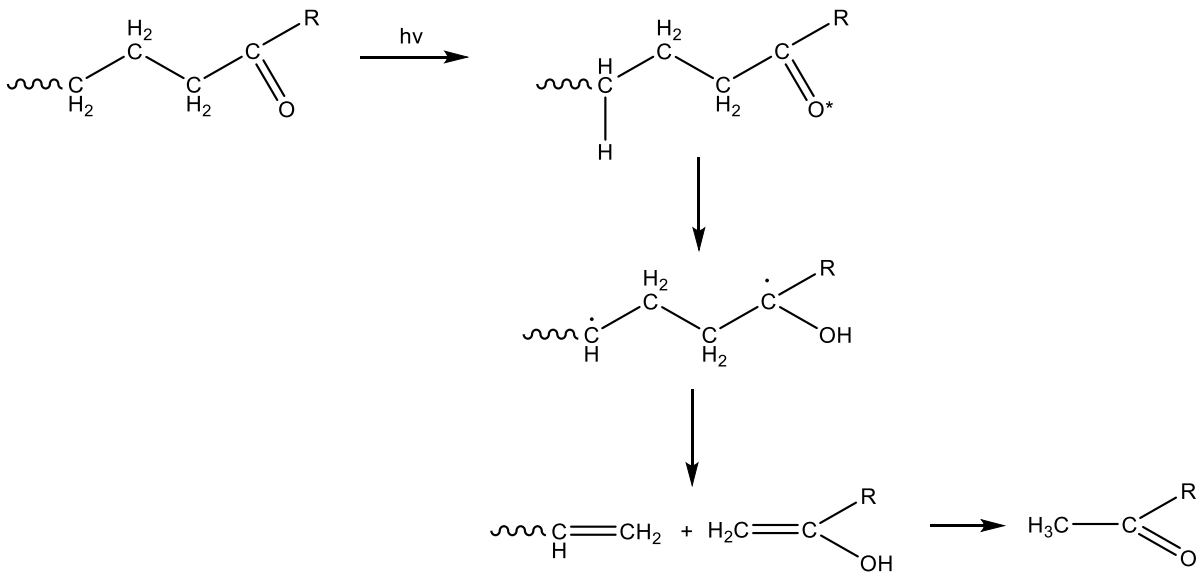
1. Norrish type I reaction (α-scission) (see Scheme 2.9)
2. Norrish type II reaction (β-scission) (see Scheme 2.10)



Where * = excited state

• = free radical

Scheme 2.9



Scheme 2.10

The actual wavelength of light required to initiate the reaction is dependent on the atom and the associated structure, although in the case of most polymers the UV-C region is generally the most active in terms of polymer degradation and breakdown, primarily through free radical initiation.

If there is oxygen present in the system, then it has been reported that carbonyl compounds have the potential to be involved in the formation of singlet oxygen ($^1O_2$). This is believed to occur through charge transfer between the carbonyl group to the oxygen molecule. The lifetime of the singlet oxygen is sufficient to allow for the reaction between the oxygen and carbon-carbon double bonds present in the resin system. This in turn leads to the formation of alkyl hydroperoxides.

2.2.4 Cure Mechanism

All vinyl esters can be cured by introducing a source of free radicals, or initiator, into the resin system. This is the most common commercial route, and if the right initiator is used then the desired properties from the cured resin can be obtained. Initiator radicals ($I^{\bullet}$) react with a suitable molecule (M) to form a molecular radical ($I\text{-}M^{\bullet}$) to begin the polymerisation process. In the subsequent reactions more molecules react with the radical to form a macro radical $I\text{-}[\text{-}Mn]^{\bullet}$. This means that at any given time during the polymerisation process there will be initiator radicals, molecular radicals and macro radicals present in the system. These can react not only with other molecules present,

but also with each other. This is done by either coupling reactions or disproportionation, thereby completing the life cycle of initiation, propagation and termination.[45]

As mentioned above free radical polymerisations involve the simultaneous generation and elimination of initiator radical, molecular radicals and macro radicals. Dependent upon the temperature, within a reasonably short period of time the total concentration of all the radical species reaches a constant level, or steady state. The free radical polymerisation is completed in theory when all the radical sites have been exhausted, however it is much more common that polymerisation is completed when there is a combination of various molecular weight polymers formed as well as various macro radicals which are unable to propagate or terminate due to steric hindrance and a general lack of mobility of polymer chains.

2.2.5 Inhibitors

Inhibitors are antioxidants whose primary purpose is to prevent premature polymerisation, this distinction has arisen from the thermoplastic processing industry, as the term antioxidants is normally reserved for the use of compounds that are intended to prevent scorching and other heat related issues during processing in injection moulding equipment. This terminology has been adopted by the thermoset polymer industry as well, even though in many cases the same classes of materials are used interchangeably as either antioxidants or polymerisation inhibitors as the same modes of action are required.

The primary use of inhibitors in the resin system is to stabilise the resin in storage and prevent premature polymerisation, however if the concentration is too great then the intended polymerisation at the desired time may also be inhibited. It is a very careful balancing act to get the correct inhibitor package at such a concentration that is sufficient to ensure a commercially acceptable shelf life, yet will also allow the resin to polymerise when so desired without requiring high concentrations of activators and initiators.[49]

There is an increasing awareness of the additives that are used in various polymer formulations, particularly those which are not reacted into the polymer structure, hence are liable to leach out over time, or under certain conditions. Various pieces of legislation have been introduced in various countries and regions in the past 10 years

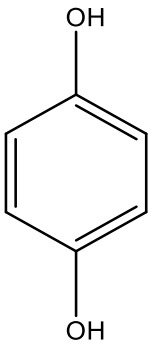
that are forcing most companies to revisit their product's formulations in order to keep them on the market. The European Union has lead the world with the introduction of REACH as a general overarching chemical registration system, as well as various industry specific directives and regulations.

A working definition of an inhibitor is a substance that when added to a polymerisation mixture will react with radicals, either from an intentionally added source or natural source, to consume and deactivate them. Similarly a retarder is a substance that will deactivate any radicals present in a polymerisation mixture. There isn't a clear cut boundary between an inhibitor and a retarder, as the end results are in many cases in the short term identical. In the long term an inhibitor should eliminate the radicals generated, while a retarder will only slow down the generation/release of the radicals. Often the use of the terms inhibitor or retarder come down to a combination of industry sector and/or personal preference.

Common inhibitors used include phenols, quinones, nitro and nitroso-compounds, stable radicals, phenothiazine and oxygen. Oxygen acts as a double edged sword for it can act as a charge transfer agent, inhibitor and initiator. As mentioned previously the problem of oxygen inhibition is a major problem with UV curing of resins, particularly with regard to surface cure. The vinyl groups present at the surface react with the ozone generated by the UV source, rather than the photo initiator in the resin, causing an incompletely cured top layer of the coating.

2.2.5.1 Phenols

Phenolic inhibitors such as hydroquinone (HQ) (**13**), 4-methoxyphenol (also known as monomethyl hydroquinone) (PMP) (**14**), methyl hydroquinone (MeHQ) (**15**), 3,5-di-*tert*-butylcatechol (DTBC) (**16**), 4-*tert*-butylcatechol (TBC) (**17**) and 2,6-di-*tert*-butyl-4-methylphenol (as known as butylated hydroxy toluene) (BHT) (**18**) are found in many commercial resin systems. Studies have shown that, in the cases of simple radicals, carbon centred radicals react with phenols by abstracting an aromatic hydrogen.



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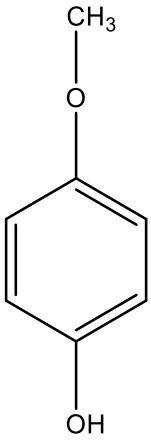

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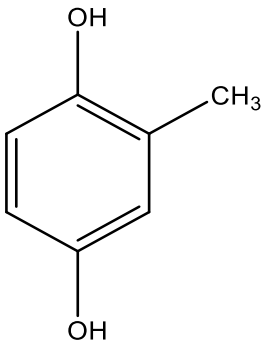

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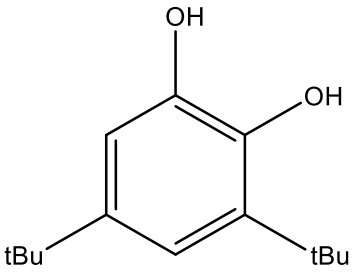

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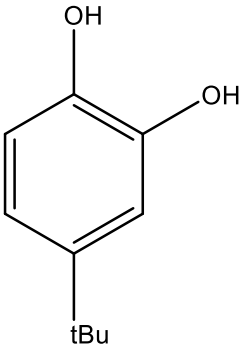

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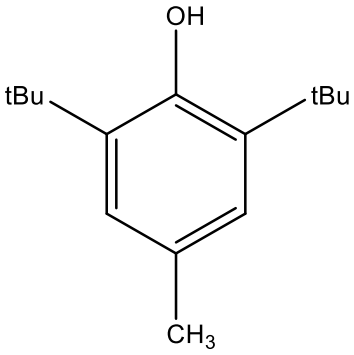

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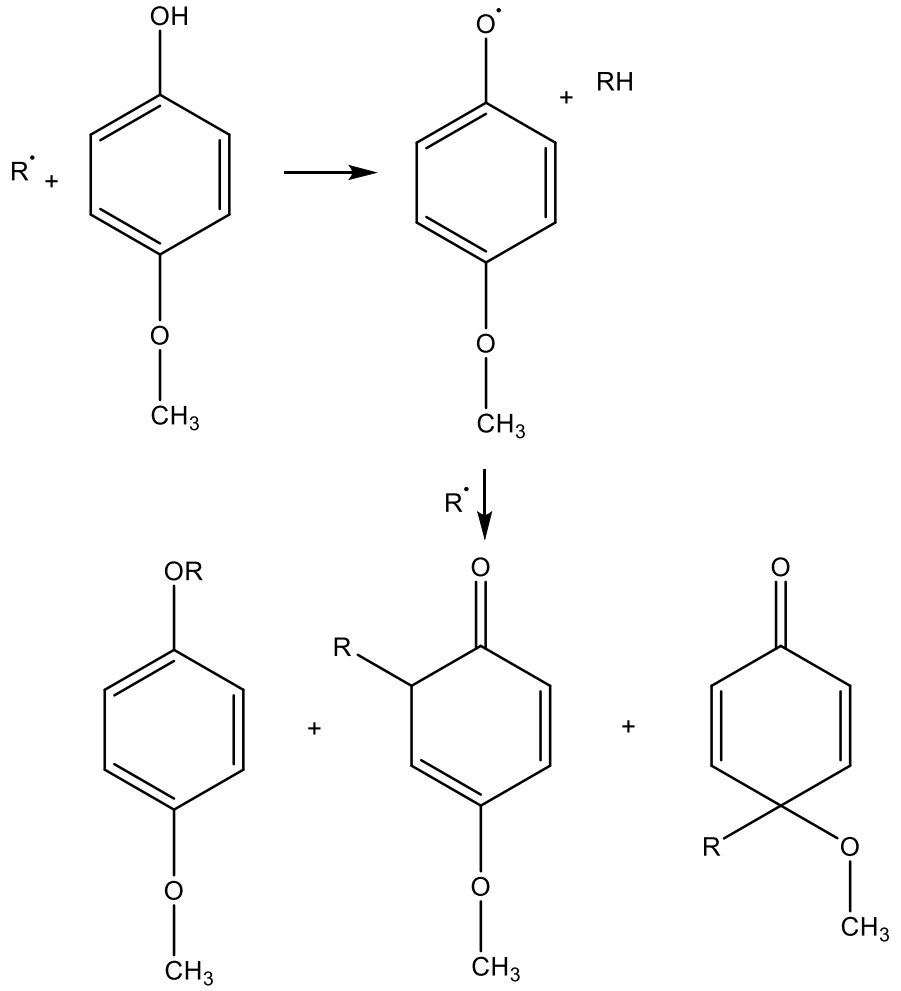
Phenoxy radicals may then scavenge a further radical by carbon-carbon or carbon-oxygen coupling. In the case of hydroquinone, the loss of a hydrogen produces a quinone. From a stoichometric perspective, 2 or more moles of radical sources may be terminated for every mole of phenolic present (see Scheme 2.11).



Scheme 2.11

It should be noted that in the majority of cases phenolics are very poor polymerisation inhibitors on their own. For maximum efficiency the phenolics work best in the presence of oxygen. This is why most commercial (meth)acrylate solutions are sold in containers with a certain amount of head space and that the head space requires regular replenishment with fresh air.

Within the (meth)acrylate industry the use of PMP has become very common, with an number of papers and patents issued over the years concerning its use, primarily for the stabilisation of (meth)acrylic acid. This is the ideal compound for doing studies on as it is very reactive, yet comparably low toxicity, low molecular weight and is easy to purify, compared to vinyl ester oligomers and polymers. Also the processing of (meth)acrylic acid is both well known and, due to its wide use as a basic building block chemical, subject to continuous improvement.

Levy[50,51] under took a lot of work looking at the use of PMP in acrylic acid storage and found at room temperature there was very good stability over time, but this rapidly dropped off as the temperature was increased to 100°C as the inhibitor was rapidly consumed by the free radicals generated. More recently Becker and Vogel[52] have undertaken a similar study looking at acrylic acid as it is distilled as part of work on improving acrylic acid processing. They found that the use of PMP results in a linear correlation between acrylic acid polymerisation and temperature up to 60°C, but above this temperature the polymerisation/temperature response changes to an exponential response.

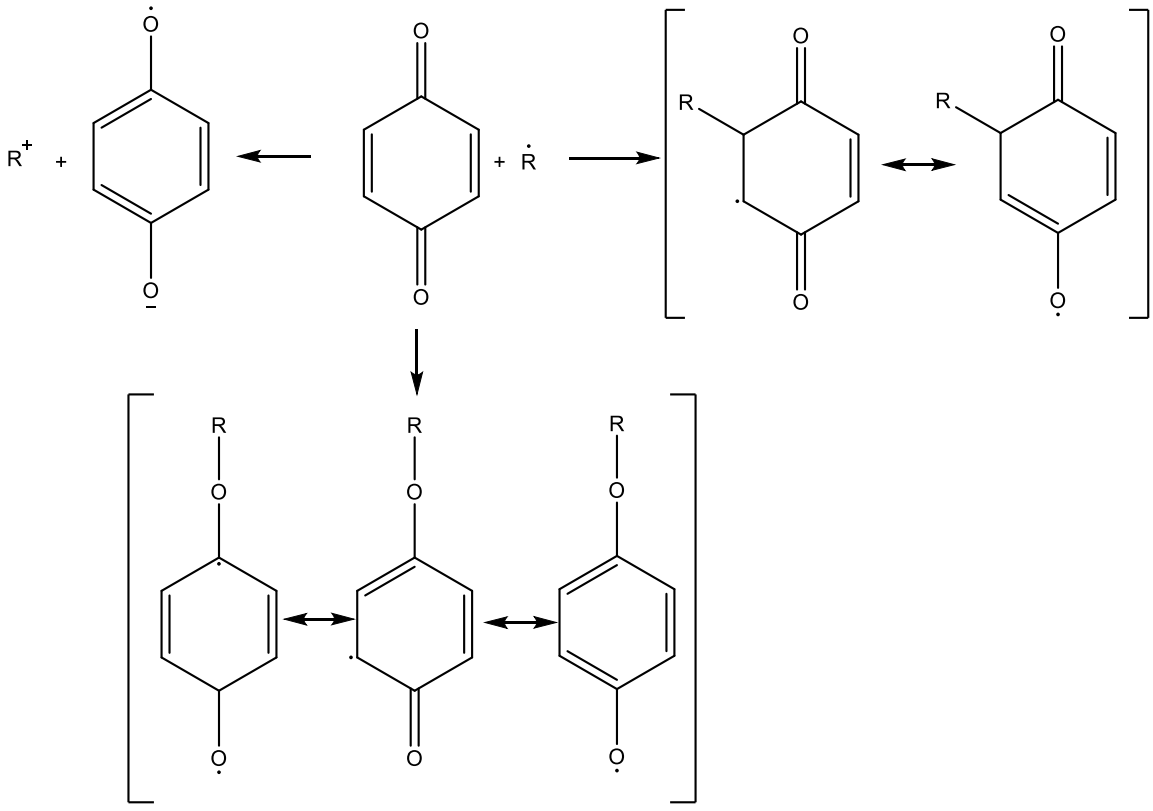
The use of micro/millireactors has generated interest over the past few years as an efficient method of continuous production of various chemical compounds, due to the high pressures and temperatures possible, combined with the potential for short residence times, particularly compared to conventional batch reactions. Henninger *et al*[53] have described methods to produce hydroxyalkyl (meth)acrylates based on the reaction between epoxies and (meth)acrylic acids, using various catalysts. A range of different inhibitors were utilised in the 0.005-0.050% concentration range, however the recommendation is for a blend of PMP and BHT.

Vrancken *et al* mentioned in their patent for the synthesis of polyester acrylates the use of PMP at 1000ppm.[32] Since this patent is amongst the earliest published works concerning the synthesis of (meth)acrylate resins, it has become regarded as the starting point of the acrylate resins industry and is probably the reason why PMP has become the inhibitor of choice.

The use of BHT and related compounds has been studied by Kovářová *et al* in degradation studies on low density polyethylene.[54] Although this has been done on solid polyolefins, rather than liquid resins, it is still interesting to note that even very low concentrations of inhibitors have a positive effect compared to virgin materials. Of the related compounds also studied, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate was the most promising. This particular material is commercially available as Irganox 1076 ex BASF.

2.2.5.2 Quinones

Quinones, such as HQ, may react with carbon centred radicals by addition at a carbon or oxygen atom, or by electron transfer. Normally the preferred reaction route is dependent upon the radical and the quinone, halogenated quinones preferentially react by electron transfer. The subsequent radical formed may then react with another radical to eliminate both. The complexity of the reaction mechanism, which is influenced by the redox potential of the quinone in question, means that the stoichiometric efficiency of the quinone in any given system can vary from 0.05 to 2 (see Scheme 2.12). The reaction mechanism involves the formation of an intermediate, although these are inherently unstable and will preferentially revert back to the more stable quinone form.

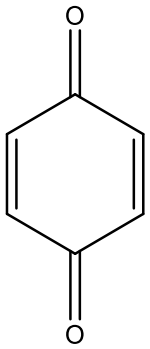


Scheme 2.12

While PMP has become the inhibitor of choice for the acrylate industry, the related unsaturated polyester industry have traditionally preferred the use of hydroquinone and other related quinones. Grohens *et al*[55] looked at the use 4-benzoquinone at a loading of 35ppm to enable the polyester to be synthesised, but this did not prevent gelation during

long term storage (>6 months at 20°C). The addition of up to 120ppm of either BHT or TBC. The use of a *tert*-butylcatechol did improve the high temperature stability of the resin, but it did require higher concentrations of peroxide to effect a cure compared to using a di-*tert*-butyl hydroquinone, which did not provide very good high temperature stability.

A commonly encountered inhibitor found in unsaturated polyesters is 1,4-benzoquinone (BQ) (**19**), and has found to be particularly effective used in conjunction with acrylic acid. Clonce *et al*[56] looked at a number of benzoquinones, and found that although BQ was effective, at 500ppm concentration both 2,5-diphenyl-4-benzoquinone and phenyl-4-benzoquinone offer better stability.



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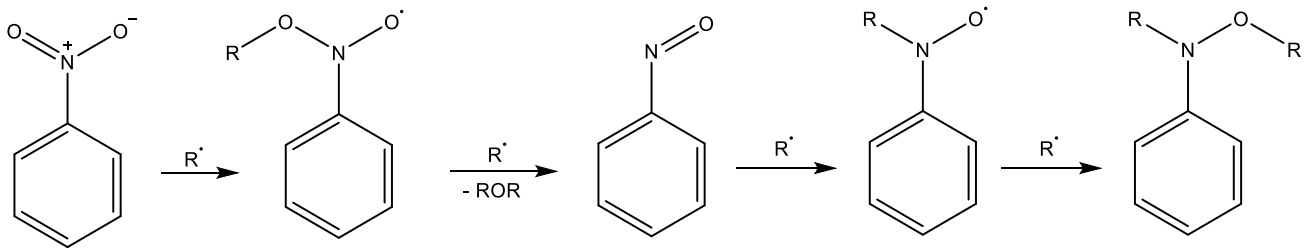
It should be noted that in the majority of the studies looking at phenolic inhibitors, air (or oxygen) is required in order to activate the free radical scavenging, however the availability of air is not as critical for quinones.

2.2.5.3 Nitro- and Nitroso-Compounds

Many nitro- and nitroso compounds have been utilised as spin traps in EPR spectroscopy, which has proved useful in determining radical reaction mechanisms. These same properties are very useful for use as polymerisation inhibitors. In particular aromatic nitro compounds have found an increasing commercial acceptance. Nitrobenzene is a case in point, which due to the various intermediates that the reaction mechanism goes through, up to 4 moles of radical sources may be eliminated for each mole of nitrobenzene (see Scheme 2.13).



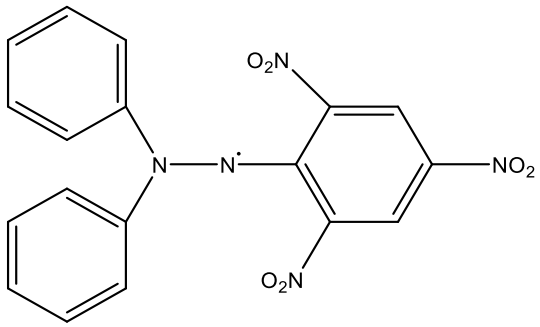
Scheme 2.13

2.2.5.4 Stable Radicals

In some respects this is the poacher turned gamekeeper. For radicals to be useful as inhibitors, the following characteristics are desired;

1. They should not add to, abstract from or otherwise react with monomers, oligomers, polymers, etc
2. They should not undergo self reaction or decomposition
3. They must react rapidly with other radicals present

There are a number of radicals that meet the above criteria that have been reported in the scientific and commercial literature, diphenylpicrylhydrazyl (DPPH) (**20**), triphenylverdazyl (**21**), Koelsch radical (**22**), triphenylmethyl (**23**), galvinoxyl (**24**) and 2,2,6,6-tetramethyl-1-piperdinyloxy (TEMPO) (**25**).



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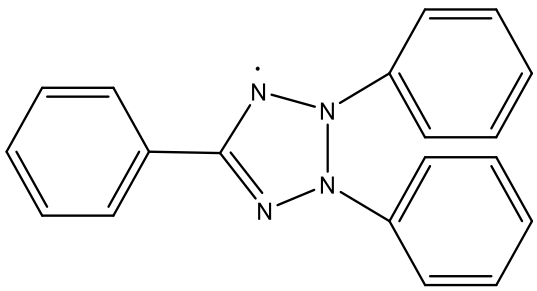

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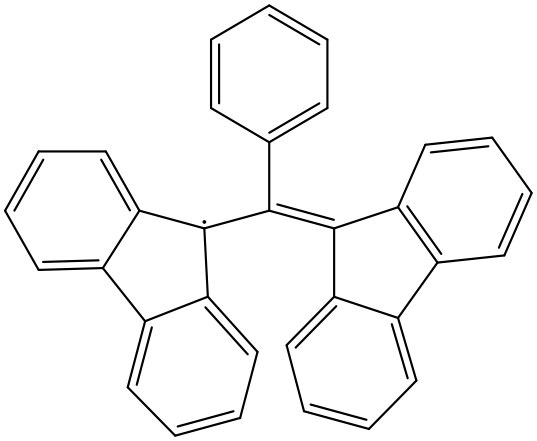

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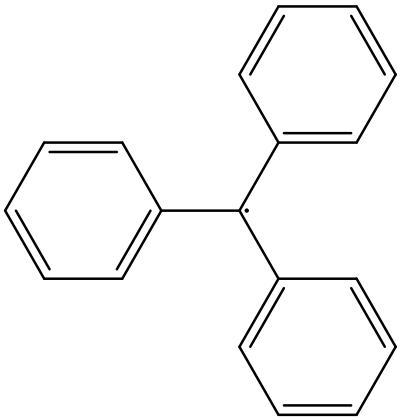

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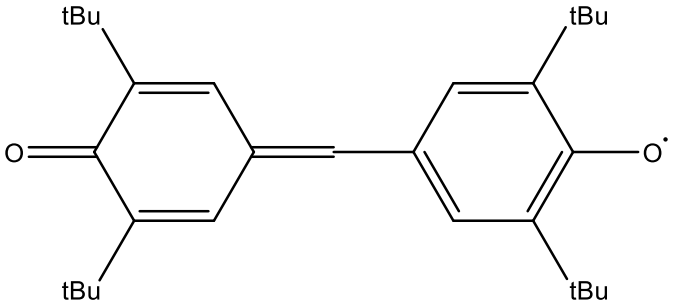

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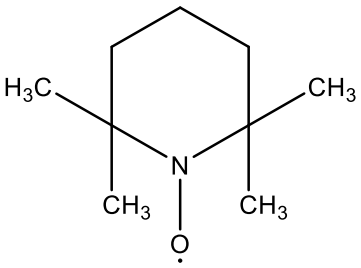

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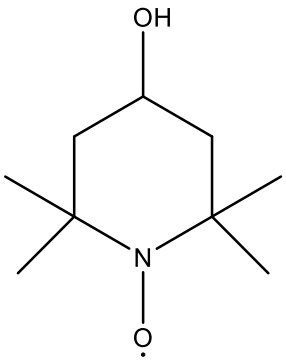

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All of the above have been used for practical applications, as well as been used for determining initiator efficiency and mechanistic pathways. It has been found that nitroxides do not trap oxygen centred radicals, but will react readily with carbon centred radicals. DPPH on the other hand shows no sign of selectivity in its reactivity and overall is a very efficient inhibitor.

The efficiency of stable radicals as a group is heavily dependent upon the reaction conditions. At elevated temperatures some of the stable radical-radical reactions may become reversible, which might lead to premature polymerisation. Some stable radical-radical reaction products may decompose to form a stable radical, hence become available for further radical elimination.

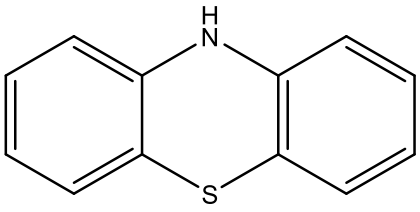
Bevington *et al*[57,58] investigated the effect of various stable radicals upon the resultant molecular weight (M_w), molecular weight number average (M_n) and polydispersity (M_w/M_n) of methyl methacrylate when polymerised by using benzoyl and lauroyl peroxides. In general as the inhibitor concentration increases, the average Mw decreases and the polydispersity becomes tighter. The effect on polydispersity was more noticeable with TEMPO and 4-hydroxy-2,2,6,6-tetramethyl-1-piperdinyloxy (4H-TEMPO) (**26**), than with DPPH. Ionita[59] reported that DPPH was experimentally found not to favour scavenging oxo-centred free radicals, despite theoretical kinetic data suggesting the contrary.

Fruchey *et al*[60] reported that the addition of 4H-TEMPO at 50ppm gave 30 to 46 hours of stability at temperature, compared to 1.5 hours for a combination of HQ and PMP (100 and 50ppm respectively). Satomoto *et al*[61] were looking at the inhibitor concentration in various (meth)acrylic monomers (acrylic acid, HEA, HEMA, HPA, HPMA, methyl methacrylate, etc) and found that even at very low concentrations 4H-TEMPO (0.01-1.0ppm) was comparable for stability to a number of phenolic inhibitors at higher concentrations (0.1-13.0ppm).

The use of 4H-TEMPO has attracted a reasonable amount of attention both in studies and industrially. Industrially the use of 4H-TEMPO was slightly cheaper than TEMPO, but since the patents on its manufacture have lapsed, the cost of the material has dropped significantly and made it commercially viable to use.

2.2.5.5 Phenothiazine

Phenothiazine (PTZ) (**27**) is known to be a good scavenger of both carbon and oxygen centred radicals. This is accomplished by hydrogen atom transfer. PTZ will work with almost equal efficiency in either aerobic or anaerobic conditions. This effect has been reported in a number of studies.



27

Becker and Vogel[62] reported that when examining the use of PTZ to stabilise acrylic acid during distillation, it give very similar performance as with PMP. However when there is no oxygen in the system, and PMP is present, the acrylic acid readily polymerises. With PTZ present the rate of polymerisation is considerably reduced, almost to the same level as when oxygen is present.

When examining the stabilisation of a butanol/acrylic acid reaction mixture, Niesbach *et al*[63] noted that when 2ppm of PTZ was added to the existing 200ppm of PMP that was present in the system, it was found that the time elapsed before the acrylic acid would begin to polymerise was double compared to only using the PMP. Additionally when the oxygen supply was withdrawn, the polymerisation of the acrylic acid occurred much quicker with only PMP present, the addition of the PTZ gave similar results compared to the times obtained with oxygen present.

Schröder[64] reported that during the esterification of (meth)acrylic acid with alcohol, if the alcohol used was too old (>7 days), then the concentration of hydroperoxides that has built up over time is sufficient to cause the acid to polymerise on to the catalyst beds that are used. In order to minimise, or eliminate, the undesirable polymerisation, the addition of 1000ppm of PTZ (based on alcohol concentration), plus an additional unspecified antioxidant (80-100ppm based on the peroxide number of the alcohol), was sufficient to prevent the premature polymerisation. This enabled the desired esterification reaction to proceed. Although the antioxidant is not specified, based on common industrial practices it is likely to be a compound related to BHT.

Levy[51,65] also looked at the use of phenothiazine for acrylic acid storage, and found that in all cases when compared to PMP, the use of PTZ in comparison was almost doubled the stability for the same concentration, even at elevated temperatures.

2.2.5.6 Transition Metal Salts

Some transition metals have been used as antioxidants and free radical scavengers. Under certain conditions it has been noted that rather than acting as a polymerisation inhibitor, the metal salts act as polymerisation catalysts. This appears to occur when the oxygen levels within the resin are depleted. Also since transition metal ions are introduced, they are often coloured, which can be a serious issue with the customer. In the 1990's some epoxy acrylates from certain manufacturers had a distinct green hue to them due to the presence of Cu_2O added as an inhibitor. Vrancken *et al*[32] reported in a study using Cu_2O as an inhibitor in the manufacture of polyester acrylates at 1000ppm.

Tweedy *et al*[66] looked at the synthesis of (meth)acrylic esters using microwaves. It was found that use of $Cu^{II}O$ at 500ppm gave 600s of stability during exposure to the microwaves, compared to 120s with 500ppm of hydroquinone and less than 90s with no inhibitor present. Since it is known that metal particles will reflect microwave energy, the extended time recorded could actually be a combination of polymerisation inhibition and energy reflection and dissipation.

In general it has become good practice to reduce the intentional presence of metal ions in resin systems to as low a level as possible to enable the resultant resin to be used in as wide a range of applications as possible and to minimise any possible substance migration.

2.3 Summary

There are a number of different resins that can be classified as vinyl ester resins. Commercially unsaturated polyesters are by far the largest volume, but the (meth)acrylate resins are normally more expensive per unit mass compared to polyesters. It is for this reason that the main focus of this study will be looking at (meth)acrylate resins, as they have a greater value per kilogram. There is also a wide range of inhibitors available, and no consensus over which is the most effective. Each segment of the resin industry has a preferred inhibitor, mainly due to historic practice. Likewise many companies have their own preferred inhibitor or blend that is used. In many cases the initial work was done many years ago and has not been reviewed or comparative testing undertaken. This study will evaluate a number of the more

commonly used inhibitors side by side under controlled conditions in a limited number of resins and determine which is better for each resin type.

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3 Resin Synthesis

3.1 Formulation Research

All of the experimental procedures are based on industrial bulk processes, which have been modified for manufacture on laboratory scale. The background to all of these industrial processes can be found in the patent and scientific literature, as well as various polymer chemistry textbooks,[1] and where only acrylates are mentioned, the use of the methacrylate analogue can be assumed due to the similarity in chemistry. In general the initial development work on epoxy and urethane chemistry was done in the 1930's, it was not until the 1950's that acrylated adducts were studied and reported. It then took a further 20 to 30 years for industrial processes to be worked up and commercial products released onto the market. Since then there has been continuous development in terms of the process and equipment used, but the fundamental underlying chemistry has remained unchanged.

Although the Michael addition reaction and mechanism was described by Michael[2] (1887), it was Hube[3] (1956) who was assigned a patent for the process of synthesising amine acrylates for use in paper manufacture and associated coatings. Gaske[4] (1974) reported the synthesis and use of amine acrylates in UV curable resins for the use of reducing oxygen inhibition at the surface of coatings, primarily for printing ink formulations.

The reaction of acid groups to epoxide group as a method of curing epoxies has a long history in the patent literature, however epoxy acrylates were patented by Payne and Smith[5] (1957) through a synthesis route of bisphenol A diglycidyl ether (BADGE) (**1**) and peracetic acid. Parker[6] (1959) was assigned a patent for the synthesis of an epoxy methacrylate via polymeric bisphenol A diglycidyl ether and methacryl chloride. The more typical reaction scheme of BADGE and acrylic acid was assigned to Hall[7] (1958), but with the use of triethylamine as the catalyst. The use of triphenylphosphine as a catalyst for opening the epoxide ring for further reactions was reported by Wittig and Haag[8] (1955) and was promoted by Degussa. A study by Neelam *et al*[9] (2004) has confirmed the esterification mechanism between BADGE and acrylic acid using triphenylphosphine as the catalyst. Other phosphorous containing groups were looked at in the 1950's as possible catalysts[10], but the low cost of triphenylphosphine prevented the commercialisation of these materials. However in recent years there has been a surge in interest as a potential method to introduce flame retardancy into a resin system. The use

of phosphine oxide containing compounds has been investigated by Espinosa *et al*[11,12] and Shau and Wang[13], and phosphorous amines by Mercado *et al*[14].

Similarly the reaction of an acid group with an alcohol to synthesis an ester is well known and recorded, Woodhouse[15] (1938) was assigned a patent for a synthesis process for esters of methacrylic acid from alcohols and methyl methacrylate. Neker *et al*[16] (1954) developed a synthesis process for acrylic esters using acrylic acid. It was not until Vrancken *et al*[17] (1976) that mention was made of using a radiation source as a method of curing the synthesised polyester acrylates. The majority of what are termed (meth)acrylate monomers within the UV curing industry are actually low molecular weight polyester (meth)acrylates, often a polyether glycol reacted with the correct molar stoichiometric quantity of (meth)acrylic acid. A good overview of the processes involved in the synthesis of unsaturated polyesters is given by Braun *et al*[18] and Sorenson *et al*.[19]

The original patent assigned to Bayer[20,21] (1942) for the synthesis of urethanes and polyurethanes mentions the reaction of diisocyanates with 2-hydroxyethyl acrylate (HEA) (**4**) and 2-hydroxyethyl methacrylate (HEMA) (**5**). This was further developed by Kleiner *et al*[22] (1953) in a patent describing the synthesis of polyurethane adhesives. Initially thermal curing of acrylates and methacrylates was the prime focus of the early patents, but Stiling *et al*[23] (1970) were assigned a patent to cover the use of UV light for the curing of monomers, oligomers and/or polymers containing vinyl groups.

3.2 Polymer Synthesis

3.2.1 Materials

The bulk of the materials used were commercially available grades, purchased where possible direct from the manufacturer, otherwise materials were purchased from either Fisher Scientific, Sigma-Aldrich or VWR. The materials were used as supplied without any additional processing unless otherwise mentioned.

3.2.2 Analytical Methods

The acid value[24] was determined by taking between 1-5g of the sample and dissolving in 50g of a 2:1 neutralised toluene/methanol solvent blend. 4-5 drops of 1% phenolphthalein solution was added and then titrate against 1.0N potassium hydroxide solution until light pink in colour. The acid value was then calculated as per equation 3.1

$$\text{Acid Value (mgKOH/g)} = \frac{\text{Titre (ml)} \times 56.1 \times \text{KOH Molarity}}{\text{Sample mass (g)}}$$

Equation 3.1

The isocyanate content[25] was determined by taking 5g of sample and dissolving in 100ml of dry methanol and 25ml of dibutylamine. 5 drops of bromophenol blue indicator was added and then titrated with 1.0N hydrochloric acid to a colour change from blue to yellow. The isocyanate content was calculated as per equation 3.2

$$\text{NCO content (\%)} = \frac{[\text{Blank} - \text{Sample titre (ml)}] \times 4.202 \times \text{HCl Molarity}}{\text{Sample mass (g)}}$$

Equation 3.2

The amine value[26] was determined by taking 1g of sample and dissolved in 50ml of neutralised propan-2-ol. 5 drops of bromophenol blue indicator was added and then titrated with 1.0N hydrochloric acid to a colour change from blue to yellow. To measure the tertiary amine value 10g of acetic anhydride would be added to the sample after dissolving it in propan-2-ol and leaving for 5 minutes at room temperature. Then continue as normal adding 5 drops of bromophenol blue and titrating with hydrochloric acid. The amine value is calculated as per equation 3.3.

$$\text{Amine value (mgKOH/g)} = \frac{\text{Titre (ml)} \times 56.1 \times \text{HCl molarity}}{\text{Sample mass (g)}}$$

Equation 3.3

The epoxy value[27] was determined by taking 0.5 – 5.0g of sample and dissolving in 10ml of 20% solution of tetraethyl ammonium bromide in glacial acetic acid. 1 drop of crystal violet solution was added and titrated with 1.0N perchloric acid from purple to apple green. The epoxy value is calculated as per equation 3.4.

$$\text{Epoxy value (mgKOH/g)} = \frac{\text{Titre (ml)} \times 56.1 \times \text{HClO}_4 \text{ molarity}}{\text{Sample mass (g)}}$$

Equation 3.4

The following charts show the typical reaction profiles encountered for an 1,6-hexandiol amine acrylate reaction (see Chart 3.1), a bisphenol A epoxy acrylate reaction (see Chart 3.2) and an isophorone polyethylene urethane acrylate reaction (see Chart 3.3).

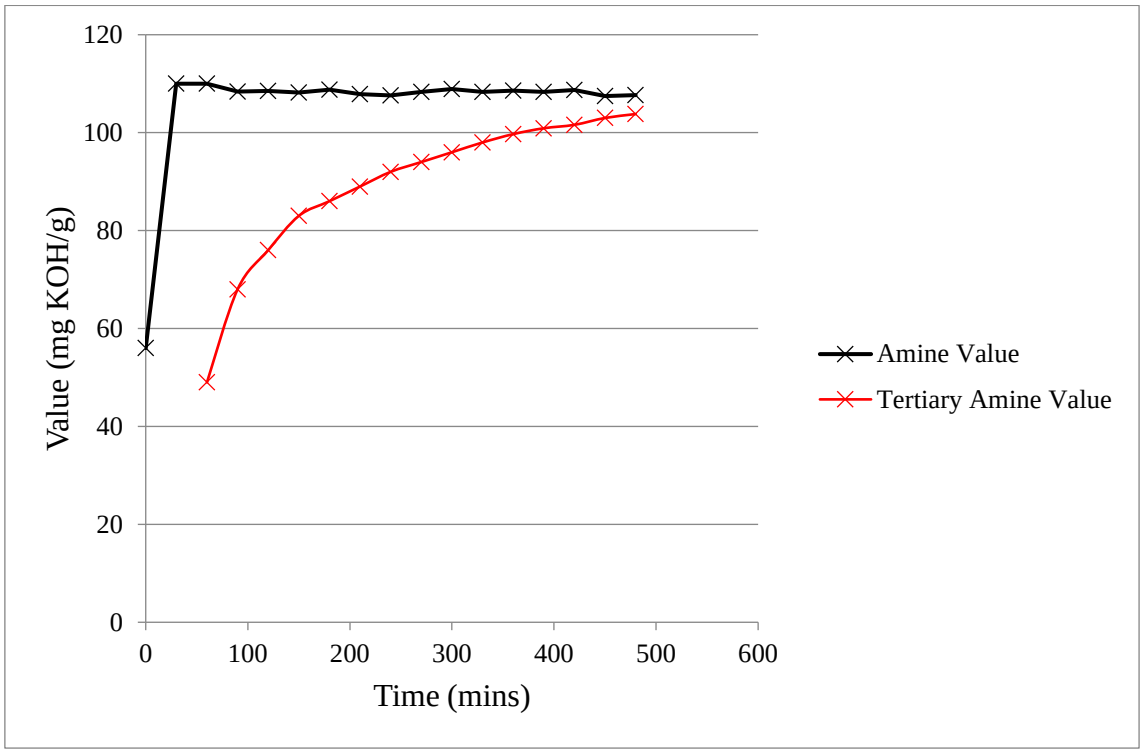


Chart 3.1 – Amine Acrylate Reaction Profile

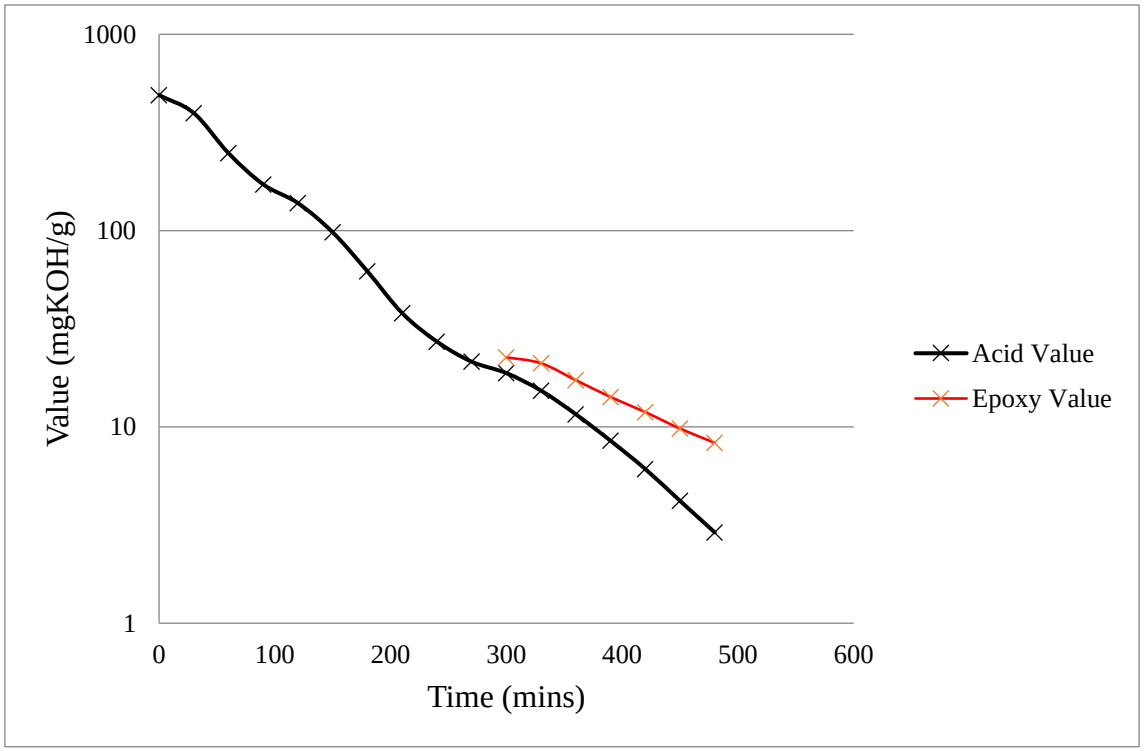


Chart 3.1 – Epoxy Acrylate Reaction Profile

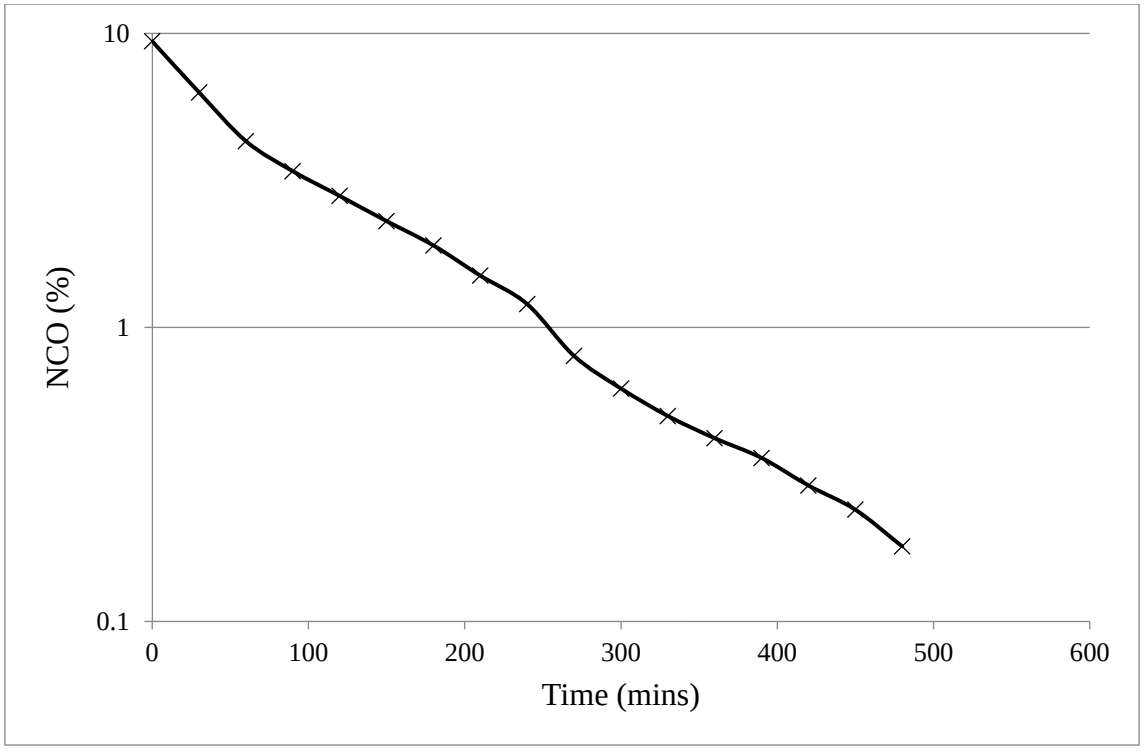


Chart 3.3 – Urethane Acrylate Reaction Profile

The resins produced above were characterised by FT-IR (Bruker ALPHA with a Platinum ATR accessory) and GPC (Agilent PL-GPC50 Plus with 2 x PLgel MIXED-E columns and a refractive index detector, using polystyrene reference standards) to ensure reactions were complete and the desired structure and molecular weight material was synthesised.

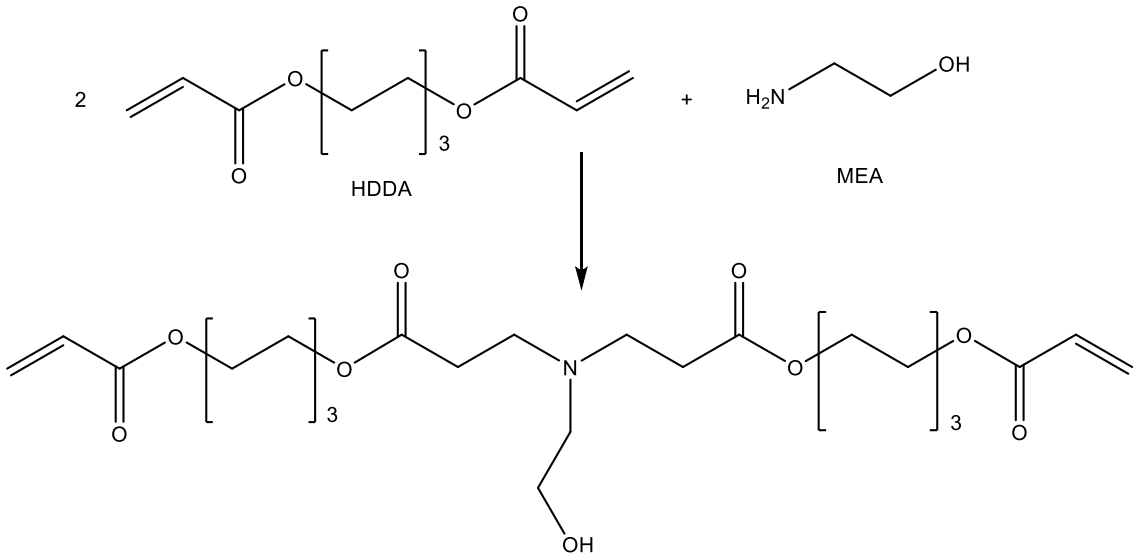
The viscosities of the samples were checked after reaching the required specifications, and again after 24 hours to ensure that the reaction was complete using a Brookfield CAP 2000 cone and plate viscometer, fitted with an appropriate cone for the anticipated viscosity range.

3.3 Amine Acrylate and Methacrylate Synthesis

3.3.1 1,6-Hexanediol Amine Acrylate

The synthesis of 1,6-hexanediol amine acrylate was carried out under standard atmosphere and pressure using a jacketed reaction vessel connected to a temperature controller filled with glycol heating fluid. In a 1 litre reaction vessel, equipped with an anchor stirrer, sampling port, temperature probe and an air cooled condenser, 666.7g (2.95 mol) of 1,6-hexanediol diacrylate (SR238 ex Arkema) and 45.0g (0.737 mol) of ethanolamine (MEA ex BASF) was charged. The vessel was allowed to exotherm to a

maximum temperature of 90°C, then cooled to 40°C with the stirrer switched on. The vessel was held at temperature for 30 minutes, then 45.0g (0.737 mol) of ethanolamine was charged. The vessel was allowed to exotherm and then cooled to 60°C after the exotherm had peaked and held at temperature. After 30 minutes the reaction mixture was sampled to determine the amine value. Additional ethanolamine was charged to bring the amine value to 100-110mgKOH/g, the exact amount required is determined by the purity of the diacrylate used. After 30 minutes the reaction mixture was sampled to determine both the amine and tertiary amine values, to enable the reaction progress to be monitored. The reaction mixture was sampled hourly until both the amine and tertiary amines values obtained agree within 5mgKOH/g. Compound HDDA-MEA (**28**).



HDDA-MEA - **28**

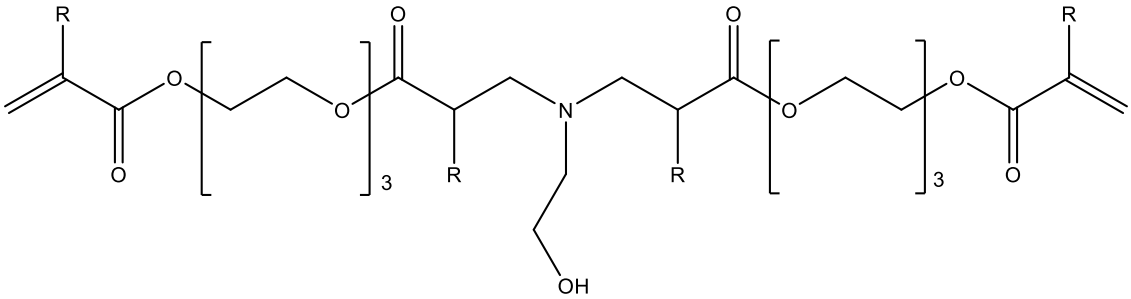
Scheme 3.1

3.3.2 Other Amine Acrylates and Methacrylates

Following the same process and equipment set up as above, three other compounds were synthesised, an additional acrylate, and the methacrylate analogues for comparison. The monomers used were, 1,6-hexanediol dimethacrylate (SR239 ex Arkema) (HDDMA), triethylene glycol diacrylate (SR272 ex Arkema) (TEGDA) and triethylene glycol dimethacrylate (SR205 ex Arkema) (TEGDMA). Formulation details are summarised in Table 3.1, the target amine values calculated based upon the purity of the (meth)acrylate and amines used.

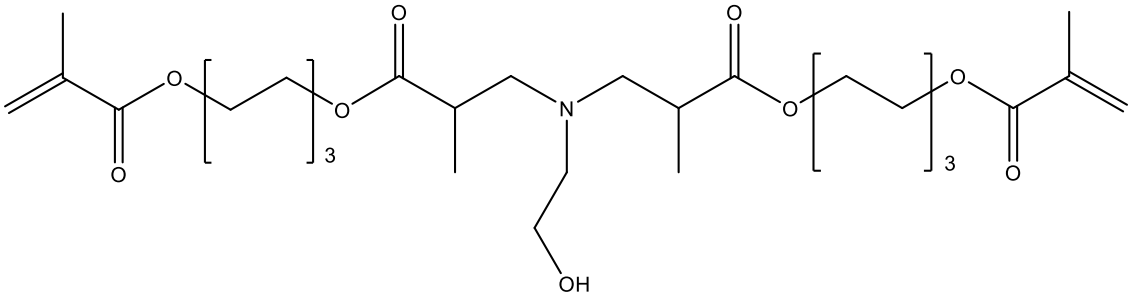
Monomer (2.95mol)		MEA (1.475mol)	Target Amine Value (mgKOH/g)	Compound
TEGDA	749.3g	90.0g	90-100	TEGDA-MEA (**29**)
HDDMA	761.1g	90.0g	85-95	HDDMA-MEA (**30**)
TEGDMA	843.7g	90.0g	80-90	TEGDMA-MEA (**31**)

Table 3.1 – Synthesis of Amine (Meth)Acrylate Compounds



Where R = H TEGDA-MEA - **29**

R = CH_3 TEGDMA-MEA - **31**



HDDMA-MEA - **30**

3.3.3 Discussion

Table 3.2 gives details of the theoretical molecular weight based upon the chemical structure, the molecular weight (Mn) and polydispersity index (PDI) obtained by GPC for the amine (meth)acrylate resins produced.

It was found that the first laboratory made samples of HDDA-MEA were prone to gelling before the reaction was complete, even when conducted at room temperature. However when the samples were remade with a fresh sample of ethanolamine from a different

manufacturer (material purchased from BASF compared to material purchased from Fisher Scientific), there was no problem experienced in utilising the same process. The most likely cause for this would be due to the presence of a high level of free radicals present in the older sample (3 years old) compared to the fresh (2 months), especially since at the time Fisher Scientific purchased their amines from BASF. There is a need to enable rapid cooling of the sample after the exotherm, so as to control the amount of heat within the reaction mixture, also step wise addition of the amine to the (meth)acrylate is required so as to minimise the formation of a polymer rather than the desired oligomer. Normally commercially manufactured resins would contain additional inhibitor to stabilise the acrylate group and to enable higher temperatures to be used and reduce processing time.

Compound	Theoretical MW	GPC MW (M_n)	PDI
HDDA-MEA	513	516	1.35
TEGDA-MEA	577	578	1.56
HDDMA-MEA	569	571	1.29
TEGDMA-MEA	633	635	1.61

Table 1.2 – Molecular Weight Comparison between Amine (Meth)Acrylate Compounds Synthesised

As discussed in section 2.1 the difference in reactivity between the acrylate and methacrylate analogues of materials with the same backbone is noticeable in the reaction between the two. The acrylate has a very rapid exotherm, over a short time scale, while the methacrylate analogue generates a similar amount of heat over a longer time scale. This can be observed in the amount of time taken to reach the desired tertiary amine value for the same heating profile.

3.4 Epoxy Acrylate and Methacrylate Synthesis

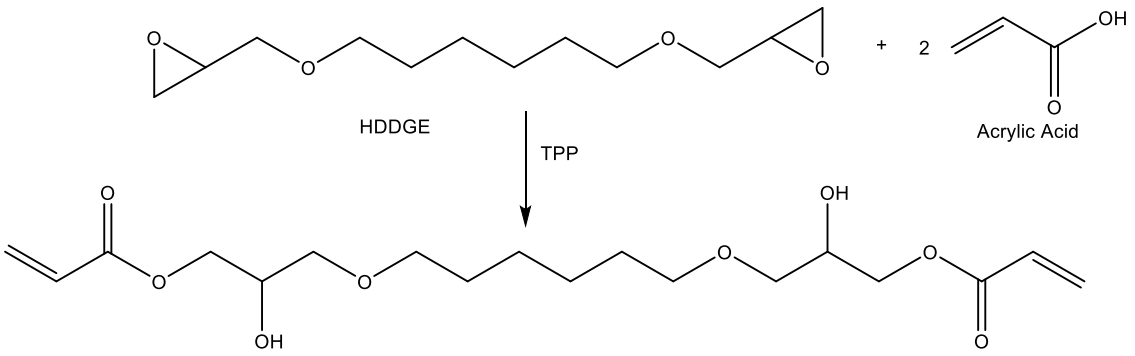
The epoxies that have been used for the synthesis are all nominally difunctional, hence can also be referred to in the literature as diglycidyl ethers.

3.4.1 1,6-Hexanediol Epoxy Acrylate

The synthesis of the 1,6-hexanediol epoxy acrylate was carried out under standard atmosphere and pressure using a jacketed reaction vessel connected to a temperature controller filled with glycol heating fluid. In a 1 litre reaction vessel, equipped with an anchor stirrer, sampling port, temperature probe and an air cooled condenser, 259.2g (3.60 mol) of acrylic acid (Glacial Acrylic Acid ex BASF) was added. The vessel was heated to 40°C with the stirrer switched on. 103.5g (0.45 mol) of 1,6-hexanediol diglycidyl ether (DER 734 ex Olin Epoxy) (HDDGE) and 0.85g ($3.25x10^{-3}$mol) of triphenylphosphine (TPP ex Evonik) was added and stirred for 10 minutes. The vessel was heated to 75°C over 20-30 minutes. The reaction was allowed to exotherm, with cooling provided if the vessel temperature exceeded 95°C. Once the exotherm had subsided, the temperature was maintained at 80-85°C and the reaction mixture sampled after 30 minutes for acid value.

When the acid value had dropped below 30mgKOH/g, then the vessel was cooled to 75-80°C. The process was repeated three more times, in each case 103.5g (0.45 mol) of HDDGE was charged to give a total of 4 epoxy charges. The same temperature profile of heating and cooling was undertaken aiming for an acid value of below 30mgKOH/g.

After the addition of the fourth epoxy charge, the standard heating and cooling profile was followed, the reaction mixture was sampled after 30 minutes for acid value. When the acid value had dropped below 25mgKOH/g, the vessel temperature was increased to 110°C and the reaction mixture sampled every 60 minutes. When the acid value had dropped below 20mgKOH/g, the reaction mixture was also sampled for epoxy value. The epoxy/acid value balance was maintained so that the epoxy value was 5mgKOH/g higher than the acid value, ensuring that there was an excess of epoxy present. Additional epoxy or acrylic acid was charged as required to maintain the epoxy/acid value balance, this is due to the batch to batch variation in the purity of the epoxy resin. The temperature was increased to 112°C if the rate of reaction had slowed. When the acid value was below 3mgKOH/g, and the epoxy value below 9mgKOH/g, then the vessel was cooled and the reaction mixture decanted off. Compound HDDGEDA (**32**).



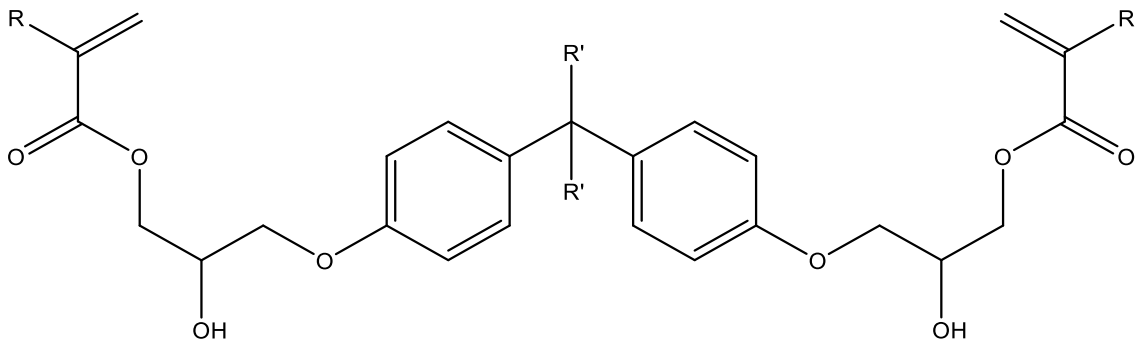
HDDGEDA - **32**

3.4.2 Other Epoxy Acrylates and Methacrylates

Following the same process and equipment set up as above, 5 other compounds were synthesised, 2 additional acrylate, and the methacrylate analogues for comparison. The epoxies used were, bisphenol A epoxy (DER 331 ex Olin Epoxy) (BADGE) and bisphenol F epoxy (DER 354 ex Olin Epoxy) (BFDGE) and methacrylic acid (Visiomer GMAA ex Evonik). Formulation details are summarised in Table 3.3.

Epoxy (1.80mol)		Acid (3.60mol)		TPP ($3.25x10^{-3}$mol)	Compound
HDDGE	422.0g	GAA	259.2g	0.85g	HDDGEDA (**32**)
BADGE	612.0g	GAA	259.2g	0.85g	BADGEDA (**33**)
BFDGE	561.6g	GAA	259.2g	0.85g	BFDGEDA (**34**)
HDDGE	414.0g	GMAA	309.6g	0.85g	HDDGEDMA (**35**)
BADGE	612.0g	GMAA	309.6g	0.85g	BADGEDMA (**36**)
BFDGE	561.6g	GMAA	309.6g	0.85g	BFDGEDMA (**37**)

Table 3.3 – Synthesis of Epoxy Di(Meth)Acrylate Compounds

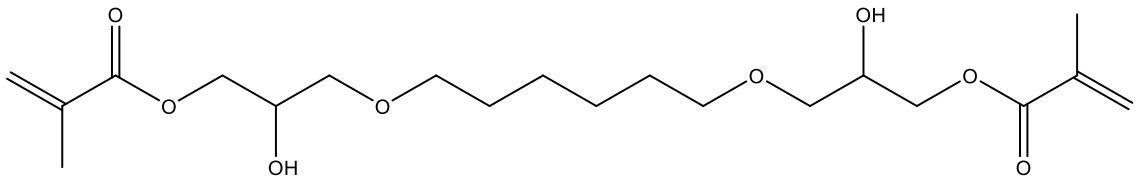


Where R = H and R’ = H BFDGEDA - **34**

R = H and R’ = CH_3 BADGEDA - **33**

R = CH_3 and R’ = H BFDGEDMA - **37**

R = CH_3 and R’ =CH_3 BADGEDMA - **36**



HDDGEDMA - **35**

3.4.3 Bisphenol A Epoxy Acrylate – Alternative Inhibitor Removal

An alternative method for removing the inhibitors used in acrylate synthesis is to first remove the inhibitors found in the acrylic acid by filtration via activated charcoal. The most commonly encountered inhibitor in commercial (meth)acrylic acid is methyl hydroquinone[28] (MeHQ) (150-500ppm) with hydroquinone (HQ) less frequently, however phenothiazine[29] (PTZ) is recommended as an emergency inhibitor to prevent polymerisation. The filtered acrylic acid is then directly used in the same process and equipment setup as described above for the BADGEDA, except that a 2 litre reaction vessel was used, with the addition of 0.5g ($4.6x10^{-3}$mol) of HQ to the acrylic acid.

HQ is water soluble (70mg/ml) and has a preference for the aqueous phase (pH 7), over the organic/resinous phase. Once the material was in specification, the reaction mixture was cooled to 40-45°C, to which 200ml of distilled water was added and the stirrer

switched on for 5-10 minutes. The stirrer was switched off and the reaction mixture was allowed to settle into 2 phases over 15-20 minutes. The aqueous phase was syphoned off and a further 200ml of distilled water added and the process repeated. After the aqueous phase was syphoned off, the resin was dried under vacuum (-0.85-0.90 bar) for 15-20 minutes. With the removal of the inhibitors, the resultant material would begin to gel within 30 minutes at room temperature. The prepared samples would be transferred to a freezer (<-5°C) and stored until required.

3.4.4 Discussion

The addition of the epoxy to the acrylic acid was found to be more consistent than the addition of the acrylic acid to the epoxy, particularly with BAGDE which has a high viscosity (12-14000 mPas @ 20°C). Care needs to be taken with the heat up rates, depending on the vessel size and the amount of reactant. If the vessel is heated too quickly and the vessel is less than half full, then there is a very high probability of a strong exotherm developing after the epoxy aliquot is charged, conversely, if a low heating rate is used, then the reaction will stall and the acrylic acid will begin to self-polymerise. Once all of the epoxy has been charged, if the temperature is not gradually increased to drive the reaction forward (as indicated by the steady decrease in the acid and epoxy values), then the free acid and/or epoxy may start to self-polymerise, and the heat generated might cause the epoxy acrylate to polymerise to form a gel.

If particles of gelled material form, then if it is possible to remove them from the reaction mixture, then it might be possible to retrieve the batch, otherwise these particles act as seeding sites. Often after a reaction there is a ring of gelled material found around the inside of the vessel at the level of the mixture, it is good practice to remove this before commencing the next batch, even if the same material is to be produced next. Generally if the gel is soft, then it is due to the acrylic acid, while a hard gel is either due to the epoxy or the epoxy acrylate, this has been confirmed by FT-IR analysis, with the presence of a peak at 900-920cm-1 due to the carbon-oxygen bond stretching of the oxirane ring, or a peak at 1630-1635cm-1 due to carbon-carbon double bond stretching of the vinyl group indicating whether the (meth)acrylate or the epoxide group has reacted respectively. The heat up rates have to be experimentally determined for each vessel used by trial and error.

As discussed previously, the epoxy ring is opened by the triphenylphosphine to allow the acid group to react, thereby creating an ester linkage. The low concentration of triphenylphosphine used does not appear to have any affect upon the flammability of the resultant resin.[30] Despite the common name there are no epoxy groups present in epoxy (meth)acrylates. Table 3.4 gives details of the molecular weight and the percentage of vinyl ester group present for the epoxy (meth)acrylate resins produced.

Compound	Theoretical MW	GPC MW (M_n)	PDI
HDDGEDA	374	375	1.27
BADGEDA	484	483	1.84
BFDGEDA	456	456	2.01
HDDGEDMA	402	404	1.37
BADGEDMA	512	513	1.79
BFDGEDMA	484	487	1.97

Table 3.4 – Molecular Weight Comparison between the Epoxy Di(meth)acrylate Compounds Synthesised

The gel time of the epoxy acrylates and methacrylates were determined by mixing 10.00 grams of resin, with 2.00g of toluene to lower the viscosity for the resins and 0.10g of N,N,Di-(2-hydroxyethyl)-*p*-toluidine (Pergaquick A150 ex Pergan) to act as the peroxide accelerator. To the mixture 0.40g of 50% dibenzoyl peroxide (Peroxan BP-50 BZ Paste ex Pergan), also known as benzoyl peroxide, was added. The stopwatch was started as soon as the peroxide was added. All the base resins had 200ppm of 4-methoxy phenol (PMP) added to them before the test. The gel times at 20°C are recorded in Table 3.5. As can be seen there is a significant difference in the time taken to gel between the acrylate and methacrylate analogues, with the acrylate being more than twice as fast as the methacrylate. There does not appear to be much difference in reactivity between aliphatic and aromatic resins. Although there are structural differences between bisphenol A and F, with the propyl group present as the bridge between the 2 aromatic rings with bisphenol A in comparison to the methyl bridge with bisphenol F. Structurally commercial bisphenol A is supplied at 97% of the 4,4’ isomer, while bisphenol F is supplied as mixture of 2,2’, 2,4’ and 4,4’ isomers in the ratio of 16.0:43.8:40.2.[31]

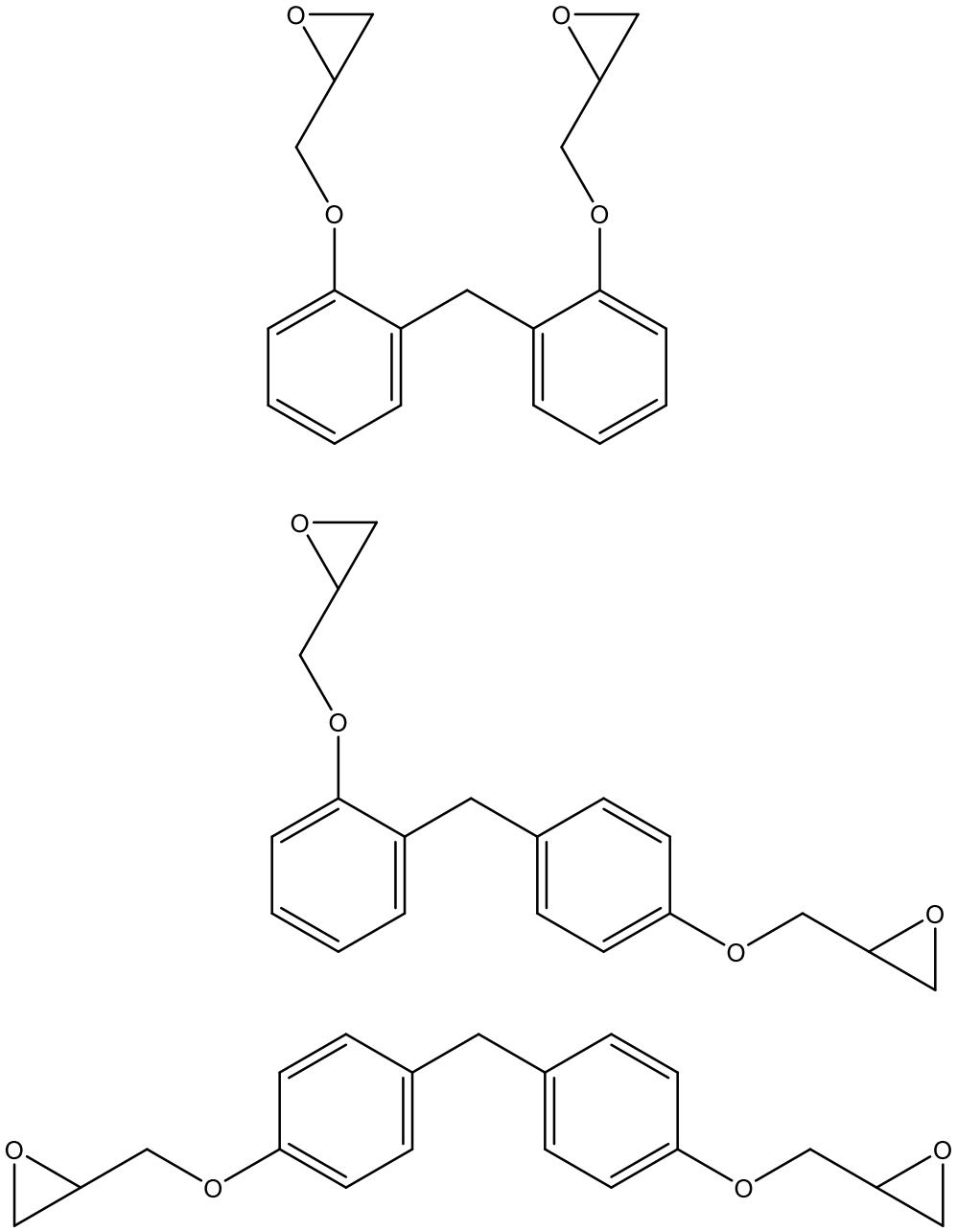


Figure 3.4 – Isomers of BFDGE – Top 2,2', Middle 2,4', Bottom 4,4'

Samples of the resins were tested under the same conditions without addition of N,N,Di-(2-hydroxyethyl)-*p*-toluidine, but all took longer than 1 hour to cure at 20°C. A cure time of less than 2 minutes was recorded with acrylate samples, and less than 4 minutes for methacrylate samples when cured at 80°C.

Resin	Gel Time (Seconds)
HDDGEDA	90
BADGEDA	90
BFDGEDA	100
HDDGEDMA	240
BADGEDMA	220
BFDGEDMA	220

Table 3.5 – Resin Relative Reactivity

3.5 Urethane Acrylate and Methacrylate Synthesis

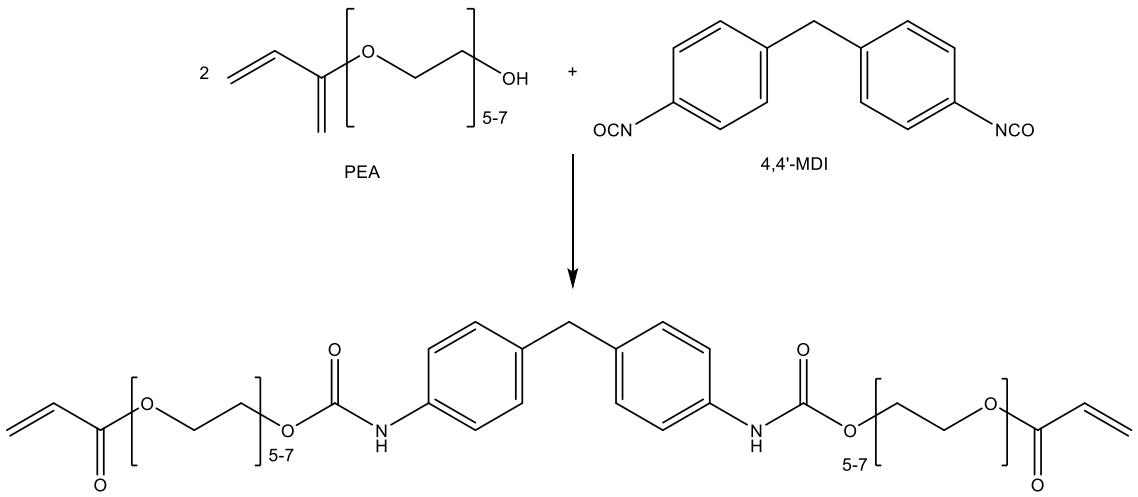
3.5.1 Polyethylene Glycol Based Urethanes

Due to the differences in reactivity between the diisocyanates, all the aliphatic diisocyanates had a small amount of metal catalyst (dibutyltin dilaurate) added to the reaction mixture to promote the urethane formation.[32] The aromatic diisocyanates were sufficiently reactive not to require the addition of a catalyst.

3.5.1.1 Diphenylmethane Polyethylene Glycol Urethane Diacrylate

The synthesis of the urethane acrylate was carried out under standard atmosphere and pressure using a jacketed reaction vessel connected to a temperature controller filled with glycol heating fluid. In a 1 litre reaction vessel, equipped with an anchor stirrer, sampling port, temperature probe and an air cooled condenser, 672.0g (2.0 mol) of polyethylene hydroxy acrylate (Bisomer PEA6 ex GEO Speciality Chemicals) (PEA) and 250.0g (1.0mol) of diphenylmethane-4,4'-diisocyanate (Desmodur 44MC ex Covestro) (4,4'-MDI) was added. The vessel was heated to 65°C with the stirrer switched on. After 4 hours at 65°C the viscosity of the reaction mixture had noticeably increased and a sample was taken to determine the isocyanate content. Sampling was continued every 60 minutes to monitor the reaction, with the temperature of the vessel increased to 70°C when the rate of reaction had noticeably decreased. Once the isocyanate content had dropped below 0.2%, then the vessel was cooled and the reaction mixture decanted off. The lower the free isocyanate content at the end of synthesis, the more stable the resultant compound during storage. The viscosity of the resin remains stable, while with free isocyanate

contents above 0.2% there is a chance of further reactions taking place during storage and the viscosity of the resin increasing over time. Compound 4,4'-MDI-PEA (**38**).



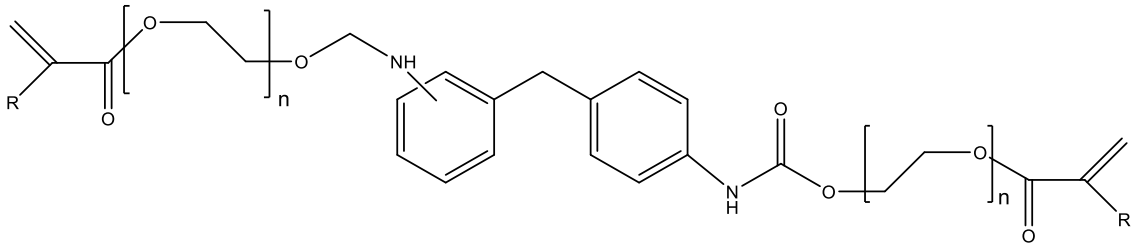
MDI-PEA - **38**

3.5.1.2 Other Polyethylene Glycol Urethane Diacrylate and Dimethacrylates

Following the same process and equipment set up as above, 7 other compounds were synthesised, 4 additional acrylate, and 3 methacrylate analogues for comparison. The diisocyanates used were, a 60/40 diphenylmethane-2,4'-diisocyanate and diphenylmethane-4,4'-diisocyanate blend (Desmodur 2460M ex Covestro) (MDI), isophorone diisocyanate (Vestanat IPDI ex Evonik) (IPDI), an 80/20 2,4-toluene diisocyanate and 2,6-toluene diisocyanate blend (Desmodur T80 ex Covestro) (TDI) and dicyclohexamethylene diisocyanate (Vestanat H_{12}MDI ex Evonik) (HMDI). The methacrylate hydroxy monomer used was polyethylene hydroxy methacrylate (Bisomer PEM6 LD ex GEO Speciality Chemicals) (PEM), while the catalyst used was dibutyltin dilaurate (DABCO T-12N ex Evonik) (DBTDL). Formulation details are summarised in Table 3.6.

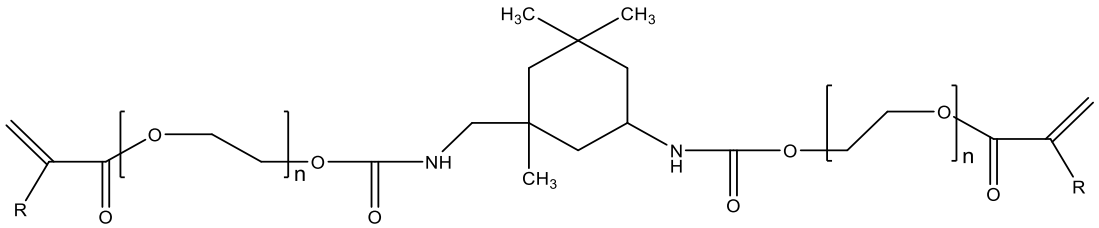
Isocyanate (1.00mol)		Hydroxy Monomer (2.00mol)	DBTDL ($1.58x10^{-3}$mol)	Compound
MDI	250.0g	672.0g	-	MDI-PEA (**39**)
IPDI	222.0g	672.0g	0.01g	IPDI-PEA (**40**)
TDI	174.0g	672.0g	-	TDI-PEA (**41**)
HMDI	262.0g	672.0g	0.01g	HMDI-PEA (**42**)
MDI	250.0g	700.0g	-	MDI-PEM (**43)**
IPDI	222.0g	700.0g	0.01g	IPDI-PEM (**44**)
HMDI	262.0g	700.0g	0.01g	HMDI-PEM (**45**)

Table 3.6 – Synthesis of Urethane Polyethylene Glycol Compounds



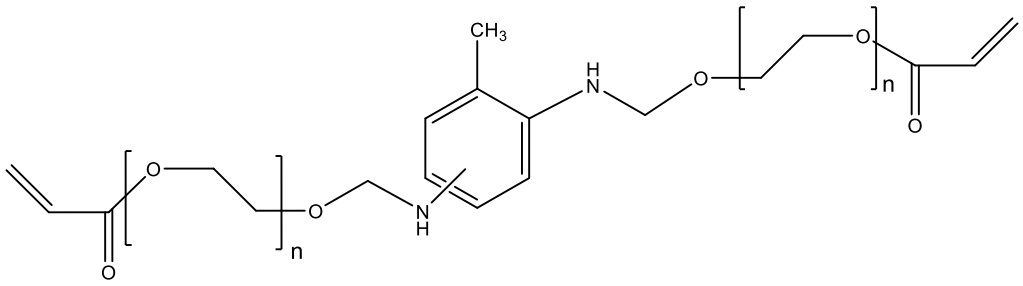
Where n = 5-7 and R = H MDI-PEA - **39**

n = 5-7 and R = CH_3 MDI-PEM - **43**

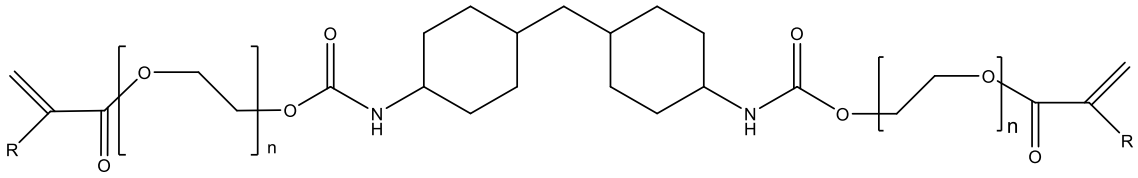


Where n = 5-7 and R = H IPDI-PEA - **40**

n = 5-7 and R = CH_3 IPDI-PEM - **44**



Where n = 5-7 TDI- PEA - **41**



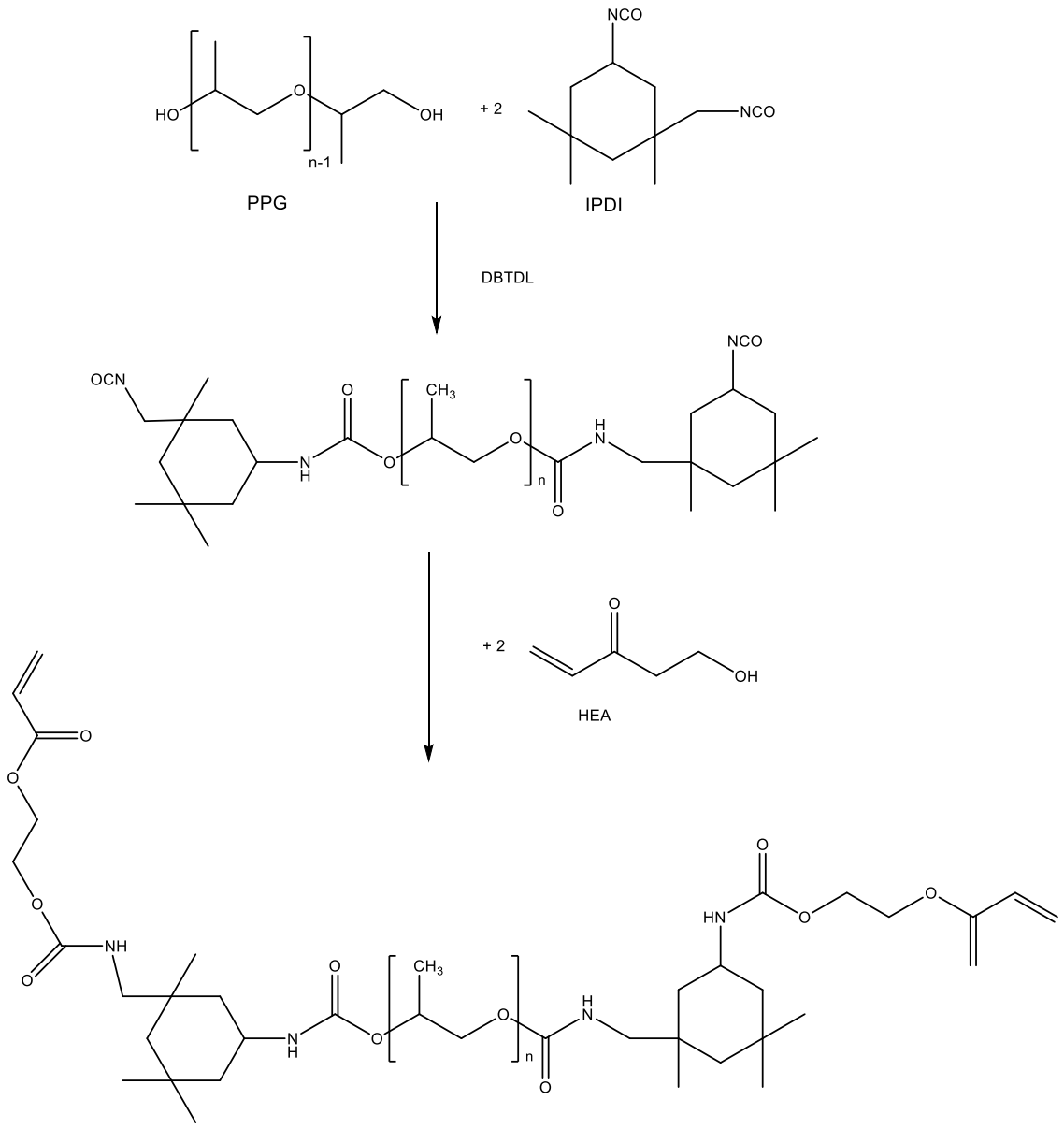
Where n = 5-7 and R=H HMDI-PEA - **42**

n = 5-7 and R=CH3 HMDI-PEM – **45**

3.5.2 Polypropylene Glycol Based Urethanes

3.5.2.1 Isophorone Polypropylene Glycol Urethane Diacrylate

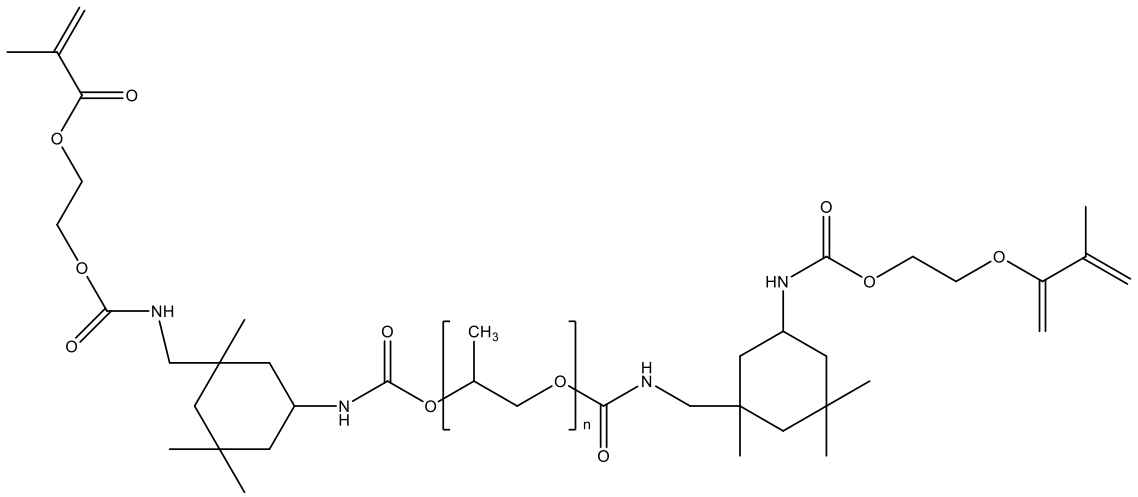
Following the same equipment set up as above, 500.0g (0.5 mol) of polypropylene glycol 1000 (Voranol 1010L ex Dow Polyurethanes) (PPG1000), 222.0g (1.0 mol) of IPDI and 0.01g ($1.58x10^{-5}$ mol) of DBTDL was charged into the vessel. The vessel was heated to 65°C with the stirrer switched on. After 2 hours at 65°C the viscosity of the reaction mixture was sampled to determine the isocyanate content. When the isocyanate content reached 12.0 – 11.5%, 116.0g (1.0 mol) of 2-hydroxyethyl acrylate (HEA ex BASF) was charged @ 65°C and allowed to react for 1 hour, before increasing the temperature to 70°C and holding for a further hour, before being sampled. Sampling was continued every 30 minutes to monitor the reaction, with the temperature of the vessel increased to 75°C when the rate of reaction had noticeably decreased. Once the isocyanate content had dropped below 0.2%, then the vessel was cooled and the reaction mixture decanted off. Due to the difference in reactivity between the 2 isocyanate groups on any diisocyanate compound it is possible to undertake this synthesis as a two stage reaction. Compound IPDI-PPGA (**46**).



Where n = 60-64 IPDI-PPGA – **46**

3.5.2.2 Isophorone Polypropylene Glycol Urethane Dimethacrylate

Following the same process and equipment set up as above, 500.0g (0.5 mol) of polypropylene glycol 1000, 222.0g (1.0 mol) of IPDI and 0.01g ($1.58x10^{-5}$ mol) of DBTDL was reacted. After 2 hours 130.0g (1.0 mol) of 2-hydroxyethyl methacrylate (HEMA ex GEO Specialities) was charged and allowed to react to specification (<0.2% free NCO). Compound IDPI-PPGMA (**47**).

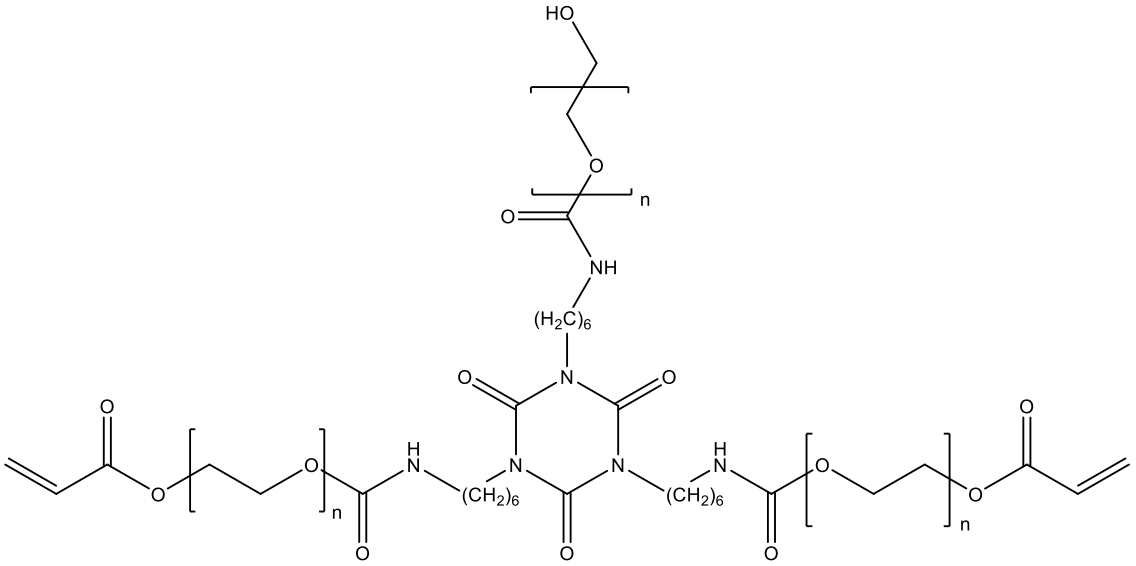


Where n = 60-64 IPDI-PPGMA - **47**

3.5.3 Water-Bourne Urethane Acrylate Synthesis

3.5.3.1 Hexamethylene Polyethylene Glycol Urethane Diacrylate

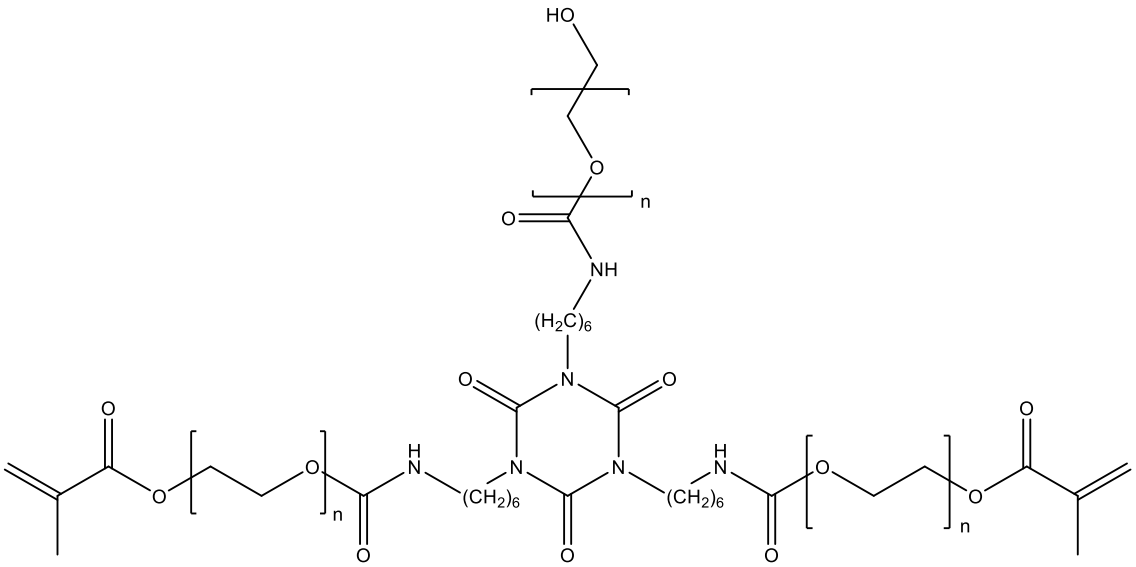
Using the same equipment as for the other polyethylene based urethanes, 201.6g (0.6 mol) of polyethylene hydroxy acrylate (PEA), 164.7g (0.3 mol) of hexamethylene diisocyanate trimer (Tolonate HDT-LV ex Vencorex) (HDT) and 0.005g (0.79x10-3mol) DBTDL was charged in the reaction vessel and heated to 65°C. The vessel temperature was held at 65°C for 2 hours before increasing the temperature to 75°C over 2 hours. Once the vessel had reached 75°C the reaction mixture was sampled to check that the isocyanate content had fallen to 3.3-3.6%. Once the specification had been obtained 120.0g (0.3 mol) of polyethylene glycol 400 (Pluriol E400 ex BASF) (PEG) was charged and reacted for 2 hours @ 75-80°C. Once the isocyanate content had reached final specification (<0.2% free NCO), the vessel was cooled down. At 50°C, 486.3g of deionised water was slowly added to give a 50% solids resin. The resultant structure with 2 acrylate groups and a PEG group reacted to the HDT centre is theoretical based on stoichiometry, however it is likely to be a mixture of compounds with 1, 2 or 3 acrylate groups reacted to the HDT. Compound HDT-PEGA (**48**).



Where n = 5-7 HDT-PEGA – **48**

3.5.3.2 Hexamethylene Polyethylene Glycol Urethane Dimethacrylate

Following the same process and equipment set up as above, 210.0g (0.6 mol) of polyethylene hydroxy methacrylate (PEM) and 164.7g (0.3 mol) of HDT was reacted to 3.2-3.4% NCO content. 120.0g (0.3 mol) of polyethylene glycol 400 was charged and reaction to final specification. 494.7g of deionised water was added to produce a 50% solids resin. Compound HDT-PEGMA (**49**).



Where n = 5-7 HDT-PEGMA – **49**

3.5.4 Discussion

It was found that when the sample of the aromatic polyethylene urethane diacrylate, using 4,4'-MDI as the sole source of isocyanate, was cooled down below 40°C, after synthesis, it turned to a soft paste like consistency. When the structure of the compound was examined and compared to the other urethane acrylates synthesised (compare 4,4'-MDI-PEA with MDI-PEA and MDI-PEM), it can be seen that it is linear. It is because of this tendency to form a paste at room temperature that a new compound was synthesised using a 60/40 blend of 2,4'- and 4,4'-MDI. The 2,4' isomer introduces a degree of non-linearity into the structure which appears to inhibit hydrogen bonding. HMDI has a 4,4' structure (HMDI-PEA/HMDI-PEM), but due to the cyclohexane ring there are actually 3 isomers[33] (cis-cis, cis-trans and trans-trans) which breaks up the linear structure, hence the resultant compounds containing HMDI are liquid at room temperature. Compound TDI-PEA is based on TDI shows the same degree of non-linearity as seen in compound IPDI-PEA which is based on IPDI.

The polyethylene glycol based urethane acrylates synthesised have a very low viscosity (2500-3500 mPas @ 20°C), in comparison with other urethane acrylates commercially available (10000 to 500000 mPas @ 20°C), due to the use of the low molecular weight hydroxyl functionalised polyethylene glycol monoacrylate. These low viscosity resins still meet the REACH requirement of a polymer despite their low viscosity and molecular weight. While IPDI-PPGA and IPDI-PPGMA are more typical of the commercially available urethane resins in that there is a difunctional polyol, reacted with two diisocyanates and then terminated with either HEA or HEMA. The viscosity of these compounds are much higher (~70000 mPas @ 20°C), although the percentage of urethane linkage in all the urethanes synthesised are roughly equal (Table 3.7).

Due to the known health and safety hazards of isocyanates, precautions must be taken to ensure that any vapours that might be generated during the reaction are contained. Normal practice is to vent the reaction vessel into a fume cupboard, although monitoring for isocyanate vapours is recommended on an annual basis to ensure that any risks can be identified and appropriate steps taken to minimise those risks. TDI is classified as very toxic by inhalation, hence particular care must be taken in handling the material, with suitable respiratory protection and local extraction used. However once the reaction is

complete, the resultant polymer is only hazardous by virtue of the (meth)acrylate terminal groups, hence a mild irritant (may cause an allergic skin reaction).

Compound	Theoretical MW	GPC MW (M_n)	PDI
MDI-PEA	922	924	1.52
IPDI-PEA	894	895	1.41
TDI-PEA	846	845	1.39
HMDI-PEA	934	937	1.74
MDI-PEM	950	949	1.56
IPDI-PEM	922	924	1.50
HDMI-PEM	962	963	1.68
IPDI-PPGA	1676	1679	1.98
IPDI-PPGMA	1704	1705	2.14
HDT-PEGA	1621	1626	1.91
HDT-PEGMA	1649	1652	2.27

Table 3.7 – Molecular Weights of Urethane (Meth)Acrylate Compounds

As previously discussed the aromatic isocyanates (MDI and TDI) are more reactive than aliphatic ones, with TDI being the most reactive of all, however there is a considerable difference in reactivity between the first and second terminal isocyanate groups. This normally results in a strong initial exotherm, then requires the addition of heat to drive the reaction forward.

With the water-borne (meth)acrylate the PEG tail length is critical to obtain the degree of solubility in water required. If it is too short then the solubility decreases, while the higher molecular weight PEG grades (<1000 M_w) are solid at room temperature.

The reactivity of the urethane acrylates and methacrylates were determined by measuring the gel time of the resins. These were obtained by mixing 10.00 grams of resin with 0.10g of N,N,Di-(2-hydroxyethyl)-*p*-toluidine (Pergaquick A150 ex Pergan) to act as the peroxide accelerator. To the mixture 0.40g of 50% dibenzoyl peroxide (Peroxan BP-50 BZ Paste ex Pergan) was added and the timer started once the peroxide was added. The results obtained are shown in Table 3.8. If the N,N,Di-(2-hydroxyethyl)-*p*-toluidine is not

used then the gel times are measured in hours as the dibenzoyl peroxide is catalysed by tertiary amines.

Compound	Gel Time (Seconds)
MDI-PEA	80
IPDI-PEA	90
MDI-PEM	250
IPDI-PEM	240

Table 3.8 – Resin Gel Times Determined Using Dibenzoyl Peroxide

As discussed in section 2.2 there is significant differences in the recorded gel time between the acrylate and methacrylate analogues, with the acrylate being almost 2½ to 3 times as fast to gel point as the methacrylate. There does not appear to be much difference in reactivity if the isocyanate backbone is changed, although the structural differences between diphenylmethane and isophorone groups are considerable. Perhaps because both the 2,4-MDI and the IPDI groups are asymmetric this accounts for the similarity in gel time reactivities observed.

Resins MDI-PEA and MDI-PEM, with 200ppm of PMP, were cast as a thin film and cured under a UV light (H type mercury bulb). 20.0g of the base resin was mixed with 0.6g of benzophenone (Speedcure BP ex Lambson) and 0.2g of a mixture of 2- and 4-isopropylthioxanthone (Speedcure ITX ex Lambson). The resultant mixture was applied as a coating on a Sheen opacity test card using a 100μm coating bar. This was passed under a Fusion-UV F300 curing equipment fitted with an H type bulb. The conveyor speed was noted at which the coating first appeared to be touch dry, ie. where a finger can be applied with light pressure and the coating does not feel wet or tacky. The slower the line speed, the greater the amount of radiation exposure the sample experiences.

Likewise resins IPDI-PPGA and IPDI-PPGMA, with 200ppm of PMP, were cast as a thin film and cured as above. 16.0g of IPDI-PPGA was mixed with 4.0g of trimethylolpropane triacrylate (SR351 ex Arkema), and 16.0g of IPDI-PPGMA was mixed with 4.0g of trimethylolpropane trimethacrylate (SR350 ex Arkema) to lower the viscosity. 0.6g of benzophenone and 0.2g of ITX were added to both mixtures as the photoinitiator package. The mixtures were applied as 100μm coating on to a Sheen test card using a 100 μm

coating bar to obtain a controlled coating thickness. The conveyor speed was noted at which the coating first appeared to be touch dry.

Compound	Speed (m/min)
MDI-PEA	10.0
MDI-PEM	4.0
IPDI-PPGA	10.0
IPDI-PPGMA	4.5

Table 3.9 – Speed Required to Cure Urethane (Meth)Acrylate Resins Under UV Light

The results in Table 3.9 would appear to indicate that the acrylate can be processed 2-2½ times than the methacrylate, when applied as a 100μm thick coating. The exposure to UV light initiates the formation of free radicals from the decomposition of the photoinitiators. Since the decomposition effectively stops when the UV light is switched off, it can be assumed that the methacrylate resins are not as susceptible to free radical attack as their acrylate analogues. This would roughly agree with the results obtained from the peroxide gel time tests for the isophorone polyethylene glycol urethane based samples. Due to the instability of the resin without any inhibitor present, the resin would gel at room temperature within 30 minutes, all of the samples run had a known quantity of inhibitor added to ensure a consistent base line for the experiments.

3.6 Inhibitor Removal

All of the acrylate and methacrylate monomers are supplied with low levels of polymerisation inhibitors present, normally 200ppm of PMP, to stabilise during storage. It has been shown that when these monomers are used in further reaction stages, effectively the majority of the inhibitor present is consumed either by the free radical processes outlined previously taking place at elevated temperatures or becoming involved in the polymerisation process due to the availability of the phenolic hydroxy group.[34] In the case of preparing the amine and urethane (meth)acrylate samples, there is sufficient inhibitor present in the monomers to allow for the synthesis to take place without gelation taking place. In the case of the epoxy (meth)acrylate, due to the presence of the (meth)acrylic acid, which has a tendency to self polymerise at elevated temperatures

(>35°C), if the reaction takes longer than 4 hours to complete, then the addition of 200ppm of HQ is often required to prevent premature gelation. This can either be removed by a water wash process, due to the high solubility of hydroquinone in water, or as described below.

The literature mentions several methods of removing inhibitors from (meth)acrylate monomers and (meth)acrylic acids either via distillation,[35] or filtering through a suitable media, such as activated charcoal,[36] alumina[37] or an ion exchange resin.[38] The problem is that the materials mentioned in the literature are low viscosity, hence the transit time for filtration is comparatively quick. This is of critical importance as once the inhibitors have been removed, the resins are unstable and have to be kept cool (<5°C) to maintain a workable shelf life in the laboratory.

Experimental work and previous experience has shown that activated charcoal is very effective at removing inhibitors, but has a long transit time due to the high porosity. Alumina is slightly less effective, but with similar transit times. Amberlite IRA900 (ex Rohm and Haas) ion exchange resin was found to be reasonably effective at removing inhibitors, but with a much faster transit time due to the more open structure. To maintain a reasonable transit time it was found that using a pump set to 5ml/min and using activated charcoal and Amberlite worked well for low viscosity materials, while for higher viscosity materials either passing the sample through Amberlite as a neat resin or diluting in acetone overcame the problems associated with viscous materials. The acetone would evaporate quite quickly at room temperature, although applying a low level of vacuum (~ -0.25bar) for 2 minutes removed the 99% of the solvent. For producing small quantities of sample passing the material through a disassembleable syringe filter, with a layer of activated charcoal, proved to be very effective.

When resins HDDA-MEA and TEGDA-MEA were filtered through activated charcoal it was found that unless the filtrate was cooled below 5°C within 5 minutes, it would begin to gel. This was not found with the methacrylic analogues (HDDMA-MEA and TEGDMA-MEA) and can only be assumed to be due to the differences in reactivity. Since amine (meth)acrylates are designed to catalyse the curing reaction, to compensate for the presence of oxygen, it would be reasonable to assume that resin would be more reactive to the presence of free radicals than the inhibitors, hence would polymerise faster than the inhibitors could inhibit the free radical production. The differences in reactivity

between the acrylate and methacrylate analogue samples are most likely to be down to the difference in reactivity of the base acrylate and methacrylate resins.

After the resins had had the inhibitors removed, the samples were immediately stored at 5°C and used with 24 hours. Resin samples older than 24 hours were disposed of to ensure quality and consistency.

3.7 References

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4 Stabiliser Evaluation

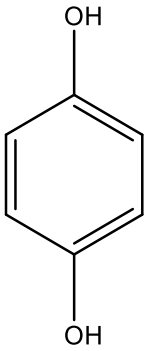
4.1 Industrial Uses of Stabilisers

The term stabiliser is used as it covers the terms of antioxidant and polymerisation inhibitor. Both antioxidants and polymerisation inhibitors are essentially present to act as free radical scavengers, but traditionally antioxidants are more associated with providing protection against thermal degradation, compared to preventing polymerisation independent of the mode of degradation.

The literature available on industrially used stabilisers is of three types, academic studies and reviews, patents and commercial literature. Most of the published academic literature is concerned about the stability of polymers used in extrusion processing (blow moulding, extrusion moulding, etc) which, although relate to higher molecular weight polymers than that which are normally encountered in (meth)acrylates and unsaturated resin systems, do offer some very good insights into polymer stability in general. There are studies looking at the effect of polymerisation inhibitors use in the processing of acrylic monomers.

Due to the commercial nature of these resin systems, a good proportion of the commercially driven development work done on polymerisation inhibitors has given rise to some interesting compounds which are first disclosed via the patent route, so as to maximise their potential revenue, and to obtain some enforceable intellectual property rights. The commercial literature is naturally biased towards the selling of the product, and rarely has any true comparative data included.

A lot of work has been done to improve the stabilisation of (meth)acrylic acid, both during manufacture and subsequent storage. As previously discussed, work done by Levy[1,2] and Vogel & Becker[3,4] on acrylic acid stabilisation studying the use of hydroquinone (HQ) (**13**) and 4-methoxyphenol (PMP) (**14**). The various processes disclosed used to manufacture acrylic acid all involve a distillation stage to separate and purify the acid. The distillation temperatures used (150-200°C) are highly conducive to initiating acrylic acid polymerisation, particularly in the packed columns used. The fouling of packed columns by polymerised material is a major source of inefficiency within the process, hence there has been a lot of work done to reduce the incidence of polymer formation. The bulk of the work has been done on studying acrylic acid stability at temperatures of 90 to 120°C.



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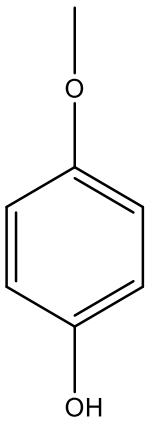

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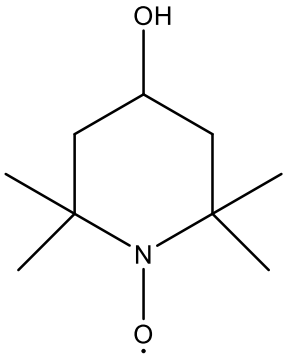
The use of 7 substituted quinone methidies was investigated by Nesvadbu *et al*[5] and found that compounds based on 3,5-di-tert-butyl-4-oxocyclohexa-2,5-dienyldene showed very good stability at 200ppm concentrations when used to stabilise styrene. Also the inhibition effects did not appear to be significantly different if the samples were prepared in a nitrogen or normal atmosphere. In the majority of cases it is known and been reported that in general phenolic based inhibitors do require the presence of air in order to activate the inhibition process, particularly the amount of oxygen dissolved into the resin is critical. This does not apply to 4H-TEMPO (**26**)**,** or to some extent to HQ and methylhydroquinone (MeHQ) (**15**).[6] Likewise the stable radicals (TEMPO *et al*) are generally active in air or inert atmospheres.[7] See Scheme 4.1 for the mechanism for 4H-TEMPO stabilising free radicals.



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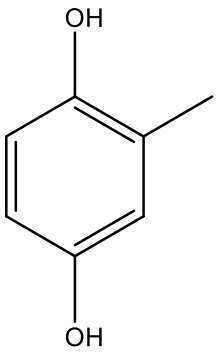

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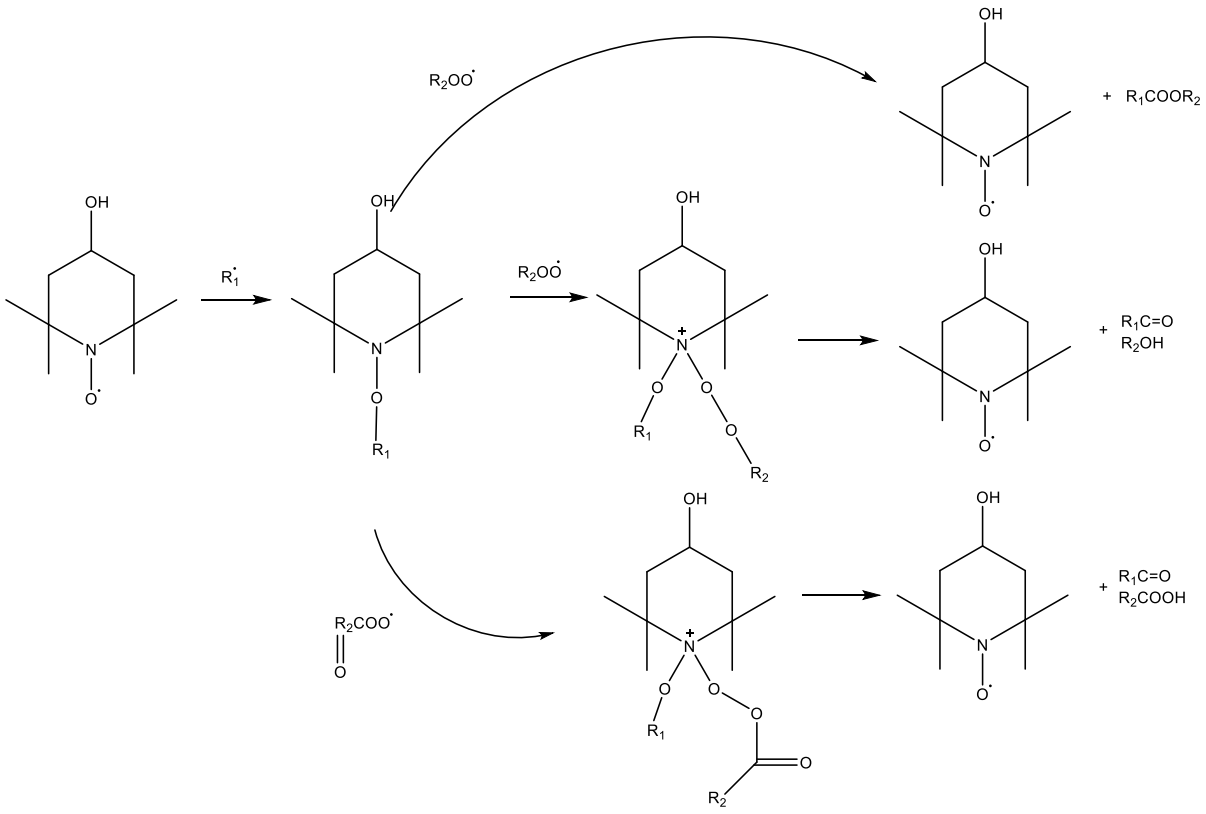
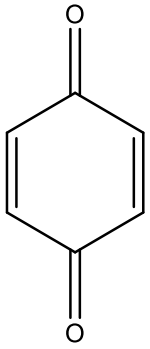


Scheme 4.1

The use of phosphites as antioxidants has been a long established practice in the manufacture of unsaturated polyesters. In the 1930's and 40's Cheetham & Evers authored a number of patents covering the use of alkyl, dialkyl, trialkyl and triaryl phosphites to produce low colour alkyl and polyester resins.[8,9] Various different ligands have been evaluated for their effectiveness,[10] but modern industrial practice is to use triphenyl phosphite as an antioxidant, as well as an inert atmosphere during the reaction stage.[11-13]

The manufacture of unsaturated polyesters have traditionally used a different range of polymerisation inhibitors compared to (meth)acrylates, normally HQ and a range of benzoquinones, particularly 1,4-benzoquinone (**19**). Clonce[14] looked at using benzoquinones in the processing of acrylic acid, and found that at 500ppm concentration phenyl-4-benzoquinone and 2,5-diphenyl-4-benzoquinone have better stability than 1,4-benzoquione.



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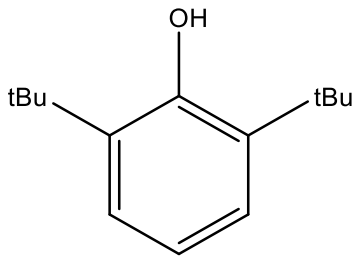
A lot of work has been reported by Gugumus[15-19] on the use of inhibitors and antioxidants in solid polyolefin systems for hot melt extrusion. Although the conditions are not the same as for liquid resins, the same issues and degradation processes take place in both types of polymer systems. In the case of the polyolefins it is during the melt and extrusion process, which can last between 1 to 10 minutes, but is carried out at 150 to 270°C dependent upon the equipment, polymer and mould types used. In a broader overview Singh *et al*[20] have summarised the mechanisms of plastics degradation, again with extruded polyolefins in mind. The discussions on the mechanisms of hydroperoxide formation and decomposition are of particular interest as they are the main source of free radicals even with resin solutions stored at room temperature.

Kovářová *et al*[21] have reported on work done with 2,6-di-tert-butyl-4-methylphenol (BHT) (**18**) and related compounds in degradation studies using low density polyethylene. Although the work has been done on solid polyolefins, it is interesting to note that even at low concentrations the antioxidants do have an effect compared to virgin material and dependent upon the substance used can dramatically increase the stability. The most promising material was octadecyl-3-(3','-di-tert-butyl-4'-hydroxyphenyl)propionate (**50**), sold commercially as Irganox 1076 ex BASF. There are a number of different alkylated phenolics available commercially which have a greater or lesser antioxidative ability.



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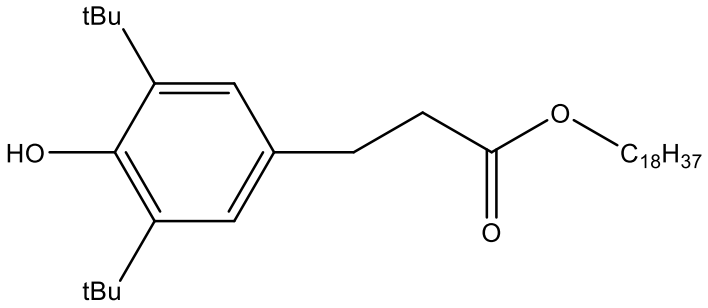

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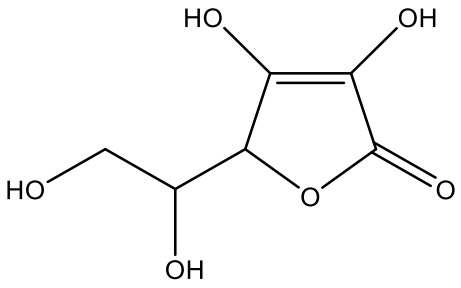
Commercially BASF (formerly Ciba) have been regarded as the leaders in the production of phenolic antioxidants, particularly under the Irganox tradename. These are a range of substituted phenol derivatives, with some organometallic complexes, sulphur based (Irganox 1035 and PS800) and phosphorous based (Irgafos range). The bulk of the commercially available antioxidants are either direct copies of BASF products (after the expiry of the patents) or are directly related to them, mainly from manufacturers based in the Far East.

There have been a number of studies undertaken to look at the potential for such commercially available materials to leach out of thermoplastics, with Denberg *et al*[22] studying the leaching out of phenolic antioxidants from high density polyethylene (HDPE) water pipes, and Ho *et al*[23] looking at similar effects in HDPE bottles and their contributions to off flavours. Li *et al*[24] determined the levels of antioxidants and UV stabilisers in polypropylene (PP) over time, while Dazzi *et al*[25] used atomic force microscopy to study the morphology of Irganox 1076 on the surface of HDPE after leeching out.

A potential route of interest is the work reported by Niki[26] on the use of ascorbic acid (AA) (**51**) and tocopherol (**52**) as oxygen radical scavengers. It was found that ascorbic acid is an effective and rapid scavenger, but tocopherol was more efficient and longer lasting, the two substances combined gave a synergistic effect. The work was done on blood samples, but the antioxidant effects reported should be repeatable on any liquid/solution providing that ascorbic acid and/or tocopherol are soluble. Finlay[27] had a patent application issued to cover the use of BHT in combination with a long chain antioxidant, with tocopherol given as an example, for the inhibition of surface oxidation on acrylic polymers. Although both ascorbic acid and tocopherol are natural products, the

bulk of the supply is via synthetic routes due to insufficient supply from natural feed stocks.



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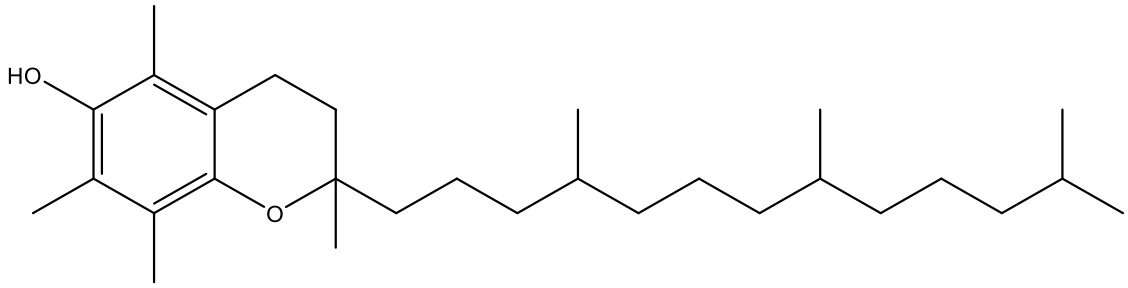

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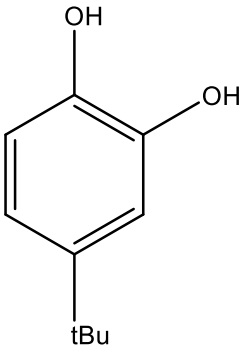
The majority of the work reported in the literature has been done looking at phenolics, quinones and stable radicals. These appear to offer good results, but there is little apparent agreement as to what is the ideal substance or combination of substances to use. Patents by their very nature have to show some "novelty" in order to be granted, so these will always be looking at new substances and or processes. The academic literature does not show any great deal of agreement over which substance is ideal. A broad overview would be that phenolics, quinones and stable radicals do provide some degree of polymerisation inhibition when used in a normal atmosphere. However if the atmosphere is inert, or the oxygen levels in the resin system are depleted to a very low concentration, then in general stable radicals with some quinones provide the resin system with some inhibition.

4.2 Stabiliser Selection

The compounds selected for investigation were chosen due to their relevance to the acrylate industry. However there is some degree of commonality as regards to stabiliser selection across the different sectors of the polymer industry, so the results generated could potentially be applied across to other situations with different polymers. The most commonly encountered stabilisers are HQ, PMP, BHT, 4-tert-butylcatechol (BTC) (**17)**

and phenothiazine (PTZ) (**27**). MeHQ is more often encountered in the production of high molecular weight polyester (meth)acrylates and unsaturated polyesters, while TEMPO (**25**) is not used commercially as it has been replaced by the use of 4H-TEMPO due to its better solubility. 2,6-di-tert-Butylphenol (DTBP) (**53**) is included as it is the starting point for a number of alkyl phenol based antioxidants.



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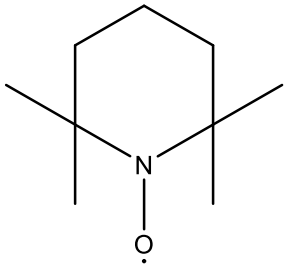

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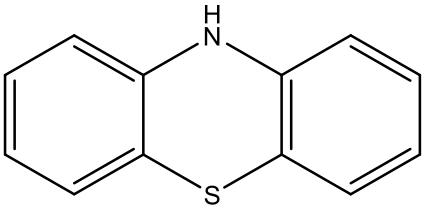

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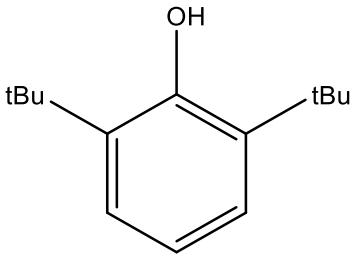

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Since in industry the majority of formulations are calculated on a weight basis, the standard convention is to quote inhibitor concentrations in terms of parts per million (ppm), Table 4.1 shows the conversion to $molg^{-1}$ for each of the inhibitors selected.

Compound	50ppm	100ppm	200ppm	500ppm	1000ppm
HQ	$4.54x10^{-7}$	$9.08x10^{-7}$	$1.82x10^{-6}$	$4.54x10^{-6}$	$9.08x10^{-6}$
PMP	$4.03x10^{-7}$	$8.06x10^{-7}$	$1.61x10^{-6}$	$4.03x10^{-6}$	$8.06x10^{-6}$
MeHQ	$4.03x10^{-7}$	$8.06x10^{-7}$	$1.61x10^{-6}$	$4.03x10^{-6}$	$8.06x10^{-6}$
BTC	$3.01x10^{-7}$	$6.02x10^{-7}$	$1.20x10^{-6}$	$3.01x10^{-6}$	$6.02x10^{-6}$
BHT	$2.27x10^{-7}$	$4.54x10^{-7}$	$9.08x10^{-7}$	$2.27x10^{-6}$	$4.54x10^{-6}$
4H-TEMPO	$2.90x10^{-7}$	$5.81x10^{-7}$	$1.16x10^{-6}$	$2.90x10^{-6}$	$5.81x10^{-6}$
PTZ	$2.51x10^{-7}$	$5.02x10^{-7}$	$1.00x10^{-6}$	$2.51x10^{-6}$	$5.02x10^{-6}$
AA	$2.42x10^{-7}$	$4.85x10^{-7}$	$9.69x10^{-7}$	$2.42x10^{-6}$	$4.85x10^{-6}$

Table 4.1- Inhibitor Concentrations in $molg^{-1}$

4.3 Stability Testing

A couple of observations that apply to all samples regardless of the sample type and test conditions, 4H-TEMPO, PTZ and AA do impart a strong orange, light pink or yellow colouration, respectively, to the samples, dependent upon the concentration in the sample, from the beginning of the test. It is well known that in solution HQ changes colour from colourless to a dark brown as it is oxidised, this is often a reliable guide as to how the stability test is progressing along with a visual assessment of the viscosity. The resin samples were left with an air gap to provide both a fixed volume atmosphere and to allow for the determination of the viscosity of the sample by inverting the sample container. The air gap becomes a bubble which by observing the speed at which it travels up the container allows for an evaluation of the viscosity and to determine if any gel formation has taken place and if so the degree of gelling and the location within the sample (top, middle or bottom).

4.3.1 Test Setup

10.00g (±0.01) of the sample resin, together with the stabiliser under investigation, was placed in a 12ml glass sample vial and sealed with a metal crimp cap and a butyl rubber septum ensure a good air tight seal. As previously discussed the resin samples were

filtered prior to use through activated charcoal to remove any remaining inhibitor in the resin. The samples were placed in the appropriate incubator and monitored for viscosity accordingly;

Temperature	Inspection Frequency
Room Temperature (20°C)	Weekly
40°C	Daily
80°C	Daily
120°C	30 Minutes

Table 4.2 – Resin Sample Inspection Frequency

For the majority of stabilisers to function oxygen needs to be present in the resin. Normally this is supplied via the atmosphere, in the case of the samples the head space left in the sample vials is a known volume. By ensuring that a good seal is established at the beginning of the stability test, it can be assumed that the head space cannot be replenished, hence any oxygen in both the resin and the head space will be used up by the antioxidant mechanisms previously outlined.

To simulate non-standard conditions, some of the samples had the headspace replaced by nitrogen gas for 5 minutes prior to being sealed, while others were sparged for 10 minutes with nitrogen at 1 bar pressure. In the cases of the samples which had been sparged, this represented the extreme scenario of a system where the dissolved oxygen had been displaced by nitrogen and the sole source of oxygen would be due to any peroxides present formed during the synthesis of the resin. Exposure to light was minimised to ensure that free radical propagation due to UV radiation was also kept to a minimum.

It is standard industrial practice to supply acrylates, methacrylates and unsaturated polyesters in containers which effectively prevent oxygen being transferred from the atmosphere to the resin inside, ie. HDPE, PP and steel (lacquer lined, usually with phenol novolac resin). To maintain the shelf life a head space in the container is left (usually 20-25 litres in a 210 litre drum), and the instruction that the material is to be stored between 15-25°C and the head space to be renewed after 3-6 months and the material thoroughly mixed. Even with these precautions a standard shelf life of only 6 months is given or guaranteed by the manufacturer.

When a vinyl ester resin is subsequently used in a formulation in an uncured and/or unmodified state the storage conditions of the resultant mixture are often not conducive to long term stability due to the use of non-oxygen permeable packaging and little or no airspace. To try to replicate such conditions, the aim was to submit a set of samples to the same temperature regime, but with different atmosphere head spaces.

It should be noted that the density of the resin samples were generally in the region of 0.95 to 1.05gcm^{-3}. This gave a head space of 2ml in a 12ml sample vial, or 20% of the resin, compared to 25 litres on 180-200kg of resin in a 205lt tighthead drum or 12.5% of the resin.

4.4 Results

The results obtained from the stability testing of primary stabiliser systems are summarised below. The discussion has been divided up according to the resin type, with the results obtained in chart format shown in the Appendices.

4.4.1 Amine Acrylates and Methacrylates

As previously discussed, amine (meth)acrylates are mainly used to improve the surface cure of UV cured resins. Without taking any precautions, most UV cured resins will suffer from poor surface cure, relative to the degree of cure experienced in the body of the resin film. This does depend on a number of factors, including the amount of energy experienced by the resin during the cure process. The UV lamp systems used create varying amounts of ozone, although with LED lamp systems the amount of ozone generated compared to the traditional mercury based systems is minimal, and the oxygen present inhibits the surface cure. The problem is particularly acute with high line speeds due to the amount of energy being generated needed to cure the resin. It has been surmised that the nitrogen lone pair of electrons help to reduce the effect of the oxygen by stabilising the charge from the oxygen, be it as a free radical or as ozone.[15-19, 26]

When a coating is cured via a UV light source, often the surface will still be tacky to the touch, however this tacky layer will only be a few microns thick, with the bulk of the coating fully cured. The cause of this poor surface curing is due to oxygen inhibition, caused by oxygen in the atmosphere becoming energised and interacting with the substances in the top layer of the coating. The traditional method of reducing the effects of this oxygen inhibition effect is to add a suitable amine, which acts as a synergist with

the photoinitiator to overcome the inhibition effect. There are 3 problems with using free amines, yellowing, smell, and a high probability of the amine leaching out of the coating.

In order to minimise the above risks, amine acrylates have been developed, with the free vinyl group available to bind the oligomer into the resultant polymer matrix. Since the amine acrylate's are as good a synergist as the free amine equivalent, then they have the same degree of reactivity towards oxygen and any oxygen radicals that might be present.

The HDDA-MEA (**28**) and HDDMA-MEA (**30**) resins are the acrylate and methacrylate analogues with a 1,6-hexanediol backbone, while the TEGDA-MEA (**29**) and TEGDMA-MEA (**31**) resins are based on a triethyl glycol backbone. It has been shown that the reaction times of the methacrylate functional group are longer than the acrylate equivalent, this generally translates into the stability of the resin with methacrylates stable for longer compared to their acrylate analogues.

HDDA-MEA and HDDMA-MEA resins were tested at 40°C (see Charts A1.1.1 and A1.2.1), 80°C (see Charts A1.1.2 and A1.2.2) and 120°C (see Charts 4.1, A1.1.3 and A1.2.3), with HQ, MeHQ and TBC all showing good performance, however 4H-TEMPO shows the best performance.

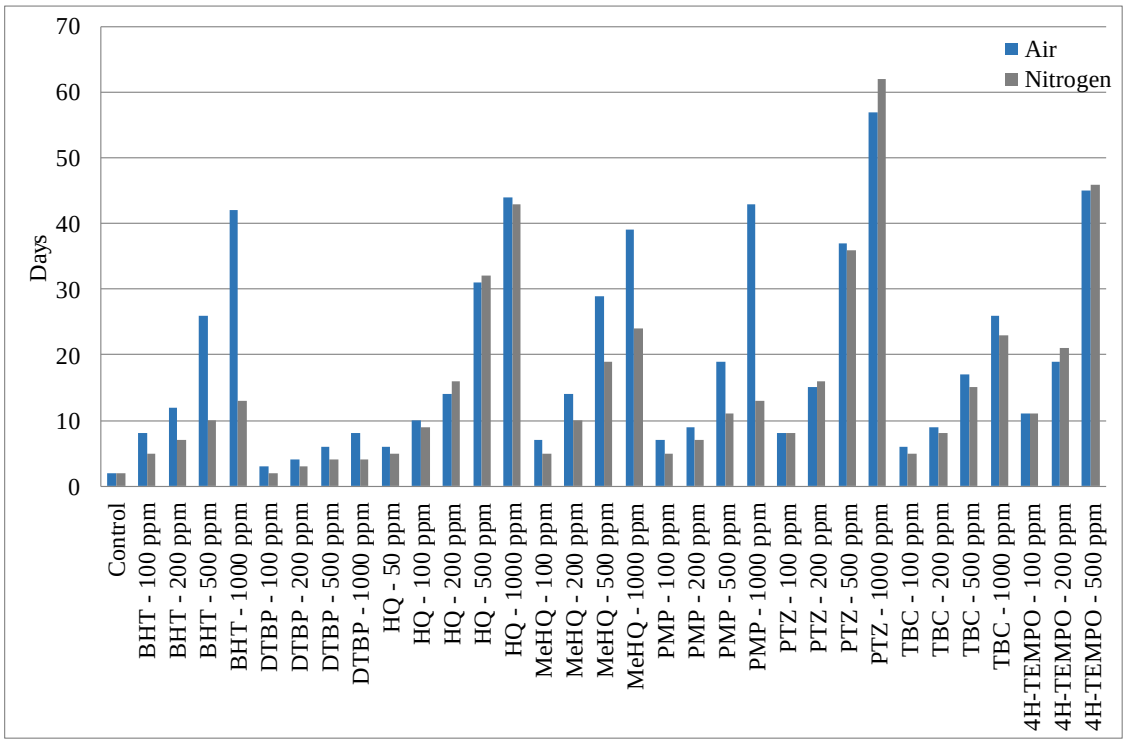
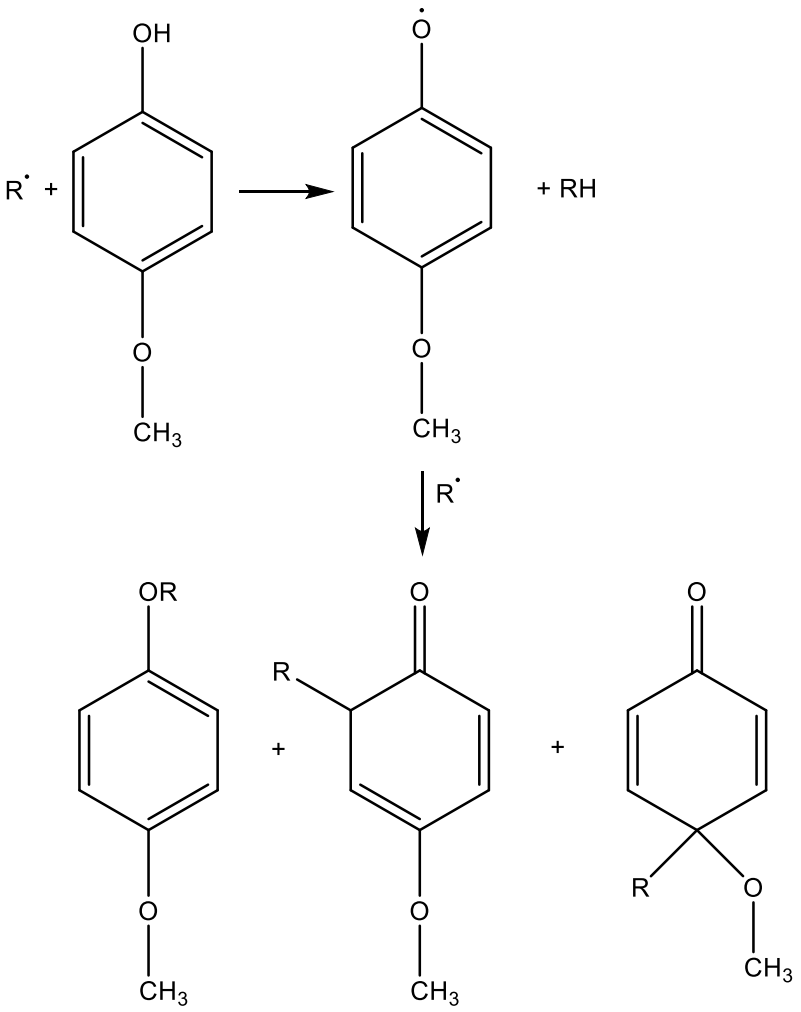


Chart 4.1 – Stability of HDDA-MEA @ 40°C

Both BHT and PMP show relatively poor performance, with DBTP the worst. The headspace composition of the sample shows some very clear differences, with BHT, DBTP and PMP all performing worse with a nitrogen atmosphere than the analogue samples with a standard air atmosphere, while for the other inhibitor systems evaluated the results are a little more varied, but overall the type of atmosphere used as a headspace does not appear to be such a concern.

It is mentioned in the literature that both BHT and PMP require oxygen present to enable the scavenging of free radicals[1-4], so the poor performance in samples with a nitrogen headspace is not unexpected. The logical assumption is that whatever oxygen is dissolved in the sample is consumed by the inhibitor during the scavenging mechanism, then once the oxygen is depleted the inhibitors would either become deactivated or inert. There is no literature for the use of DTBP as an inhibitor, but since it is structurally similar to BHT it would be logical to assume similar properties, and this has been borne out. Since DBTP is used as the precursor in the production of various commercial antioxidants/inhibitors (50% of the Irganox range from BASF for example), it is apparent that the various ligands added to and modifications may account for the antioxidant activity of the new substances, compared to the performance of DBTP. The Irganox range of phenolic antioxidants was developed by Ciba (now BASF) and was covered by various patents, as these have expired over the years other companies now also produce these compounds as well as use them as the basis for further developments.

Both the quinones, HQ, MeHQ, and TBC are known not to require oxygen present to act as an active free radical scavenger, although a low concentration (<10ppm) of oxygen does appear to improve the efficiency of the inhibition mechanism.[1,4] TBC is the inhibitor of choice for stabilizing styrene, which due to its flammability is stored in bulk under a nitrogen atmosphere. It is known that PTZ remains active under either aerobic or anaerobic environments[2], while 4H-TEMPO due to its stable free radical is well known for its ability to remain active in most environments. See Scheme 4.1 for 4H-TEMPO inhibition mechanism and Scheme 4.2 for HQ.



Scheme 4.2

The TEGDA-MEA and TEGDMA-MEA resins were tested at 80°C (see Charts A1.1.4 and A1.2.4) and 120°C (Charts A1.1.5 and A1.2.5) with both air and nitrogen headspaces. Both TEGDA-MEA and TEGDMA-MEA appear to have a lower inhibiting effect compared to HDDA-MEA and HDDMA-MEA in an air atmosphere. This could be due to structural differences between the two polymer backbones, although both are linear and are synthesised via esterification. The inclusion of 4H-TEMPO and PTZ is due their known activity in reduced/free oxygen environments. Certainly from the evidence above it would appear that 4H-TEMPO does not suffer from any reduction in activity due to a nitrogen headspace, nor does HQ or PTZ. In all cases the use of PMP does not appear to be much more effective than the control samples, and at 80°C is markedly reduced in activity in the nitrogen samples compared to the air, this falls in line with both the literature and past experience. The results for PMP at 120°C show very little difference between atmospheres, which is unusual as it does not tie up with the literature or past

experience, which would expect that the stability should be worse in the nitrogen atmosphere.

Of the commercially available amine acrylates, diethylamine is the most commonly encountered amine used in the synthesis of monomeric amine acrylates, while ethanolamine is used in the synthesis of oligomeric and polymeric amine acrylates. Commercially there are a number of amine acrylate products on the market, but very few, if any, methacrylate equivalents. This is due to the slower cure speeds encountered with methacrylates compared to acrylates and the fewer suitable methacrylate monomers available as reactants compared to acrylates. This is despite the lower hazard classifications associated with methacrylates compared to acrylates.

4.4.2 Epoxy Acrylates and Methacrylates

The samples were tested at 20, 40, 80 and 120°C, although bisphenol A and F epoxy (meth)acrylates are viscous, it is possible to determine the formation of gelled material due to polymerisation by careful observation at 20°C, at higher temperatures the resin viscosity is lowered sufficiently to easily allow the detection of gelled material. It was found that there was no significant difference in performance or when characterised by FT-IR and GPC between the two methods of inhibitor removal undertaken with BADGEDA (**33**). Therefore the results obtained can be taken to apply to either method.

Charts A1.3.1 to A1.4.12 show the results obtained for the stability testing of the epoxy acrylate and methacrylate samples from 20 to 120°C. As seen with the amine (meth)acrylate samples described above the methacrylate resins take longer to gel than their acrylate analogues. As would be expected the higher the concentration of inhibitor, the longer the shelf life. As a general indication BHT, HQ, PTZ and 4H-TEMPO show good overall performance.

Charts A1.3.1 to A1.3.4 show the results obtained with HDDGEA (**32**), Charts A1.3.5 to A1.3.8 for BADGEDA (**33**) resin and Charts A1.3.9 to A1.3.12 for BFDGEDA (**34**) covering the epoxy acrylate resins tested. The results from the methacrylate analogues are shown in Charts A1.4.1 to A1.4.4 for HDDGEDMA (**35**), Charts A1.4.5 to A1.4.8 for BADGEDMA (**36**) and Charts A1.4.9 to A1.4.12 for BFDGEDMA (**37**).

The resin samples were tested with an air headspace for all temperatures, while with a nitrogen headspace at 40, 80 and 120°C, and with nitrogen sparing at 80 and 120°C.

Although all 6 resins were difunctional, HDDGEDA and HDDGEDMA resins were synthesised using a 1,6-hexanediol aliphatic backbone, while BADGEDA and BADGEDMA resins were bisphenol A backbone based and BFDGEDA and BFDGEDMA bisphenol F, both of which are structurally similar aromatic compounds. Looking at the overall pattern of the results obtained, it appears that the following pattern of relative stability can be determined, which is the reverse of the degree of reactivity. Where 1,6 hexanediol is the most stable and bisphenol A the least, with bisphenol F in the middle.

In general it appears that for epoxy (meth)acrylate samples tested, HQ and 4H-TEMPO appear to offer the best performance, however at 120°C HQ gives the best performance. To synthesise the resins (meth)acrylic acid is used to provide the (meth)acrylate functionality. At temperatures above 120°C the stability of the vinyl carbon-carbon double bond is very weak and will readily break apart and form new carbon-carbon single bonds with other suitable groups resulting in a gel.

It is noticeable the effect of nitrogen sparging has on the stability of the other inhibitors submitted for evaluation. It is known in the literature[1-4] that BHT, HQ, MeHQ and PMP do require oxygen to be present in the system so that the free-radical termination step is not uni-molar (ie. 1 mole of antioxidant to react with 1 mole of free-radical species), but multi-molar (ie 1 mole of antioxidant to react with 2 or more moles of free-radical species). However it is logical to assume that when the sample has been sparged with nitrogen, any dissolved oxygen will have been displaced and the only oxygen present would be due to the presence of peroxides. The concentration of peroxides present was sufficient to cause the rapid gelation of the resin, as well as to overwhelm the inhibitor present.

When the air and nitrogen headspace values are looked at it can be seen that the use of HQ does lead to a more stable resin system. This is on par with, if not better than, the use of PTZ. The different headspaces do not appear to be affecting the performance of HQ and MeHQ to the same extent as BHT and PMP where the use of a nitrogen headspace results in a considerable drop in performance. This confirms the assumption that BHT and PMP require a higher level of dissolved oxygen in the system, compared to HQ and PMP.

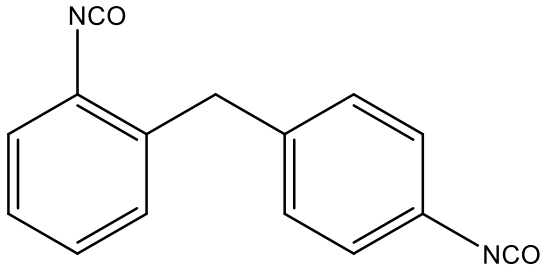
It had been noticed that in the lower concentration samples (up to 500ppm) the samples showed signs of gelation at the bottom of the sample container, but with a top layer still mobile. This gelation could be seen to progressively increase with time until all the sample had gelled. When this situation had occurred the gel time was recorded from when 50% of the sample had gelled. All of the inhibitors showed some signs of this phenomenon occurring, regardless of the test temperature with all the resin samples tested in this project, but it was found to be most pronounced with the epoxy based resins.

Work with TBC in styrene has shown that in enclosed systems the headspace oxygen concentration has dropped over time, this would lead to the assumption that an osmotic system is in place to balance the oxygen concentrations between the gas and liquid systems. Providing that the headspace was kept regularly topped up with air and that the oxygen in the headspace did not drop below 5% then there was sufficient oxygen present in the styrene to enable the TBC to work efficiently.

4.4.3 Urethane Acrylates and Methacrylates

Urethane (meth)acrylate samples were put in to test at room temperature (20°C), 40, 80 and 120°C, with the results shown in Charts A1.5.1 to A1.5.14 for the acrylate polyethylene based resin samples, Charts A1.6.1 to A1.6.11 methacrylate polyethylene based resin samples, Charts A1.7.1 and A1.7.2 for the IPDI-PPGA (**46**) and IPDI-PPGDA (**47**) resins respectively. In the case of the water-borne urethanes, HDT-PEGA (**48**) and HDT-PEGMA (**49**) the stability testing carried out at 85°C was reported in Charts A1.8.1 and A1.8.2.

The MDI-PEA (**39**) and MDI-PEM (**43**) resins were based on a diphenylmethane backbone (MDI **9a** and **9b**) with polyethylene (meth)acrylate termination, were placed into stability test at 20, 40, 80 and 120°C (see Charts A1.5.1 to A1.5.4 and A1.6.1 to A1.6.4 acrylate and methacrylate respectively). 4H-TEMPO was found to give the best performance regardless for the resin type or the conditions, followed by PTZ. Similarly the results for The IPDI-PEA (**40**) and IPDI-PEM (**44**) resins were based on an isophorone backbone (IPDI **10**) with polyethylene (meth)acrylate termination, were placed into stability test at 20, 40, 80 and 120°C (see Charts A1.5.5 to A1.5.8 and A1.6.5 to A1.6.8) again show the effectiveness of 4H-TEMPO as an inhibitor regardless of the resin type or conditions. Likewise, again the use of PTZ for the acrylate appears to be a good second choice.



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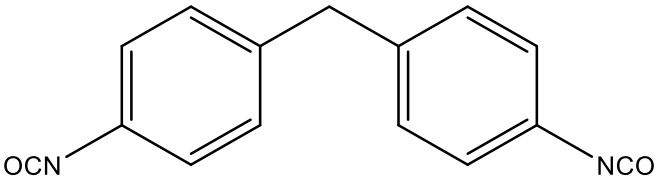

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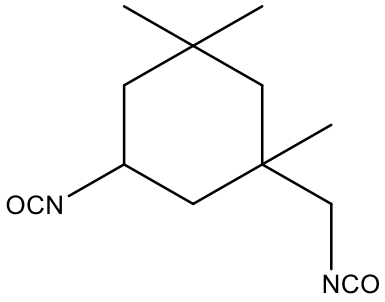

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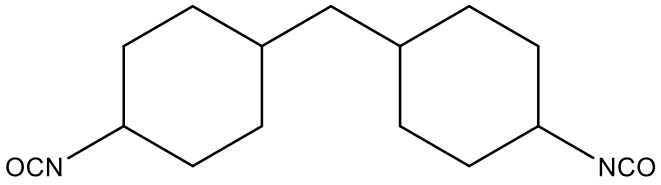
As would be predicted from the results obtained looking at the epoxy (meth)acrylate test series, the nitrogen sparged samples show deleterious effect upon the stability when BHT, HQ, MeHQ, PMP and TBC are used as the inhibitor. Generally HQ and MeHQ do show good performance under both air and nitrogen headspaces, although TBC does perform better for both the acrylate and methacrylate @ 80°C, and similarly for the methacrylate @ 120°C, but at lower temperatures only performs as well as BHT. As expected from the results obtained from other test series, although BHT shows reasonably good performance in air, when a nitrogen headspace is used, the performance is significantly reduced.

Taking into account the known fact that PMP does not act as an effective inhibitor under nitrogen, the poor results obtained in air when compared to the likes of BHT and HQ are unusual although industrial experience has shown that in the case of urethane resins the addition of BHT stabilises the resin far better than the use of the same amount of PMP.

This appears to be more the case for aromatic based resin systems, than the aliphatic equivalent.

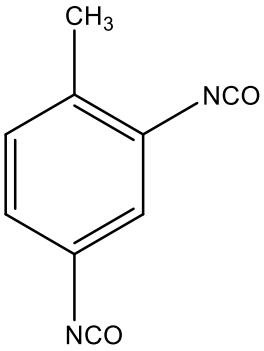
It could be argued that the two aromatic rings present in the structure of the diphenylmethane based resins, compared to the single aliphatic ring present in the isophorone, are giving a degree of stabilisation due to delocalisation. This would allow some of the free radicals present to be stabilised. It also needs to be taken into account that the structure of isophorone is asymmetrical, hence any substances further synthesised from such a base will likewise be asymmetric in its structure. These structural differences most probably are the explanation for the differences in the results obtained between the two different resin systems when comparing acrylate against acrylate, and methacrylate against methacrylate. There is an aliphatic analogue of MDI, dicyclohexylmethane-4,4'-diisocyanate (HMDI) (**12**), available which when synthesised into acrylate and methacrylate resins, HMDI-PEA (**42**) and HMDI-PEM (**45**), (see Charts A1.5.12 to 1.5.14 and A1.6.9 to 1.6.11) show behaviour that is very close to that seen for the isophorone based resins.



12

This would appear to indicate that some degree of stabilisation is taking place due to the presence of the aromatic rings. Toluene diisocyanate (TDI) contains a single aromatic ring with the isocyanate functional groups in an asymmetrical layout, either as 2,4 (**8a**) or 2,6 (**8b**) isomers, although the grade of TDI used is predominantly (78-82%) the 2,4 isomer. TDI-PEA (**41**) resin was synthesised and the results obtained (see Charts A1.5.9 to A1.5.11) show that the behaviour observed is halfway between that seen for resins **39** and **40**. This would appear to confirm that some degree of stabilisation take place due to the presence of aromatic rings. However in terms of colour stability then certainly the presence of aromatic rings does lead to the development of colour, particularly noticeable at higher temperatures (80 and 120°C), yet the samples under test still remain liquid, although it can be taken as a sign that the resin samples in question are close to gelation point. It would be a logical to assume that the same mode of free radical attack that causes

the colouration, also causes the (meth)acrylate carbon-carbon double bond to be broken leading to gelation.



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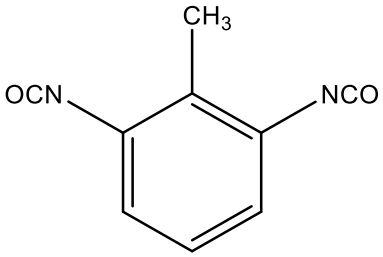
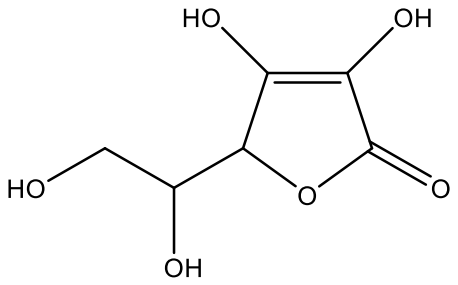


8b

TDI-PEA (**41**) resin was synthesised and the results obtained (see Charts A1.5.9 to A1.5.11) show that the behaviour observed is halfway between that seen for the MDI-PEA and IPDI-PEA resins. This would appear to confirm that some degree of stabilisation take place due to the presence of aromatic rings. However in terms of colour stability then certainly the presence of aromatic rings does lead to the development of colour, particularly noticeable at higher temperatures (80 and 120°C), yet the samples under test still remain liquid, although it can be taken as a sign that the resin samples in question are close to gelation point. It would be a logical to assume that the same mode of free radical attack that causes the colouration, also causes the (meth)acrylate carbon-carbon double bond to be broken leading to gelation.

Looking at the results obtained between the IPDI-PEA and IPDI-PPGA (**46**) resins (see Charts A1.5.3 and A1.7.1), there is virtually no difference in the stability results, and likewise between the IPDI-PEM and IPDI-PPGMA (**47**) resins (see Charts A1.6.3 and A1.7.2), this would indicate that the stability of a resin system is more dependent upon the active terminal functional groups, than on the polymeric backbone for resins of a similar functionality and molecular weight range.

Both HDT-PEGA (**48**) and HDT-PEGMA (**49**) are water-borne urethane resin systems with a nominal 50% solids. The inhibitors used are all, to varying degrees, soluble in water with ascorbic acid (AA) (**51**) completely soluble in water, but conversely completely insoluble in the polymer phase.



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All of the resins with a polyethylene backbone are water tolerant to some extent, but only to a maximum water addition of 15-17%. The resin systems were only tested at 85°C (see Charts A1.8.1 and A1.8.2) with air and nitrogen headspaces. The temperature of 85°C was chosen as it has been found that it was the highest temperature at which a water based system could be stored without a significant amount of water vapour being generated. 4H-TEMPO gave the best stability, followed by HQ. Although AA is only soluble in the water phase, it gave a level of performance similar to MeHQ and only slightly behind BHT. This would suggest that the dissolved oxygen and free radicals can transfer between the polymer and aqueous phases, most likely in an osmotic relationship. This would explain how AA would be able to function as an inhibitor as the concentration of free-radicals would tend to be equal in both phases, and as the free-radicals were terminated in the aqueous phase due to reaction with the acid, then more free-radicals would be drawn to the aqueous phase to maintain equal concentration levels.

4.5 Inhibitor Blends

In the case of higher molecular weight polymer systems there has been much discussion of the synergistic effects and benefits in using blends of antioxidants/inhibitors. Cooray and Scott[84] have discussed such effects in relation to polyvinyl chloride (PVC) processing, as have Gömöry and Gömöryova.[85] While for polypropylene (PP) there is a large body of literature by Gugumus[26, 52-55] discussing the relative merits of antioxidant blends in processing as well as work done on the kinetics of antioxidant synergism in polypropylene by Verdu *et al*.[86]

At the other end of the scale, mention has already been made of the work done by Levy,[30,32] and Becker and Vogel,[34] on looking at the effect of inhibitors upon the synthesis and distillation of acrylic acid and the use of PMP and PTZ.

The potential economic benefits of using such synergistic blends for lower molecular weight polymers, such as the vinyl ester resin systems that form the basis of this work, could be significant. Also the potential to have a lower concentration of free substances within the resin system does have potential health and safety benefits. It would reduce the exposure risk to such low molecular weight substances to both the employees handling the materials during synthesis and subsequent processing, and also to the general public who handle the cured resin. Low molecular weight substances are known to migrate towards the surface of cured resins, particularly if in contact with liquids.

There is little explanation given as to the reasons why such blends are chosen, some blends are recommended by the manufacturers of inhibitors as a method of promoting their own products. Where found, published academic reports on such blends are normally funded and supported by industrial sponsors, which have the result that a restricted range of materials are evaluated and reported. From experience the use of blends appears to come under the following categories,

- Synergistic effects, ie. the effects of two or more inhibitors combined are greater than the sum of the parts
- Cost reduction, either due to synergistic effects to reduce the amount required or blending a cheap material with an expensive one
- To broaden the service conditions/life, ie. combining an aerobic inhibitor with an anaerobic one

Sulphur has been reported as having a synergistic effect with a number of different inhibitors, primarily in the stabilisation of styrene and methyl methacrylate monomers. Although the work was originally done using elemental sulphur added directly as a powder due to experience in the rubber processing industry, PTZ offers a more suitable sulphur based complex for this study.

4.6 Binary Stabiliser Blends

From the literature, and 24 years of industrial experience, it is known that the combination of BHT and PMP is a widely used blend and within the acrylate industry is often quoted as showing some synergistic effects. Table 4.3 shows the current samples under test and the inhibitor concentrations used. AA and 4H-TEMPO were not examined in this batch of testing due to previous results which have eluded to the excellent stability imparted by

the use of the latter and the converse in the case of the former. The base resins used in this study are the same as those synthesised for previous stability studies.

Blend	1	2	3	4
BHT/HQ	50-50ppm	100-100ppm	250-250ppm	500-500ppm
BHT/MeHQ	50-50ppm	100-100ppm	250-250ppm	500-500ppm
BHT/PMP	50-50ppm	100-100ppm	250-250ppm	500-500ppm
BHT/PTZ	50-50ppm	100-100ppm	250-250ppm	500-500ppm
HQ/MeHQ	50-50ppm	100-100ppm	250-250ppm	500-500ppm
HQ/PMP	50-50ppm	100-100ppm	250-250ppm	500-500ppm
HQ/PTZ	50-50ppm	100-100ppm	250-250ppm	500-500ppm
MeHQ/PMP	50-50ppm	100-100ppm	250-250ppm	500-500ppm

Table 4.3 – Binary Inhibitor Blends

4.6.1 Results and Discussion

The epoxy acrylate and methacrylate BADGEDA and BADGEDMA resins were evaluated at 40, 80 and 120°C. The results obtained are shown in Charts A2.1.1 to A2.1.6. In the cases were either an air or nitrogen headspace is used, then the use of PTZ whether blended with BHT or HQ appears to offer the best performance, followed by HQ blended with either BHT or PMP. The BHT/PMP blend performs reasonably well. In all cases it appears that there does appear to be some synergistic effects with the blend of inhibitors, even in the case of the MeHQ/PMP blend, where the inhibitors are isomers.

However where a nitrogen sparge has been used then it appears that the resin stability is uniformly adversely affected, expect where PTZ is used in the blend. Even when PTZ is used in the blend, the stability is still only approximately half that of the results obtained with an air headspace, indicating that only the PTZ component in the blend was fully active. This would show that some residual oxygen is required to be present within the system in order to be efficient. This does tie up with the results obtained from single inhibitor systems.

The urethane (meth)acrylate resins IPDI-PEA, IPDI-PEM, MDI-PEA and MDI-PEM were studied at 80 and 120°C and the results obtained shown in Charts A2.2.1 to A2.2.8.

As with the epoxy (meth)acrylate resins above the most conspicuous result is with the use of the nitrogen sparge, which as would be expected with the phenolic inhibitors has considerably reduced the stability, but with the blends containing PTZ, reduced the stability to approximately half of the level seen with an air headspace. Again the reduced level of stability with PTZ is approximately the level that would be expected with the concentration of the sole material.

The other noticeable result is the antagonistic response seen with the BHT/PMP blend when used in urethane based resins compared to the epoxy resins. It has been shown that PTZ is not as effective in urethane systems, but it does appear not to be antagonistic towards quinones, HQ and MeHQ. The use of BHT/HQ blend in air and nitrogen headspace conditions also give good stability, it appears that the best synergistic combinations are between aerobic and anaerobic inhibitors, as this allows for the use of the blend in the widest range of conditions. Otherwise it does not appear to be the evidence to suggest that there are any true synergistic effects taking place.

4.7 General Discussion

From the results obtained with the epoxy and urethane (meth)acrylate resins it appears that HQ, PTZ and 4H-TEMPO offer good performance in an enclosed environment.

Industrial users, when they declare the inhibitors, most commonly use BHT or PMP8. The main reason is due to cost and that the products do not discolour as they oxidise. Both HQ and PTZ are comparatively cheap but either discolour the product at the time of addition or produce a coloured oxidation product. However due to their superior performance and efficiency both HQ and PTZ are used in the production of many (meth)acrylate monomers, particularly when high temperature processing is required, and then stripped out, with BHT, MeHQ or PMP used for stabilisation during transport and storage.

Both TEMPO and 4H-TEMPO were developed by Ciba (now BASF) and until comparatively recently still under patent protection, both for production and covering a wide range of different application areas, which has effectively hindered their use as a stabilisation additive and/or antioxidant in a polymer formulation, as well as being expensive. There are now a number of companies in China that are now producing both materials and the price has dropped considerably, yet is still more expensive that the more

usual materials, recent changes in legislation have led to a number of Chinese chemical plants being closed. There is also the continuing question over whether these companies can legally import the material in to the EU due to REACH legislation. Another major disadvantage with both is the colour, which is red (TEMPO) or orange (4H-TEMPO) and the tinting strength of the substances, which does limit the range of applications.

The use of AA is limited due to its insolubility in most polymers and solvents. However it does have excellent solubility in water and offers a good level of inhibition performance. With the increasing drive to more environmentally sustainable production processes and products, waterborne products and the associated production methods are regularly entering the market, which could offer an advantageous use of AA in the future. Of the other inhibitors evaluated in this study, only HQ and 4H-TEMPO have any significant degree of water solubility, however as previously mentioned 4H-TEMPO is coloured and HQ discolours after oxidation. AA when dissolved in water is colourless and remains colourless and in solution when oxidised.

The use of blends of inhibitors could offer certain advantages in combining a cheaper inhibitor with a more expensive one as a method to extent the storage life of a resin at a reduced cost, particularly as a method to ensure that the resin is protected against periods of atmospheric oxygen starvation. Although it is normal industrial practice to only quote a maximum 6 month storage life of most vinyl ester resins, it is well known that the storage life can be extended by renewing/replenishing the air in the head space of the container on a regular basis, ideally every 3 months. However it is inevitable that there will be cases where material will be neglected or forgotten and the use of a blend containing either HQ, PTZ or 4H-TEMPO would advantageous. The major downside, apart from the significant cost difference using 4H-TEMPO compared to other inhibitors, would be the resultant colouration of the resin as previously mentioned.

In general the results appear to indicate that the use of a blend of two inhibitors is of an additive nature. There does not appear to be any confirmation of the belief in a synergistic effect in the use of a blend of BHT and PMP, however since the tests have only been conducted at elevated temperatures, it could be that the synergy may only be seen at room temperature storage conditions (20°C). The use of a blend of two inhibitors, where one functioned in an aerobic environment and the other functioned in an anaerobic would be logical to provide maximum stability during the shelf life of the resin, especially towards

the end of the resin shelf life when the dissolved oxygen in the resin has effectively been used up.

4.8 Inhibitor Modelling

From the data obtained from the stability experiments it is possible to derive a relationship for each resin type and inhibitor across a defined temperature range. This could then be further refined to enable a set of equations/relationships to be defined which could then be incorporated into mathematical models of both short term stability during synthesis, and long term stability during storage for certain types of polymers.

4.8.1 Calculation and Discussion

The results obtained for each inhibitor and resin combination were plotted at 100 and 1000ppm concentrations and the trend line was calculated using the least squares method. It was found that an exponential relationship proved the best line of fit for the data points for all cases. Charts 4.2, 4.4 to 4.6 show the acrylate resins containing BHT and the temperature stability data obtained, while Chart 4.3 shows the degree of correlation obtained when the trends obtained from BHT, HQ and PMP are compared in BADGEDA resin.

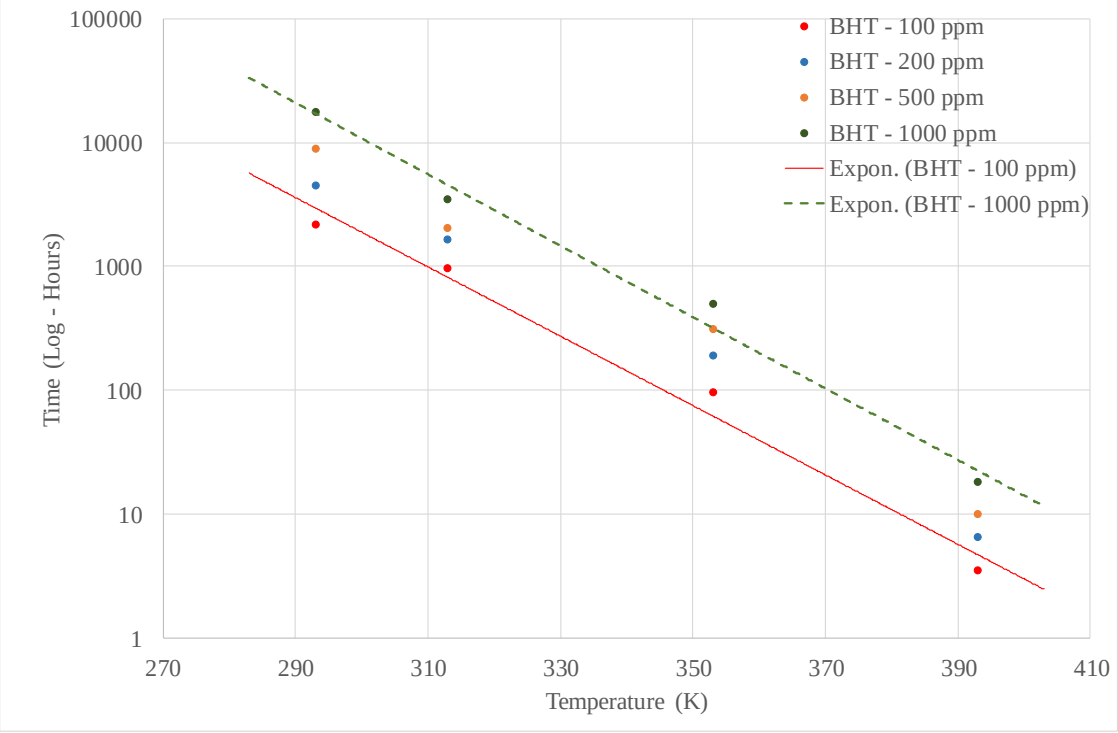

Chart 4.2 – BADGEDA Resin, Air Headspace with BHT as the Inhibitor

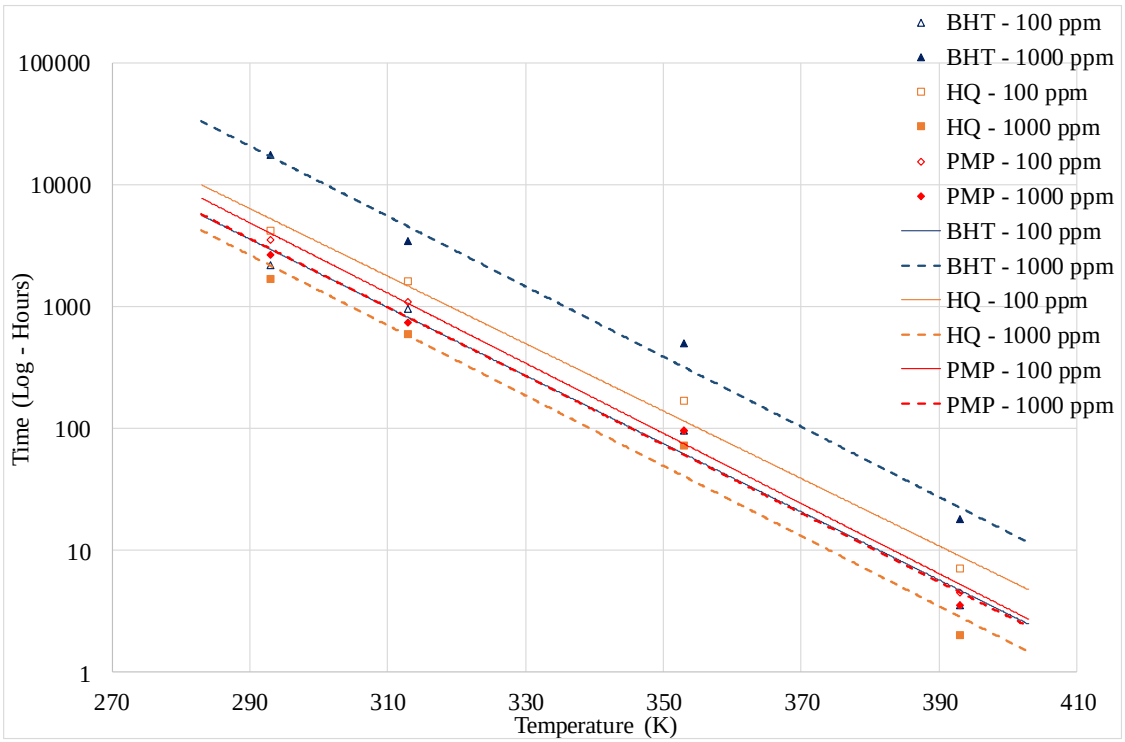

Chart 4.3 – BADGEDA Resin, Air Headspace Inhibitor Trends

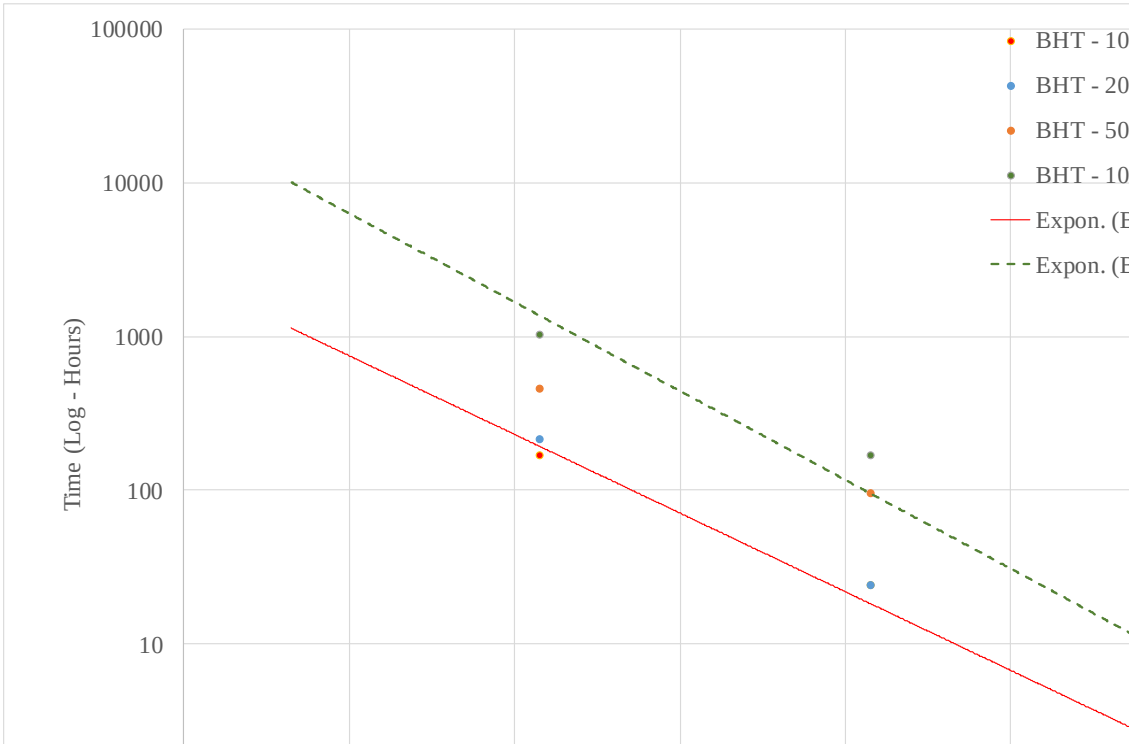

Chart 4.4 – HDDA-MEA Resin, Air Headspace with BHT as the Inhibitor

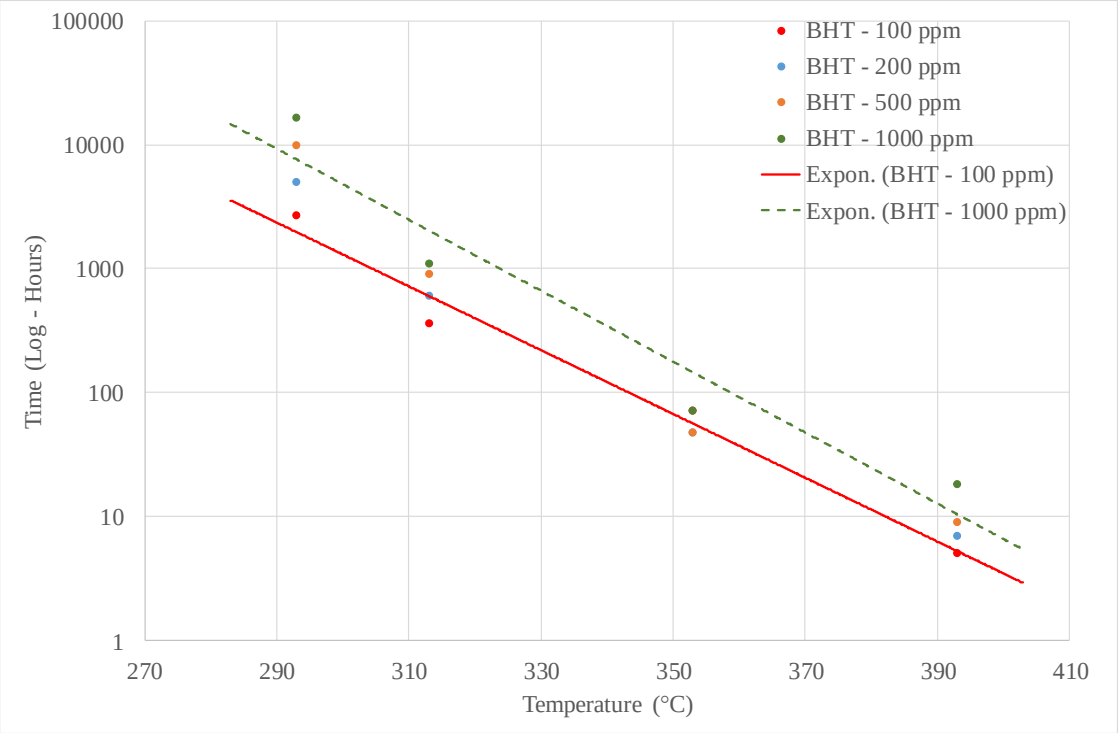

Chart 4.5 – MDI-PEA Resin, Air Headspace with BHT as the Inhibitor

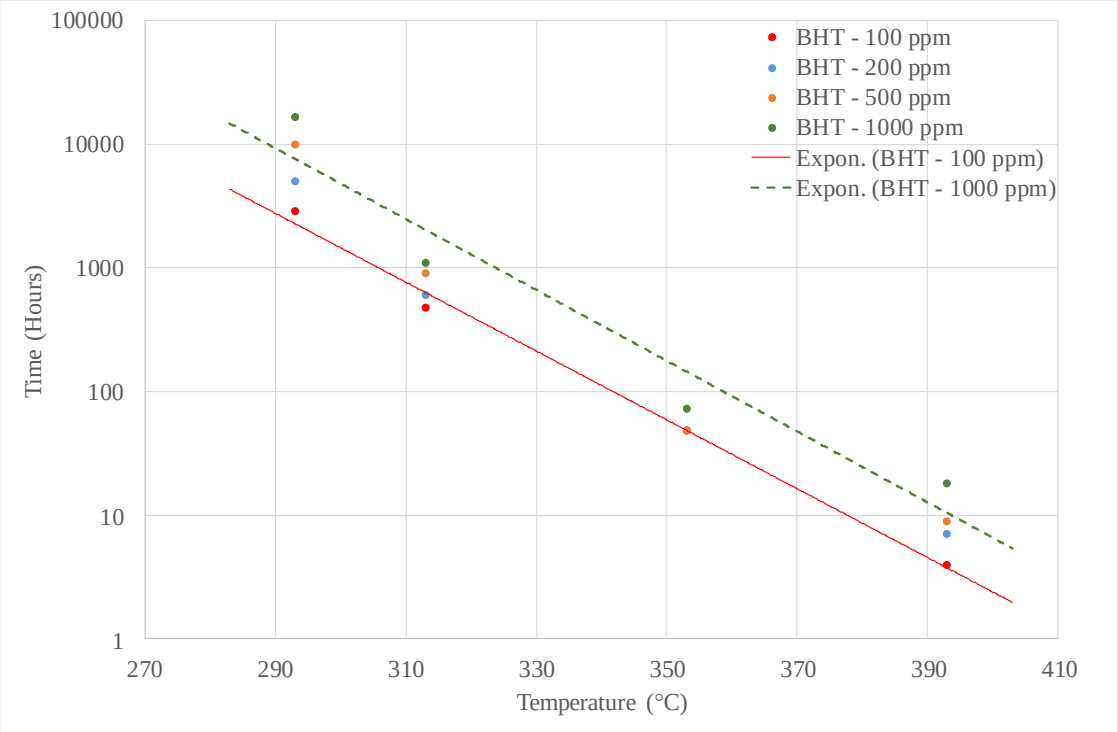

Chart 4.6 – IPDI-PEA Resin, Air Headspace with BHT as the Inhibitor

The equation for the line of best fit can be represented as;

$$y = ax10^{b}e^{-c}$$

Equation 4.1

Where y = maximum stability time in hours, x = the resin temperature (K). a, b and c are constants for each resin type and inhibitor concentration. The temperature is quoted in K so as to allow for the prediction of the inhibitor stability at low temperatures (<0°C/273K).

The values obtained from the resins evaluated are shown in the Appendix in Tables A3.1 to A3.12, with the values calculated for HDDA-MEA shown in Table 4.4. The results for the amine (meth)acrylate HDDA-MEA and HDDA-MEA resins are given, along with all of the epoxy (meth)acrylate resins. In the case of the urethane (meth)acrylate resins, the results are given for IPDI-PEA, IPDI-PEM, MDI-PEA and MDI-PEM resins.

In general the lines of best fit for the upper (1000ppm) and lower (100ppm) inhibitor concentrations for the resins are parallel, hence a median line can be calculated and used to derive an equation to predict the stability of the inhibitor in a defined environment. Although the majority of the data derived from the resin stability have produced parallel best lines of fit, there is some data that show convergence, typically at the higher temperatures (120°C/393K). Since the rate of inhibitor consumption is at its highest at these temperatures, it becomes more difficult to accurately measure the true stability time with certain inhibitor/resin combinations. Chart 4.4 shows such a convergence with HDDA-MEA and BHT.

The median line of best fit was calculated for the above mentioned resin and inhibitor combinations by taking the average time to gelation between the inhibitor concentrations at each temperature. This was calculated to be at 525ppm concentration for HQ and 550ppm for all other inhibitors evaluated. As previously the same exponential equation (Equation 4.1) was found to give the best line of fit for the generated values, and lay between the upper and lower concentration lines of best fit. The values of a, b and c as mentioned in the previous equation were calculated and have been described in Tables A3.13 to A3.24, together with the R^2 value to give an indication as to how well the equation fits to the calculated values obtained.

Inhibitor	Air Headspace						Nitrogen Headspace					
	100ppm			1000ppm			100ppm			1000ppm		
	a	b	c	a	b	c	a	b	c	a	b	c
HQ	9.6604	9	0.0571	2.7457	10	0.0532	5.4572	10	0.0607	9.5160	9	0.0507
PMP	2.0078	10	0.0590	1.5595	12	0.0666	1.2171	10	0.0571	2.8158	13	0.0751
MeHQ	6.2096	9	0.0553	7.4837	10	0.0567	5.0612	8	0.0484	8.7111	10	0.0565
TBC	1.2171	10	0.0571	2.5706	9	0.0475	5.4953	8	0.0484	4.1168	9	0.0484
BHT	3.7838	10	0.0607	6.5974	13	0.0778	9.6604	9	0.0571	1.9623	11	0.0603
4H-TEMPO	3.3886	10	0.0582	9.4573	10	0.0554	2.6222	10	0.0571	6.2417	10	0.0536
PTZ	5.9336	9	0.0543	7.5837	10	0.0560	9.3098	9	0.0548	6.6215	10	0.0550
DTBP	3.6004	8	0.0484	2.8205	9	0.0520	3.6004	8	0.0484	1.0377	10	0.0557

Table 4.4 – Data for Equation 4.1 for HDDA-MEA Resin

Looking at the R^2 values calculated, it is found that the majority of the inhibitors lie within the 0.9700-0.9999 region, particularly for the epoxy (meth)acrylate resins, however with the amine and urethane (meth)acrylate resins there is a far wider range of R^2 values, 0.07797 to 0.9985 in the case of amines and 0.7709 to 0.9999 for urethanes. In the case of HDDA-MEA and HDDMA-MEA resins it could be due to the effects of hydrogen bonding between the nitrogen lone pair and the hydrogens present in a linear molecule, which at low temperatures results in gel formation taking place. Otherwise interactions, such as van der Waals forces could be playing a significant contribution. The amine group does appear to have an adverse effect upon the stability of the resin, particularly when the structurally similar 1,6-hexanediol based resins are compared, HDDA-MEA and HDDGEDA in the case of the amine and epoxy acrylates respectively and HDDMA-MEA and HDDGEDMA for the methacrylate. The amine based systems are considerably less stable, than the epoxy.

It is well known that the urethane bond begins to breakdown at temperatures of 130°C and above. The stability testing of the resins at 120°C would have the effects of not just the formation and degradation of free radicals, which would attack the vinyl carbon-carbon double bond, but also the slow breakdown of the urethane bond at the same time. The inhibitors under investigation were primarily chosen for their ability to control the effects of free radical attack, rather than the stabilising effect upon the urethane bond. This would help to explain the dip seen in the stability of the urethane resins, when compared to the epoxy. MDI-PEA and MDI-PEM resins have a structurally similar central backbone to BFDGEDA and BFDGEDMA.

In general the methacrylate resins appear to produce results that are more variable compared to their acrylate analogues, this is shown in the R^2 values. However there does not appear to be a pattern as to which inhibitor produces the greatest variability, as the R^2 values do not show any clear inter-relationship.

Looking at the values obtained for a and b, it can be seen that in many cases there is a factor of 10 between the values for 100 and 1000ppm for each inhibitor and resin combination. It is then possible to derive an equation to predict the lifetime of an inhibitor within a specific resin system, providing that the temperature and the inhibitor type and concentration are known. If the below are assumed, then an equation can be derived to give a predication concerning the stability of a given resin system;

1. The upper and lower trend lines are effectively parallel,
2. The midpoint trend line represents the mean of the data collected,
3. There is a linear proportionality between the upper and lower concentrations.

Based on the line of best fit data derived from the stability data the following logarithmic relationship can be used;

$$y = (az + b)e^{-cx}$$

Equation 4.2

Where x = temperature (K), y = time (hours), z = concentration (ppm), a = resin constant, b = resin constant and c = resin constant.

The values calculated in Tables A4.1 to A4.12 are for the amine (meth)acrylate resins, epoxy (meth)acrylate resins and the urethane (meth)acrylate resin with 2 different head space atmospheres, air and nitrogen. Since the core data has been taken from the 20 to 120°C region, then the times calculated are only valid within the temperatures specified. Again the R^2 values are provided to give an indication of the degree of fit to the actual values, with the line gradient determined by the calculated mean as discussed above. It would be ideal if the R^2 values were 1.0, however as a good approximation it has been shown that even when the values are as low as 0.9, then the values generated for a given temperature and inhibitor concentration do match up quite closely to the values recorded. Table 4.5 shows the percentage of the R^2 values that are greater than or equal to 0.9. In general it does appear that the epoxy (meth)acrylate resins in air can be modelled with a reasonable degree of accuracy, with the degree of certainty of modelling reduced when a nitrogen atmosphere is introduced. There does not appear to be any clear cut situation with the amine (meth)acrylates, however with the urethane methacrylates it appears that the nitrogen atmosphere allows for a better modelling.

Resin	Air Atmosphere	Nitrogen Atmosphere
HDDA-MEA	25.0%	50.0%
HDDMA-MEA	62.5%	37.5%
HDDGEDA	100.0%	50.0%
BADGEDA	100.0%	50.0%
BFDGEDA	87.5%	87.5%
HDDGEDMA	87.5%	37.5%
BADGEDMA	62.5%	25.0%
BFDGEDMA	100.0%	62.5%
MDI-PEA	62.5%	62.5%
IPDI-PEA	37.5%	12.5%
MDI-PEM	50.0%	62.5%
IPDI-PEM	50.0%	75.0%

Table 4.5 – Analysis of R^2 Values ($\geq$0.9)

Looking at the data in Tables A4.1 to A4.12 there does not appear to be any one combination of inhibitor and atmosphere that gives rise to poor modelling, it does appear to be random scatter. From the figures below the nitrogen atmosphere with IPDI-PEA resin gives rise to the greatest difficulties to predictive modelling, with all bar one (BHT) of the inhibitors resulting in poor predictive modelling.

Unfortunately there does not appear to be any pattern to the vales of a, b and c generated that could correlate the values generated to either the resin type, the test atmosphere used or the inhibitor. The variation within each set of data generated is too wide to allow for anything more than some generalised conclusions to be drawn.

4.9 Conclusions

The results generated have shown that 4H-TEMPO is a very good inhibitor to provide excellent stability for both air, nitrogen and even nitrogen sparge conditions, for a given concentration when compared to the other compounds evaluated, this is in contrast to DBTP which has shown very poor response in almost all conditions. As previously discussed the major limitations on the commercial use of 4H-TEMPO are the colouration issue and the cost. PTZ is the next best contender, along with HQ for providing good all round performance, followed by MeHQ. These compounds are known to be able to be able to operate in anaerobic conditions, unlike the remaining compounds which all require aerobic conditions to act as polymerisation inhibitors and/or free radical scavengers. This also includes AA, which is water soluble and only active in the aqueous phase which contains some dissolved oxygen present.

Looking at the equations derived from the experimental data for modelling purposes, further data points particularly at lower temperatures would allow for further refinement of the resultant equations, particularly in the 5 to 30°C (278-303K) region. At lower temperatures the time taken for the resins to gel would be significantly longer than at >60°C, but it is in this temperature region that the majority of resins are stored and used at, hence is potentially of greater interest than high temperatures which are normally only encountered during the initial synthesis of the resin and potentially during the final curing regime.

In commercially produced resins at the end of the synthesis process a charge of fresh inhibitors is added to provide the required storage stability and then rapidly cooled to allow the manufacture of the next batch of material. It is very rare for resins of the types described in this report to be held at high temperatures for prolonged periods. For the majority of resins it would be possible to predict the required concentration of an inhibitor to allow for a minimum of 1 year of storage stability from the date of manufacture and to allow for a reasonable safety buffer.

4.10 References

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5 Resin Curing

The main direction of the work described thus far has been to examine the use of polymerisation inhibitors to prevent the resin system from polymerising during storage. This is naturally very important from a commercial perspective, but at some point the resin will be processed in a form where controlled polymerisation is the desired outcome.

There is a balance to be struck between the two conflicting requirements of a stable resin system that does not polymerise during storage, and then the need for the same resin to polymerise quickly during the curing process. Studies were undertaken looking at how the resins examined thus far behave during curing. There is the slow polymerisation that can take place during storage due to the polymer inhibitors becoming exhausted, which is often referred to as a gel, and then there is the rapid polymerisation that is deliberately induced, normally by the addition of a free radical catalyst and a source of energy (either radiation or thermal).

5.1 Gel Formation

It has been postulated that the reason why vinyl ester resins gel during storage, and processing, is due to the build up of free-radicals which can attack the carbon-carbon double bond of the (meth)acrylate group. The major source of free radicals in vinyl ester resins are due to naturally occurring peroxides. Once the inhibitor added to the resin system has either become exhausted, or deactivated, then either the peroxide concentration will begin to increase or the existing peroxides will be able to react with the resin. The peroxide formation and reaction with other substances has been found to be temperature dependant.

There is a substantive body of literature on peroxide formation in thermoplastics due to extrusion moulding, the use of peroxides to cure vinyl ester resins (by the deliberate introduction of peroxides) and of peroxide formation during the manufacture of monomers. Similarly there is a significant amount of literature concerning the introduction of free radicals into vinyl ester resins to enable UV curing to take place. However there is very little in the way of how vinyl ester resins gel during storage, and what reaction mechanisms are taking place to cause gel formation to occur.

Taking a sample and sampling at various points during its life time it should be possible to determine the nature of the gel formation, and in turn relate it to the effects of the inhibitors added in terms of extending the shelf life of the resin. By using rheology it was

possible to study the changes on a macroscale, while using FT-IR spectroscopy to look for any changes due to bond cleavage/formation.

5.1.1 Rheology

Since the area of interest is to determine how stable resins are at temperature it was decided to instigate a rheological study of the resins where the temperature was fixed and time was varied. The assumption was that the resin would begin to show changes before a visible gel occurred, hence the use of a rheometer to obtain as much data as possible, compared to using a viscometer which can only generate viscosity data. To allow for a quantifiable correlation between samples to be made, a series of rheological studies were undertaken to look at how the samples gel under various ideal conditions.

Work done by Winter *et al*[1,2] looking at the gel point of polydimethylsiloxane was undertaken using oscillation rheology. This was the basis for a standard method which was developed as a suitable method for determining the gel point of mixed epoxy resin systems to determine safe working temperatures. Typically a temperature sweep would be undertaken using a sample of freshly mixed resin. The temperature sweep would start at room temperature (~20°C) and then increased at a defined temperature ramp to a temperature where the resin begins to gel. This would also have the advantage of enabling the method to be used for industrial applications due to the widespread use of rheometers within industry.

The rheological data was obtained using a TA Instruments AR 2000 Rheometer, equipped with an external furnace to allow high temperature cure measurements to be run, and able to accept parallel plate measurement geometry. A second instrument, TA Instruments AR 2000 EX, with the same accessories and software was also used to provide additional data for cross checking.

To determine the gel point of a resin system it is common practice to apply a temperature sweep to the sample, while maintaining a constant applied frequency. As the temperature increases the viscosity of the resin will initially decrease until the gel point is reached, then will sharply increase. This information is particularly useful in determining both resin stability data as well as minimum cure temperatures. From the work reported by Winter and co-workers[1,2] it is known that the crossing point of G' (storage modulus) and G'' (loss modulus) is taken to be the gel point of the resin system.[3] This gel point will

actually occur before there is any significant increase in the viscosity of the system. The storage modulus represents the elastic component of the material, while the loss modulus the viscous component. Figure 5.1 shows the graphical results of a rheology experiment, where the G' and G'' crossing point can clearly be seen, as can the increase in viscosity (η) as G' increases.

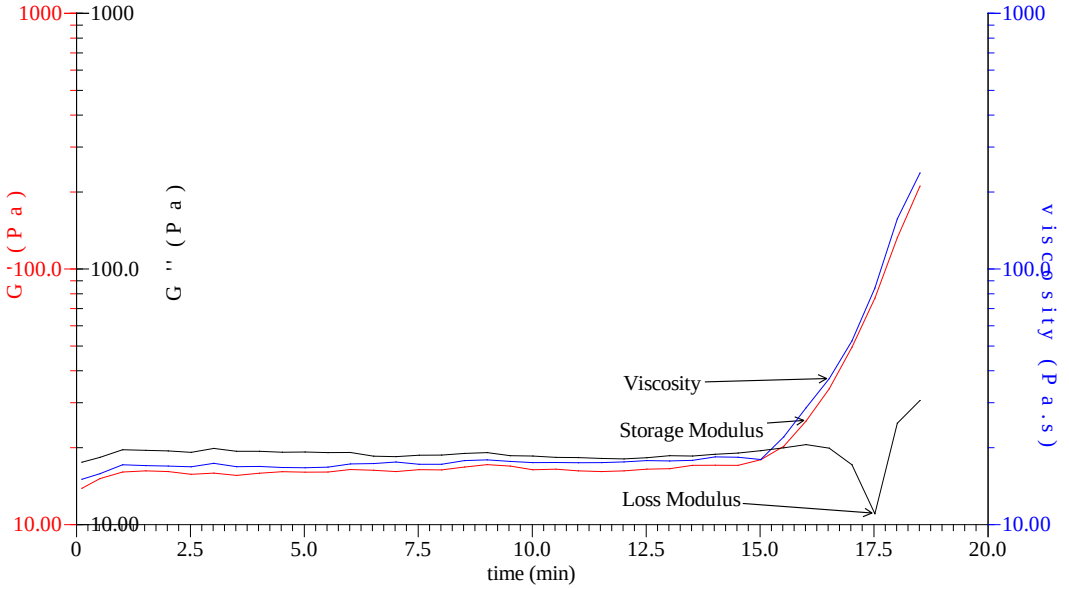


Figure 5.1 – IPDI-PEM Resin Oscillation Response @ 2Hz

5.1.1.1 Equipment Setup

An aluminium disposable geometry was used with a 25mm diameter upper platen and 40mm diameter lower platen, the two surfaces in contact with the sample were polished with 1000 grit wet and dry paper to minimise potential interference due to surface irregularities (see Figure 5.2). The cured resins samples could be removed from the aluminium platens by soaking them in N-methyl pyrrolidone @ 80°C for 48 hours. The equipment was serviced every 12 months with the temperature of both the Peltier plate and external furnace calibrated at the same time. The equipment was calibrated once a month against standard viscosity oils. Before each series of runs, the geometry was mapped on a daily basis, or when the plates had been changed. The gap was set to 1000μm, which when combined with the upper platen dimensions, gave a sample volume of 0.49mm^2. The samples were measured in oscillation mode at various temperatures.

The amount of strain applied to the samples had to be sufficient to induce a sufficient viscoelastic response, but not enough to either induce mixing within the sample when

liquid, or to cause the sample to be fractured when curing or cured. Experiments were carried out to determine a suitable level of strain and frequency to be applied (see Charts 5.1 and 5.2). Previous temperature sweep curing studies carried out on epoxy, epoxy acrylate and polyester resin systems were done applying 3.259Pa at a frequency of 1 Hz, these figures were used as reference points. It was found that when looking over an applied stress range of 0.1 to 32.59Pa there was a slight upward trend in the gel time as the stress was increased, but that applying a stress of 3.259Pa gave reasonably consistent results. When a similar series of runs were made looking over an applied frequency range of 0.1 to 10Hz, the gel time trend was reasonably consistent up to 1Hz, then the gel time trends shows a definite increase. Since the point of inflection is in the 1-2Hz region, it was decided to remain with the original experimental parameters.

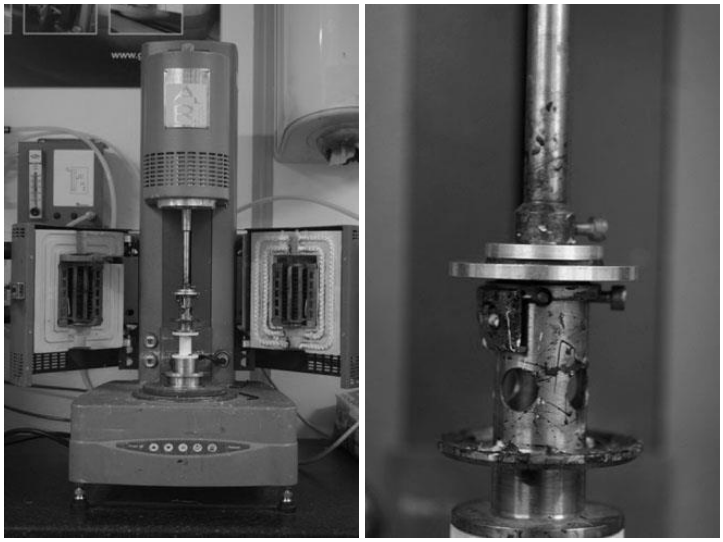


Figure 5.2 – Rheology Experimental Setup With Parallel Plates

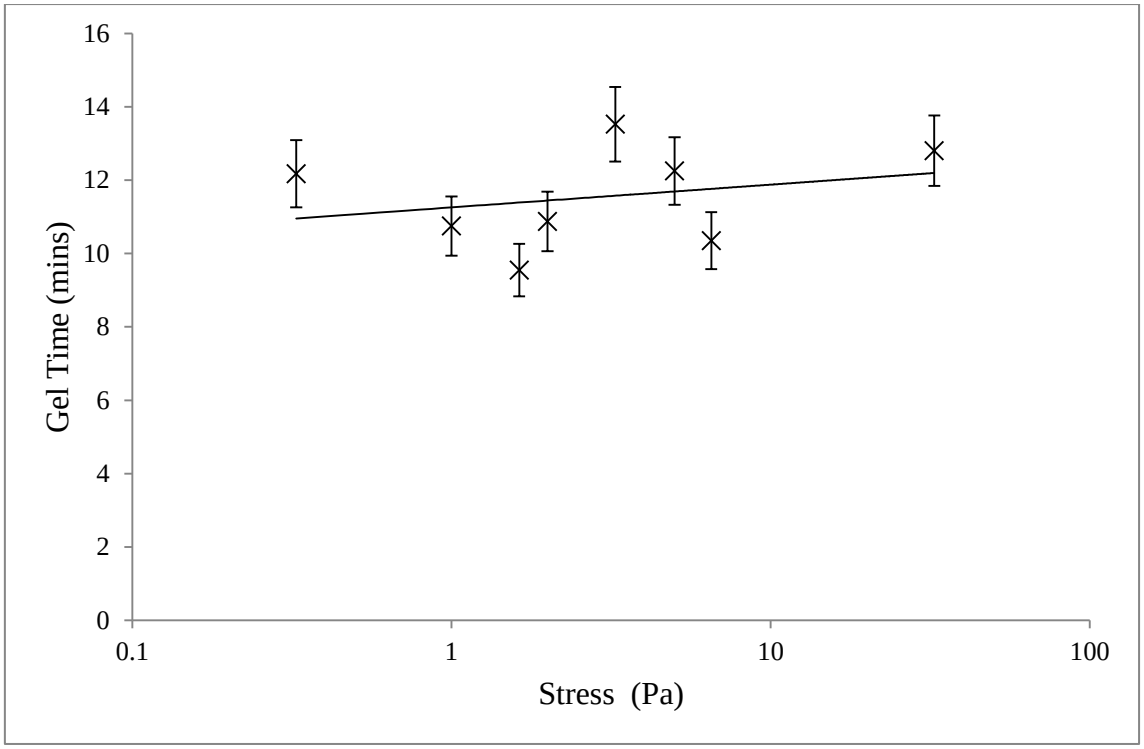


Chart 5.1 – Stress Sweep of IPDI-PEM Resin @ 2Hz, 120°C

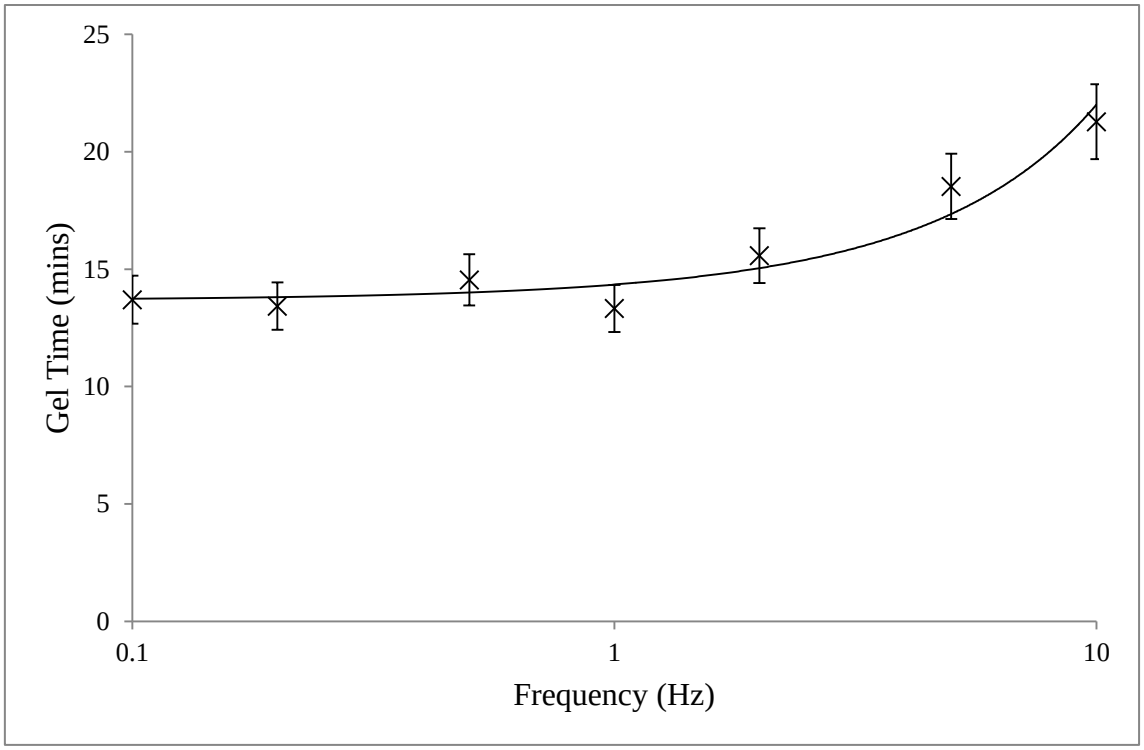


Chart 5.2 – Frequency Sweep of IPDI-PEM Resin @ 3.259 Pa, 120°C

Figures 5.3 to 5.5 show a series of rheology traces describing the change in G' and G'' with time at a fixed temperature. Figure 5.3 shows a textbook response where the crossover point is clear and unambiguous, followed by a rapid increase indicating gel

formation due to the polymer network being formed. Figure 5.4 shows where there is no crossover due to G' being greater than G'' from the start of the measurement. This situation is not that uncommon and is remarked upon in several texts, in which case the G' inflexion point is taken as the pseudo crossover point. Figure 5.5 shows where there is a "noisy" baseline and there are multiple crossovers, in which case the final crossover at the inflection point is taken as the definitive value.

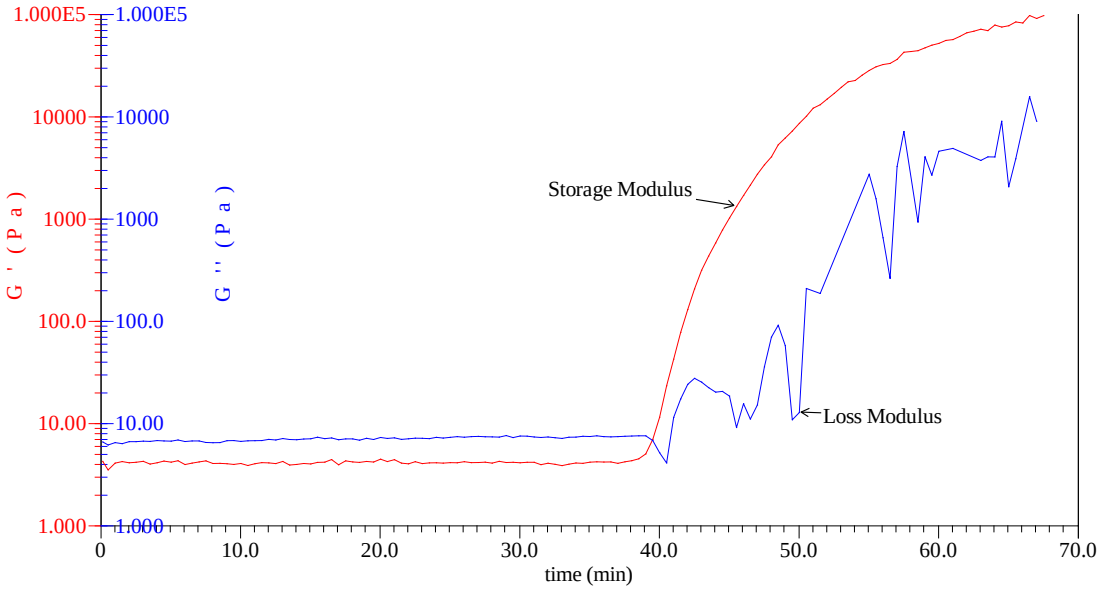


Figure 5.3 – IPDI-PEA Resin with 1000ppm of BHT @ 120°C under Oscillation

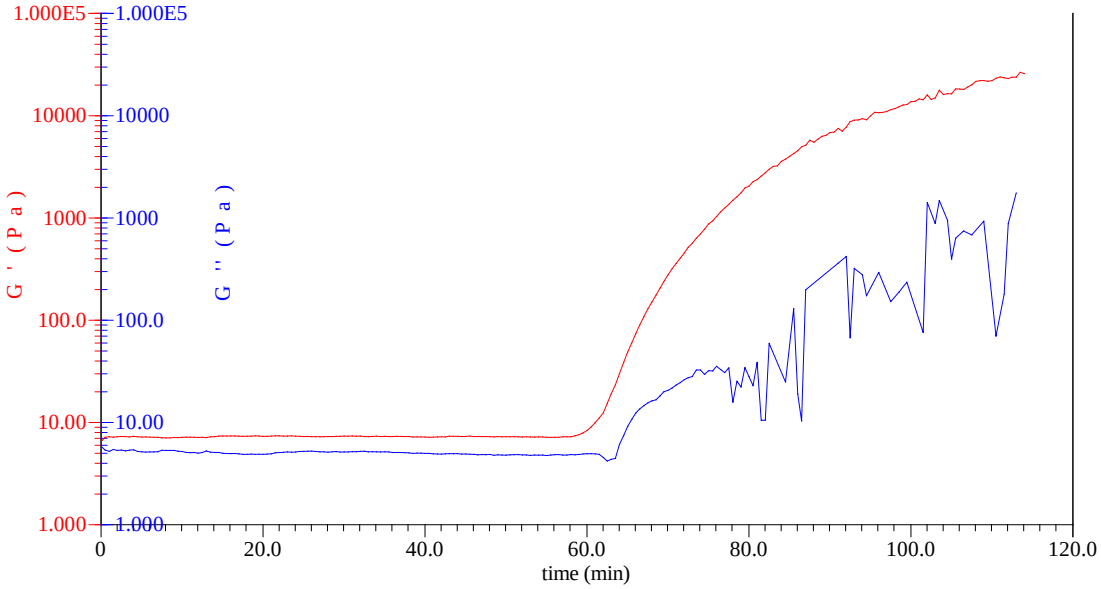


Figure 5.4 – IPDI-PEA Resin with 1000ppm of BHT @ 90°C under Oscillation

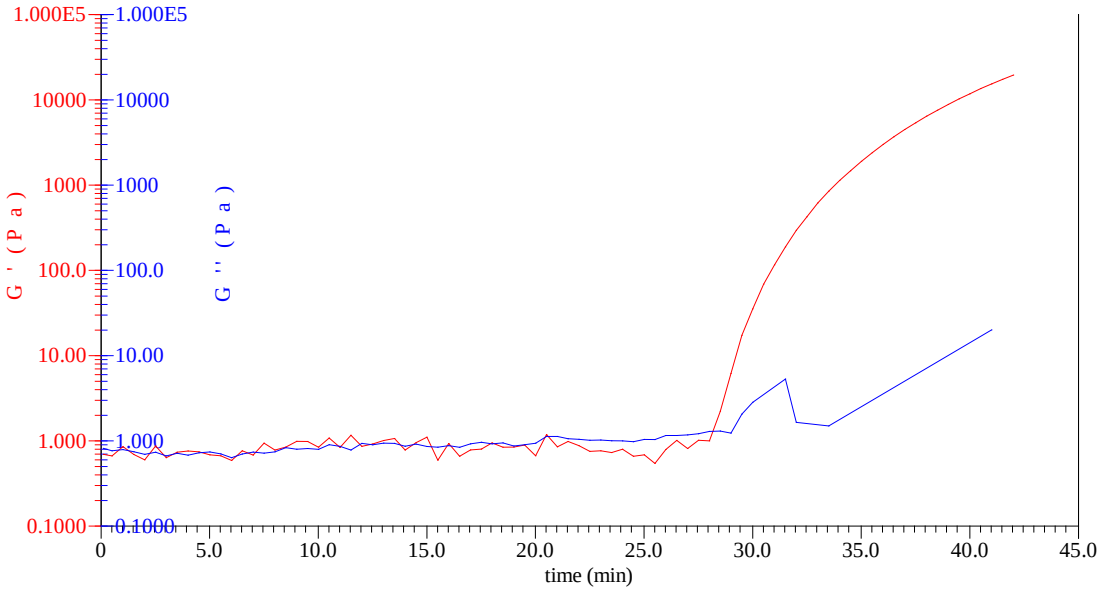


Figure 5.5 – IPDI-PEM Resin with 1000ppm of BHT @ 120°C under Oscillation

5.1.1.2 Results and Discussion

Charts 5.3 to 5.5 show the average gel time (or the time when the G' and G'' crossover took place) of the resin samples tested. As seen with the stability samples discussed in Section 4, the general trend of increased stability with increased inhibitor concentration is observed, even with a smaller sample volume used for testing. Generally it is the case that the methacrylate appears to be more stable than the equivalent acrylate as discussed in Section 2.1.[4] However in the case of the urethane resins, IPDI-PEA, IPDI-PEM, MDI-PEA (**39**) and MDI-PEM (**43**), the reverse is the case when 4H-TEMPO (**26**) is used as the inhibitor. The samples containing 4H-TEMPO had by far the longest experimental run times, which might have been a contributory factor, with external influences playing a part, although the runs were repeated on a different rheometer in a different laboratory and obtained a similar set of results. In the case of the epoxy (meth)acrylate samples, BADGEDA (**33**) and BADGEDMA (**36**), it was found that the methacrylate was by far the most stable regardless of the inhibitor used. The amount of residual epoxy left after the resin synthesis does have a significant effect upon the curing profile at elevated temperatures. Providing that the epoxy value of the epoxy (meth)acrylate is 8mgKOH/g or below (0.99% unreacted epoxy), then the effect of the remaining epoxy groups reacting due to the elevated temperatures has a minimal effect due to either crosslinking, or bonding to the test geometry. However higher levels of unreacted epoxy groups to lead

to crosslinking to form harder segments, compared to the crosslinking due to (meth)acrylate double bond opening up and crosslinking.

The samples were examined after each run, and it was found that if the run was stopped as *G′* was still increasing, then the sample showed discrete areas of gel formation surrounded by liquid. However when *G′* had reached a plateau then the sample had completely gelled into a single continuous mass, since the material was a polyethylene based urethane polymer, it was quite flexible as would be expected if cured via a normal route.

It is very noticeable that 4H-TEMPO certainly gives the best performance in terms of longevity. The experiment was tried using 1000ppm of 4H-TEMPO in IPDI-PEM and had to be abandoned after 15 hours @ 90°C due to the sample still being liquid due to the inhibitor remaining active even after this time.

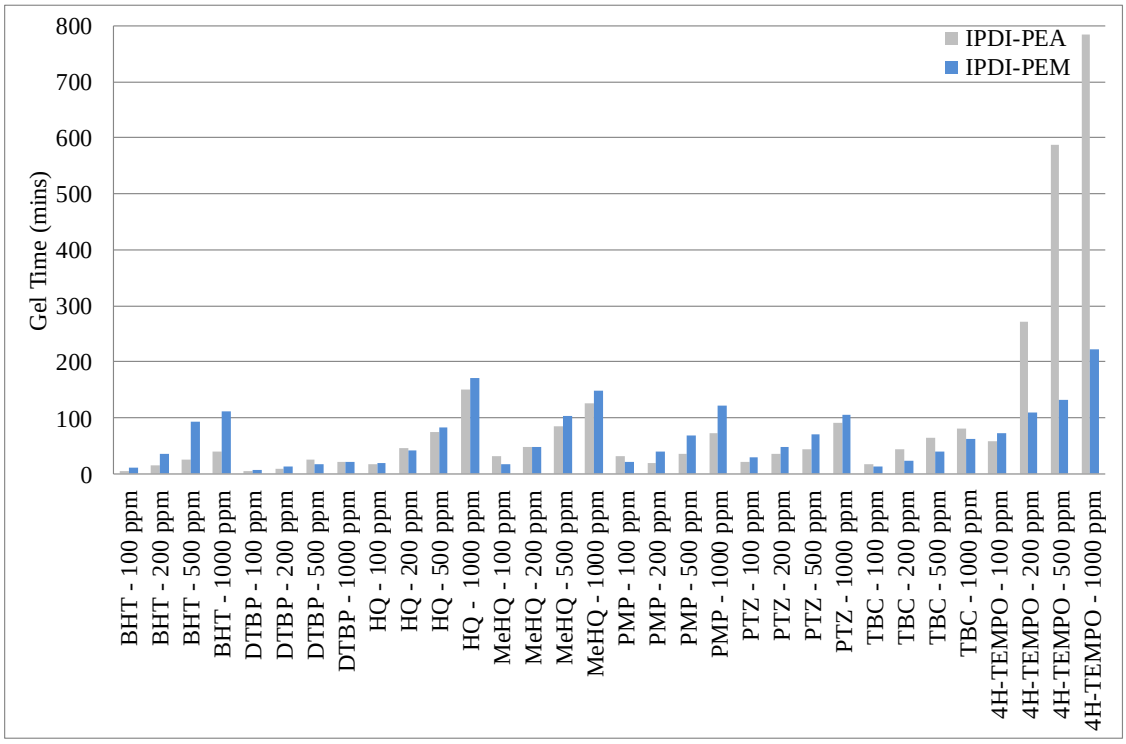


Chart 5.3 – Comparison of IPDI-PEA and IPDI-PEM Resins Oscillation @ 120°C

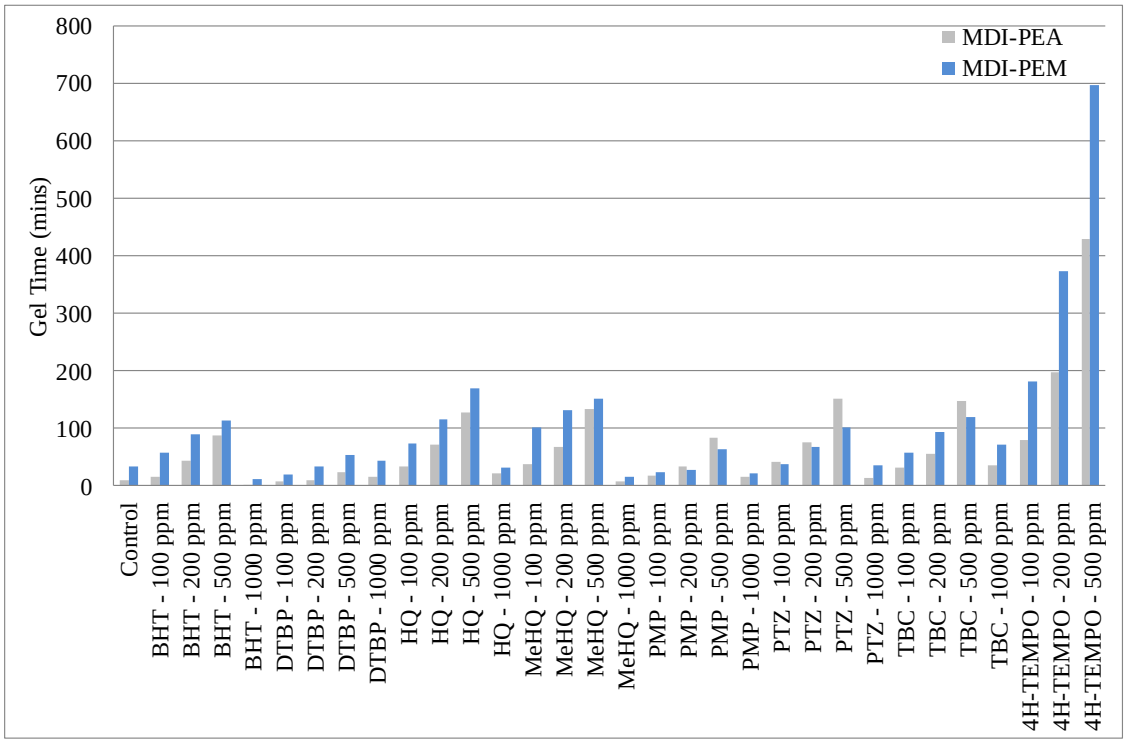


Chart 5.4 - Comparison of MDI-PEA and MDI-PEM Resins Oscillation @ 120°C

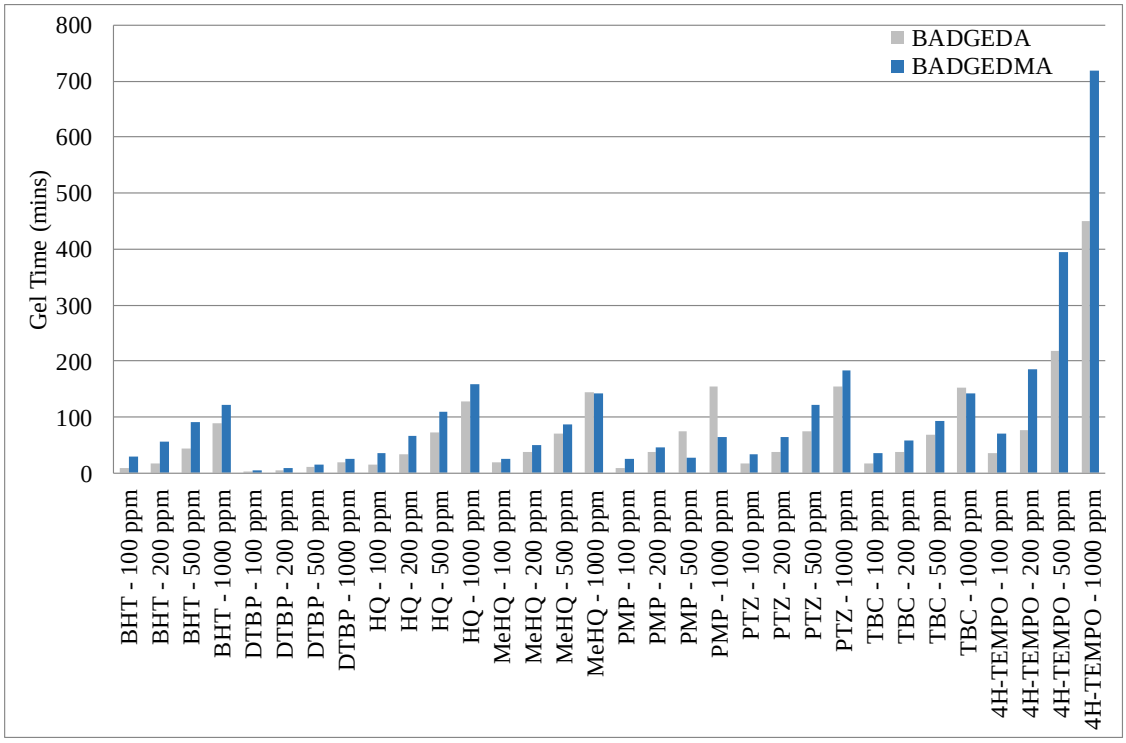


Chart 5.5 - Comparison of BADGEDA and BADGDMA Resins Oscillation @ 120°C

Work was done to determine the stability of the uninhibited base resin at different temperatures. As would be expected, as the temperature increases, the gel time for the sample decreases (see Charts 5.6 to 5.8) showing a logarithmic relationship, which appears to hold for both acrylate and methacrylate samples. Generally the methacrylate resins are more stable than the acrylate, even in the uninhibited state, however this relationship is reversed for the isophorone based urethane resins IPDI-PEA and IPDI-PEM examined.

The highest temperature that was studied was 130°C, where the gel times were occurring within 5 minutes of starting the experiment. Since the (meth)acrylate carbon-carbon double bond is known to become unstable at temperatures above 130°C and increasingly becomes prone to polymerisation even with the presence of inhibitors.[5,6] The epoxy (meth)acrylate resin contains not just a residual amount of unreacted epoxy, but also trace amounts of TPP catalyst. At 130°C the epoxy ring can open up in the presence of the residual amounts of TPP present and either cross-link with other epoxide groups, or react with hydroxyl groups on the surface of the aluminium geometries used. Since epoxies are well known to have excellent adhesion to the majority of most commonly encountered substrates due to the epoxy groups being able to react with the hydroxyl groups present on the surface of most substrates, it would be logical to assume that the results of the epoxy (meth)acrylate testing would be similar regardless of the substrate used.

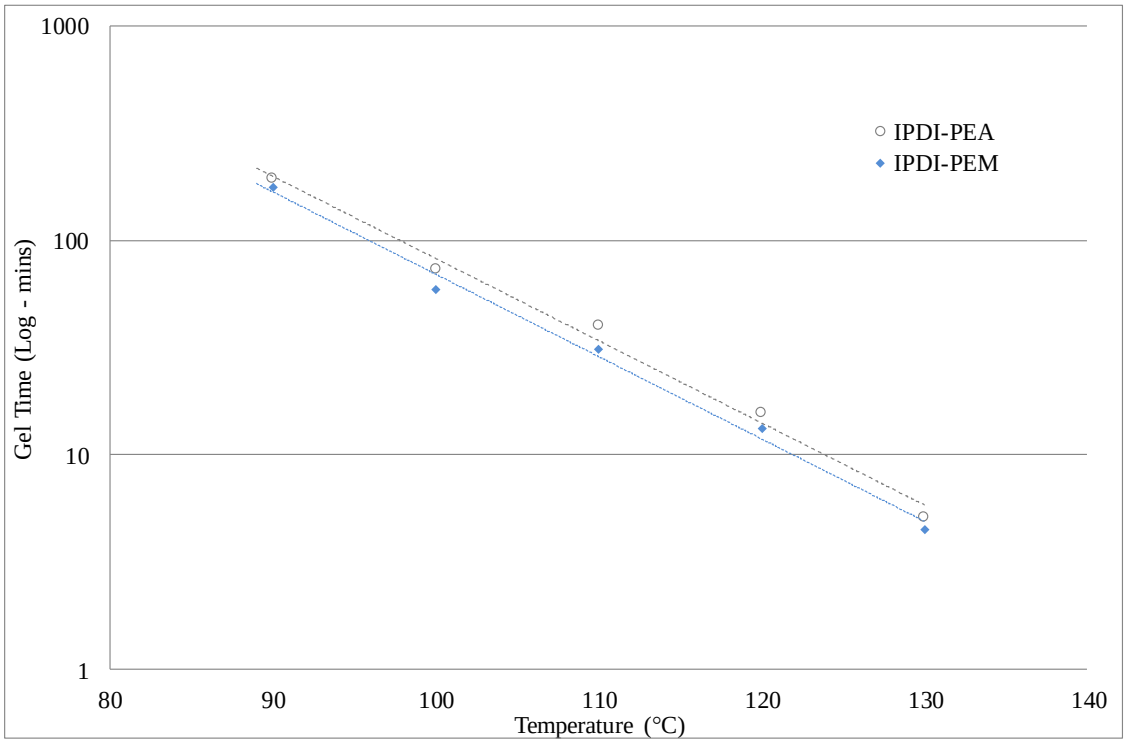


Chart 5.6 - Comparison of IPDI-PEA and IPDI-PEM Resins Oscillation between 90-130°C

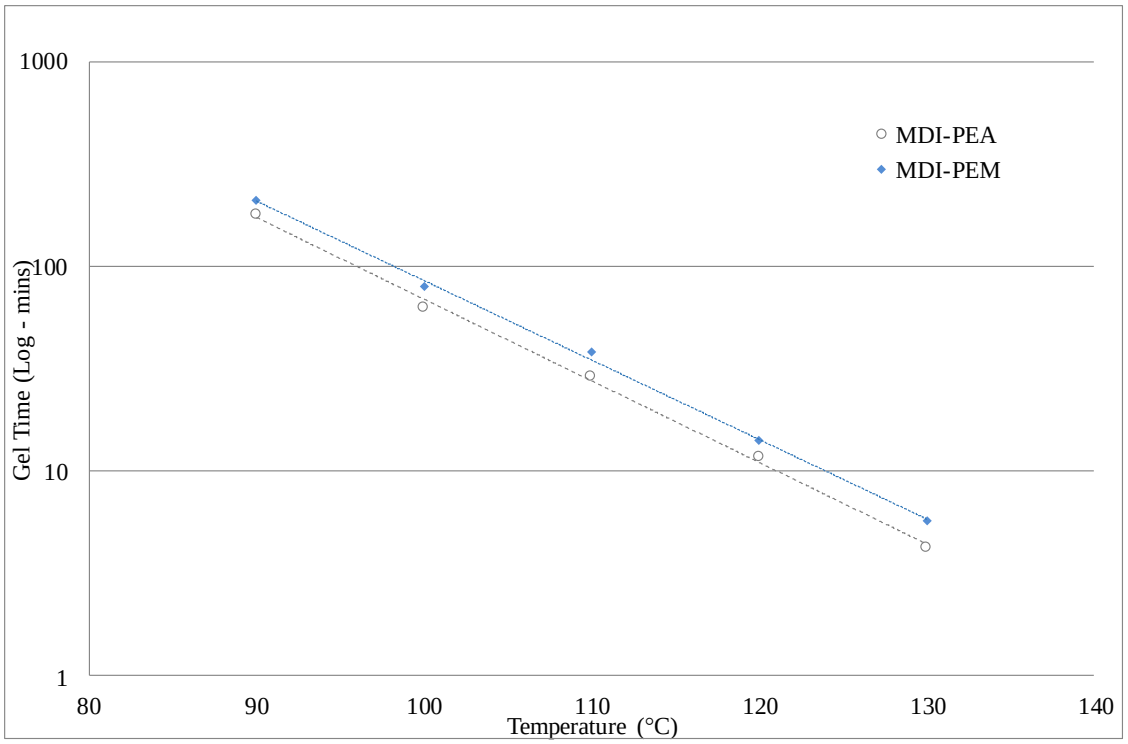


Chart 5.7 - Comparison of MDI-PEA and MDI-PEM Resins Oscillation between 90-130°C

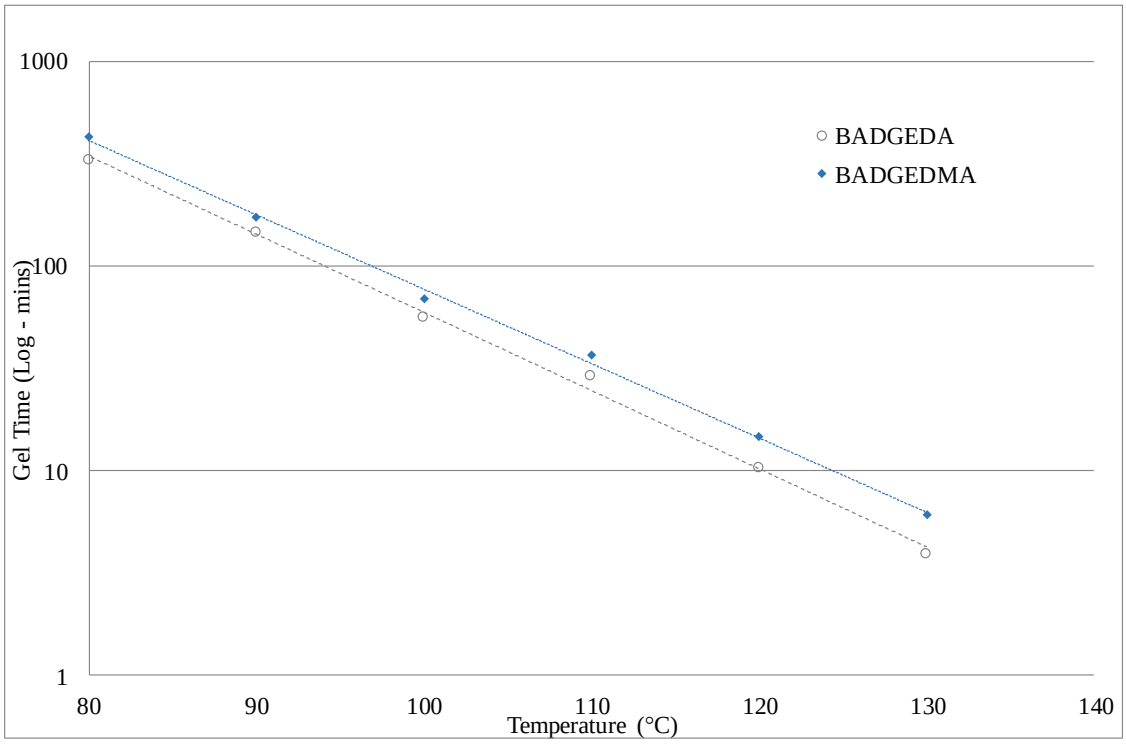
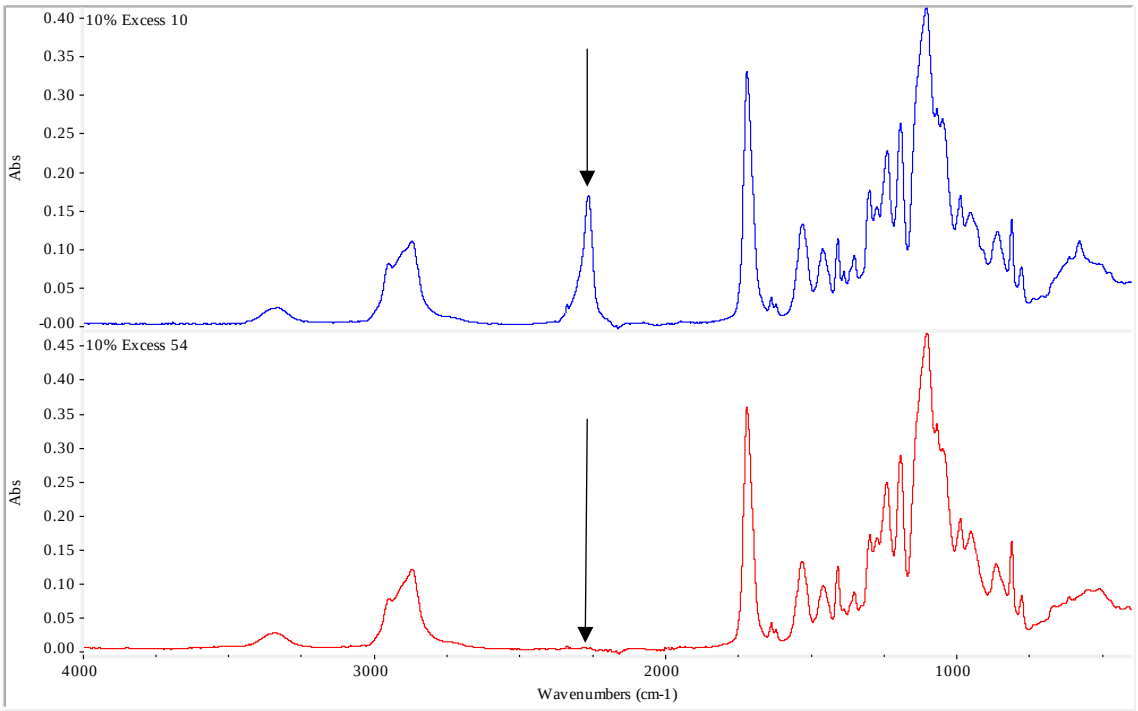


Chart 5.8 - Comparison of BADGEDA and BADGEDMA Resins Oscillation between 80 and 130°C

5.1.2 FT-IR Spectroscopy

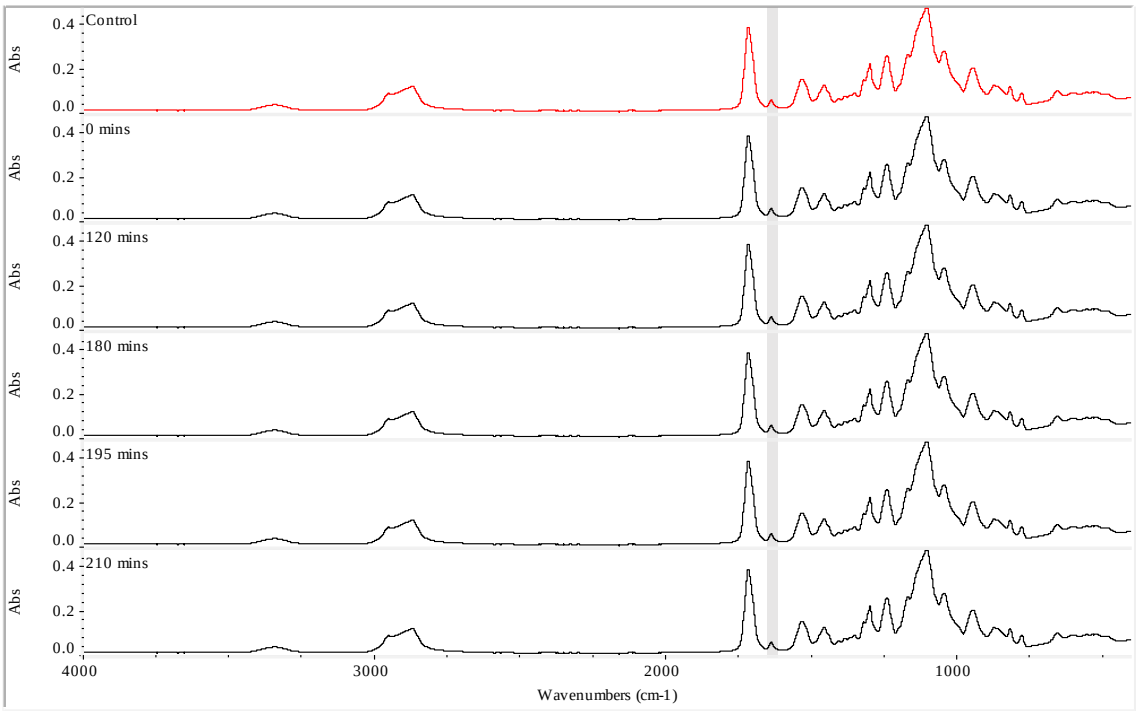
The samples were characterised using a Bruker ALPHA FT-IR spectrometer with a Platinum ATR accessory. The initial work was done on IPDI-PEA and IPDI-PEM. Samples of both resins were analysed check that the reaction was fully complete for absence of a peak at 2270cm^{-1} due to NCO stretching.

Two samples were made up based on IPDI-PEA as the only reactants, with 0.1% DBTDL as a catalyst. These were reacted for 4 hours at 50°C to completion. The sample with a 10% excess of IPDI clearly shows the unreacted isocyanate due to the peak at 2270cm^{-1} (see Spectra 5.1), while the spectra directly below is from the sample with a 10% excess of PEA, which does not have a peak at 2270cm^{-1}, indicating that all the isocyanate had been reacted. Since the ATR accessory is not equipped with a heated stage, the temperature stability experiment was done in the same oven as the 120°C stability testing. 20g of IPDI-PEA and IPDI-PEM with 100ppm of BHT was made up and placed in an oven at 120°C. Samples were taken out every 30 mins until the remaining material had started to gel, then every 15 minutes until full gelation had occurred. FT-IR spectra were run on the samples taken.



Spectra 5.1 – IPDI-PEA Resin, Upper – Excess IPDI, Lower – Excess PEA. Isocyanate Stretching Peak Indicated

Spectra 5.2 show the results from a selection of the samples taken, unfortunately as can be seen the peak at 1635-40cm^{-1} (C=C bond stretching due to (meth)acrylate group) is visible in all the spectra, as highlighted in the spectra. The gelled samples were determined for degree of cure by undertaking a 24 hour extraction test at 50°C in hexane as out lined by Park *et al*,[7] which is a modification of the appropriate ASTM standard.[8]



Spectra 5.2 – Curing Profile of IPDI-PEM Resin Measured Over 210 Minutes

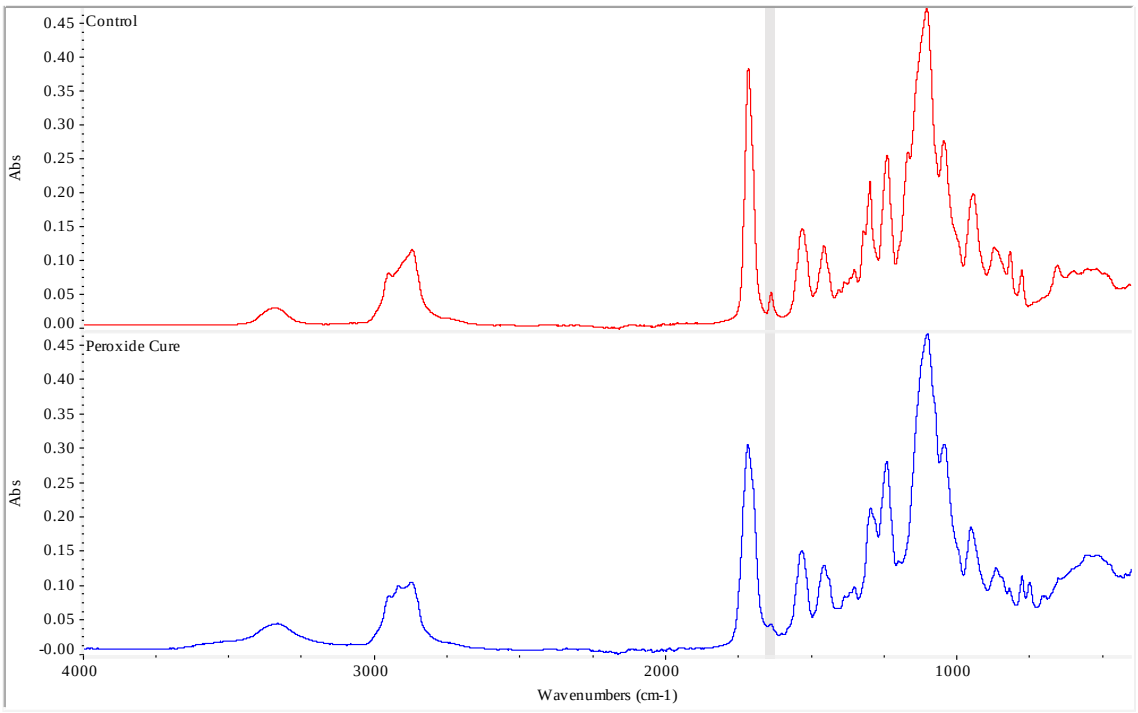
Table 5.1 shows the degree of cure of the samples together with the results of the peak height at 1640cm^{-1} normalised to the control sample. Also included are samples from the same batch of resin cured by peroxide (1% dibenzoyl peroxide - Peroxan BP-50 BZ Paste ex Pergan). As can be seen by the degree of cure test, the samples are curing, but the FT-IR spectra are suggesting otherwise (see Spectra 5.2 and 5.3). The peak at 1635-40 cm^{-1} for the peroxide sample is much reduced in intensity compared to uncured material, it is still present.

One possible explanation could be that since the ATR only penetrates a limited distance into the sample (2µm with the diamond crystal used), before being reflected back,. The spectra that is being recorded could be due to any residual uncured material left on the surface. The samples were prepared so as to remove any unreacted material prior to taking the spectra. Also an additional problem associated with ATR equipment is that with solid

and semi-solid materials do not generate very good spectra due to poor contact with the crystal material unless pressure is applied. The spectra generated for the UV cured sample is considerably more noisy than the others suggesting that there was poor contact as it was not possible to apply too much pressure to the sample particularly the samples in a semi gelled state. Since the carbon-carbon double bond peak at 1635-40cm^{-1} is particularly weak, it could be lost in the noise.

Time (mins)	Degree of Cure (%)		Normalised Peak @ 1640cm^{-1}	
	IPDI-PEA	IPDI-PEM	IPDI-PEA	IPDI-PEM
Control	0	0	1	1
0	0	0	1.01	1.01
30	0	0	1.03	1.05
60	0	0	0.96	0.99
90	0	0	1.00	0.97
120	0	0	0.94	0.98
150	21.4	0	0.87	0.96
165	52.5		0.94	
180	94.5	19.3	0.91	0.97
195		42.7		0.98
210		92.3		0.97
Peroxide Cure	98.1	98.9	0.94	0.95

Table 5.1 – Comparison of Cure between IPDI-PEA and IPDI-PEM Resins



Spectra 5.3 – IPDI-PEM Resin, Upper – Thermal Cure, Lower – Peroxide Cure

A thin cross-section from each sample was taken, were rerun as a transmission sample using the transmission accessory. The results obtained were too weak as it was not possible to obtain a thin enough slice to allow the IR radiation to pass through the sample due to the gelled nature of the material. The cross-section samples were also subjected to ATR spectroscopy, and similar results were obtained with the carbon-carbon double bond not reducing in intensity, despite the material gelling. In addition samples of the gelled material from between the plates in the rheology experiments were examined with FT-IR ATR spectroscopy, with the carbon-carbon double bond peak at 1635-40cm^{-1} still present despite the material being gelled.

5.1.3 General Discussion

The data obtained from the evaluation of epoxy (meth)acrylate and urethane (meth)acrylate resins it is realistic to use a rheometer equipped with a suitable method of heating the samples to obtain data to give an idea of the potential stability of a resin/inhibitor system. It is worth noting that a similar pattern between the different inhibitors as seen in the stability trials is reproduced with the work done using the rheometer to measure the rate of gel formation. The amount of time required to obtain some of the data points would preclude the use of the method for either low temperature

studies (<100°C) and/or high inhibitor concentrations, however it is a comparatively quick method to determine if a material to close to its gel point, or low has a low active inhibitor concentration.

The use of FT-IR spectroscopy on the other hand has not been as successful as wished for due to the thickness of the resin sample, the semi-gelled nature of the material and the effects of oxygen inhibition.

5.2 Resin Curing

The addition of antioxidants to vinyl ester resins is to ensure that the resin system will remain stable during storage, however at some time the resin will be further processed and cured to produce the designed polymeric material. It is a careful balance between ensuring the stability of the resin during storage, the speed and ease of curing the resin into the final polymer and finally ensuring that the cured polymer also remains stable during its service life. Often the same substances that are used to maintain the resin shelf life will also help to maintain the service life of the cured polymer.

The normal methods for curing vinyl ester resins are either by free radical sources (peroxides or photoinitiators) or by thermal curing. The use of photoinitiators will be further examined in the work described in the following sections.

5.2.1 UV Curing

The use of ultra-violet (UV) lamps for curing resins has become increasing more important as it offers a very fast method of curing resins and allows for a high throughput of material compared to traditional thermal curing with the associated equipment requiring a comparatively small foot print. The high initial cost of the equipment and the different chemistries involved were the main reasons for the slow up take of the technology.

The main method of curing is to use a mercury vapour lamp which produces energy in a broad range from UV-C through to infra-red. Although the energy of interest lies between UV-A to UV–C, this only accounts for 20-25% of the energy output, with the bulk of the energy being emitted either as visible light or heat. The advantage of the mercury vapour lamp is that there are 4 types, standard mercury or H type, iron doped mercury or D type, gallium doped mercury or V type and indium doped mercury or Q type. These emit energy

over different wavelengths, each favouring a different type of photoinitiator. The amount energy emitted is very high across the full frequency range, allowing for efficient curing.[9]

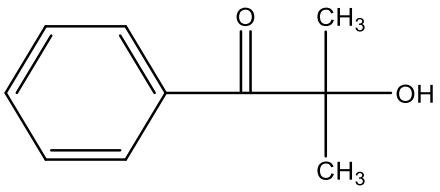
Electron beam technology has been promoted for as long as the use of mercury vapour lamps, but do not require the use of a photoinitiator as the energy emitted can break open the vinyl carbon-carbon double bond. However the equipment is more expensive and the actual area that can be cured at a time is quite small compared to a mercury lamp. The latest advance is in the use of UV light emitting diode (LED) technology. It is only in the past 10 years that the technology has become mature enough to be considered for industrial application. The main disadvantage is that the LED's will only emit in one wavelength, rather than the broad spectrum of the mercury lamps, and currently only 3 wavelengths are commercially available, all in the UV-A region, 360, 395 and 405nm.[10] Currently the energy output from the LED's are considerably lower than that which is possible from a mercury lamp, but the advantages are lower power consumption, as up to 40% of the energy is emitted in the UVA region, longer working lives (with claims of greater than 20,000 hours), no drop off in performance as the LED's age (mercury lamps degrade with time resulting in lower power and spectral changes in output) and finally do not use mercury. Since the energy emitted by the LED's is only in the UV-A region, this has meant that the majority of the traditional photoinitiators are not suitable as they mainly absorb in the UV-B and –C regions. This in turn has led to the development of a new class of photoinitiators, mainly based on phosphine oxides chemistry.

5.2.1.1 Equipment Setup

Photoinitiators used in free radical UV curing are classified as either Norrish Type I or II depending upon the fragmentation of the compound to form the free radical species when subjected to UV light.[11] Each photoinitiator has a different absorbance spectrum, hence the selection of the photoinitiator depends upon a combination of the curing equipment used, the thickness of the resin to be cured, the types of filler used and the degree of colouration permissible in the cured resin. A number of photoinitiators are either yellow or turn yellow during the UV curing process. To reduce the number of different parameters the resins were left unfilled and the amount of photoinitiator added fixed to 1%. In general the amount of photoinitiator added is between 1-3% depending on the speed of cure required, and also the amount of filler present. A lot of recent work[12-13] has shown that only between 10-40% of the photoinitiator is actually used in the curing

process, this came to public attention in 2006-7 when isoproylthioxantone (ITX) was found in cartons of baby milk. The coating on the outside of the carton had been cured with a photoinitiator blend that included ITX, and the milk fat had drawn the unreacted ITX from the outer coating, through the cardboard and inner polyethylene layers into the milk.

The photoinitiators selected for use with a mercury lamp system were 2,2-dimethyl-2-hydroxyacetone (Omnicure 1173 ex IGM) (DMHA) (**54**),[14] a Type I α-hydroxyketone, and benzophenone (Genocure BP ex Rahn) (**55**), a Type II aryl ketone. Both photoinitiators are well known and have become general purpose materials, DMHA gives both good surface and depth cure. BP gives good surface cure, with limited depth cure, however it is probably the cheapest photoinitiator on the market, hence is still used in considerable quantity despite its disadvantages.



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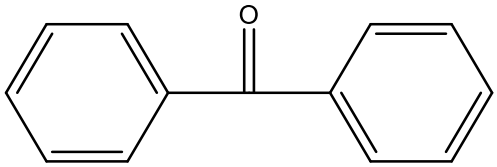

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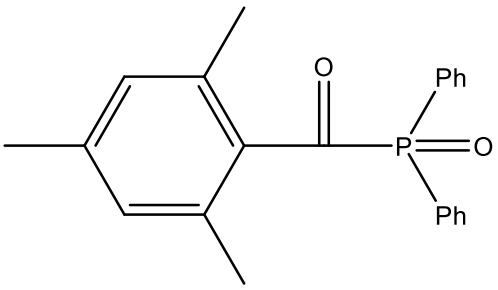
The photoinitiators selected for use with a LED lamp system were 2,4,6-trimethylbenzoyldiphenylphosphine oxide (Omnicure TPO ex IGM) (**56**) and bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (Omnicure 819 ex IGM) (**57**) also known as BAPO, both Type I acylphosphine oxides. Both photoinitiators will absorb in the UV-A region in concentrations greater than 0.01% which make them suitable for LED systems. Both are yellow powders and colour the resin, however phosphine oxides do photo-bleach when exposed to UV light, so the degree of yellowing is reduced during the cure process.



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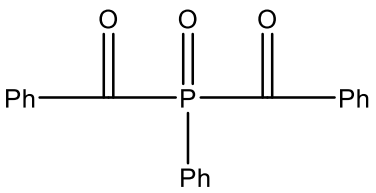

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The curing equipment used was an H type 120W/cm mercury lamp (Jenton International), and an OmniCure AC8150 2W/cm 395nm LED lamp (Excelitas Technologies), both with the height adjusted to be 50mm above the top of the surface of the sample (see Figure 5.7). The equipment was equipped with a power control system to allow for variable power output to both lamp systems, and with a variable speed conveyor belt. The lamp outputs were regularly checked using an EIT Instruments Power Puck II radiometer.

A silicone mould was made to allow ten 10 x 10 x 5mm blocks to be created to allow for the curing of samples at depth, as well as using a 100µm coating bar to prepare thin film samples on standard coating opacity test cards (ex Sheen). The exposure times are given for each experiment. The samples examined were the epoxy BADGEDA resin and urethane IPDI-PEA and IPDI-PEM resins. All of the samples had 1% by weight of the required photoinitiator added and heated to 50°C for 5-10 minutes to allow the photoinitiator to melt/dissolve in to the resin, before being mixed. Once mixed the samples were stored in the dark. It was found that samples containing BAPO would cure to an unusable condition, within 2 hours at room temperature under standard fluorescent lighting used in the laboratory.

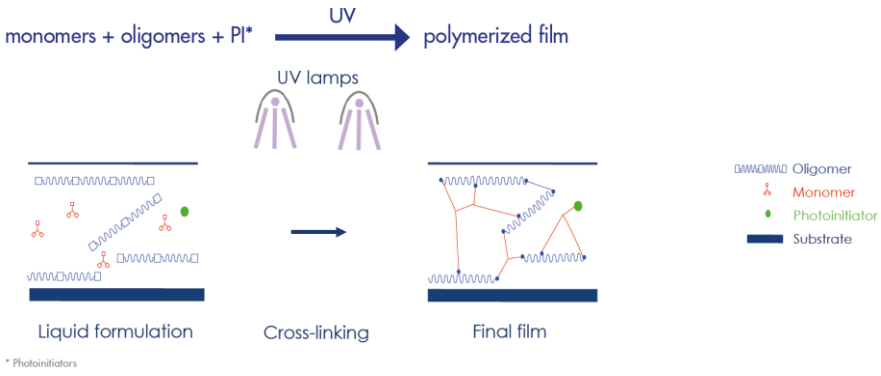


Figure 5.6 – UV Curing Principles. Courtesy Arkema[15] © 2019

The cured blocks were measured using calibrated micrometers to determine the depth of cure after 15, 30, 45 and 60 seconds of exposure. Afterwards the degree of cure in the cured sections was determined following the method outlined by Park *et al.*[7] The cured samples were weighed and then placed in hexane for 24 hours @ 50°C. The samples were re weighed and the degree of gel determined by mass loss since the cured material is insoluble in hexane. Since in the majority of the sample the material was not fully cured to the 5mm depth, the degree of cure data obtained is only valid for the cured material and does not take into account the uncured material at the bottom.

5.2.1.2 Results and Discussion

As would be expected the use of DMHA did give good surface and depth cure, while using BP resulted in a good initial surface cure, and a subsequent depth cure. With BP, material at the edges of the mould cured first, even at depth, followed by the centre of the block. With TPO there was good surface and depth cure, while BAPO gave mixed results, probably due to the sensitivity to the florescent lighting used in the lab as previously noted, also due to the lower power output of the LED lamp compared to the mercury. It will also be noted that for the samples that cured quickly, after 60 seconds of UV exposure there is a marked drop in the sample depth, this is due to the resin shrinking due to the curing. It is understood that UV cured resins are subject to high shrinkage rates, although this can also be applied to all vinyl ester resins, due to the replacement the weak van der Walls forces between the resin molecules with shorter and stronger covalent bonds formed during the conversion of the vinyl C=C to C-C bonds during polymerisation.[11] The degree of shrinkage is dependent upon the resin structure and functionality, since the urethane based resins under evaluation are difunctional the shrinkage is normally in the 2-5% range, while the epoxy based resin is nominally difunctional and the shrinkage can vary from 4 to 10%.

The results obtained are shown in the Appendix in Charts A5.1.1 to A5.1.24 and A5.2.1 to A5.2.5. Charts A5.1.1 to A5.1.4 show the cure development in the IPDI-PEA resin, the samples contained an increasing concentration of PMP (**14**) and a standard 1% addition of photoinitiator and cured under the mercury lamp with DMHA and BP, and the LED lamp with BAPO and TPO. As can be seen the DMHA provides excellent depth cure, while the BP takes longer to provide the required depth cure. It should be noted that as previously mentioned the depth begins to decrease after 60 second of exposure, this is due to the cured resin shrinking. As the concentration of PMP increases, the rate of cure rapidly decreases when TPO is present. With BAPO present the overall rate of cure is significantly decreased compared to the other photoinitiators examined. The development of cure can be seen on all the charts. Experimentation has shown that the degree of cure exceeds 85% that the shrinkage becomes measureable, in the case of the difunctional (meth)acrylate resin used. It does appear that as the concentration of PMP increases, there is some noticeable polymerisation inhibition effect as regards to the resin cure rate.

Charts A5.1.5 to A5.1.8 show the data obtained using the same resin (IPDI-PEA), photoinitiators and curing set up, but with 4H-TEMPO as the inhibitor. As has been seen in previous work done in this study the inhibition effect shown by 4H-TEMPO compared to PMP is far greater, and this is borne out in the data obtained. Again the samples containing DMHA show far better depth of cure compared to a similar sample containing BP, likewise a similar pattern has been observed with regards to the samples containing BAPO and TPO. Compared to the use of PMP, 4H-TEMPO particularly at high concentrations does significantly inhibit the depth of cure and also the rate of cure within the cured samples.

Due to the poor cure depth performance of both BP and TPO, the degree of cure data obtained is rather scattered, but generally shows the trend that the closer to the surface that was exposed to UV energy, the better the rate of cure. The samples obtained were often reasonably well cured on the surface, with the material beneath a gel like consistency with a noticeable decreasing degree of cure relative to depth.

Charts A5.1.9 to A5.1.12 show the depth of cure data obtained using IPDI-PEM resin, but due to the lower reactivity of the methacrylate terminal group compared to the acrylate, the depth of cure obtained over the same time scale as with the previous samples using IPDI-PEA is lower. The data presented is to the same time scale, but further work has shown that between 120 and 150 seconds UV exposure is required to obtain the same depth of cure (see Chart 5.9). A similar pattern emerges in that as expected the samples with DMHA cure better at depth compared to those containing BP and that PMP has a lower inhibition effect compared to a similar concentration of 4H-TEMPO.

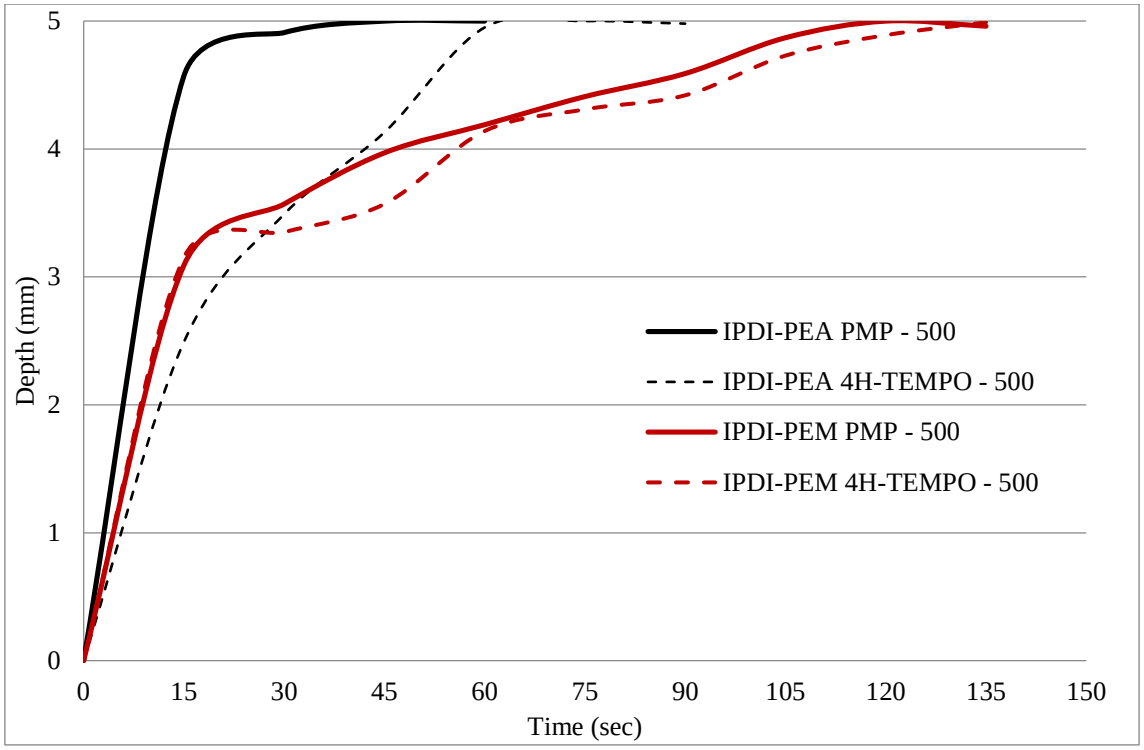


Chart 5.9 – Comparison between IPDI-PEA and IPDI-PEM Resins and 4H-TEMPO Inhibitor With 1% DMHA

Charts A5.1.13 to A5.1.16 show the curing rates obtained when BADGEDA resin is used with PMP. In this case it appears that using BAPO and BP in such a system does have an impact upon the development of the cure depth, in the presence of PMP does have an adverse effect. The degree of cure measured does not appear to show a clear pattern across the range of samples examined. In comparison with IPDI-PEA cured with the same inhibitor and photoinitiator combination (Charts A5.1.1 to A5.1.4), the degree of cure obtained is greater, although the depth of cure is reduced for the same exposure time, regardless of the lamp type used.

Charts A5.1.17 to A5.1.20 show the curing rates obtained when BADGEDA resin is used with 4H-TEMPO. In this case it appears that using BAPO and BP in such a system does seriously impact upon the development of the cure depth, in which the use of 4H-TEMPO is very deleterious. The degree of cure measured does not appear to show a clear pattern across the sample containing BAPO and BP, however the samples containing DMHA and TPO are much more predictable and the degree of cure is related to the concentration of the inhibitor, with the greater the concentration of inhibitor, retarding the curing process by the greater extent.

In comparison with IPDI-PEA (see Charts A5.1.5 to A5.1.8) with the same photoinitiator, the use of 4H-TEMPO has a greater polymerisation retardation effect, both in terms of depth of cure and degree of cure.

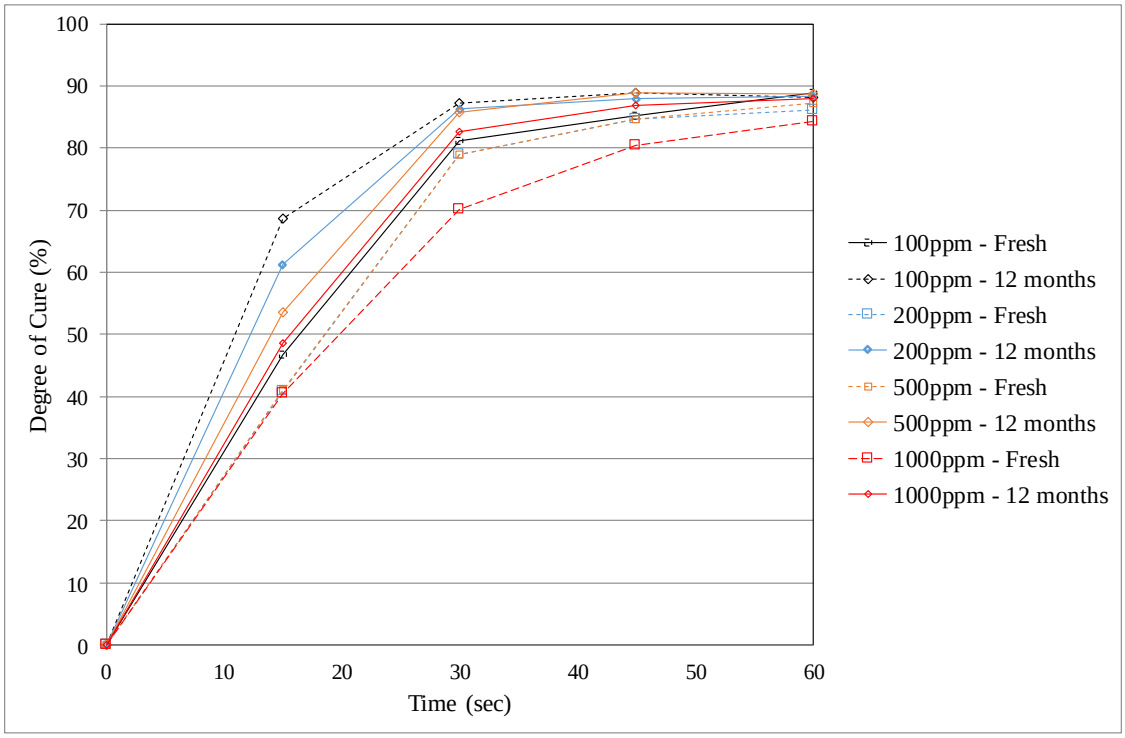


Chart 5.10 – Degree of Cure of IPDI-PEA Resin and PMP Inhibitor with 1%DMHA Over 12 Months Storage

Since 4H-TEMPO is a stable free radical, it would be logical to assume that it would have an effect upon free radical based curing systems. The work done shows that 4H-TEMPO does have a greater effect on UV curing compared to PMP. As would be expected the greater the concentration of inhibitor, the greater the retardation upon the polymerisation/curing reaction. Limited work was done on year old samples, to compare against the fresh samples used in the experimental results previously presented. Chart 5.10 shows a shift in the degree of retardation seen when looking at IPDI-PEA resin and PMP. As would be expected from the stability work done, all the concentrations of inhibitor have been used up by differing degrees, hence there is overall a better response to UV radiation. It can be seen that the 12 month old samples have a better initial UV response comrade to the fresh material, however overall the degree of cure after 60 seconds of exposure remains reasonably similar regardless of the concentration of inhibitor used or the age of the sample, which appears to indicate that the UV process will only allow for a maximum degree of cure of 80-90%. The samples which have been

subjected to cure times of greater than 30 seconds of UV exposure also experience significant amounts of thermal energy. After 30 seconds the temperature of the samples have increased from 20 to 40°C, while after 60 seconds the temperature is up to 38-70°C. Work has shown that UV cured materials will continue to polymerise when subjected to a thermal post cure. The mercury lamp systems are inefficient in terms of generating UV energy, only 40% of the output is in the UV region, 40% in the IR region and the remainder in the visible.

Following the methods outlined by Park *et al*[7] and Amerio *et al*[16] for epoxy acrylate and Kunwong *et al*[17] for urethane acrylate resin systems, work was done to see if it was possible to correlate the above work with FT-IR with thin film transmission samples. Previous work has shown that using FT-IR ATR spectroscopy does not appear to indicate that the material has cross linked due to the reaction of the carbon-carbon double bond due to the presence of the vinyl group. With the transmission method the effect of any uncured material at the surface can be minimised, however it is a known fact that UV curing does suffer from oxygen inhibition at the surface, which appears to cause problems using the ATR method.

Four resins were examined, IPDI-PEA was used as the base with 1173 and BP as the photoinitiators. A 50μm thick film of the resin under test was applied to a thin KBr window mounted in a cardboard holder and then cured under mercury lamps. Spectra were taken using two different Bruker ALPHA FT-IR spectrometers fitted with a transmission accessory. A set of spectra were taken before curing, then one every 5 seconds up to 30 seconds total exposure. The subsequent spectra were analysed looking at the bands in the following regions 1710-15cm^{-1} (stretching of the carbon-oxygen bond attributed to the carbonyl group), 1630-35cm^{-1} (stretching of the carbon-carbon double bond attributed to the vinyl group) and 810-15cm^{-1} (twisting of the carbon-carbon double attributed to the vinyl group). The following equation was used to evaluate the degree of cure evaluating the peaks at 1715 and 1635cm^{-1} by calculating the relative concentration of carbon-carbon double bonds were present after exposure to UV radiation.

$$\text{Carbon} - \text{carbon double bonds (\%)} = \frac{A_{1635}^{UV}/A_{1715}^{UV}}{A_{1635}^{0}/A_{1715}^{0}} \times 100$$

Where A_{1635}^{UV} = Absorbance of UV cured material at 1635cm^{-1}, A_{1715}^{UV} = Absorbance of UV cured material at 1715cm^{-1}, A_{1635}^{0} = Initial absorbance of material at 1635cm^{-1} and A_{1715}^{0} = Initial absorbance of material at 1715cm^{-1}. The absorbance was calculated by taking the peak height from a normalised baseline. The same equation was used to evaluate the relative concentration of carbon-carbon double bonds present by the evaluation of the peaks at 1715 and 815cm^{-1} as a double check. Since the carbonyl group does not partake in the process of free radical initiated polymerisation, it is used as the internal reference to compensate for the differences found in spectral intensities between different spectra.

The FT-IR data collected is shown in Charts A5.1.21 & A5.1.22 and A5.1.24 does appear to show that contrary to the gel formation data presented, there is no sign of the carbon-carbon double bond attributed to the vinyl group, being broken and used in the process of cross-linking/polymerisation. Although Chart A5.1.23 does show that in the case of the 4H-TEMPO with 1% DMHA does show the sort of behaviour that would be expected due to polymerisation due to the vinyl carbon-carbon double bond partaking in the polymerisation process. A possible explanation of this could be that the layer of material applied was not thick enough to overcome the effects of oxygen inhibition. One way to overcome the problems associated with oxygen inhibition is to use nitrogen inerting, which the current equipment set up does not allow to be undertaken. The use of amine acrylates is well known to reduce the effects of oxygen, but this then introduces another variable into the matrix, hence was rejected as a possible solution.

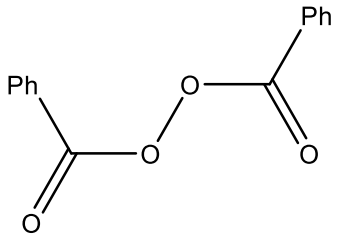
5.2.2 Peroxide Curing

The use of peroxides to cure vinyl esters is well known and there is a substantial body of literature, both academic[18,19] and commercial,[20,21] on this method of curing. The manufacture of vinyl ester resins rely on the use of polymerisation inhibitors to ensure the stability of the resin during processing (and storage), but also to control the cure speed when the desired peroxide is used. In the case of unsaturated polyesters, hydroquinone is the inhibitor of choice to slow down the cure when the peroxide is added. However it should be noted that the rate at which free radicals are generated by peroxides is actually quite slow, even with peroxides which are optimised for room temperature curing. It is

for this reason that for room temperature curing the use of an accelerator is needed, otherwise heat is used to catalyse the reaction.

The great advantage of peroxide curing over either thermal or UV curing methods, is that with careful selection of the peroxide and the accelerator it is possible to cure resins at room temperature. There is a wide range of peroxides that are available, with different industries favouring certain peroxide/accelerator combinations over others. For curing epoxy acrylates the most common peroxide used is benzoyl peroxide (BPO) (**58**), which has good stability at room temperature and is readily commercially available diluted to different concentrations in a range of different diluents. Previous work done in Section 3 has shown that polyurethane based acrylates show good curing and cured properties when benzoyl peroxide is used. It has been found that tertiary amines are good accelerators for diacyl peroxides in general,[21] of which benzoyl peroxide is a member of the group, commercially four amines have become industrial standards,

1. N,N-Diethylaniline – low reactivity, for long gel times
2. N,N-Dimethylaniline – medium reactivity, for medium gel times
3. N,N-Di(2-hydroxyethyl)-4-methylaniline (DHEMA) (**59**) – medium/high reactivity for short to medium gel times
4. N,N-Dimethyl-4-methylaniline – high reactivity, for short gel times



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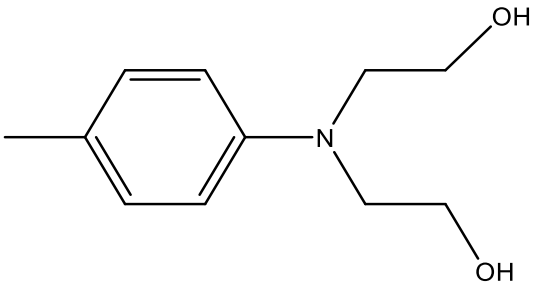

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The work done for this study used N,N-di(2-hydroxyethyl)-4-methylaniline (Pergaquick A150, ex Pergan) and 50% benzoyl peroxide paste (Peroxan BP 50BZ paste, ex Pergan). The sample of BPO paste was stored at 5°C to extend the life of the product, the theoretical active oxygen content of the material was quoted as 3.30%, testing of the material prior to use showed that the sample contained 3.26% active oxygen (see section 6.1.2.1 for further details on the active oxygen test). IPDI-PEA and IPDI-PEM resins are used to compare the differences between a urethane acrylate and the methacrylate

analogue. In order to simplify the data set obtained, the concentration of BPO powder used throughout the study was fixed at 2.0% based on resin, which equates to 1.0% of pure BPO. Chart 5.11 shows the initial work undertaken to determine the amount of accelerator required to give a reasonable gel time based on using 25g of resin (0.5g of BPO (0.002mol)) using IPDI-PEA with 100ppm of PMP. In all cases the accelerator was mixed into the resin before the addition of the peroxide. Mixing the accelerator with the peroxide without any resin or filler present results in a very exothermic reaction which can be dangerous.

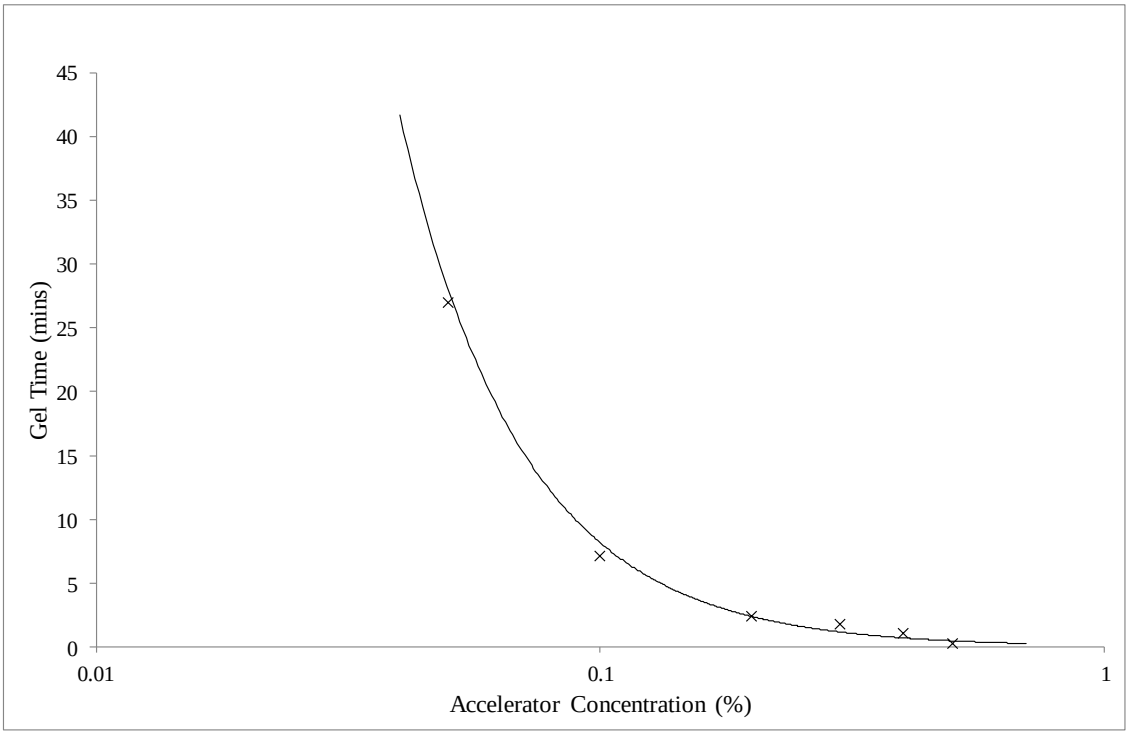

Chart 5.11 – Gel Time of IPDI-PEA Resin Using DHEMA as the Accelerator

Chart 5.11 shows the effect of varying the amount of accelerator, based on this work it was decided to add 0.1% of DHEMA (0.25g, 0.00128mol) to the resin. Both IPDI-PEA and IPDI-PEM resins were tested to determine the gel time with different concentrations of three different inhibitors, HQ, PMP and 4H-TEMPO. When determining the gel time, a modified version of ASTM standard test method[22] was used, where the gel point was determined when a wooden spatula could not easily penetrate the resin surface. It was noted that with all the resins at 100 and 200ppm inhibitor loadings the time between the gel time and cured was very short (less than 60 seconds due to the exotherm generated), with the 500 and 1000ppm concentrations the exotherm was not as great and this was observed by the greater time gap between the gel and cure times (2 to 5 minutes), although

with 1000ppm of 4H-TEMPO the gap between gel and cure time was almost 30 minutes with the methacrylate resin.

Chart A5.2.1 shows the effect of inhibitor and concentration with IPDI-PEA, and Chart A5.2.2 for IPDI-PEM, while Charts A5.2.3 and A5.2.4 show the effect of storage of the resin after 12 months at room temperature (20°C). The accelerator was added to the 12 month old resin just before the addition of the peroxide, so the accelerator was not aged in the same way as the resin. There is an obvious difference between the acrylate and methacrylate functionalities in terms of the reactivity, with the methacrylate resin being in general 2-2½ times less reactive than the acrylate analogue. It is been shown that the storage of the resin at room temperature will lead to a reduction in the stability of the resin, and this has been shown in the results obtained after 12 months storage, with a general reduction in the gel time obtained compared to freshly prepared material. Chart A5.2.5 shows the relative gel times obtained with the IPDI-PEA and IPDI-PEM resins with PMP as the inhibitor. As previous results have shown the relative efficiency of the inhibitors studied above can be shown to be PMP < HQ < 4H-TEMPO.

5.2.3 Thermal Curing

The stability testing work has shown that vinyl ester resins will cure via thermal means. The greater the level of inhibitor in the resin, the longer the incubation time required at the desired temperature. Likewise the higher the temperature, the shorter the cure time. It is known that free radicals are formed during the initial resin synthesis, and are propagated over time. It would be logical to assume that it is the presence of these free radical species are the main driver towards the heat curing of vinyl esters.

Industrial experience[21] has shown that relying solely on heat to cure vinyl esters, can be hit and miss in terms of both the degree of cure finally obtained and the length of time required. In order to obtain some degree of reliability and consistency it is far better to deliberately incorporate a free radical source, either in the form of peroxides or UV initiators as previously discussed.

5.3 Conclusions

The use of inhibitors does have an effect upon the stability of the resin to delay the onset of gelation. It is not possible to totally prevent the risk of gelation during storage, as this

would mean that the resin was effectively inert, and could not be then subsequently processed to form a cured resin, either as a thick or thin film.

Curing resins up to 5mm thick using UV initiators and radiation as the free radical source, is not that common, but is used commercially for some specialised applications, but it does allow the depth and degree of cure to be more accurately plotted. This allows for some comparisons to be drawn against the use of peroxides, which are far more commonly used in commercial applications at thicknesses greater than 1mm. UV curing is typically done with coatings up to 100μm thick, and typically applied as a top coat on high speed application and curing lines, with line speeds up to $100 m.min^{-1}$. At the moment UV curing is in the middle of a switching over from mercury lamps to LED ones. The main problems with the LED lamps have been discussed earlier, but with the power and efficiency of the LED's improving each year then many of these problems concerning the lower amount of radiation energy and the narrowness of the frequencies being emitted are being overcome meaning that this technology has become more widely accepted and used.

The addition of either peroxides or UV initiators to the resin to make up a typical commercial formulation (0.5 to 2.0% for peroxides and 1.0 to 5.0% for UV initiators) are at such a high loading that the much lower amounts of inhibitors used (50 to 1000ppm) do not appear to have significantly affected the curing performance of the resin. It can be seen that HQ, PTZ and 4H-TEMPO are very effective inhibitors in terms of ensuring that the resin remains stable during storage, and would be the preferred compounds of choice. Since these compounds will either discolour the resin upon addition, or over time due to the coloured by products formed, then the use of PMP would be preferred.

5.4 References

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6 Oxygen and Blocked Isocyanates

As has been discussed eariler,[1-6] oxygen plays a major role in the stability of a resin system, either by being a free radical source, or by activating certain types of inhibitors. Normally at room temperature these effects due to the presence of oxygen can only be measured over a period of months by monitoring the viscosity of the resin. However at elevated temperatures the rate of oxygen consumption increases and the effects of the inhibitors are much more easily observed. To prevent a runaway polymerisation from occurring within the resin, often extra inhibitor is added, but it might also be possible to use a compound which will break down at temperature to release an inhibitor. To this end creating a blocked isocyanate with the inhibitor could be a viable option.

6.1 The Role of Oxygen

It is important to determine how much dissolved oxygen there is present in the resin system of interest in order to account for this into the results of the stability trials. It is well known that for both BHT (**18**) and PMP (**14**), dissolved oxygen is required to be present in order for the inhibitors to function properly. Since PMP is widely used as an inhibitor in both the raw materials (acrylic and methacrylic acids both contain PMP at 200-250ppm) and the finished resins, it is of commercial importance to know the dissolved oxygen level in order to accurately determine the storage life of such materials. The heat of polymerisation for acrylic acid is 77.5KJ/mol and has been the cause of a number of serious fires at chemical plants over the years.

As a crude, but effective, method of determining the effect of oxygen in the mechanism of inhibition in the samples, the replication of the samples in oxygen free conditions, by virtue of sparging the sample with nitrogen gas to displace the oxygen dissolved in the resin, does have its merits. Likewise the sparging of samples with compressed air does allow for the maximum dissolved oxygen concentration to be obtained. This does not answer the question as to how much oxygen is present in the resin, but only gives the two extremes of the potential range of oxygen concentration. Also it is known that atmospheric oxygen will dissolve into the resin at the interface, hence the requirement for the test samples to be sealed so as to create a closed system.

6.1.1 Oxygen in Polymer Chemistry

It is widely recognised that oxygen plays a major role in polymer chemistry. Since oxygen is a well-known inhibitor of polymerisation reactions and radical scavenger, it would be

assumed that there would be a significant body of literature[1-6] on the subject, which there is but it does not make many claims to measure the amount of oxygen in the polymer during the polymer synthesis, except for emulsion polymerisation. Since the process takes place in an aqueous medium the measurement of the dissolved oxygen concentration is quite easy with standard probes. Unfortunately the actual reaction does not take place in the aqueous phase, but inside micelles formed by the interaction of the reactive monomers, catalyst and surfactant used. The size of the micelles is such that it is physically impossible to insert a probe into them.

Huo *et al*[7] looked at the effects of impurities on emulsion polymerisation, and treated oxygen as an impurity, but without differentiating between the different impurities. The overall conclusion was that impurities in the aqueous phase would delay the onset of the reaction, but not the actual polymerisation mechanism. However impurities in the monomer phase would both delay the onset of the reaction and also affect the polymerisation mechanism. These effects have been observed and reported in the literature many times, but without knowledge of which impurities are present in which phase and in what concentration, the statement can only be a general summary.

De Arbina *et al*[8] looked at the effect of oxygen on emulsion polymerisation by using calorimetry to measure the change in kinetics of a series of butyl acrylate/styrene copolymerisation reactions with and without nitrogen gas being bubbled through. It was found that the reactions in the nitrogen environment had a more rapid reaction on set point and that the reaction kinetics were faster compared to the normal oxygenated systems, thereby providing proof that oxygen does have a polymerisation inhibition effect.

Following on from this work Cunningham *et al*[9] looked at the kinetics of styrene emulsion polymerisation at different levels of oxygen saturation. In this work a dissolved oxygen probe was used to measure the oxygen concentration in the aqueous phase. The reported results show that an increased oxygen concentration increased the inhibition effect upon the polymerisation kinetics. Again unfortunately it was not possible to directly measure the oxygen concentration of the monomers used, nor inside the micelle where the actual reaction was taking place.

6.1.2 Measurement of Dissolved Oxygen

The normal method of measuring dissolved oxygen is by using a dissolved oxygen meter fitted either with an electrochemical or optical sensing probe. The electrochemical probe measures the conductivity of the solution under test and then relates this against a stored set of calibrated results, the amount of oxygen present will alter the conductivity of the solution. A variation of this is to apply a current to the solution and then measure the change in air pressure within the probe. The change in air pressure is directly related to the amount of oxygen present in the sample.

The optical probe passes a beam of light at a set frequency onto a membrane which has been impregnated with a dye that will luminesce at a different frequency. This is then monitored by a sensor. The oxygen present in the solution will, depending upon the dye used, either cause a reduction in the intensity of the luminescence, or a frequency shift. This can then be related to a stored set of calibration data.

A lot of work has been done on using various different electrodes for conductivity measurement of dissolved oxygen. Capuano[10] patented the use of a pH type electrode with a thalium and a calomel electrode pair measuring the voltage thus generated across due to the presence of dissolved oxygen. The equipment is described for the measurement of dissolved oxygen in liquids, although it is primarily designed for use in aqueous systems.

Hahn *et al*[11] and Floate and Hahn[12] have developed gold electrodes for the measurement of oxygen and carbon dioxide gases with the use of dimethyl sulphoxide (DMSO) as the non-aqueous solvent. The use of DMSO is to improve the resolution of the measurements as the gases when bubbled through are more readily dissolved in DMSO compared to aqueous systems and also to prevent any side reactions due to hydrogen. While Berkh *et al*[13] reported the development of a coated gold micro electrode for the measurement of dissolved oxygen in fungi broths.

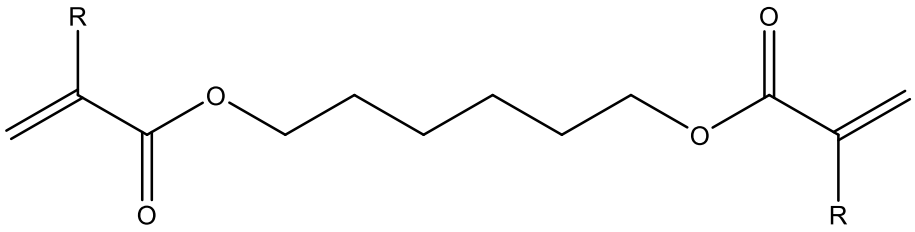
6.1.2.1 Measurement of Dissolved Oxygen Using a Dissolved Oxygen Meter

Samples of 1,6-hexanediol diacrylate (HDDA) (**60**) and triethylene glycol diacrylate (TEGDA) (**61**) were obtained as samples of low viscosity polyester acrylate monomers for testing, along with their methacrylate analogues, 1,6-hexanediol dimethacrylate (HDDMA) (**62**) and triethylene glycol dimethacrylate (TEGDMA) (**63**).

Monomer	Inhibitor	Inhibitor Concentration (ppm)	Water Content (ppm)	Viscosity @ 25°C (mPas)
HDDA	PMP	198	87	7.5
TEGDA	MeHQ	134	93	14.8
HDDMA	HQ	95	63	7.8
TEGDMA	PMP	226	83	10.6

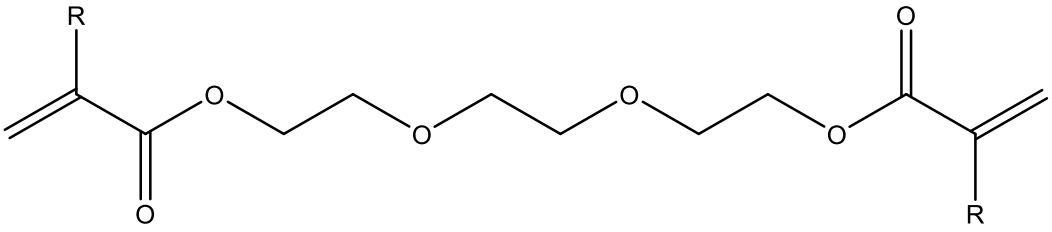
Table 6.1 – Properties of Monomer Samples

The values quoted in Table 6.1 have either been extracted from the Certificate of Analysis for the sample, and the water content was determined by Karl-Fischer titration. The dissolved oxygen was measured using a Mettler-Toledo SevenGo pro SG68 fitted with a InLab 605-ISM conductivity probe, and a Mettler-Toledo SevenGo Duo pro SG98 fitted with a OptiOx optical probe.



Where R = H **60**

R = CH_3 **62**



Where R = H **61**

R = CH_3 **63**

The equipment used was calibrated using standards supplied by VWR and the samples were left to equilibrate at 20°C for 30 minutes prior to measurement. In the case of the conductivity probe a reading of 0.0mg/lt of O_2 was recorded for both samples after numerous attempts, both with and without the PTFE membrane at the end of the probe in place. In the case of the optical probe, when the sample of HDDA was tested with the PTFE membrane in place, a reading of 0.0mg/lt of O_2 was obtained, however when the PTFE membrane was removed a reading of 100.9mg/lt of O_2 was first obtained, followed by a second reading where an error message was obtained. The probe was placed in some deionised water to clean it and then checked against the calibration standards previously used. It was found that the readings were approximately 40% lower than before testing.

The readings obtained could not be regarded to giving an accurate value of the dissolved oxygen within the samples. It is known that polymers are good electrical insulators and this would explain the low readings obtained with the conductivity probes, also the low water contents of the samples in comparison to the aqueous standards used would negate the results. In the case of the optical probe, it would appear that the polymer has attacked the dye membrane, and either caused the dye to be deactivated or leach out. A simple conductivity test using a micrometer attached to a data logger was also run over 24 hours at 20°C to record any changes in current without any success for any of the samples.

HDDA, HDDMA, TEGDA and TEGDMA have very low viscosities in comparison to the majority of vinyl ester resins on the market, which are in the region of 1000-100,000mPas @25°C. At these viscosities it would be relativily hard for the oxygen molecules to move within the polymer. Also assuming oxygen behaves the same when dissolved in a polymer and/or diluent and/or solvent as it does in water, then the higher the temperature of the medium, the lower the maximum potential oxygen concentration.

6.1.2.2 Measurement of Dissolved Oxygen by Titration

The measurement of dissolved oxygen via titration is used to measure the dissolved oxygen in water[14] and was first described by Winkler.[15] This relies upon the simple reaction of oxygen with iodine, then doing a simple titration with a thiosulphate solution to determine the amount of iodine oxidised by the reduction of the thiosulphate. The water sample has to be dosed with a known amount of transition metal salt, under basic conditions, to fix the dissolved oxygen at the time of sampling, $MnCl_2$ being most often quoted. The sample is then acidified to release the hydroxide ions from the $MnO(OH)_2$.

The hydroxide ions are then free to react with the KI solution, then after a suitable reaction time be titrated against standardised $Na_2S_2O_3$.

There are have been a number of papers in the past discussing the inaccuracies inherent in the test method, as well as the method of collecting and storing the samples. The main problems lie in ensuring that the sample does not get contaminated with oxygen from other sources, ie. the atmosphere, the indicator used and the accuracy of the test reagents used. Since the introduction of cheap and reliable electronic dissolved oxygen meters, this test method has been all but forgotten, and is only really now used to teach environmental science students the basic theory behind dissolved oxygen in water and biological oxygen demand (BOD). However it is still used as a calibration method for the sensors that measure dissolved oxygen in solution.

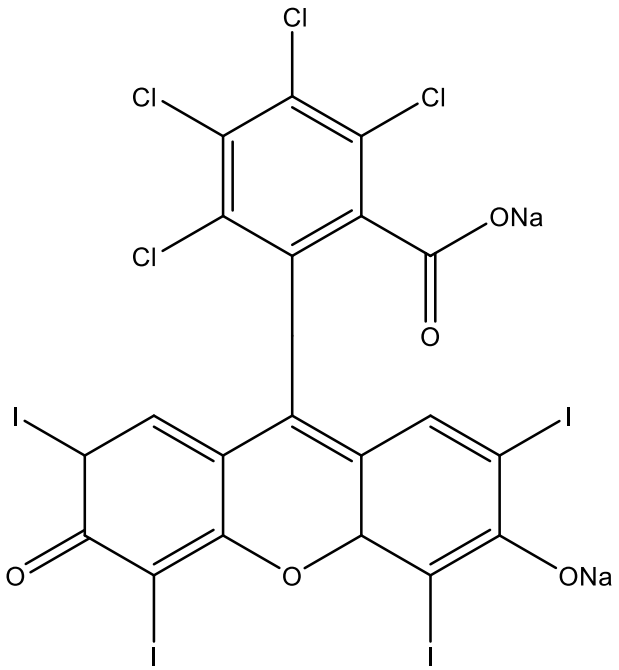
A similar test method, based on Winkler, is widely used to measure the active oxygen of peroxides.[16] From the amount of oxygen present it is possible to determine either the age of a sample of peroxide, or the samples thermal history. Since the half-lives of most commercially available peroxides are known it is possible to back calculate either the age, or if the date of manufacture is known, what the maximum temperature a sample has been exposed to. Active oxygen contents the results are normally quoted to 0.1% ±0.05%. Depending up on the molarity of the reagents used and the accuracy of the burette it might be possible to get down to a detection limit of 100ppm, but for a greater degree of reliability and repeatability 1000ppm is more realistic.

6.1.3 Spectroscopic Methods of Oxygen Determination

Smith and Newnham[17] reported on the use of near infrared spectroscopy for the detection of oxygen in gases. All the work was done using gas cells and peaks due to oxygen reported at 7894-7897cm^{-1}, 7970-8035cm^{-1}, 9369-9374cm^{-1} and 9411-9429cm^{-1}. The most likely explanation for these peaks is not due to the O_2 molecule itself but the result of $O_2 \cdot O_2$ collisions. Kusaka *et al*[18] reported on work done with near infrared spectroscopy for the measurement of dissolved oxygen in cerebral blood in infants. The region of interest is 700-900nm (11100-14280cm^{-1}), but it is the changes in the structure of the haemoglobin as oxygen is associated with the molecule, that is being analysed rather than the oxygen directly. This is not surprising as since the oxygen molecule is perfectly symmetrical, there is no dipole moment for infrared vibration to be set up.

The oxygen molecule can be directly measured using fluorescence spectroscopy, however this is not a widely used industrial technique. Related to this is the use of a suitable dye which can convert the ground triplet state oxygen to the excited singlet state. As this takes place the molecular structure of the dye changes and can be monitored either by the change in light absorption frequency or the change in intensity of the original frequency. Howard and Mawer[19] submitted just a method based on the use of indigo-carmine salts for use as a standard method for the determination of oxygen in beer. However beer is a predominantly aqueous system.

Franco and Olmsted[20] reported on work to use Rose Bengal (4,5,6,7-tetrachloro-2',4',5',7'-tetraiodofluorescein disodium salt) (**64**) or Methylene Blue (3,7-bis(dimethylamino) phenazathionium chloride) (**65**) as "oxygen sensitizers" and 1,3-diphenylisobenzofuran as the oxygen acceptor as a method for determining the dissolved oxygen content of solvents and other non-aqueous media. The use of a UV-Visible spectrometer to take a quick reading does have potential commercial application as the equipment is widely available.



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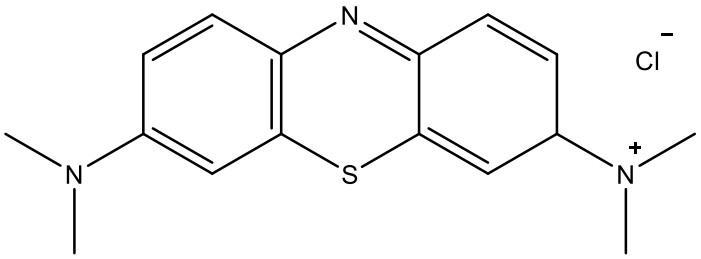

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However Guo *et al*[21] reported that in the case of acrylate monomers the 1,3-diphenylisobenzofuran reacts with the terminal carbon-carbon double bonds and results in an unstable reading which deteriorates over time. Due to solubility issues they propose the use of 5,10,15,20-tetraphenyl-21H,23H-porphine zinc as a singlet oxygen generator, instead of Rose Bengal or Methylene Blue, and 9,10-dimethylanthracene as the "singlet oxygen trapper" instead of the 1,3-diphenylisobenzofuran. Although they do give some dissolved oxygen concentration data on a limited range of acrylate monomers, which had been saturated with air (see Table 6.2). The bulk of their work has been done on 2-hydroxyethyl methacrylate (HEMA). The main problem with their preferred compounds is that although they are very good at their respective roles, as a potential commercial test method they suffer from being expensive.

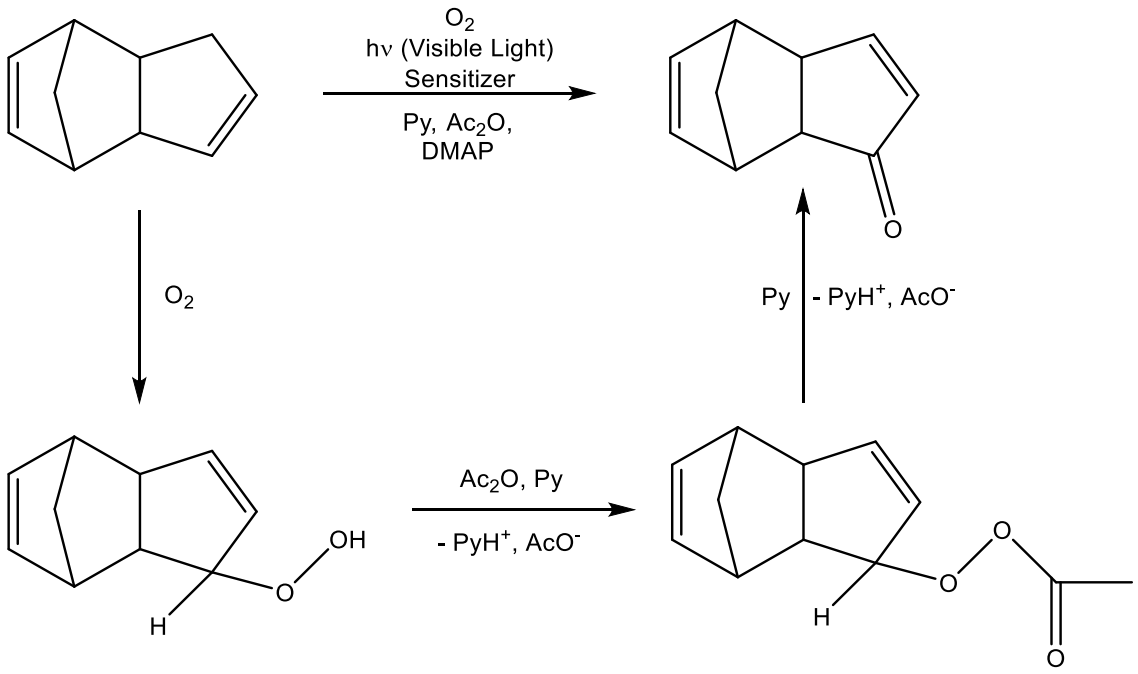
Sample	O_2 Conc. ($mollt^{-1}$)	ppm
HEMA	0.82×10^{-3}	26.2
HDDA	1.17×10^{-3}	37.4
TEGDMA	0.98×10^{-3}	31.4
TMPTA	1.05×10^{-3}	33.6
TPGDA	1.43×10^{-3}	45.8
H_2O	0.22×10^{-3}	6.9

Table 6.2 – Monomer Oxygen Concentation[21]

Silvestrini *et al*[22] looked at how to determine the oxidative capability of organic pigments used in commercial water colours. The singlet oxygen generated by the interaction of the pigment with dissolved oxygen and light was reacted with dicyclopentadiene into a

hydroperoxide. This was further reacted with acetic anhydride and pyridine into a stable ketone (see Scheme 6.1), which then was detected using GC equipped with a flame ionisation detector (FID). It was found that after 40 minutes the levels of ketone thus generated remained stable.

This test method does have potential to be used to determine the dissolved oxygen content in polymers, particularly if a suitable singlet oxygen sensitizer can be utilised. Since the main thrust of the work was to look at the oxidation potential of different pigments, the work was done using Rose Bengal bound to polystyrene as the control. The results published show that Pigment Blue 16 (copper phthalocyanine) the most effective oxygen sensitizer, but only 21.69% as efficient as Rose Bengal. Pigment Blue 16 is a widely available pigment and is competitively priced to be used as an analytical reagent. The generation of a stable ketone offers the possibility of using other analytical methods to detect the species, particularly if no other ketones are known to be present.



Scheme 6.1

One of the problems with using the commercial pigments is their lack of solubility in the resins systems of interest. Certainly the industrial practice of ink manufacture is to grind the pigment into the polymer. The pigment is then just suspended in the polymer, so long as the pigment particle is covered in a layer of the polymer, then for most purposes this

is sufficient for its application. The fact that the pigment is just suspended in the base polymer of the ink/paint could be a contributing factor to the colour degradation seen when printed materials/paintings are left exposed to day light for a prolonged period.

Perstorp AB of Sweden have developed an industrial analytical method,[23] based on the Winkler method and a ASTM Standard Test Method,[24] using UV-Visible spectroscopy to determine the peroxide content of allyl ethers supplied on to the market. Potassium iodide solution is added to the acidifed sample and left to react, as shown below, before being placed in a UV-Visible spectrometer to determine the concentration of iodine in the sample.

$$2(\text{R-O-OH})^- + 2\text{I}^- + 4\text{H}^+ \rightarrow \text{I}_2 + 2\text{OH}^- + 2\text{H}_2\text{O}$$

The quoted detection limit is 1 ppm, with a 50ppm maximum active oxygen content quoted on the certificate of analysis.

Since this is same reaction as the Winkler titration used to determine the dissolved oxygen content in water, then it is a suitable test method to determine the amount of dissolved oxygen in the samples used in this study. It does however pose another question, in that since the iodine will react with oxygen, be it in the form of dissolved oxygen, or from a peroxide, it is not possible to determine the source of the reacted oxygen, in this respect the term “active oxygen” is most appropriate.

6.1.3.1 Spectroscopic Measurement of Dissolved Oxygen

6.1.3.1.1 Near Infrared

Samples of TEGDA and methacrylate analogue TEGDMA were prepared by sparging one sample of each with compressed air for 5 minutes, one sample of each sparged with nitrogen gas for 5 minutes and one sample of each degassed by being spun at 2500 rpm for 5 minutes. The samples were analysed with a Bruker Matrix F near infrared spectrometer equipped with a fibre optic probe.

When the samples were compared there weren’t any visual significant differences between the samples based on the same resin. When looking for substances by infrared spectroscopy in such concentrations, the substance of interest would need to have a large molar extinction coefficient to be reliably measureable.

6.1.3.1.2 UV-Visible

Following the method outlined by Franco *et al*[20] limited work has been done to date using a Cecil CE1021 UV-Visible spectrometer. This equipment does allow for the sample to be exposed to a fixed wavelength of light, to allow the triplet to singlet transition to take place, before recording the absorbance at a different wavelength. The initial work has concentrated on using Methylene Blue and 1,3-diphenylisobenzofuran in samples of TEGDA and TEGDMA. Samples were taken and one set sparged with compressed air for 5 minutes to provide an oxygen saturated environment, while another set was sparged with nitrogen gas for 5 minutes to provide an oxygen deficient environment. The initial work on determining the exposure time and wavelength for Methylene Blue has been completed, and awaiting samples of other potential oxygen sensitizers to examine differences.

Following the analytical method supplied by Perstorp work has been carried out using an Agilent Cary 100 UV-Visible spectrometer. This instrument does allow a full spectrum of the sample to be obtained over a 190-900nm frequency range. The calibration standards were made up as per the test method to generate a calibration graph to calculate the active oxygen content of the samples. The sample is dissolved in a 2:1 glacial acetic acid/2-propanol mixture and then placed in a nitrogen atmosphere for 5 minutes. A known amount of deaerated KI solution is added to the sample mixture and placed back in the nitrogen atmosphere, in the dark, for 5 minutes and allowed to react. The sample is then measured against a blank solution, the absorbance at 435nm is then plotted against the calibration curve to determine the active oxygen content of the sample.

The test method states to deaerate the sample by bubbling a stream of nitrogen gas through. While this may be suitable for determining the concentration of peroxides, this would also displace an unknown amount of any dissolved oxygen.

Samples of HEA, HEMA, TEGDA and TEGDMA were purchased and evaluated along with the resins IPDI-PEA (**40**) and IPDI-PEM (**44**). For each run five samples were prepared and the average of three readings per sample was taken. It was found that there was a wide variation in the results (see Table 6.3) obtained in terms of a dissolved oxygen value from the samples when tested just as received. When the samples were sparged with air to the point of saturation, using a similar method to that described by Guo *et al*,[21] the

results become a lot more consistent. The values obtained for HEMA and TEGDMA agree very closely with those obtained by Guo *et al*.

The samples were also sparged with nitrogen following the procedure recommended in the Perstorp test method, and although lower values were obtained compared to the as received samples, again the variation in results obtained were very high. The addition of 100ppm benzoyl peroxide (BPO) (**59**) (6.61% O_2 content) to the samples was undertaken to see if it was possible to determine a difference between dissolved oxygen due to air sparging or due to the presence of peroxide. One set of samples were cooled for 15 minutes using solid carbon dioxide to allow the temperature of the resin to cool down enough to allow any dissolved gases to escape as the solubility decreases as the temperature is lowered. The minimum resin temperature measured was -34.6°C. The samples were then placed inside a box with a small piece of solid carbon dioxide present and allowed to return to room temperature (see Table 6.4). The carbon dioxide was used to ensure that no oxygen would dissolve back into the sample as it warmed up.

Sample	As Received		Air Sparged	
	O_2ppm	Std Dev	O_2ppm	Std Dev
HEA	5.3	3.05	28.0	0.21
HEMA	4.2	2.74	25.9	0.18
IPDI-PEA	7.3	3.23	50.5	0.18
IPDI-PEM	5.1	2.37	48.2	0.22
TEGDA	6.1	3.61	32.1	0.25
TEGDMA	3.8	2.89	31.5	0.20

Table 6.3 – Monomer Oxygen Concentration Before and After Air Sparging

Sample	N_2 Sparged		100ppm DHEMA		Solid CO_2 Cooled	
	O_2ppm	Std Dev	O_2ppm	Std Dev	O_2ppm	Std Dev
HEA	3.2	3.21	10.1	2.47	3.2	0.67
HEMA	3.4	2.99	9.8	2.87	3.3	0.59
IPDI-PEA	6.3	2.77	12.4	2.97	6.2	1.03
IPDI-PEM	4.4	3.11	10.7	3.20	4.5	0.82
TEGDA	5.4	3.54	11.7	3.01	5.3	0.71
TEGDMA	3.6	2.87	9.2	2.67	3.6	0.57

Table 6.4 – Monomer Oxygen Concentration After Nitrogen Sparging, Cooling Using CO_2 and the Addition of DHEMA

In theory by sparging the sample with dry nitrogen after it has passed through a canister of molecular sieve, the bulk of the dissolved oxygen should have been removed by displacement, only leaving the oxygen present in the form of peroxides. If this is the case then a simple subtraction between the values obtained from the samples as received and the nitrogen sparged samples should give an indication of the dissolved oxygen present (see Table 6.5). However, the high standard deviation values obtained from the results would not appear to offer any confidence in this particular approach, and it is not possible to be confidant that 100% of the free dissolved oxygen has been removed/displaced.

The addition of DHEMA does as would be expected to increase the apparent dissolved oxygen content, but again the standard deviation results obtained are high. It does appear that the actual amount of dissolved oxygen present in these systems is actually quite low. Even when the samples are air sparged the amount of oxygen increases up to five times the original value, the values are still only in the order of 25-50ppm. It does also explain why the industrial practice of bubbling air through vinyl ester containing materials which are coming to the end of their shelf life does refresh the material.

By cooling the sample to -30 to -40°C it does appear that the values obtained show the amount of peroxide formed during manufacture/synthesis and subsequent storage, is very similar to the results obtained by sparging the samples with nitrogen gas, but with a better

degree of reproducibility of results, as evidenced by the standard deviations obtained, almost a factor of 10 lower. It would appear that cooling the samples is sufficient to drive out the dissolved gases to allow for an accurate peroxide determination to be made.

Sample	As Received	Solid CO_2 Cooled	Calculated Dissolved O_2
	O_2ppm	O_2ppm	O_2ppm
HEA	5.3	3.2	2.1
HEMA	4.2	3.3	0.9
IPDI-PEA	7.3	6.2	1.1
IPDI-PEM	5.1	4.5	0.6
TEGDA	6.1	5.3	0.8
TEGDMA	3.8	3.6	0.2

Table 6.5 – Calculation of the Concentration of Dissolved O_2 in Monomers

The dissolved oxygen concentration of the resins can be calculated by simply subtracting the values obtained from the solid carbon dioxide cooled samples from the values of the same samples as received. The high standard deviation obtained from the as received samples can be reduced by increasing the sample size, although it is still larger than that obtained from the cooled samples. From the calculated dissolved oxygen concentrations it would appear that in general the oxygen content is between 0.5 to 1.0ppm. The extremes in concentration seen for HEA and TEGDMA could be down to a number of different reasons, age of the material, storage conditions or how far down the original container the sample came from (in theory material sampled from near the top of the container and the headspace, would be more rich in dissolved oxygen, compared to material from near the bottom. This can be borne out by the fact that often 200 litre drums of (meth)acrylate monomers which have passed their expiry date and have been replenished with air, there is a layer of variable depth/volume which is still within specification and can be used, while at the bottom there is a layer of gelled material.

The results show that the hydroxy terminated (meth)acrylates have the capacity to retain a lower level of dissolved oxygen compared to non-hydroxy terminated (meth)acrylates,

which agrees with the findings of Guo et al. One possible explanation for this observation could be that electrostatic attraction takes place between the glycol backbone of the (meth)acrylates studied and the dissolved oxygen, this would also explain the result seen with the polyethylene glycol resins IPDI-HEA and IPDI-PEM.

6.1.4 Detection of Oxidised Inhibitor

The detection of the oxidised inhibitors could also give valuable clues as to how efficiently the inhibitors are functioning within the respective resin systems. Since the oxidised inhibitors would be structurally different, it should be possible to use mid infra-red spectroscopy to try and detect these new substances. To this end samples of the inhibitors have been dissolved in a suitable solvent (toluene or propan-2-ol) and sparged with air, as well as just being exposed to the atmosphere for a couple of months.

The work done using FT-IR spectroscopy with a diamond ATR equipped spectrometer has shown that it is possible to detect some structural changes due to oxidation of the antioxidants, however the bands are not particularly strong, and when looking for 50-1000ppm concentrations in the resin samples the peaks are too weak to be accurately determined for the majority of the epoxy (meth)acrylate and urethane (meth)acrylate samples examined to date, particularly with aromatic based resin systems due to overlaps in peaks due to aromatic ring structures.

6.1.5 General Discussion

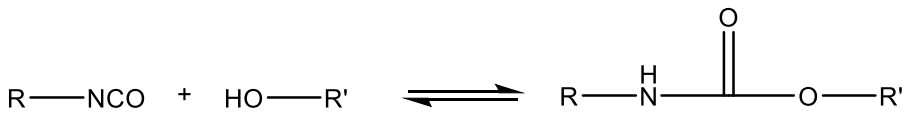
As previously discussed the role of oxygen in the mechanism of antioxidants, particularly phenolic antioxidants, is well documented. The preceding work has shown that although it is possible to determine how much oxygen is present in a resin system, by doing a two stage analytical process using the UV-Visible method outlined above. The first stage done at room temperature will measure the total dissolved oxygen concentration of the resin. The second stage determined either after sparging the sample with nitrogen gas, or by cooling the sample with carbon dioxide, to measure the amount of oxygen present due to peroxide formation. The amount of oxygen gas dissolved in the system can then be calculated by subtracting the peroxide oxygen concentration from the total dissolved oxygen concentration. The suitability of the solid carbon dioxide cooling method for an industrial test method would require further examination, as the actual temperature that

the samples were cooled to was -30 to -40°C, which is obtainable with standard laboratory refrigerated cooler.

As previously mentioned, the results obtained appear to indicate that the methacrylate samples do have a lower dissolved oxygen concentration compared to the acrylate ones, yet in general the methacrylate samples are significantly more stable that their acrylate analogues. This leads to the conclusion that although the dissolved oxygen content is important, the reactivity of the (meth)acrylate group is also critical in the overall stability of the system.

6.2 Phenolic Inhibitor Urethane Oligomers

The use of "blocked" or capped isocyanates in polyurethane chemistry has been known since the 1960's.[25] Commerical MDI based prepolymers developed in the 1960's were capped with phenol, which would uncap at a temperature range of 160-180°C as the urethane linkage is a reversible reaction (see Scheme 6.2). Different hydroxy functional compounds have been used as blocking agents and reacted with a range of different isocyanates in response to the different properties required.[26,27] However, all require higher temperatures to unblock the isocyanate group and release the blocking agent, compared to the initial reaction temperature. If the blocking agent was a phenolic with polymerisation inhibitor effects, then it is a method to enable the release of the inhibitor into a polymer system at high temperatures.



Scheme 6.2

6.2.1 Urethane Oligomer Synthesis

6.2.1.1 Diphenylmethane Diisocyanate Based Oligomers

6.2.1.1.1 MDI-PMP

The synthesis of the urethane was carried out under standard atmosphere and pressure. In a 25ml reaction vessel, on a hot plate equipped with magnetic stirrer, heating block and temperature probe, 7.5g (0.03 mol) of diphenylmethane-4,4'-diisocyanate (Desmodur 44MC ex Bayer) (MDI) (**9**) and 7.4g (0.06 mol) of 4-methoxyphenol (ex Solvay) (PMP) (**14**) was added. The vessel was heated to 60°C with the stirrer switched on. After 2 hours

at 60°C the temperature was increased to 80°C over 2 hours. The vessel was held at 80°C for 2 hours before sampling for isocyanate content. Once the isocyanate content had dropped below 0.2%, then the vessel was cooled and the reaction mixture decanted off. Compound MDI-PMP (**66**).

6.2.1.1.2 Other MDI Based Oligomers

Following the same process and equipment as the MDI-PMP synthesis, the following compounds were synthesised (see Table 6.6);

MDI (0.03 mol)	Inhibitor	Mass (0.06 mol)	Compound
7.5g	TBC (**17**)	10.0g	MDI-TBC (**67**)
7.5g	BHT (**18**)	13.2g	MDI-BHT (**68**)
7.5g	4H-TEMPO (**26**)	10.3g	MDI-4H-TEMPO (**69**)
7.5g	DTBP **(53**)	12.4g	MDI-DTBP (**70**)
7.5g	Phenol	5.6g	MDI-Ph (**71**)
7.5g	Nonylphenol	13.2g	MDI-NonylPh (**72**)
7.5g	tert-Butylphenol	9.0g	MDI-tBuPh (**73**)

Table 6.6 – Reactions with MDI

6.2.1.1.3 MDI-PTZ

Following the same process and equipment as the MDI-PMP synthesis, 7.5g (0.03 mol) of MDI and 12.0g (0.06 mol) of PTZ (**27**) were placed in a reaction vessel. Due to the high melt point of PTZ, the reaction temperature was taken to 120°C and held for 1 hour, where the reaction mixture appeared to be liquid. The reaction mixture was held for a further 5 hours at 120°C, then cooled down. It was not possible to perform an isocyanate content determination due to the insolubility of the reaction product in toluene or xylene at room temperature.

Once the reaction mixture had cooled down, FT-IR spectra showed the presence of NCO stretching at 2270 cm^{-1}. The reaction vessel was equipped with a condenser, and the reaction mixture was heated up to 100°C and then heated to 150°C @ 10°C/hour and held

@ 150°C for 4 hours. Again once the reaction mixture had cooled, the FT-IR spectra was obtained, which showed the presence of NCO. PTZ has a literature melt point of 182-187°C (185.8°C obtained from material used in experiment), which is lower than the literature boiling point of MDI (>300°C), however it was advised not to take the reaction mixture above 160°C for safety reasons. Compound MDI-PTZ (**74**).

6.2.1.2 Isophorone Diisocyanate Based Oligomers

Following the same process and equipment as the MDI-PMP synthesis the following compounds (see Table 6.7) were synthesised using IPDI (**10**) as a base;

IPDI (0.03 mol)	Inhibitor	Mass (0.06 mol)	Compound
6.7g	PMP	7.4g	IPDI-PMP (**75**)
6.7g	TBC	10.0g	IPDI-TBC (**76**)
6.7g	BHT	13.2g	IPDI-BHT (**77**)
6.7g	4H-TEMPO	10.3g	IPDI-4H-TEMPO (**78)**
6.7g	PTZ	12.0g	IPDI-PTZ (**79**)
6.7g	DTBP	12.4g	IPDI-DTBP (**80**)
6.7g	Phenol	5.6g	IPDI-Ph (**81**)
6.7g	Nonylphenol	13.2g	IPDI-NonylPh (**82**)
6.7g	tert-Butylphenol	9.0g	IPDI-tBuPh (**83**)

Table 6.7 – Reactions with IPDI

6.2.1.3 Dicyclohexamethylene Diisocyanate Based Oligomers

Following the same process and equipment as the MDI-PMP synthesis above following were synthesised (see Table 6.8) using HMDI (**12**) as a base;

HMDI (0.03 mol)	Inhibitor	Mass (0.06 mol)	Compound
7.9g	PMP	7.4g	HMDI-PMP (**84**)
7.9g	TBC	10.0g	HMDI-TBC (**85**)
7.9g	BHT	13.2g	HMDI-BHT (**86**)
7.9g	4H-TEMPO	10.3g	HMDI-4H-TEMPO (**87**)
7.9g	PTZ	12.0g	HMDI-PTZ (**88**)
7.9g	DTBP	12.4g	HMDI-DTBP (**89**)
7.9g	Phenol	5.6g	HMDI-Ph (**90**)
7.9g	Nonylphenol	13.2g	HMDI-NonylPh (**91**)
7.9g	tert-Butylphenol	9.0g	HMDI-tBuPh (**92**)

Table 6.8 – Reactions with HMDI

6.2.2 Analysis

The samples were checked by FT-IR spectroscopy to ensure that the reaction was taken to completion, by examining the 2000 – 2400 cm^{-1} region for any sign of a peak due to the presence of unreacted NCO. In half the samples there was a residual peak, <5% of the peak area when compared to a sample of the unreacted isocyanate. The samples were subjected to DSC analysis over the -30 - 300°C region (TA Instruments Q20 DSC, 7-15mg sample mass, 1 min equilibration @ -30°C, 10°C/min ramp rate, N_2 atmosphere) to determine the melt point and unblocking temperature of the substances following the method outlined by Mohammed and Sankar.[28]

6.2.3 Results

The data obtained from the DSC analysis are summarised in Table 6.9 below. TA Universal Analysis 2000 software was used to evaluate the data and to determine the melt points (taken as the peak minimum) and the unblocking temperatures (the onset temperature determined at the curve inflection point, and the peak temperature at the peak minimum). Figure 6.1 shows the DSC curve obtained for IPDI-BHT.

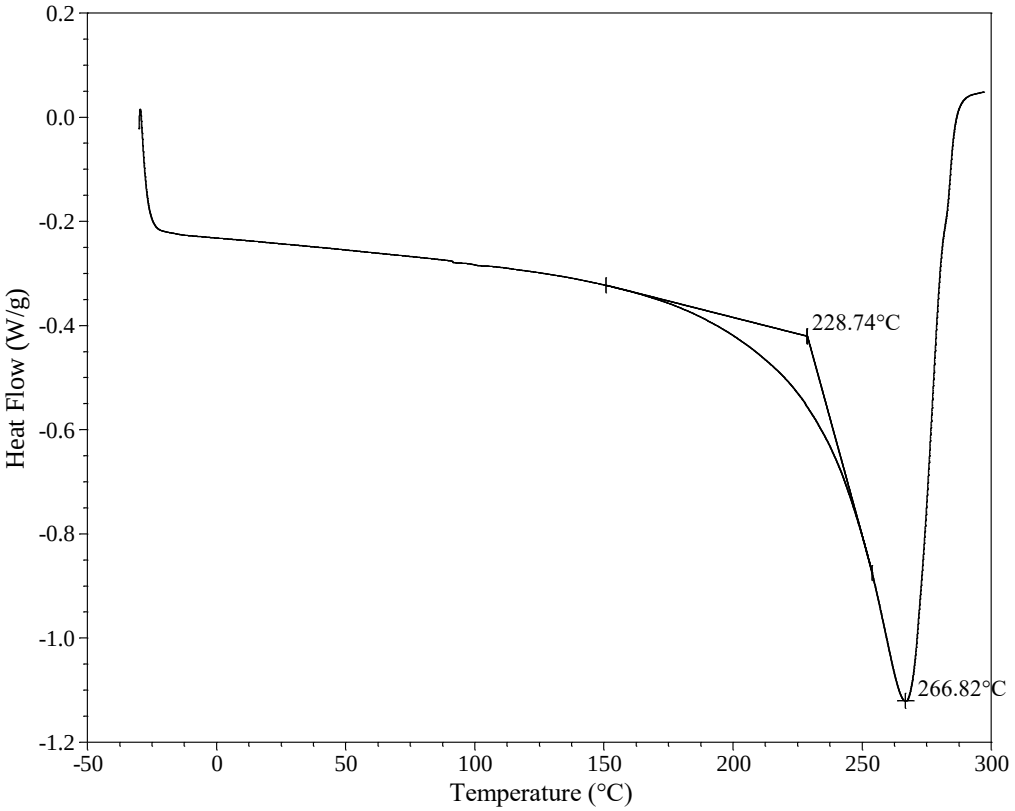


Figure 6.1 – DSC Curve Obtained for IPDI-BHT

The unblocking temperatures quoted above are determined from a sample of the pure substance, when the substance is dissolved in a resin system different values may be obtained due to solvency effects and interactions with the resin itself. In general it has been generally expected that that aromatic urethanes will unblock at lower temperatures compared to an aliphatic equivalent.

Compound	State @ 20°C	Melt Point (°C)	Unblocking (°C)	
			Onset	Peak
HMDI-BHT	Solid	97.2	210.6	210.1
IPDI-BHT	Semi-solid	19.8	241.7	284.6
MDI-BHT	Liquid	<-30	80.7	154.2
HMDI-DTBP	Solid	48.6	>300	>300
IPDI-DTBP	Solid	58.3	>300	>300
MDI-DTBP	Liquid	<-30	142.8	224.3
HMDI-Ph	Liquid	13.1	173.9	295.8
IPDI-Ph	Liquid	<-30	163.4	270.9
MDI-Ph	Solid	107.7	202.3	238.0
HMDI-NonylPh	Solid	227.7	230.2	277.5
IPDI-NonylPh	Liquid	-6.8	240.9	>300
MDI-NonylPh	Liquid	<-30	195.4	267.5
HMDI-tBuPh	Solid	153.6	231.6	>300
IPDI-tBuPh	Solid	112.7	198.5	>300
MDI-tBuPh	Liquid	<-30	200.6	251.5
HMDI-PMP	Solid	90.1	183.5	256.9
IPDI-PMP	Solid	126.4	187.2	261.8
MDI-PMP	Solid	78.3	190.6	273.2
IPDI-PTZ	Solid	58.0	196.9	266.9
MDI-PTZ	Liquid	<-30	210.4	267.1
HMDI-TBC	Liquid	<-30	75.5	149.9
IPDI-TBC	Liquid	<-30	163.4	243.7
MDI-TBC	Solid	54.9	187.8	261.9
HMDI-4H-TEMPO	Solid	166.3	187.0	247.3
IPDI-4H-TEMPO	Solid	123.0	233.5	260.2
MDI-4H-TEMPO	Solid	67.0	>300	>300

Table 6.9 – Compound Properties

The use of HMDI and MDI allow for a direct comparison between an aliphatic and aromatic structure. Although the 4,4'-MDI does consist of predominantly a single isomer (>98% 4,4'-, <1.8% 2,4'-) while the HMDI consists of a mixture of 6 isomers, predominantly 4,4'- (cis-cis, cis-trans and trans-trans) with <5% 2,4'- (cis-cis, cis-trans and trans-trans) isomers. The IPDI however is asymmetric in its structure, and consists of 2 stereoisomers, 66-70% trans and 30-33% cis.

Although PTZ is not hydroxy functionalised, it does have a secondary amine which will react with an isocyanate to create a urea. Ureas are generally heat stable, hence the high unblocking temperatures seen for IPDI-PTZ and MDI-PTZ, however the urea linkage is reversible hence the system would revert back to an isocyanate and amine group.

6.2.4 Discussion

Looking at the analytical results obtained there does not appear to be a clear pattern that emerges. It would appear that the blocking group and the diisocyanate used both play an effect, which produces a wide range in both melt point and unblocking temperature ranges. The equivalent of 200ppm, of the IPDI based compounds (**75** to **83**), was dissolved into a 10.0g sample of IPDI-PEA resin. These were placed in an incubator @ 120°C and monitored every 30 minutes. It was found that all the samples had gelled within 1.5 hours except for the samples containing IPDI-DTBP and IPDI-tBuPh. The rapid time to gel point is indicative that there was insufficient inhibitor present, which would indicate that the substances added had not unblocked and released the inhibitor. The IPDI-tBuPh gelled after 3 hours, while the IPDI-DTBP did not fail until 8.5 hours. Chart 6.1 below shows the results obtained, together with the results obtained from testing done with 200ppm of the pure substance added to the IPDI-PEA resin. From the DSC results all of the compounds tested were below their respective unblocking temperature, and for the phenolic based materials this has removed any antioxidant capability. However MDI-PTZ containing PTZ does retain some activity, probably due to the sulphur not directly connected to the urea linkage.

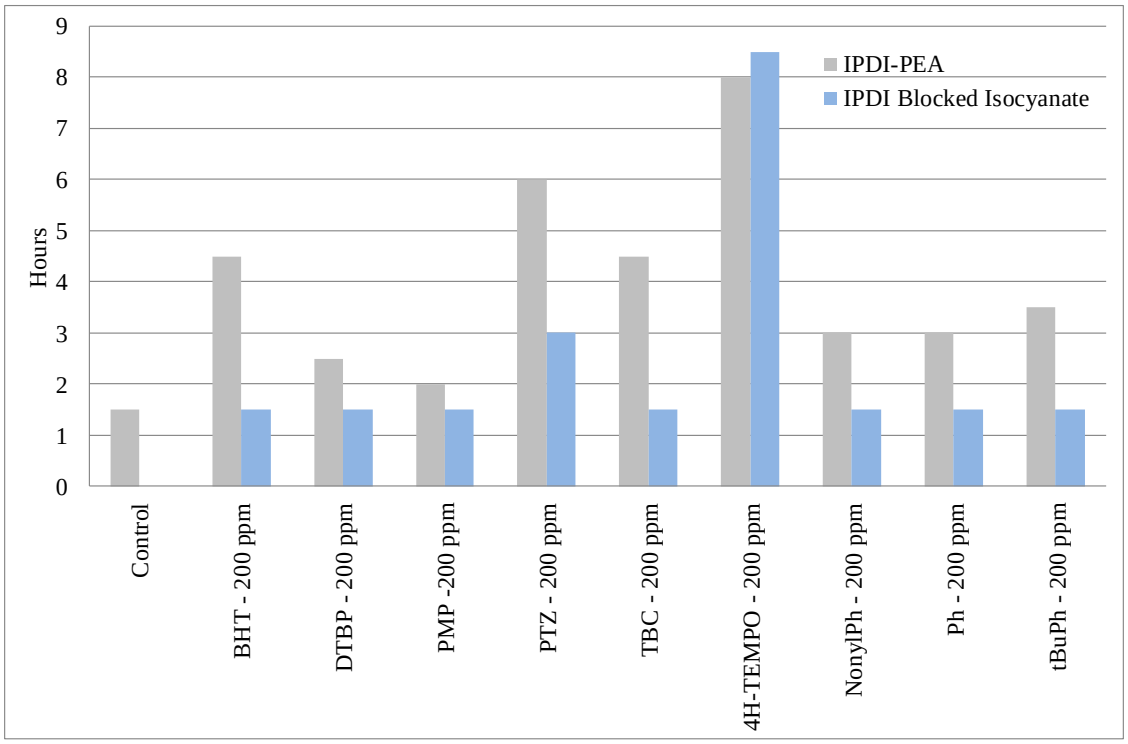


Chart 6.1 – Comparison of Gel Time between a Control and Material Containing a Blocked Isocyanate @ 120°C

The use of 4H-TEMPO does not appear to have been affected by being reacted with an isocyanate, which does prove that the method of stabilisation is due to the stable nitroxide, rather than via the hydroxyl group, which is the stabilisation route used in phenolic based inhibitors and antioxidants.

Although compounds containing HMDI or MDI were not tested, due to their analogous nature to the IPDI based ones it would be reasonable to assume that they would behave in a similar fashion.

It does appear that reacting the hydroxyl group to create a urethane linkage does provide a degree of protection for the inhibitor, and that once it is unblocked, then it is available to undertake free radical scavenging. Also it would appear that if there are any phenolic based inhibitors present in the reaction mixture during a urethane synthesis, then these are likely to be consumed. The use of 4H-TEMPO does not appear to be affected by urethane reaction, unfortunately this does mean that the nitroxide functional group is not protected, hence released at high temperatures.

The high unblocking temperatures preclude the use of the blocked compounds for use in these urethane based systems due to the urethane linkage breaking down at 120-150°C.

However the compounds would be of interest in thermoplastic processing as the temperatures involved are in the 200-300°C region. Although in normal thermoplastic processing the residence time of the polymer in an injection moulding machine, at temperature, is in the order of 30-120 seconds, if the material is left for longer than 5 minutes, then the material in the barrel has to be scrapped due to scorching and other thermal degradation. The addition of one or more the blocked compounds would help to delay the scorching due to the release of fresh inhibitor at temperature and allow for a greater leeway in processing times in case of emergencies.

Scorching is a major problem with the processing of thermoplastics, as the majority of the materials used are colourless or optically clear, hence there is the need for additives to keep the desired optical properties. One of the main criteria for such additives, apart from preventing scorching, is that the substance (and its by-products) must also be clear, at both room and elevated temperatures. To this end some of the compounds synthesised above are particularly suitable, as being colourless and also liquid, MDI-BHT being the most suitable as this study has shown that BHT has good properties and will remain colourless.

6.3 Conclusions

The presence of dissolved oxygen will occur in most resins, even though as this study has shown the amount present is relatively low. However since it is the starting point for peroxide formation, even at these low levels it has the potential to reduce the long term stability of the resin. The use of an aerobic inhibitor might be considered to be more appropriate in these situations as the presence of the oxygen will ensure that the inhibitor remains active. However the work presented earlier in this study has shown that when aerobic inhibitors are solely reliant upon dissolved oxygen in the resin due to a nitrogen gas headspace, then their active period is markedly reduced compared to anaerobic inhibitors.

As the temperature increases, the rate of oxygen consumption due to peroxide formation must be increasing as the stability of the resin decreases, as has been shown earlier. For some monomers, (acrylic acid, methacrylic acid and styrene) it is normal practice to monitor the amount of inhibitor present by gas chromatography to ensure that there is sufficient present to prevent the rate of polymerisation from getting too high. If this occurs then the polymerisation can get out of control, and become extremely exothermic. There

have been numerous fires and explosions in chemical facilities across the world over the past 40 years directly attributed to these circumstances occurring. Measuring the oxygen content of the monomer and monitoring the storage temperature would help to ensure that these conditions do not happen. It has become standard industrial practice to have sufficient inhibitor present (often dissolved into the monomer or a suitable solvent at 5-20% concentration) that can be injected into the monomer if required. The use of a blocked isocyanate containing 2 moles of the preferred inhibitor is another potential method of providing some degree of a safety margin if the normal inhibitor levels in the monomer get depleted.

Additionally there is potential for these inhibitor containing blocked isocyanates to be used in thermoplastic applications, as well as the thermoset types discussed in this study, since thermoplastics are often processed using injection moulding equipment via a hot melt stage where high temperatures (200-300°C) depending on the resin would be experienced for a short period of time.

From the studies shown the inhibitor does not appear to be as effective as when pure inhibitor is used, but it does provide a degree of extra protection if required. The reason for this reduced efficiency could be due to the unblocked isocyanate group trying to react with any suitable functional group that is available, and so reacting with the inhibitor again. The use of 4H-TEMPO does appear to be very effective when used in a blocked isocyanate, this is most likely to be because the hydroxyl functional group is not required as it is a stable radical, which terminates the free radical propagation cycle.

6.4 References

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7 Conclusions

This study has looked at the effects that the use of phenolic inhibitors have upon resin systems which contain a terminal carbon-carbon double bond functional group, also known as a vinyl group, and are liquid at room temperature. The terminal location of the functional group means that when the double bond is broken, normally by the presence of a free radical, it can react with other terminal vinyl groups to result in chain extension or cross-linking, hence polymerisation. The following observations can be drawn from this study.

- Even the addition of a low concentration (100 ppm for most of the inhibitors examined, 50 ppm for hydroquinone) of an inhibitor does improve the storage stability of a resin system.

- 4-Hydroxy-2,2,6,6-tetramethyl-1-piperdinyloxy (4H-TEMPO) is the most effective inhibitor examined within this study relative to its concentration in the resin, irrespective of the resin type and the headspace conditions. The compound does impart a distinct colour to the resin it is added to, so would not be suitable for colourless resins.

- 2,6-di-tert-Butylphenol (DTBP) has the worst performance of the compounds studied as polymerisation inhibitors, although it is used as the precursor in the synthesis of a number of commercially available inhibitors.

- The majority of the inhibitors used for commercially available acrylate and methacrylates, 2,6-di-tert-butyl-4-methylphenol (BHT) and 4-methoxyphenol (PMP) are aerobic and require a headspace that contains oxygen. If a nitrogen headspace is used with these inhibitors, then the storage life of the materials would be considerably reduced to less than half compared to a headspace containing air.

- Phenothiazine (PTZ) is a particularly effective inhibitor for use with amine acrylates and methacrylates. Hydroquinone (HQ) and methyl hydroquinone (MeHQ) are good cost effective general purpose anaerobic inhibitors.

- Ascorbic acid is effective inhibitor in the aqueous phase of the waterborne resin systems, but not in the resin phase as the compound was found not to be soluble in the resins evaluated in this study. Hydroquinone is effective in both the resin and aqueous phases, while the other inhibitors were only effective in the resin phase.

- In binary inhibitor systems studied, the effects of the 2 inhibitors are additive, rather than synergistic.

- The addition of inhibitors in concentrations up to 1000ppm does not have an adverse impact upon the ability of the resin to be subsequently cured using a source of free radicals either from peroxides or UV initiators, providing that the free radical source is added at a concentration of 1% of the resin formulation.

- A blend of an aerobic and anaerobic inhibitors would be the most effective to prolong the storage of the resin. Keeping the resin stored at 20°C will extend the storage life for as long as possible, temperature excursions to 40°C and above should be minimised to as short a time as possible.

- To maximise the storage life of the resin, it is best to add the inhibitor after the resin synthesis has been completed. It would be desirable to have some inhibitor present at the start of the resin synthesis, both the help stabilise the vinyl group during the synthesis process and to help minimise the peroxide formation that takes place during the synthesis process.

- It is possible to determine both the dissolved oxygen content and the peroxide content by determining the overall oxygen content by a combination of existing titration methods and cooling to -20/30°C.

7.1 Possible Further Studies

This study has been done looking at samples in the 20-120°C temperature range, but it would be interesting to obtain data in the 0-10°C region as this would allow further data to be incorporated into the modelling equations derived from this study, and help to enable better predictions. The time taken for these experiments would be considerable, and in the case of the epoxy and urethane resins, a new method of measuring the point at which the material begins to gel at these temperatures without disturbing the atmosphere inside the sample containers would have to be developed.

The headspace that is present in the sample containers used to store resins would warrant some further investigation, particularly for resins which have aerobic inhibitors present (2,6-di-tert-butyl-4-methylphenol and 4-methoxyphenol). The volume of headspace to offer the optimum level of protection could be determined, although there are regulations

concerning the headspace of chemicals being transported which are subject to United Nations classification. Also it would be interesting to determine just how much oxygen from the headspace does cross the liquid gas interface into the resin, and how much of an oxygen concentration gradient is setup in a container.

It is proposed to author a couple of papers based on the work presented in this report, one looking at the effect of the isocyanate group upon the properties of acrylate polymers, and the other on the measure the gel point of resins using a rheometer in an isothermal setup.

Appendices

A1.0 – Inhibitor Stability Results

A1.1 – Amine Acrylate

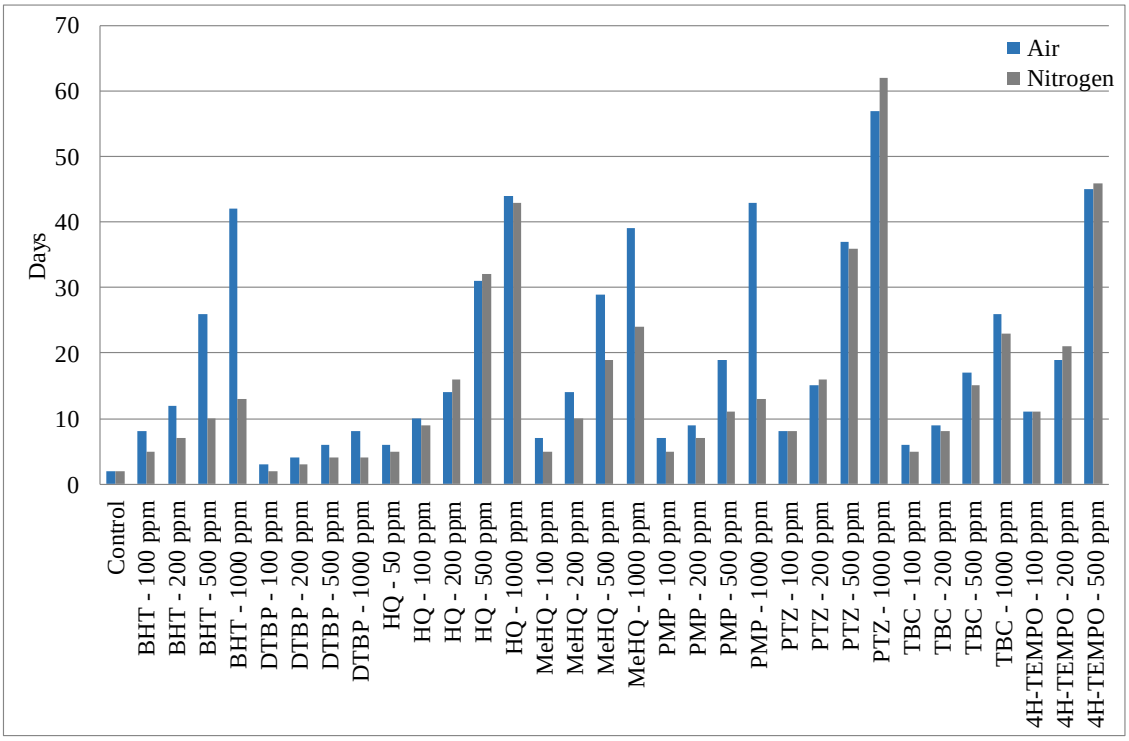

Chart A1.1.1 – HDDA-MEA Resin Stability @ 40°C

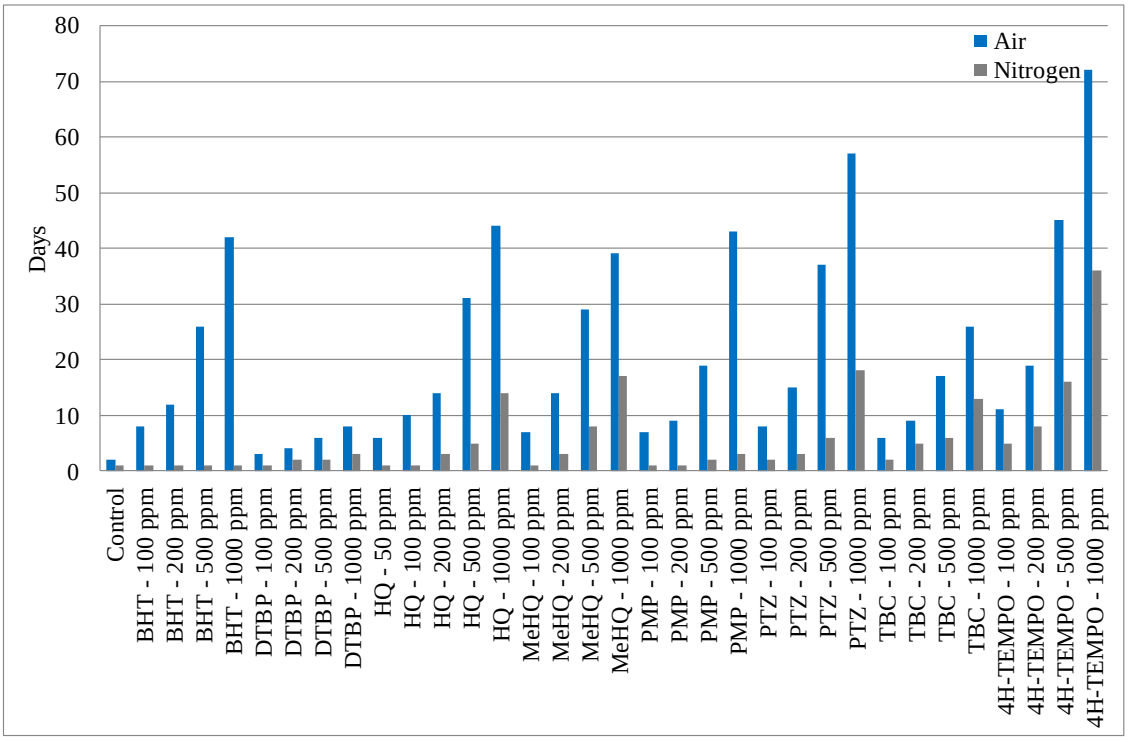

Chart A1.1.2 – HDDA-MEA Resin Stability @ 80°C

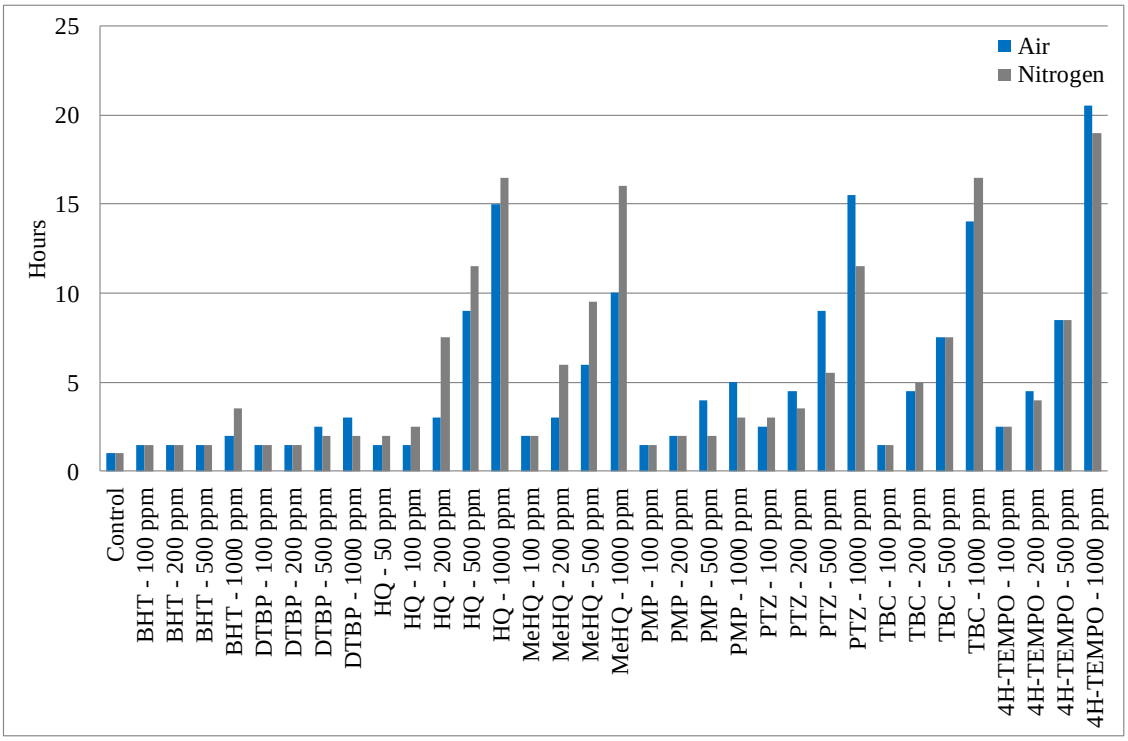

Chart A1.1.3 – HDDA-MEA Resin Stability @ 120°C

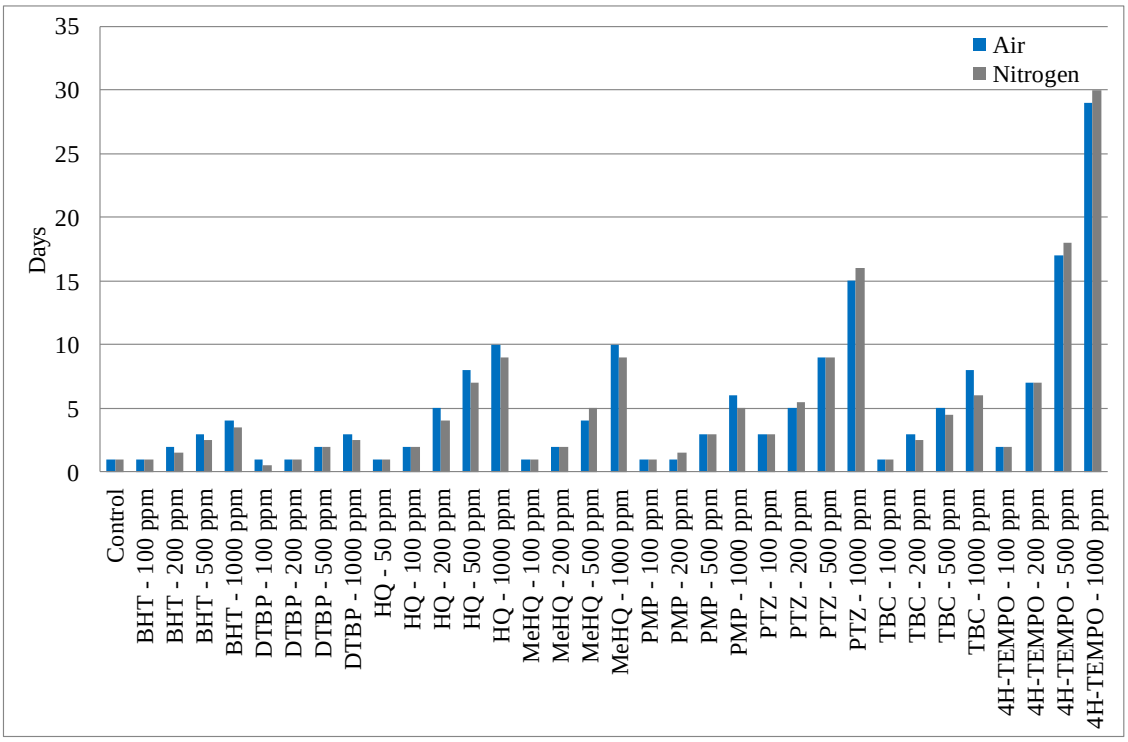

Chart A1.1.4 – TEGDA-MEA Resin Stability @ 80°C

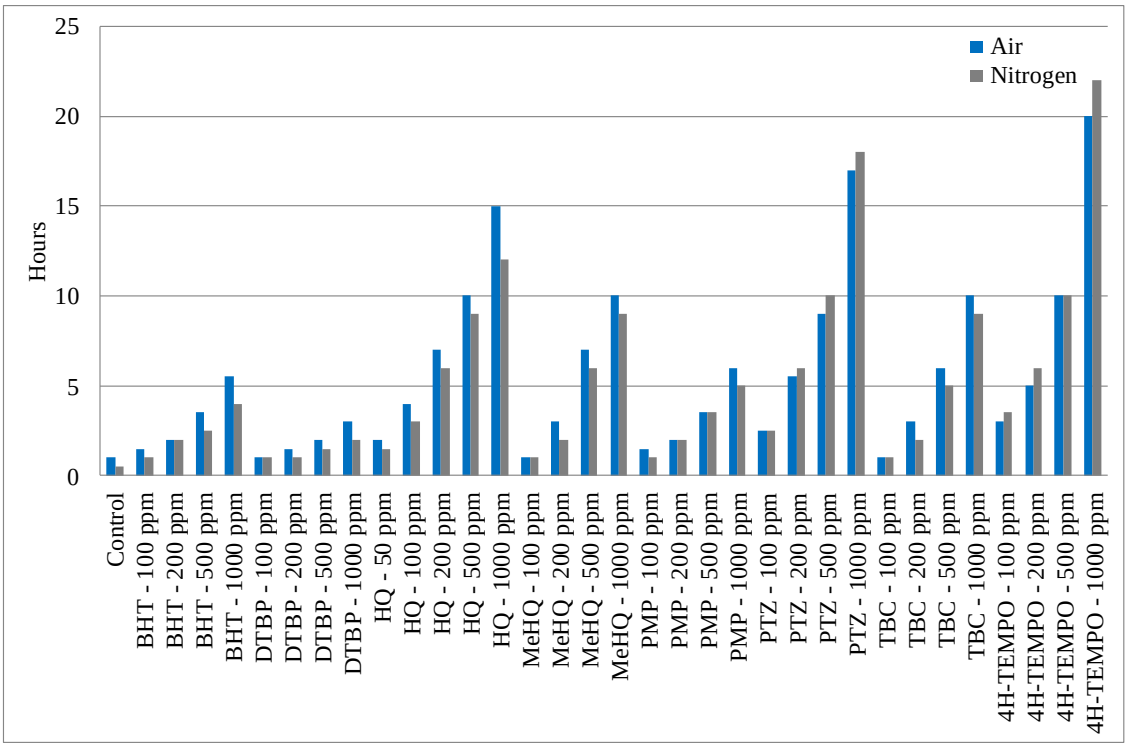

Chart A1.1.5 – TEGDA-MEA Resin Stability @ 120°C

A1.2 – Amine Methacrylate

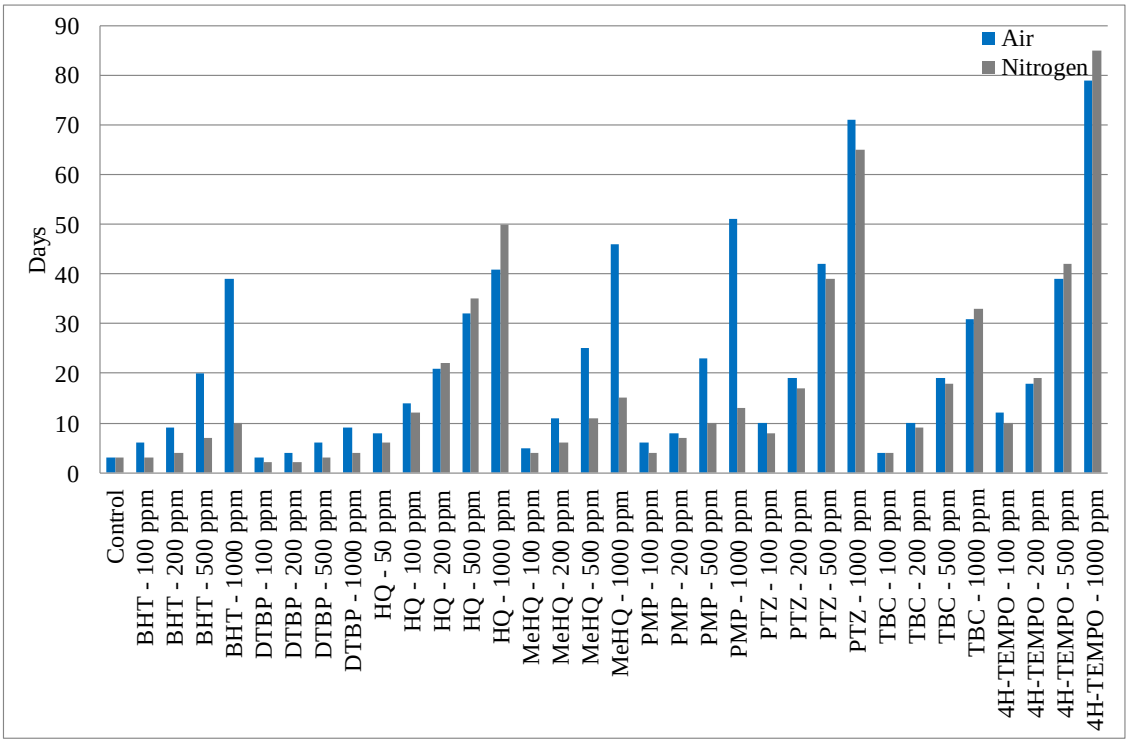

Chart A1.2.1 – HDDMA-MEA Resin Stability @ 40°C

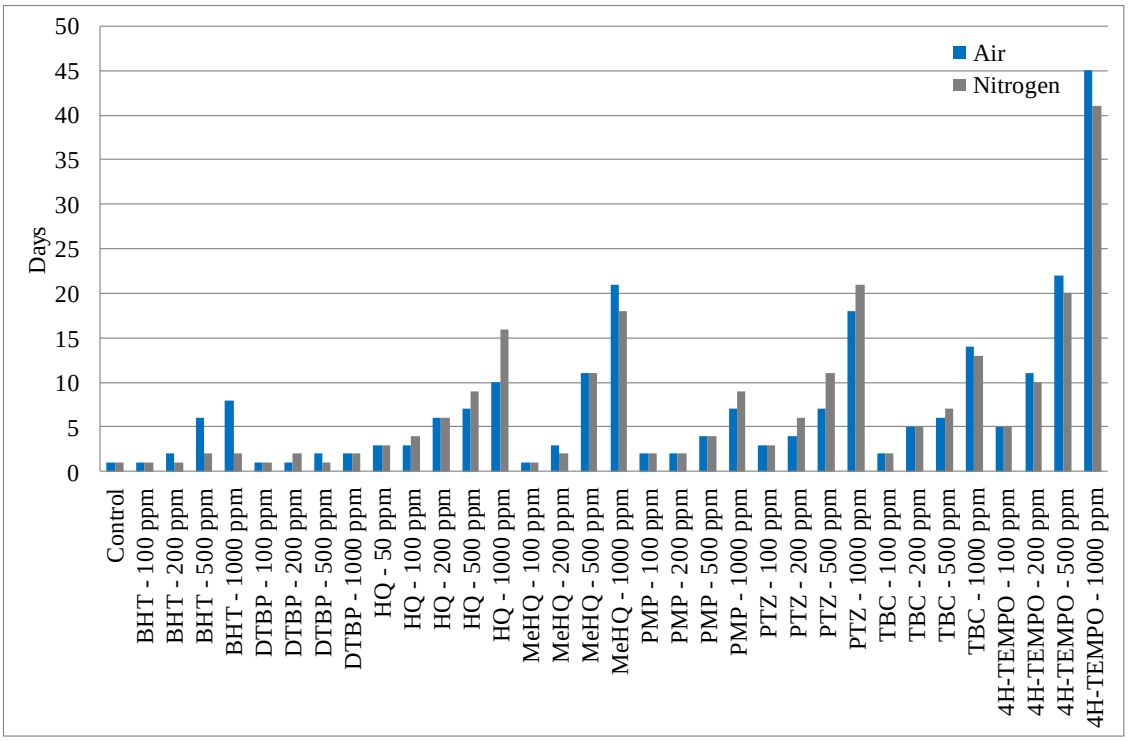

Chart A1.2.2 – HDDMA-MEA Resin Stability @ 80°C

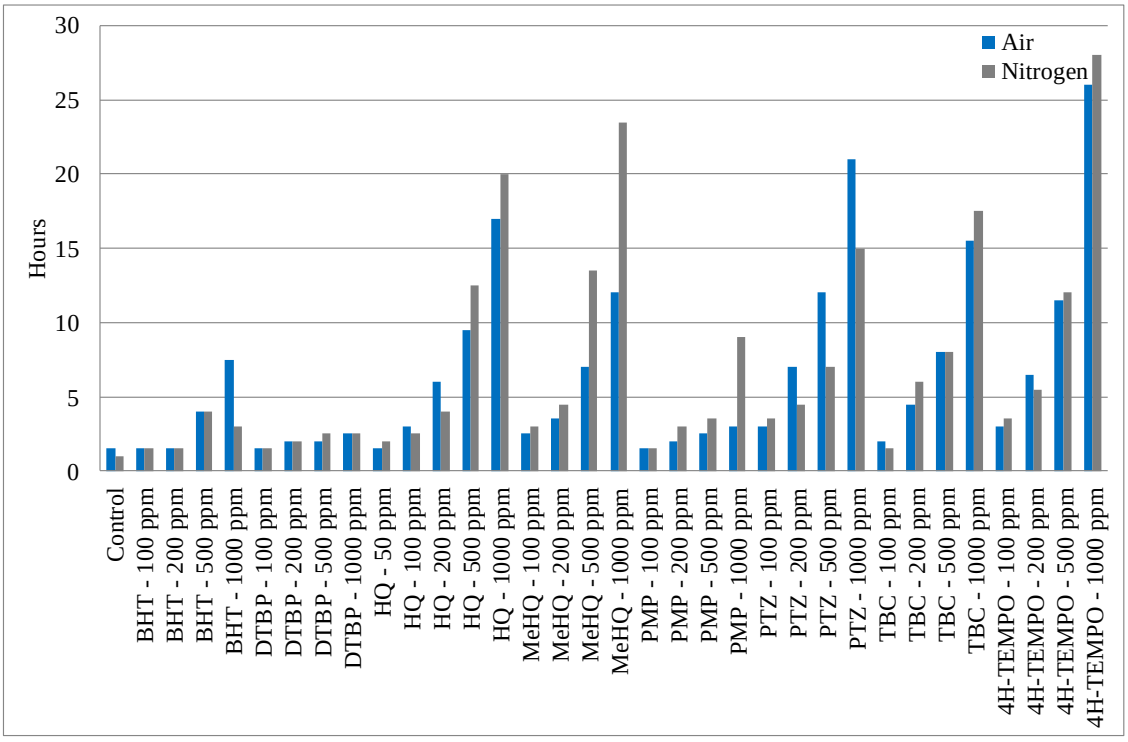

Chart A1.2.3 – HDDMA-MEA Resin Stability @ 120°C

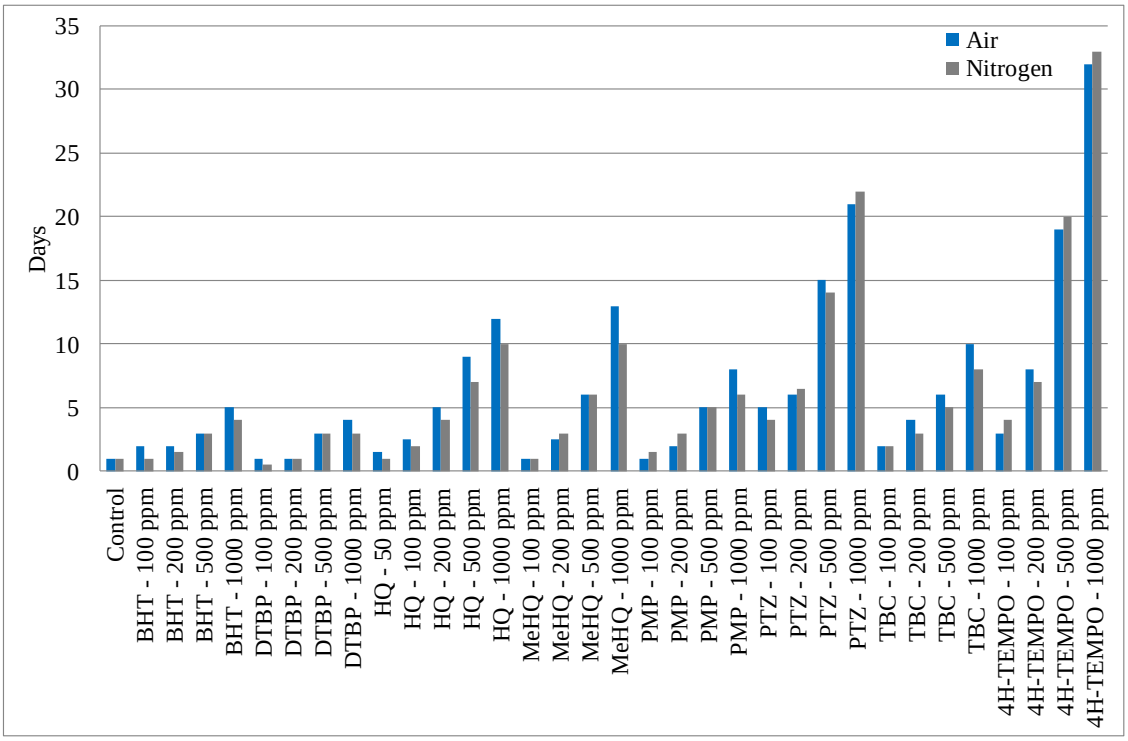

Chart A1.2.4 – TEGDMA-MEA Resin Stability @ 80°C

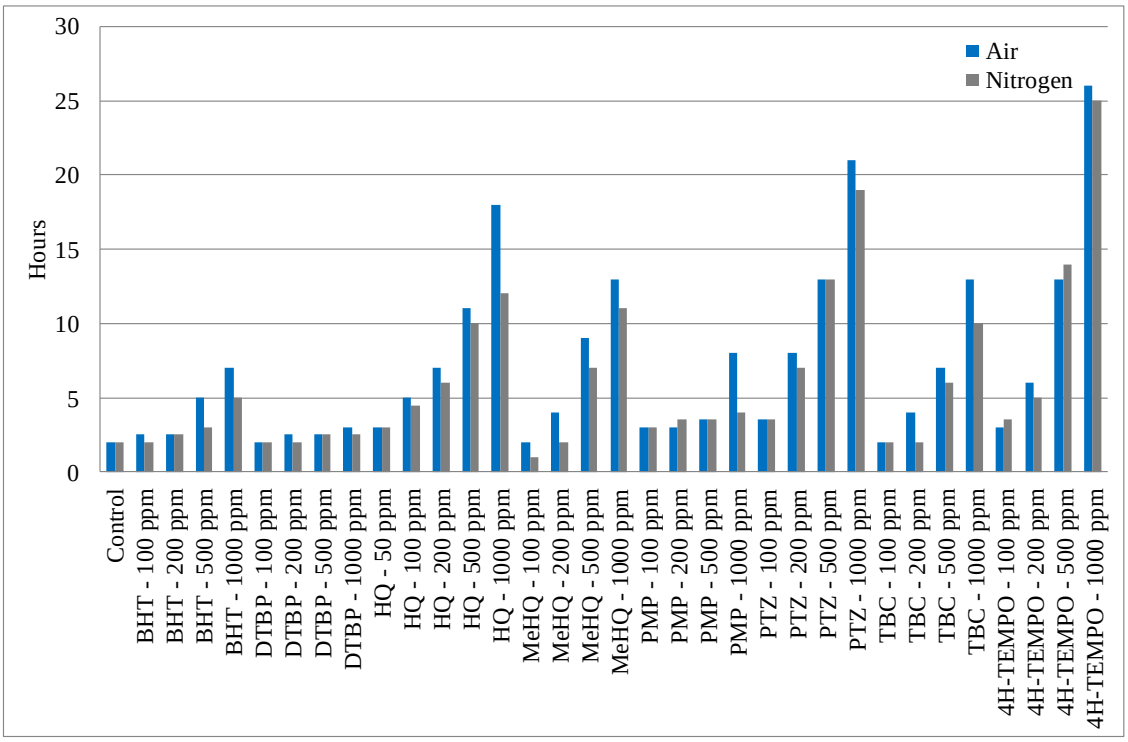

Chart A1.2.5 – TEGDMA-MEA Resin Stability @ 120°C

A1.3 - Epoxy Acrylate

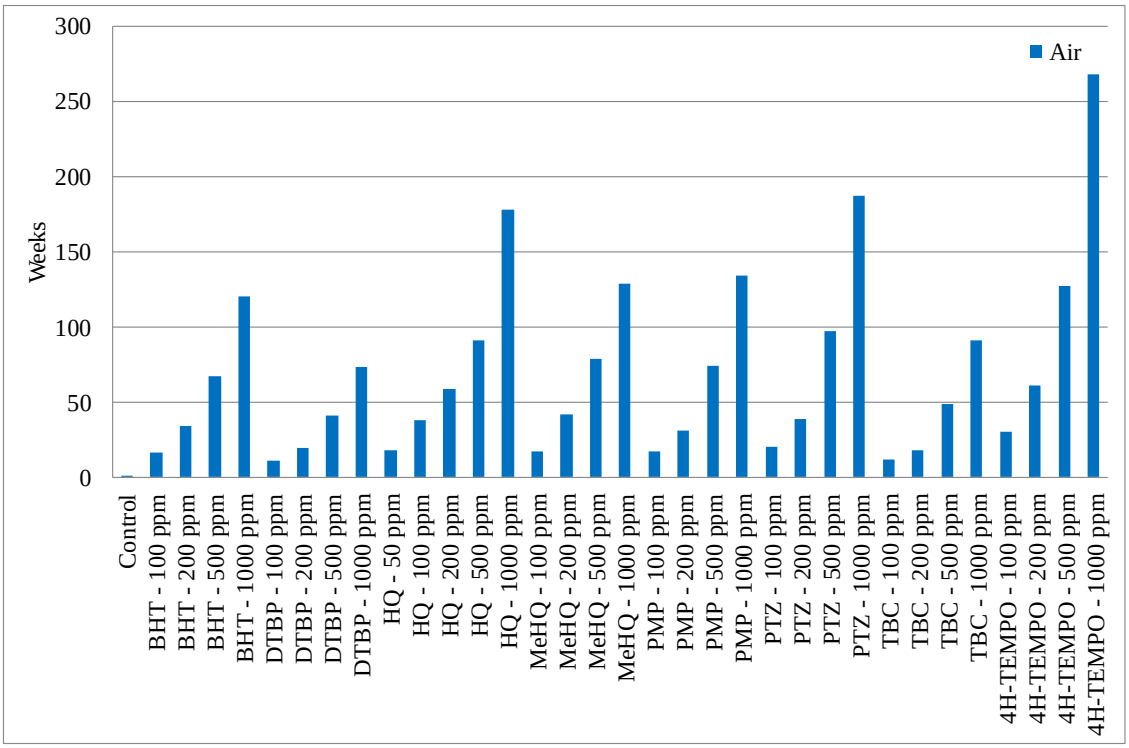

Chart A1.3.1 – HDDGEDA Resin Stability @ 20°C

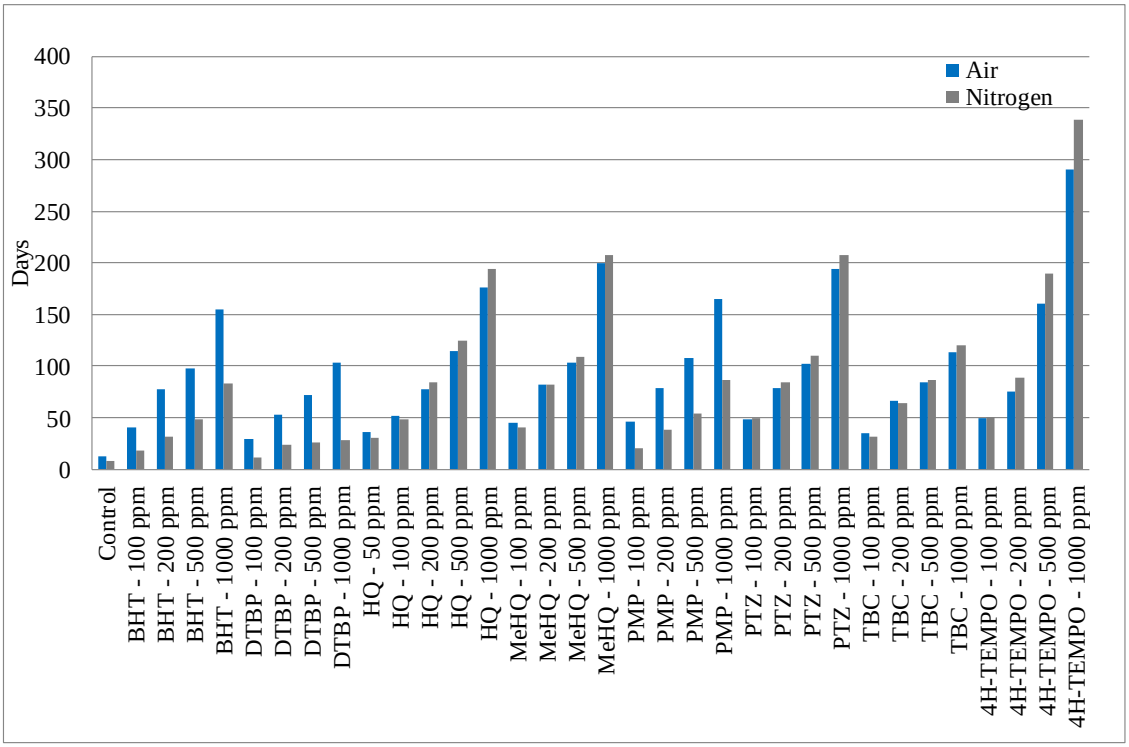

Chart A1.3.2 – HDDGEDA Stability @ 40°C

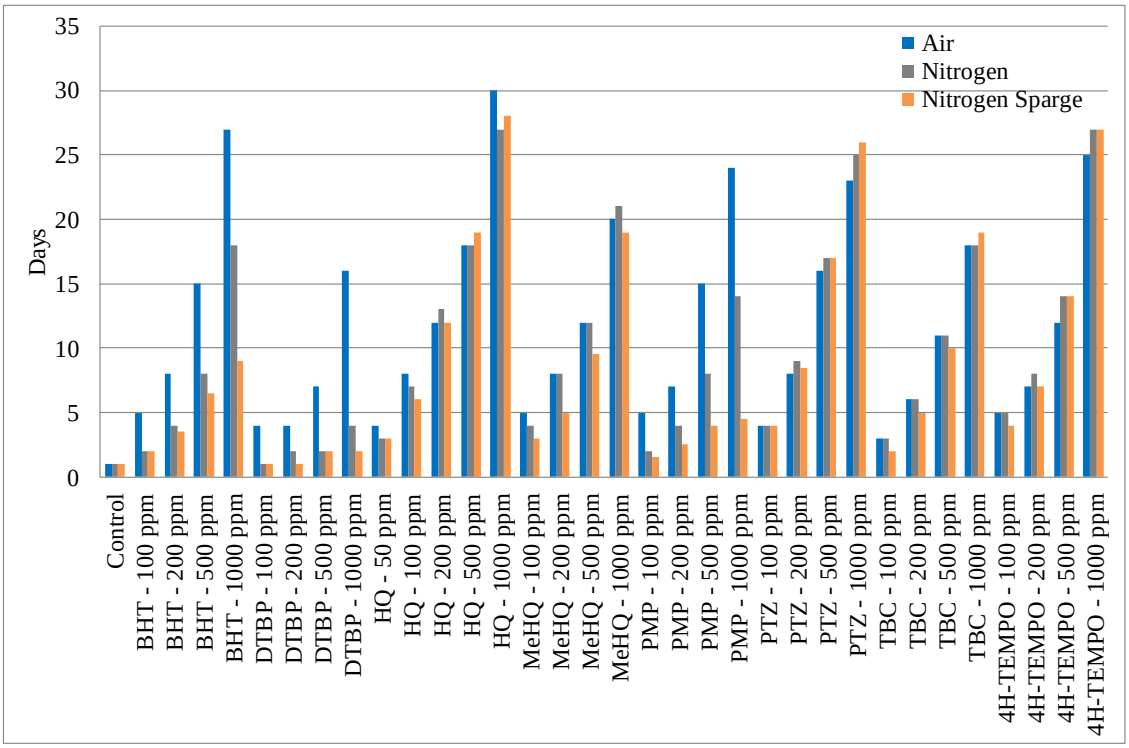

Chart A1.3.3 – HDDGEDA Resin Stability @ 80°C

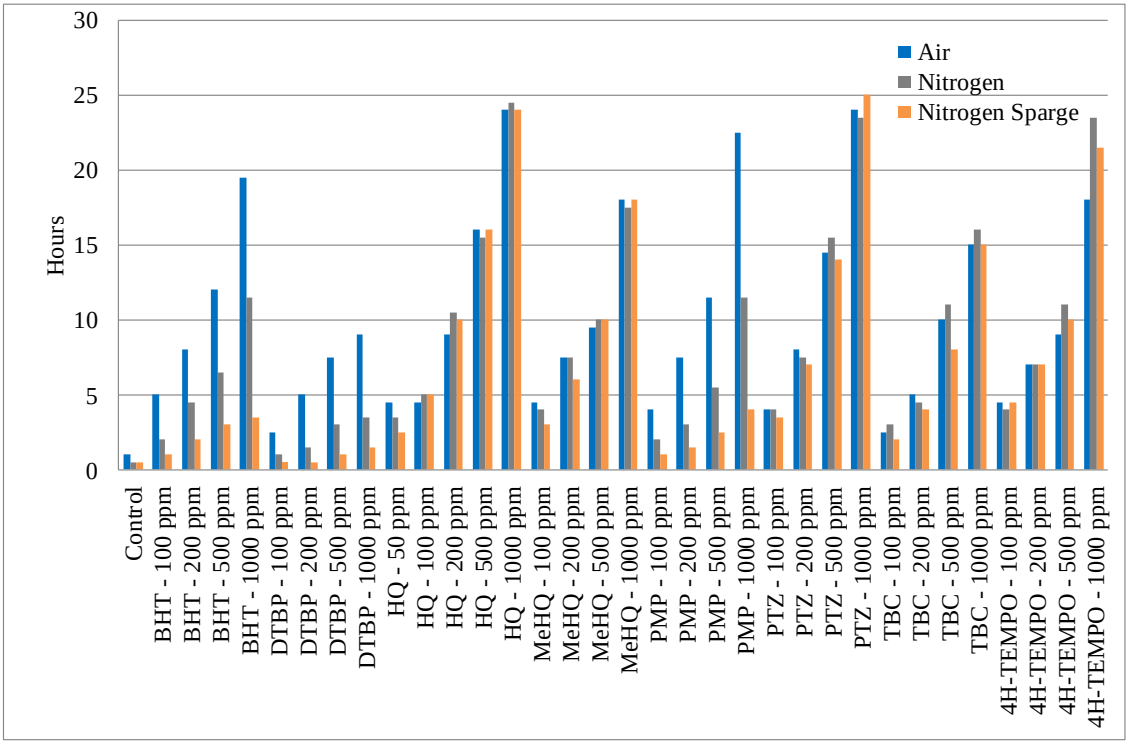

Chart A1.3.4 – HDDGEDA Resin Stability @ 120°C

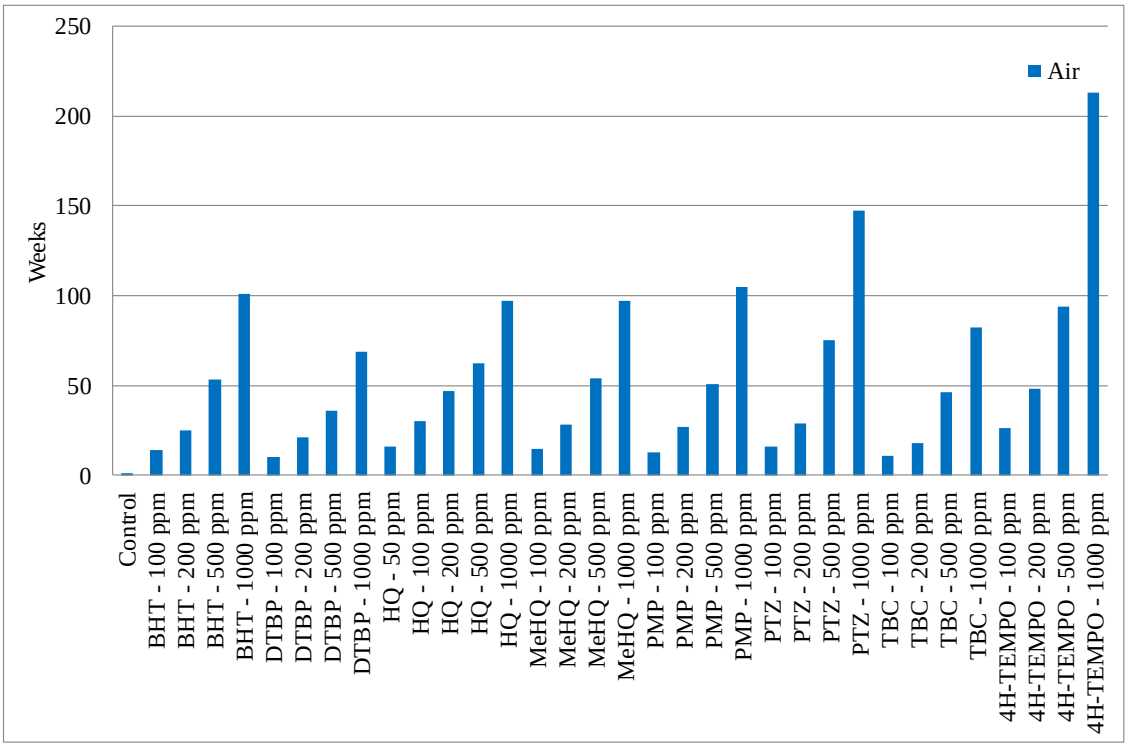

Chart 1

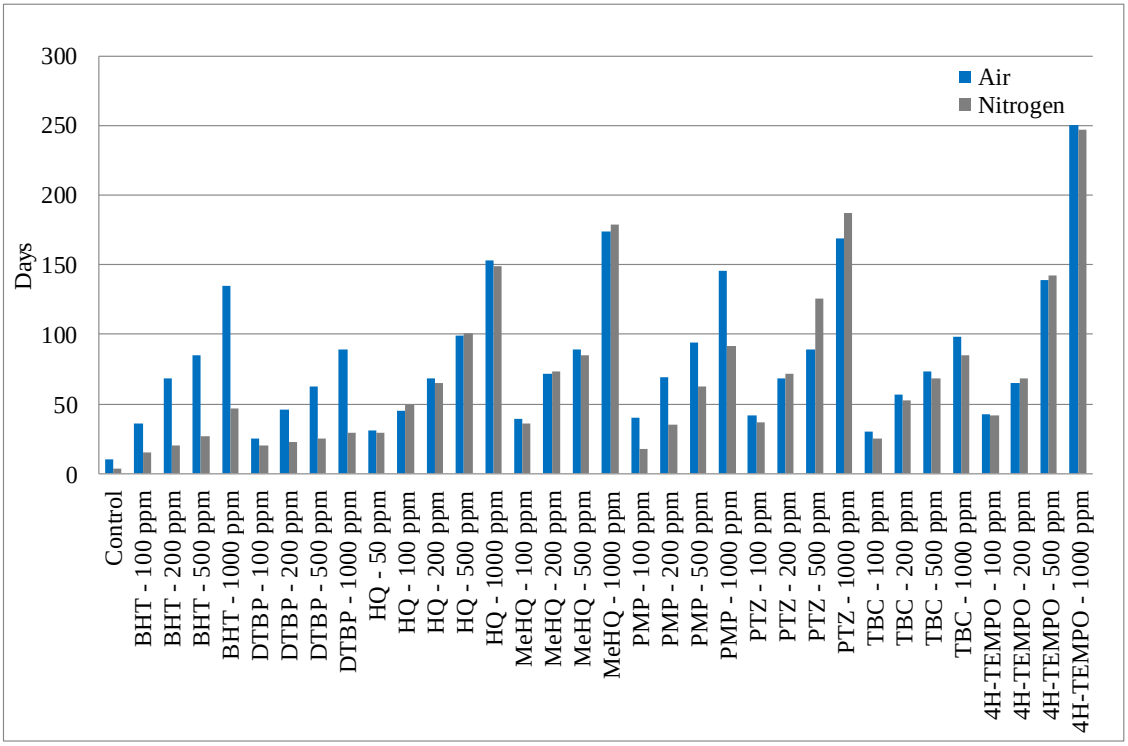

Chart A1.3.6 – BADGEDA Resin Stability @ 40°C

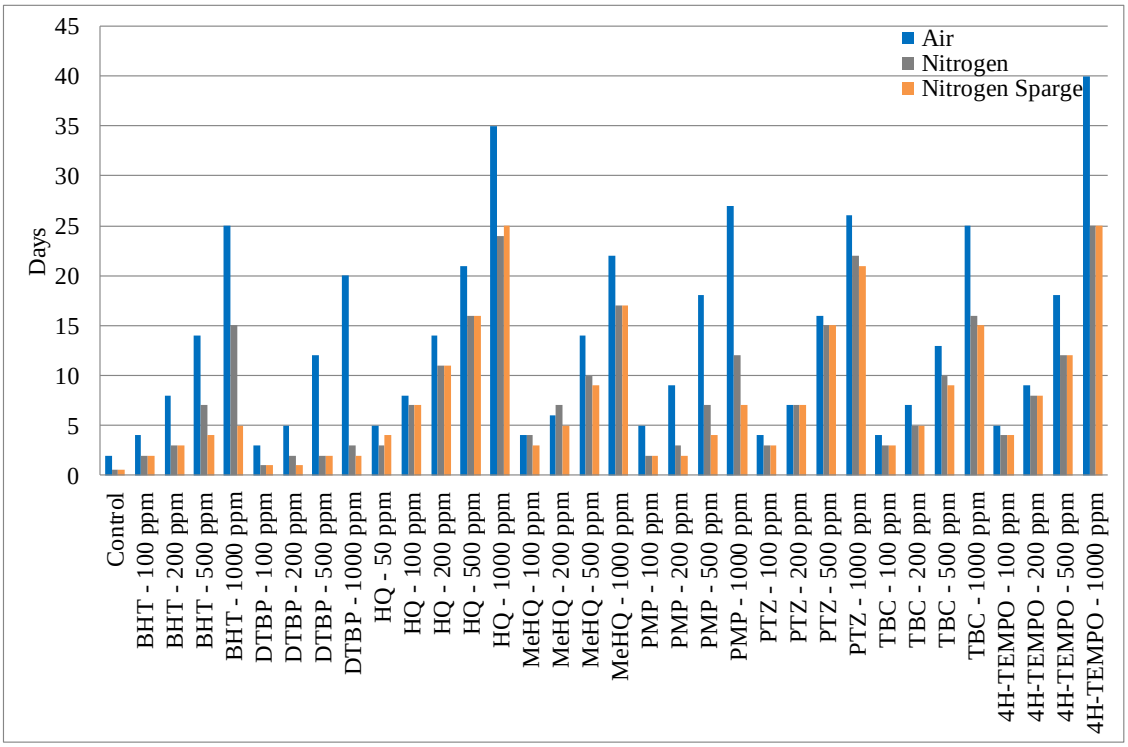

Chart A1.3.7 – BADGEDA Resin Stability @ 80°C

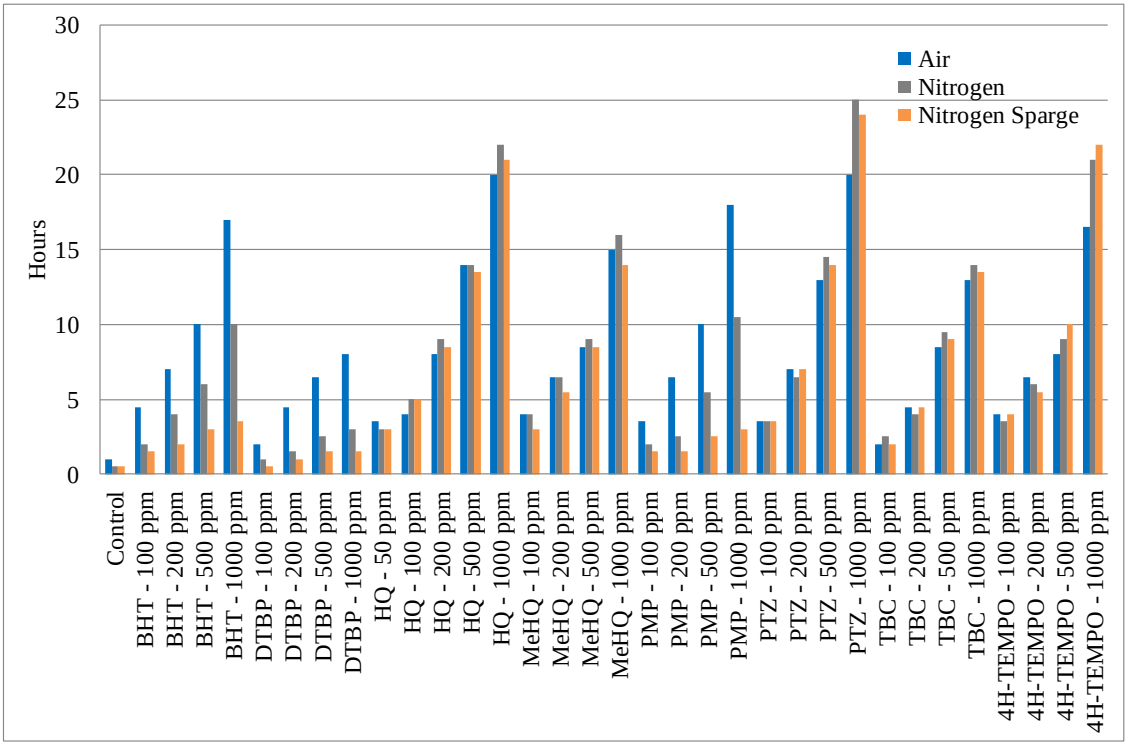

Chart A1.3.8 – BADGEDA Resin Stability @ 120°C

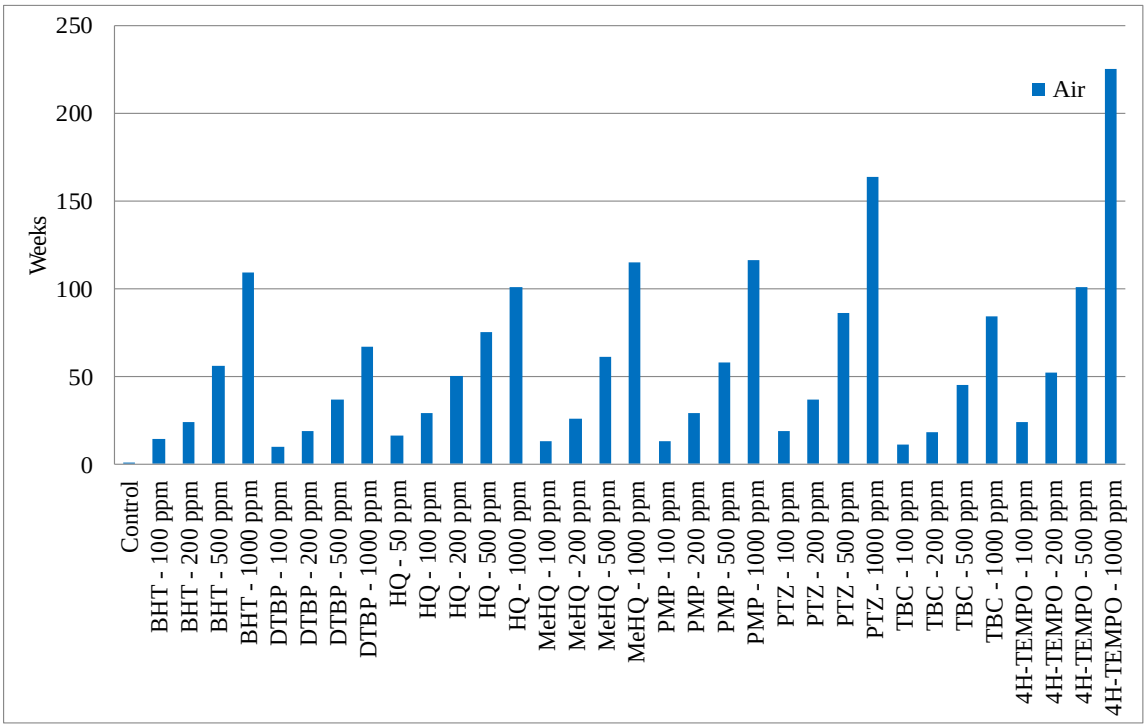

Chart A1.3.9 – BFDGEDA Resin Stability @ 20°C

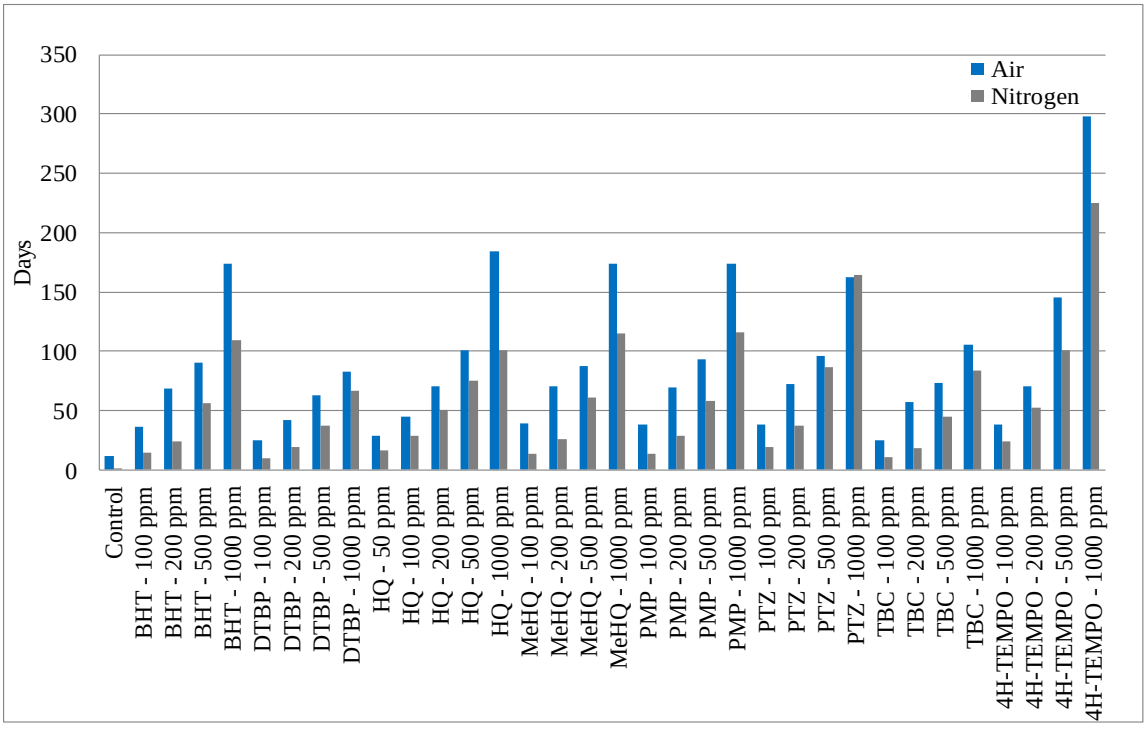

Chart A1.3.10 – BFDGEDA Resin Stability @ 40°C

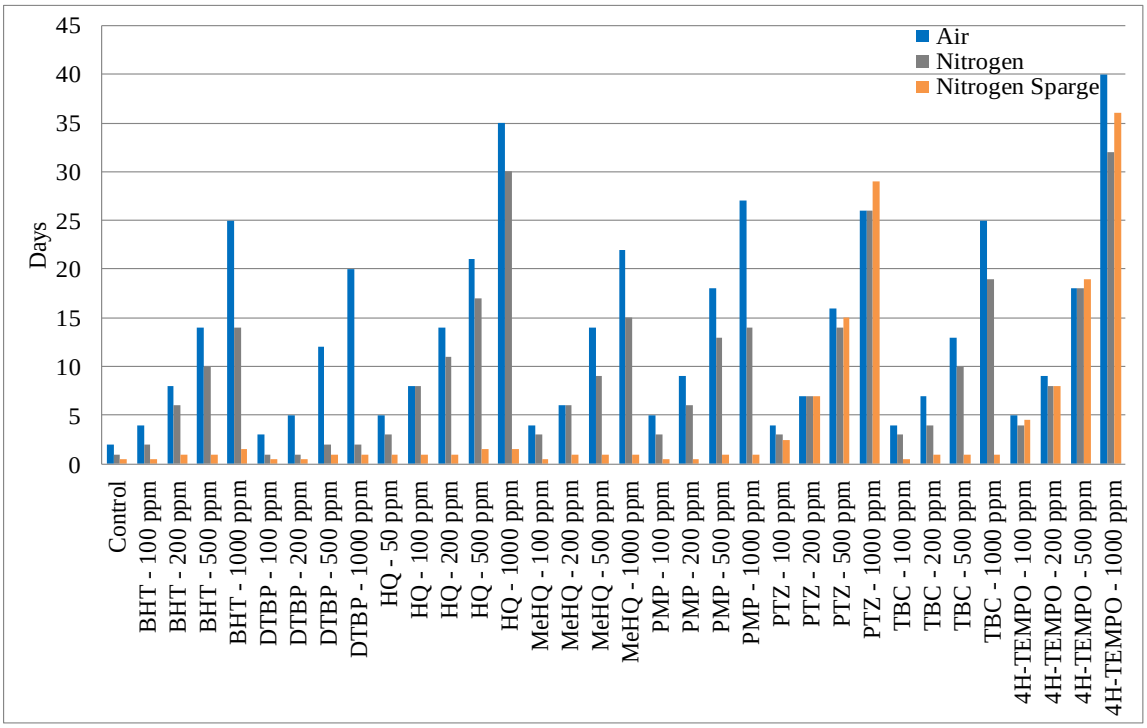

Chart A1.3.11 – BFDGEDA Resin Stability @ 80°C

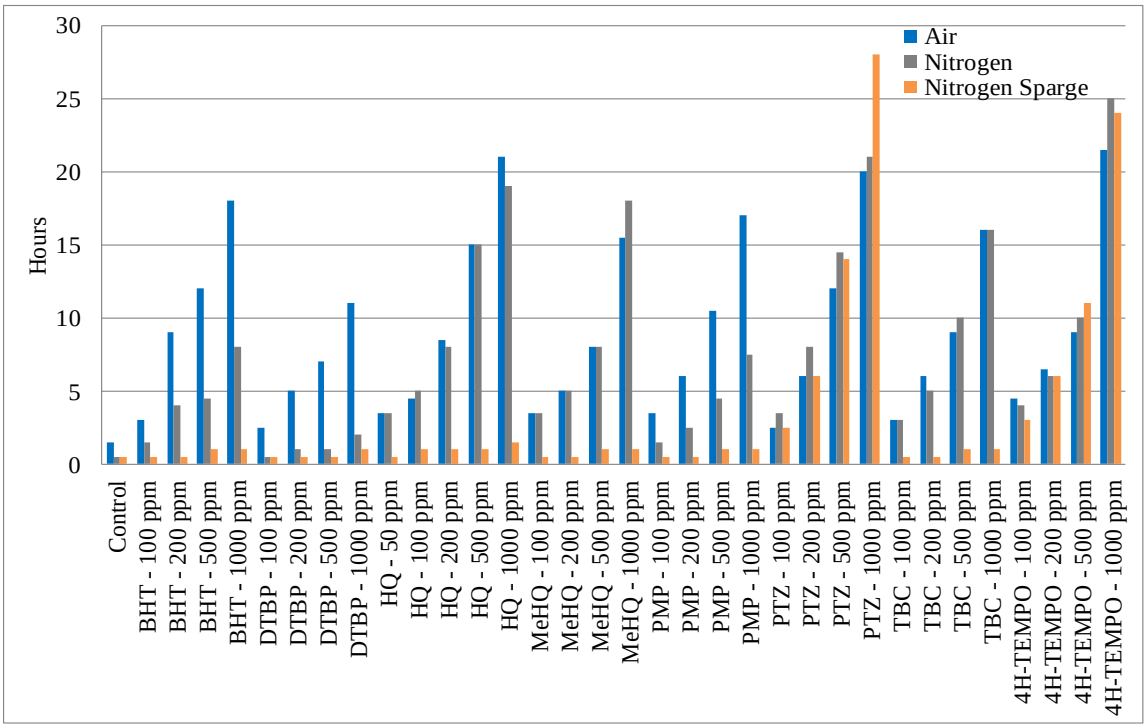

Chart A1.3.12 – BFDGEDA Resin Stability @ 120°C

A1.4 – Epoxy Methacrylate

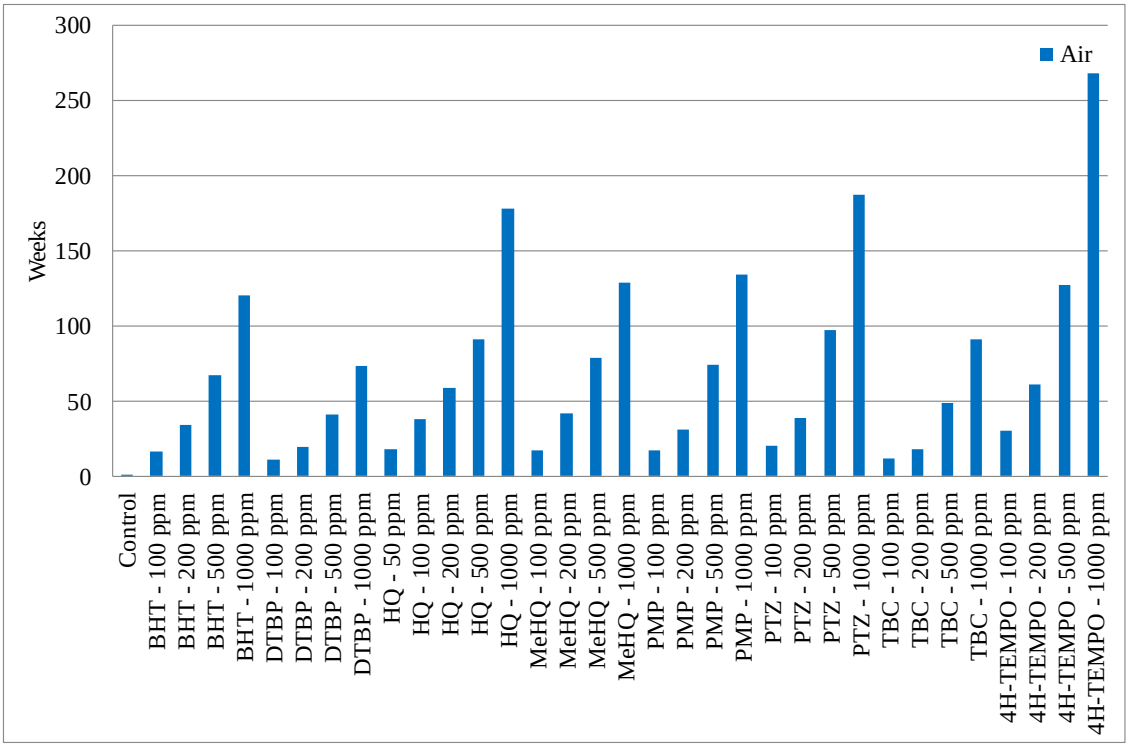

Chart A1.4.1 – HDDGEDMA Resin Stability @ 20°C

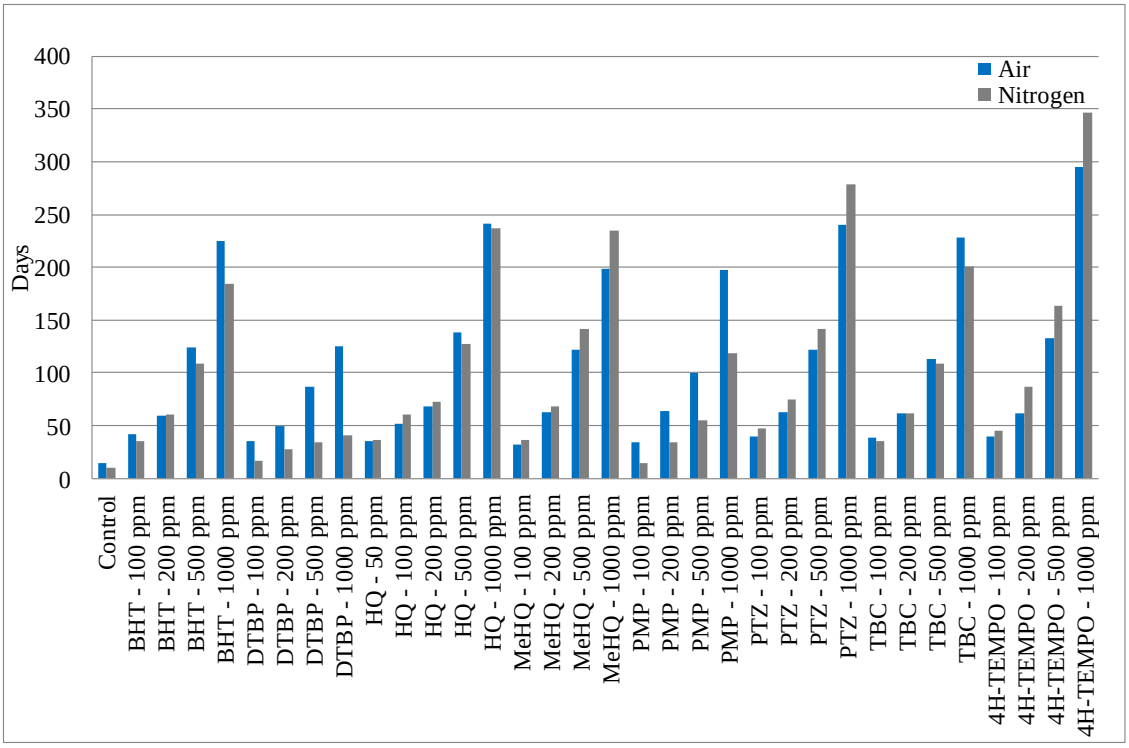

Chart A1.4.2 – HDDGEDMA Resin Stability @ 40°C

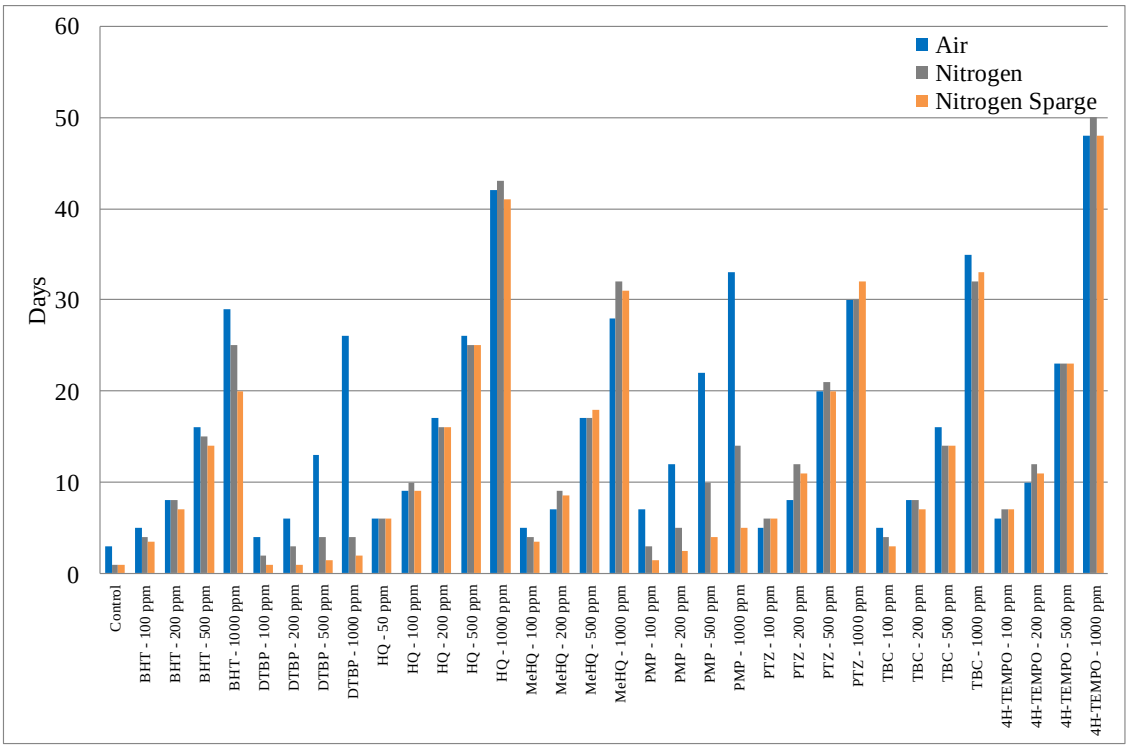

Chart A1.4.3 – HDDGEDMA Resin Stability @ 80°C

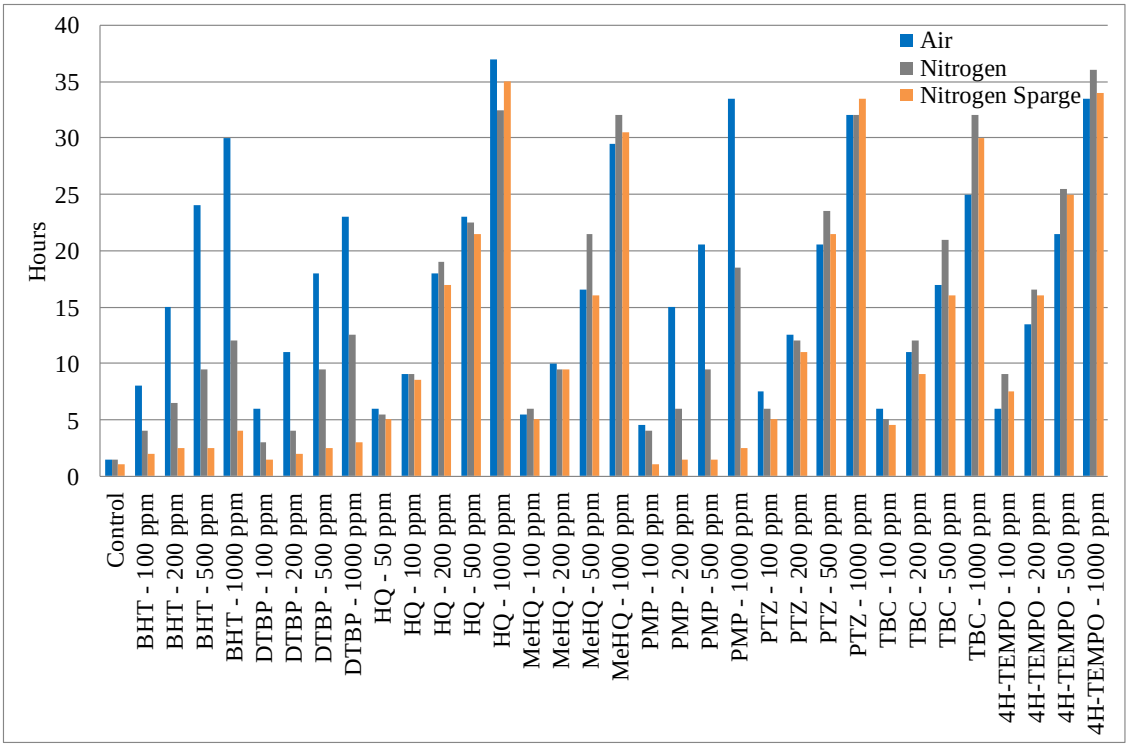

Chart A1.4.4 – HDDGEDMA Resin Stability @ 120°C

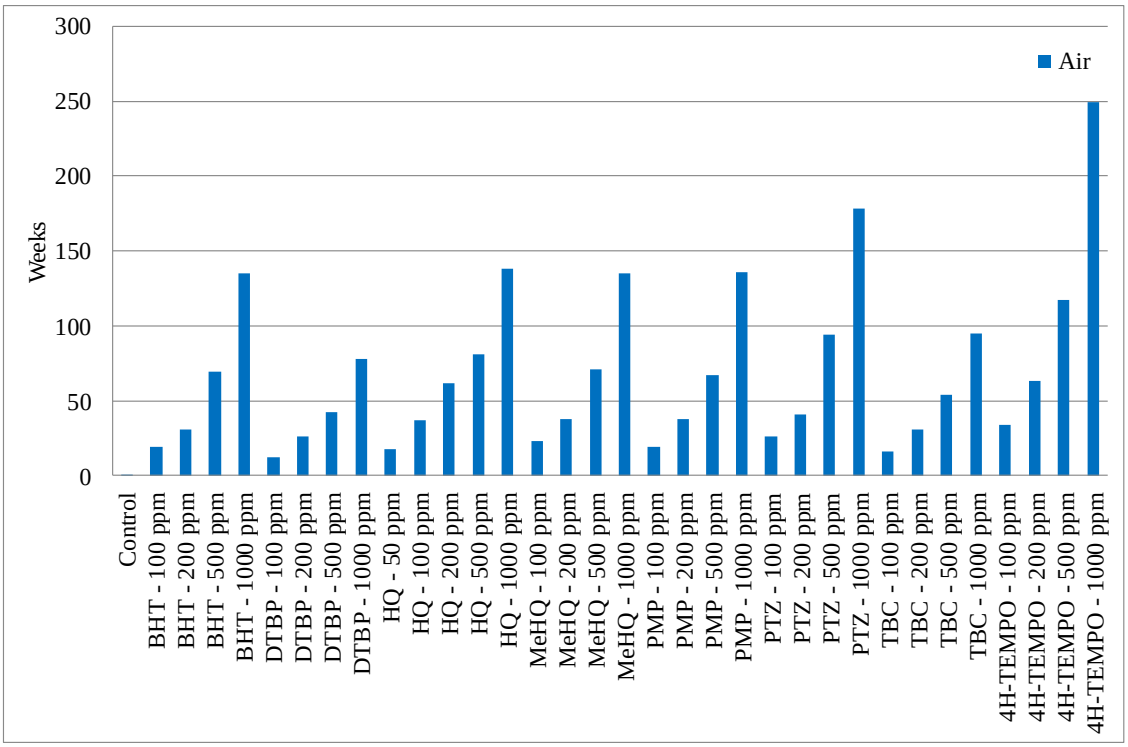

Chart A1.4.5 – BADGEDMA Resin Stability @ 20°C

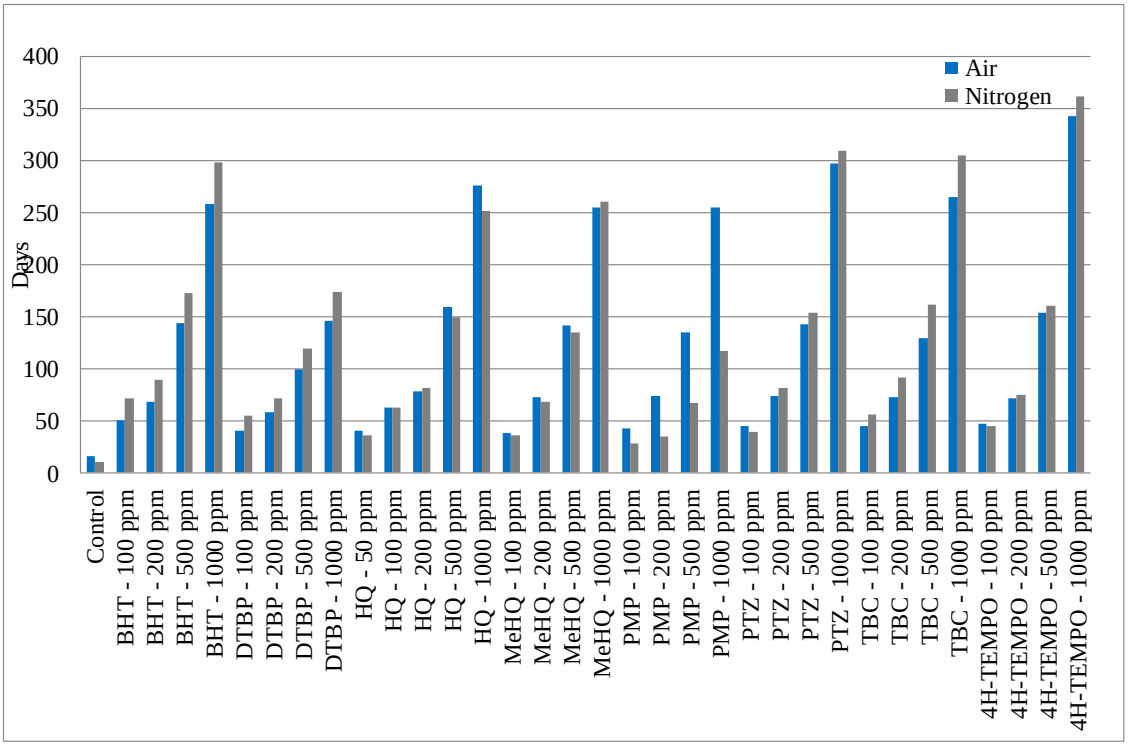

Chart A1.4.6 – BADGEDMA Resin Stability @ 40°C

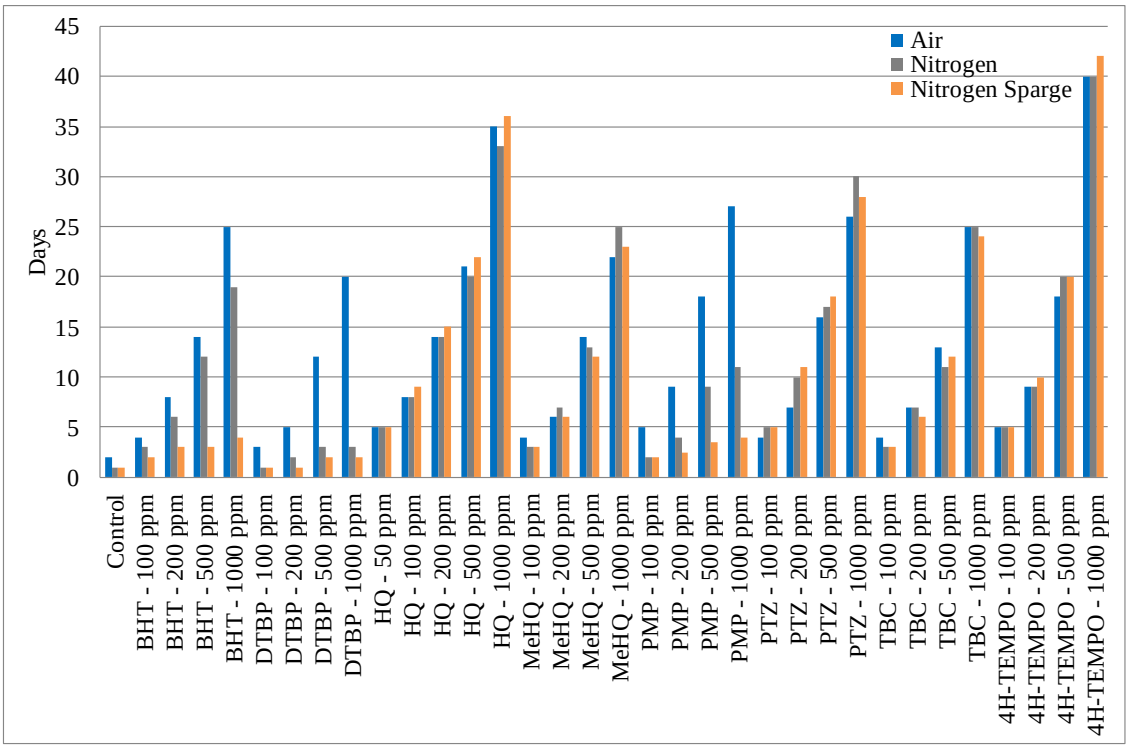

Chart A1.4.7 – BADGEDMA Resin Stability @ 80°C

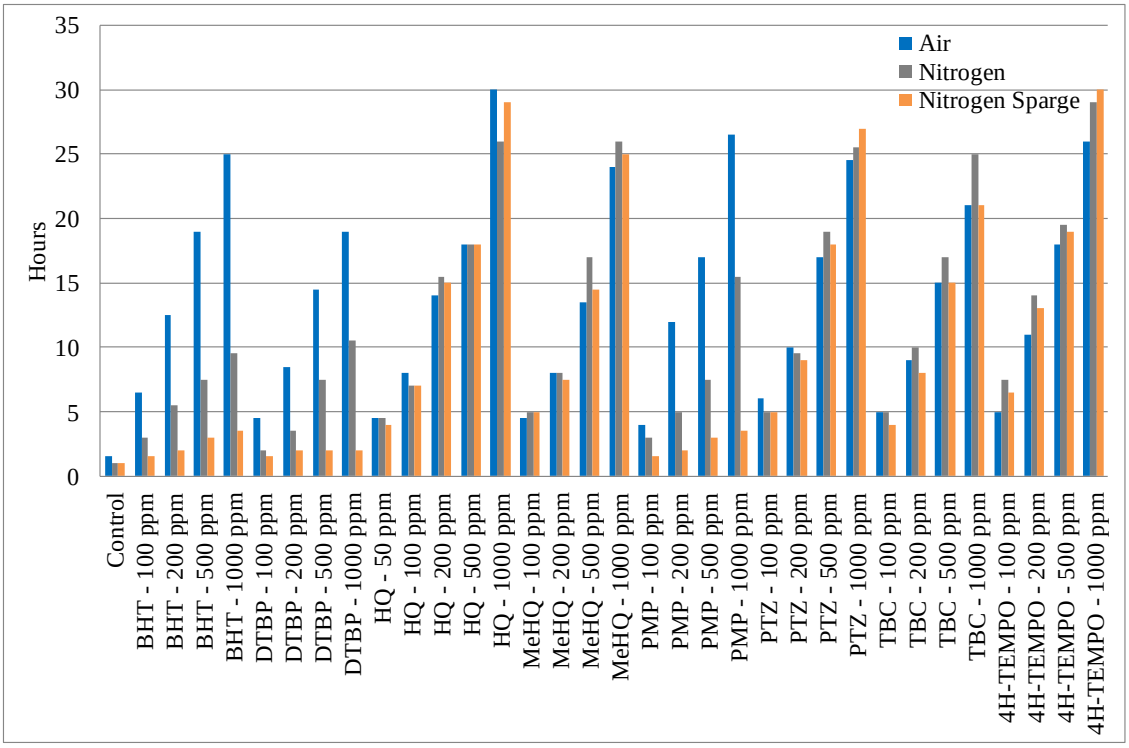

Chart A1.4.8 – BADGEDMA Resin Stability @ 120°C

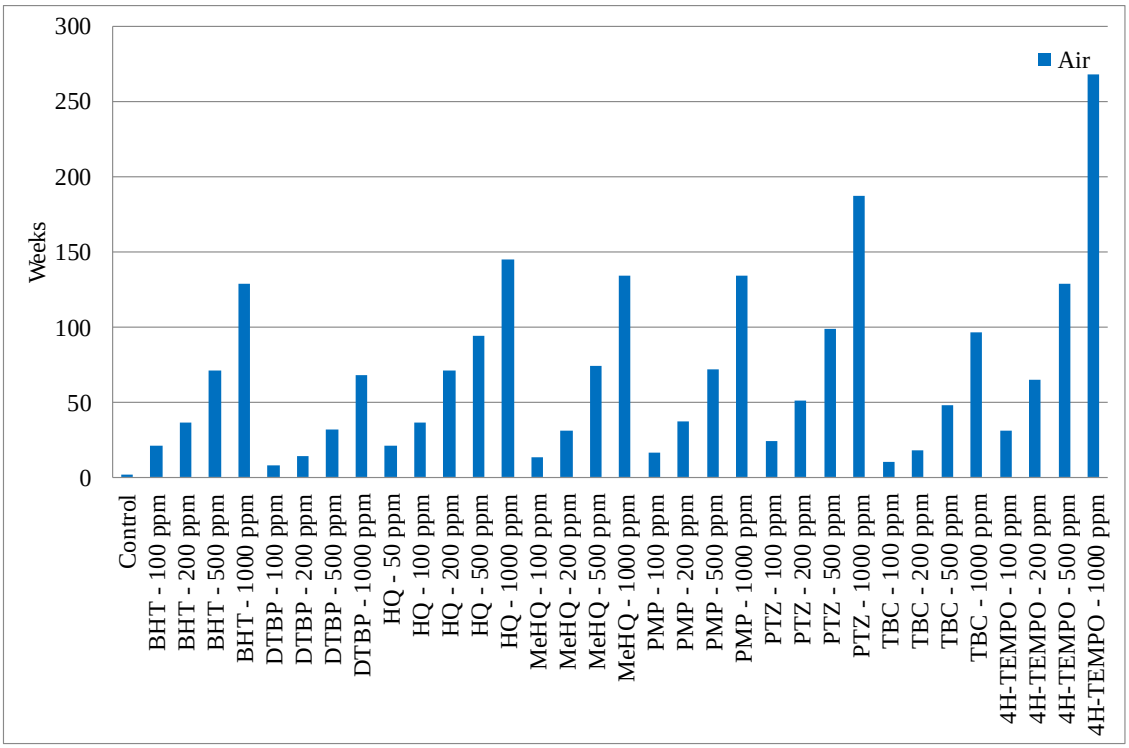

Chart A1.4.9 – BFDGEDMA Resin Stability @ 20°C

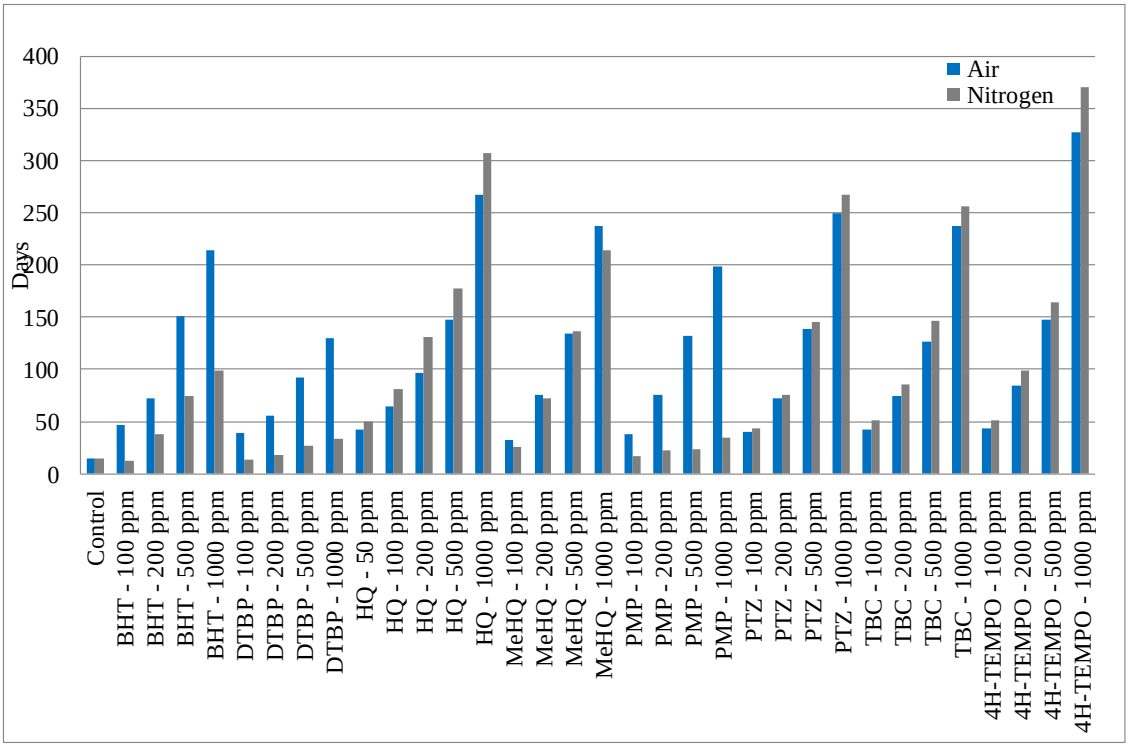

Chart A1.4.10 – BFDGEDMA Resin Stability @ 40°C

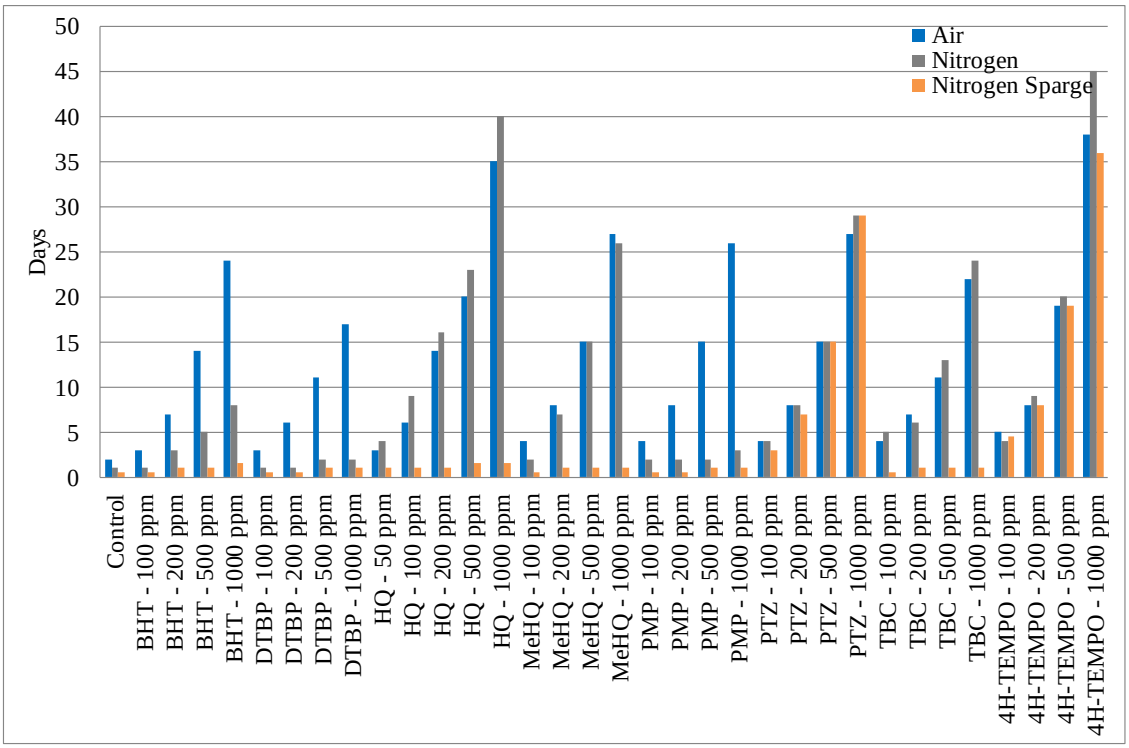

Chart A1.4.11 – BFDGEDMA Resin Stability @ 80°C

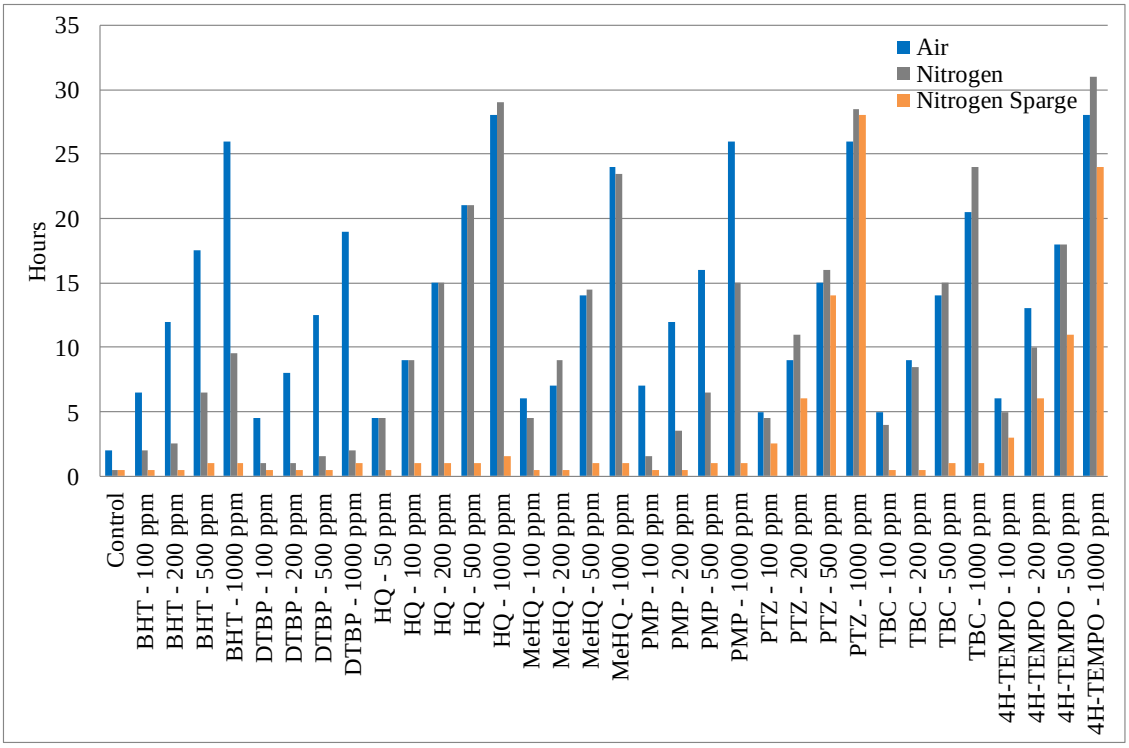

Chart A1.4.12 – BFDGEDMA Resin Stability @ 120°C

A1.5 – Polyethylene Glycol Urethane Acrylate

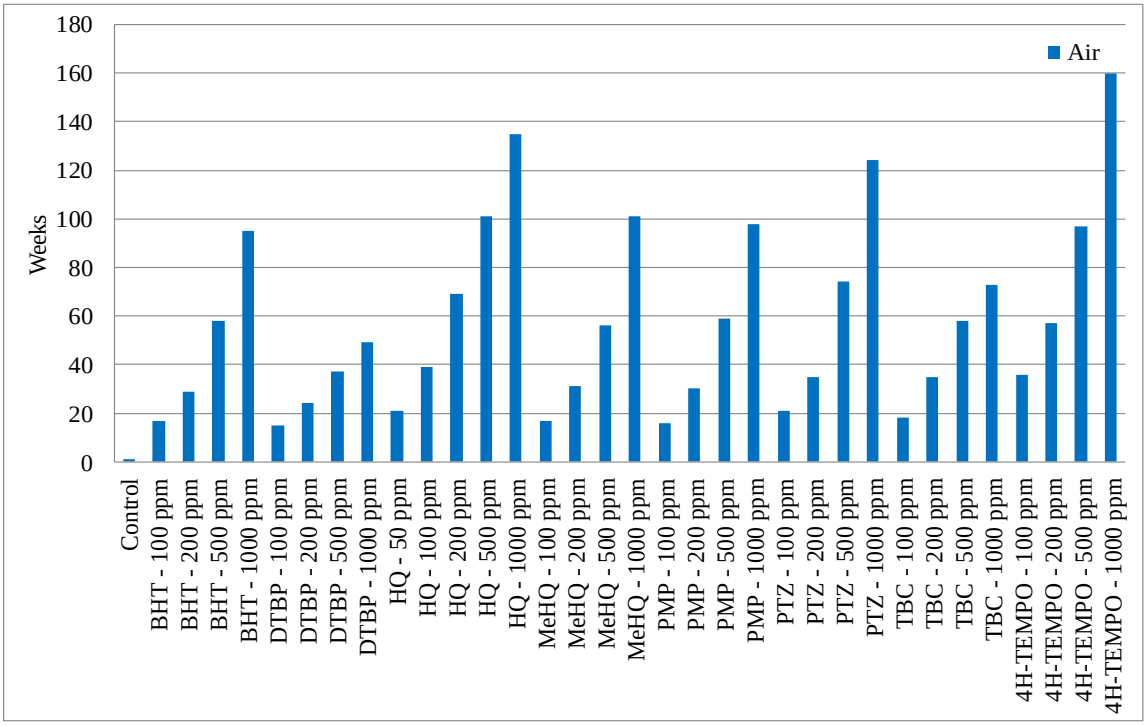

Chart A1.5.1 MDI-PEA Resin Stability @ 20°C

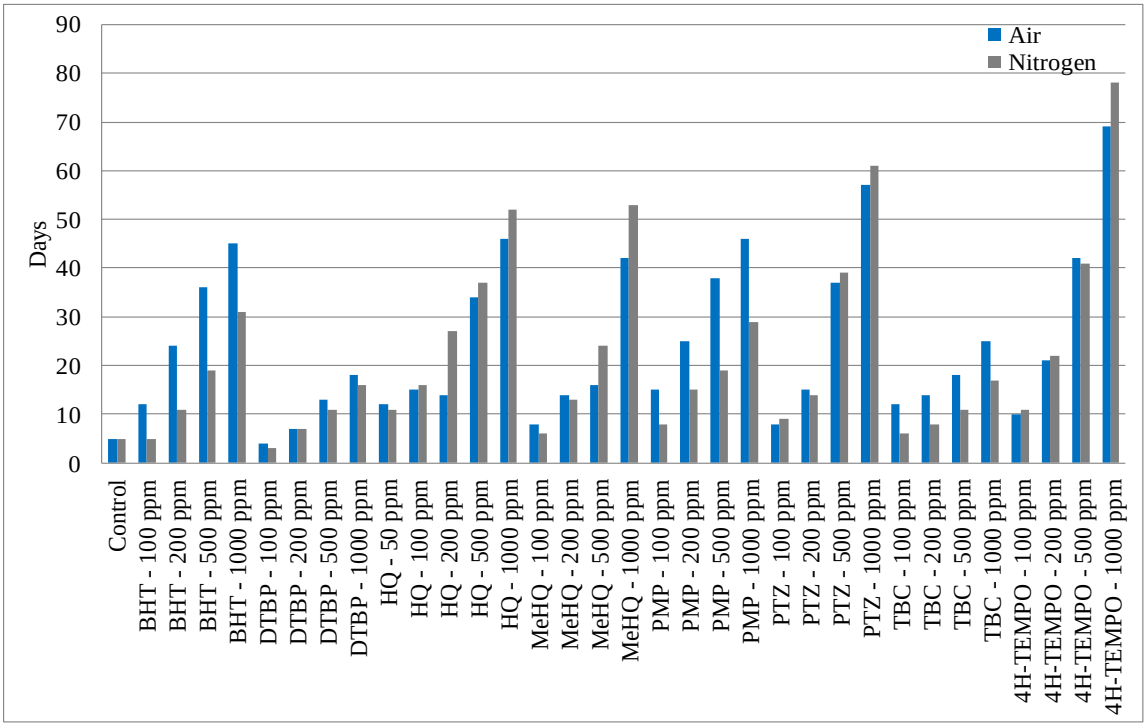

Chart A1.5.2 – MDI-PEA Resin Stability @ 40°C

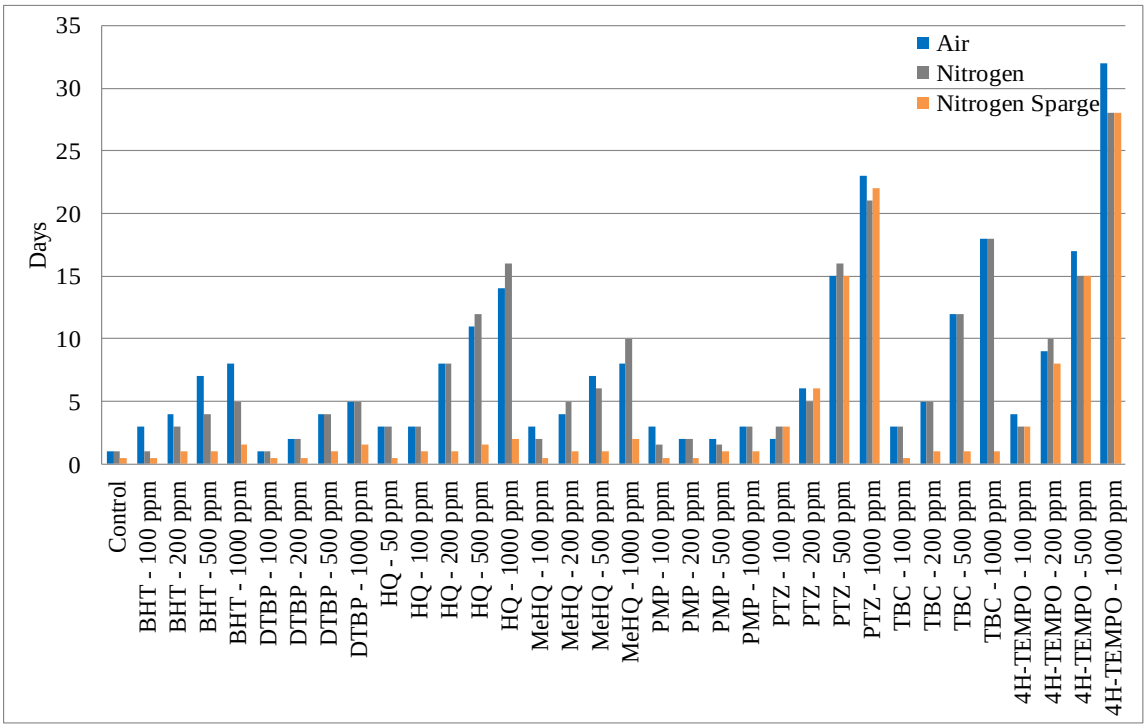

Chart A1.5.3 – MDI-PEA Resin Stability @ 80°C

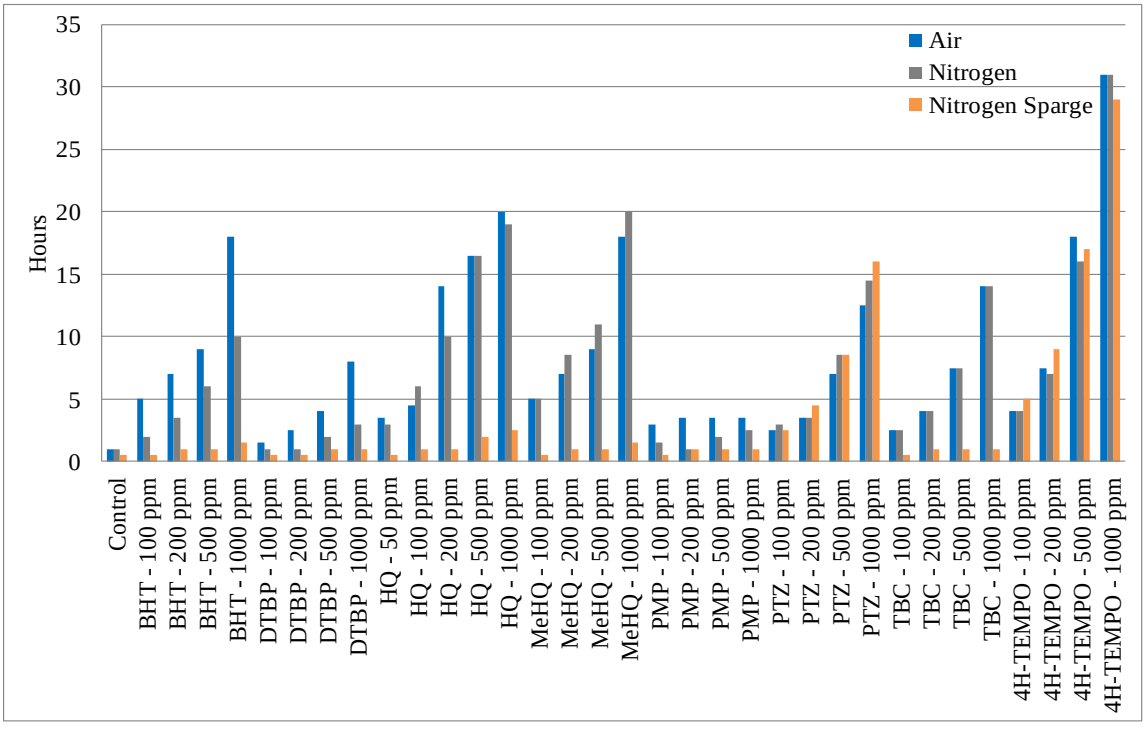

Chart A1.5.4 – MDI-PEA Resin Stability @ 120°C

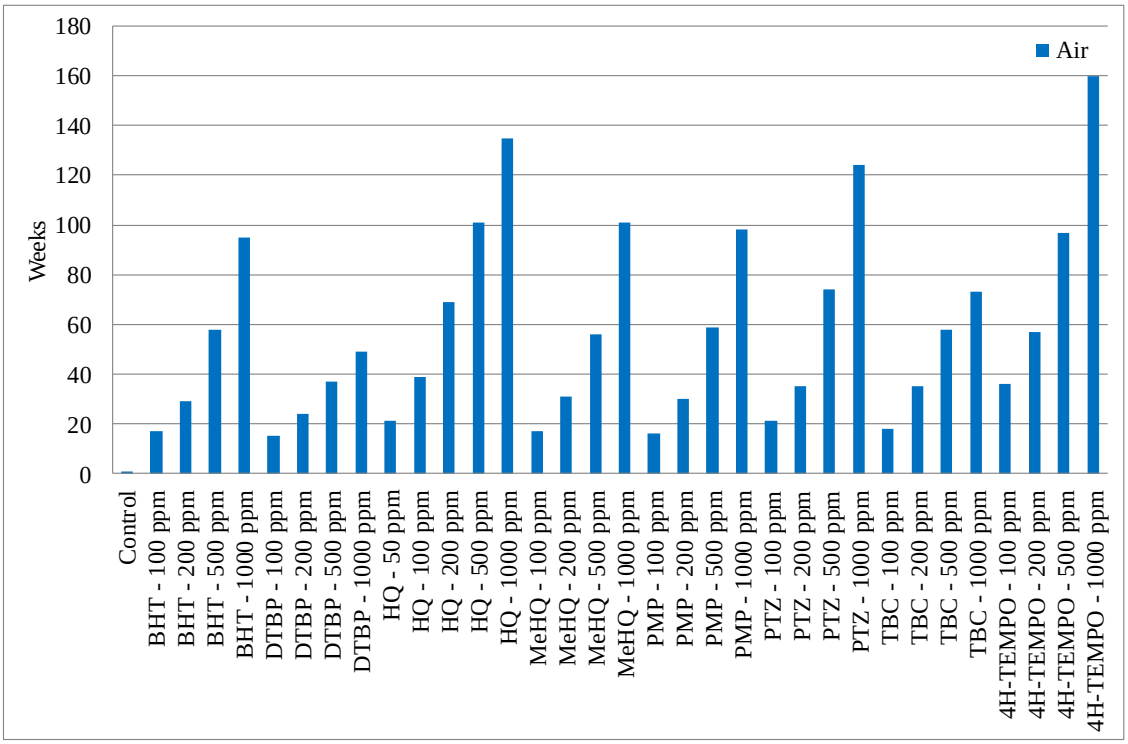

Chart A1.5.5 – IPDI-PEA Stability @ 20°C

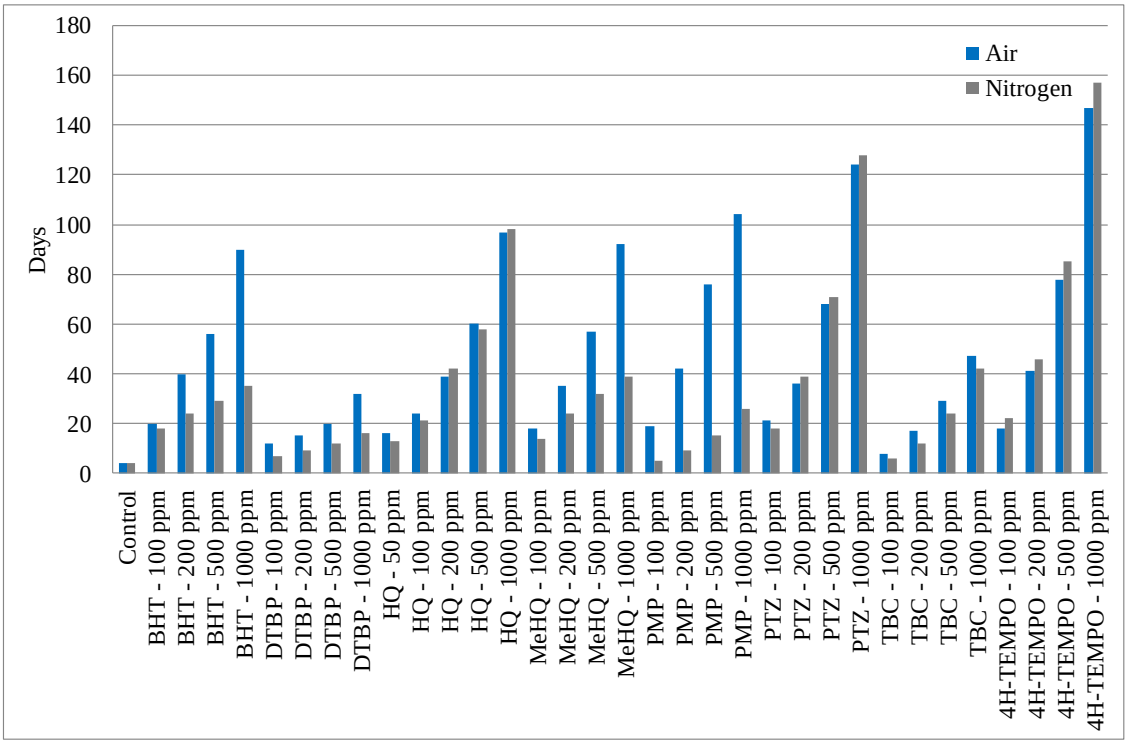

Chart A1.5.6 – IPDI-PEA Resin Stability @ 40°C

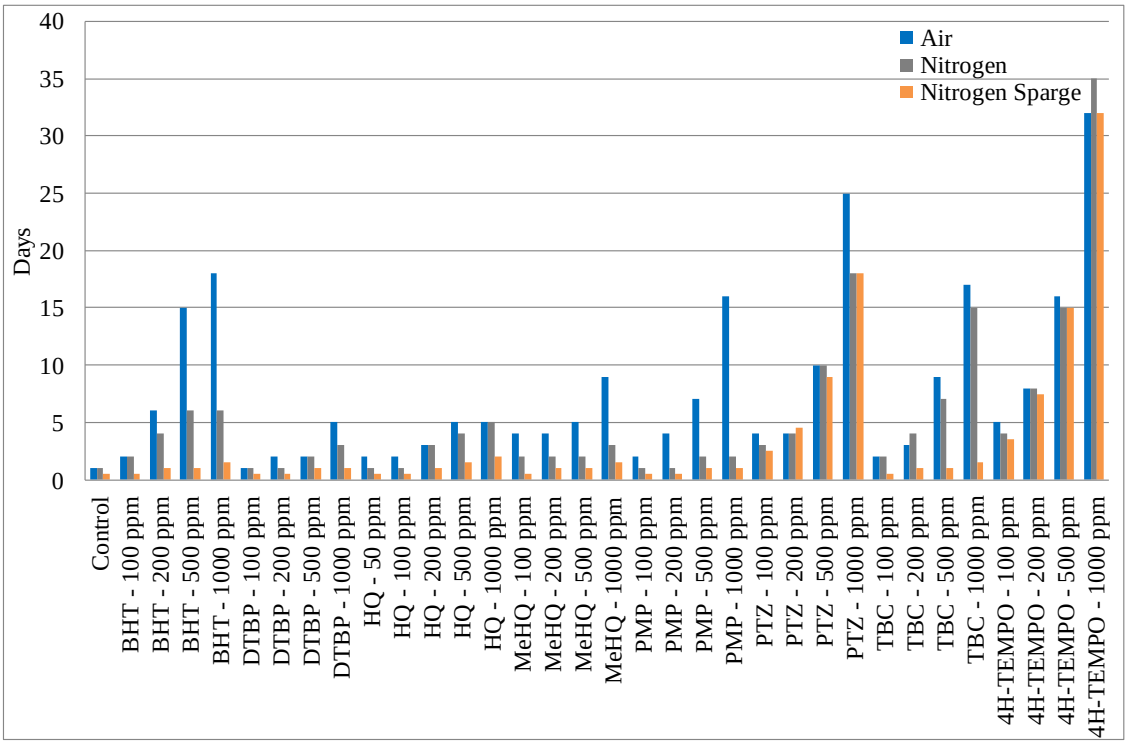

Chart A1.5.7 – IPDI-PEA Resin Stability @ 80°C

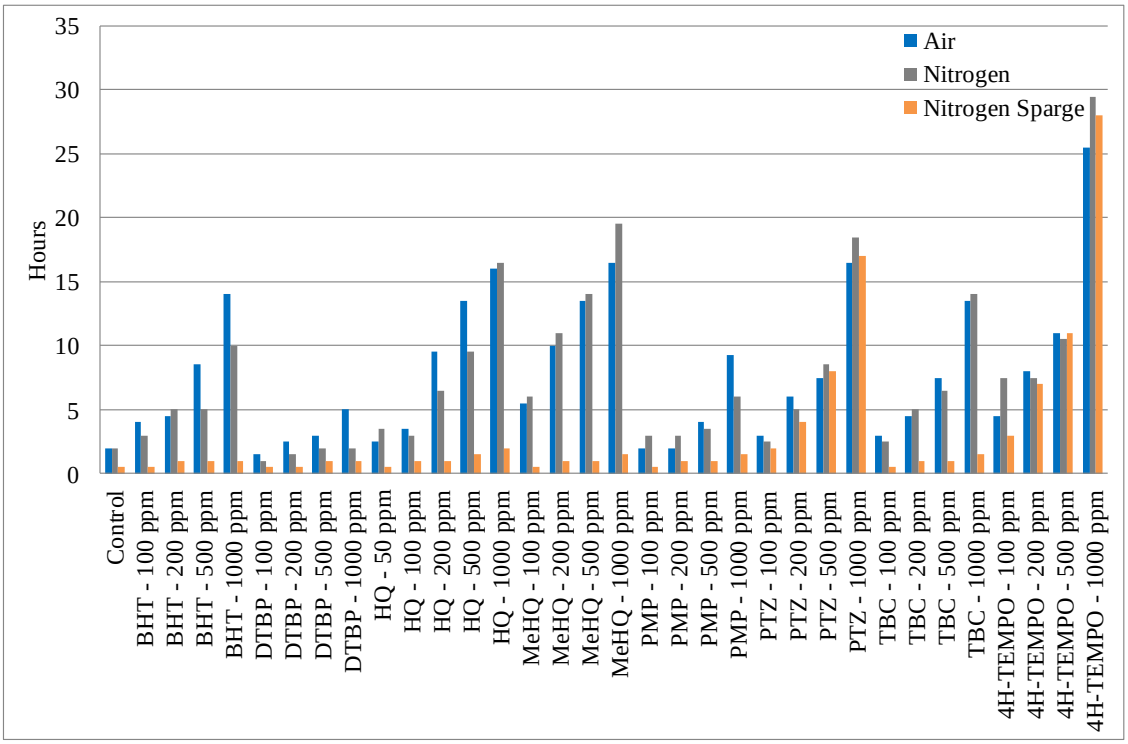

Chart A1.5.8 – IPDI-PEA Resin Stability @ 120°C

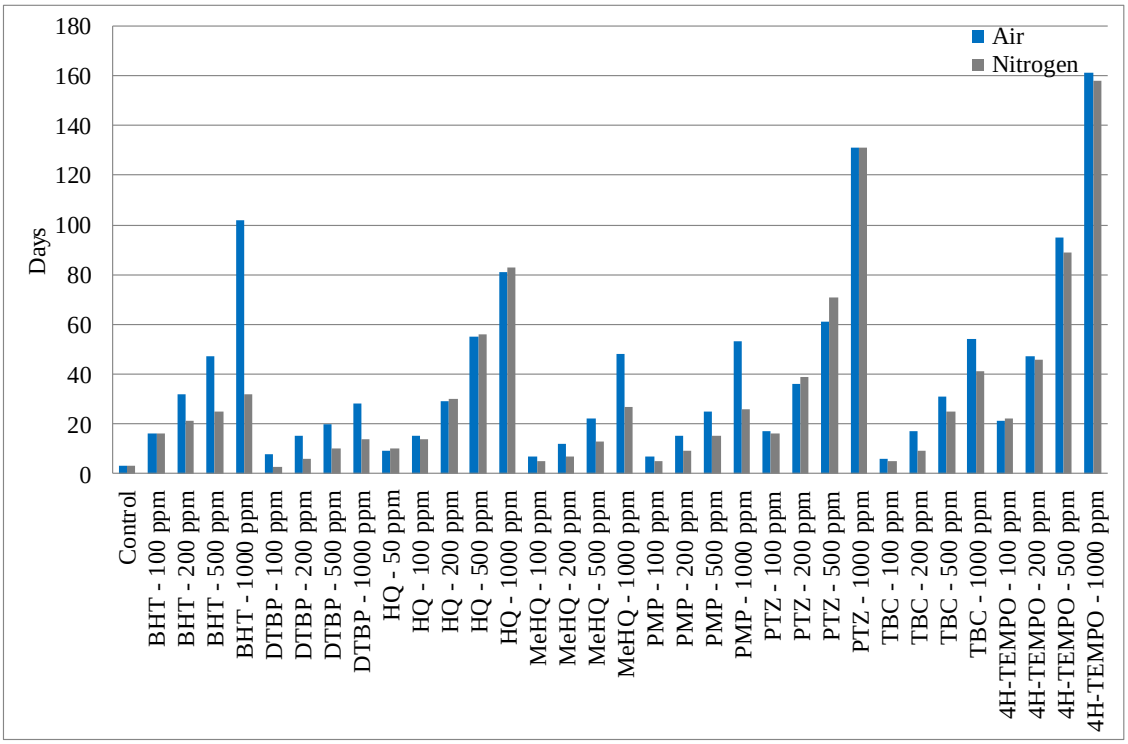

Chart A1.5.9 – TDI-PEA Resin Stability @ 40°C

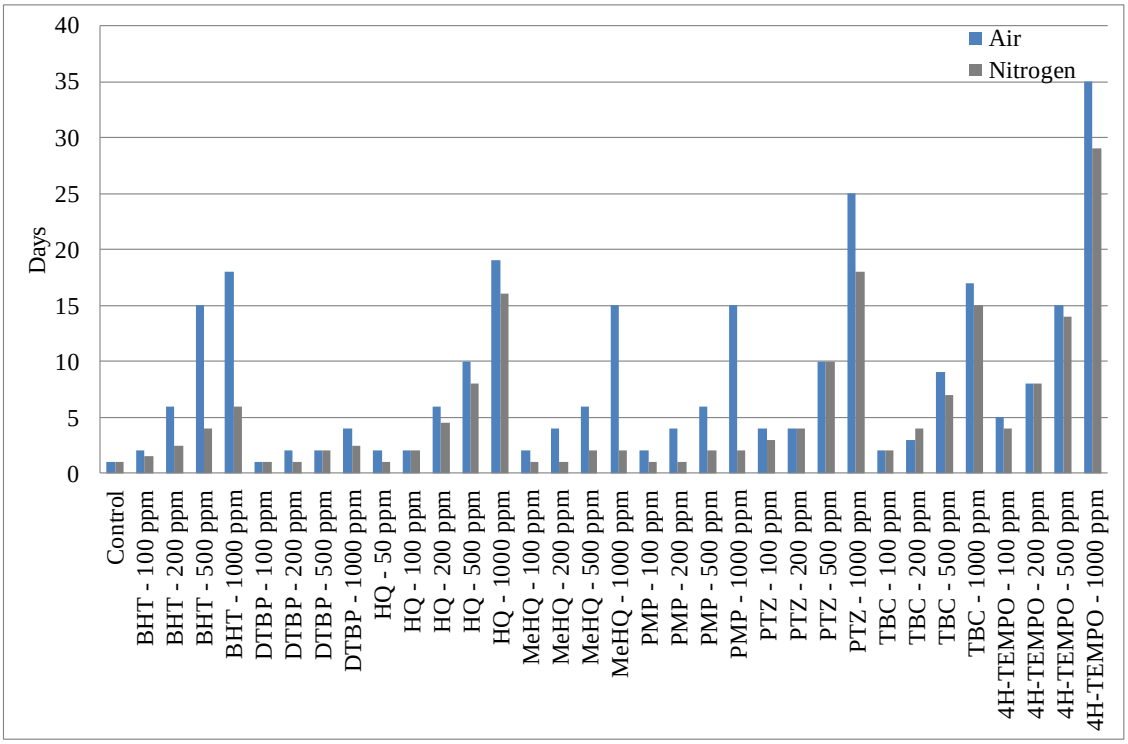

Chart A1.5.10 – TDI-PEA Resin Stability @ 80°C

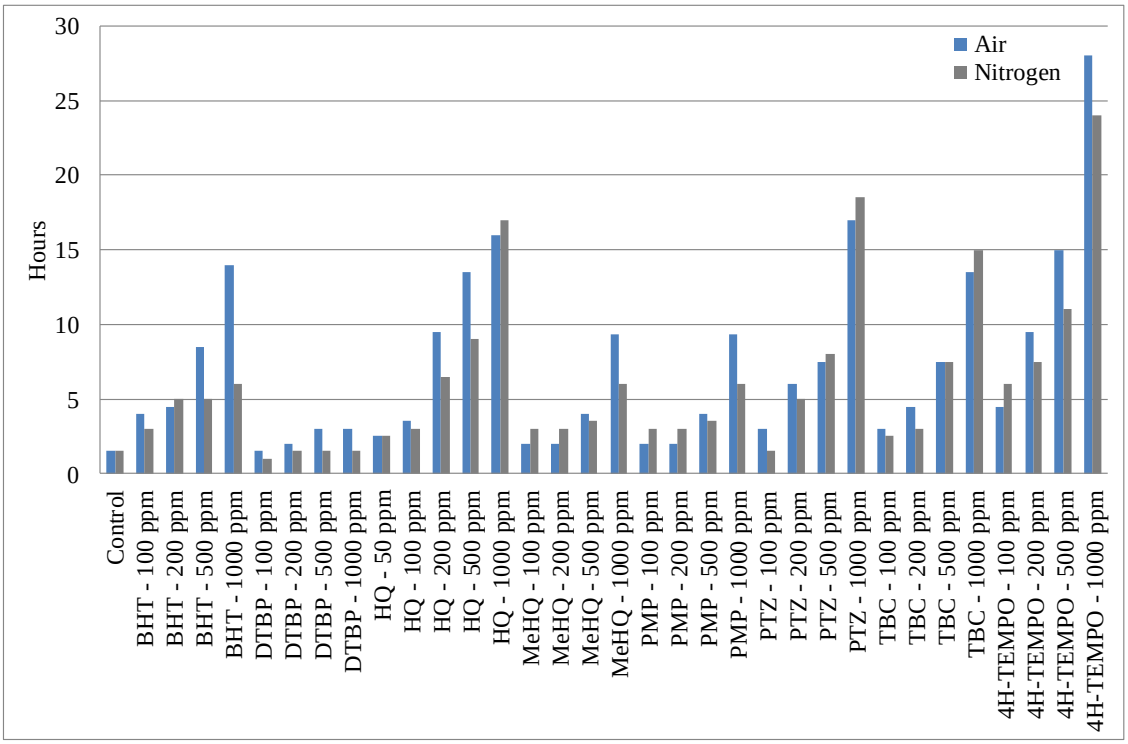

Chart A1.5.11 – TDI-PEA Resin Stability @ 120°C

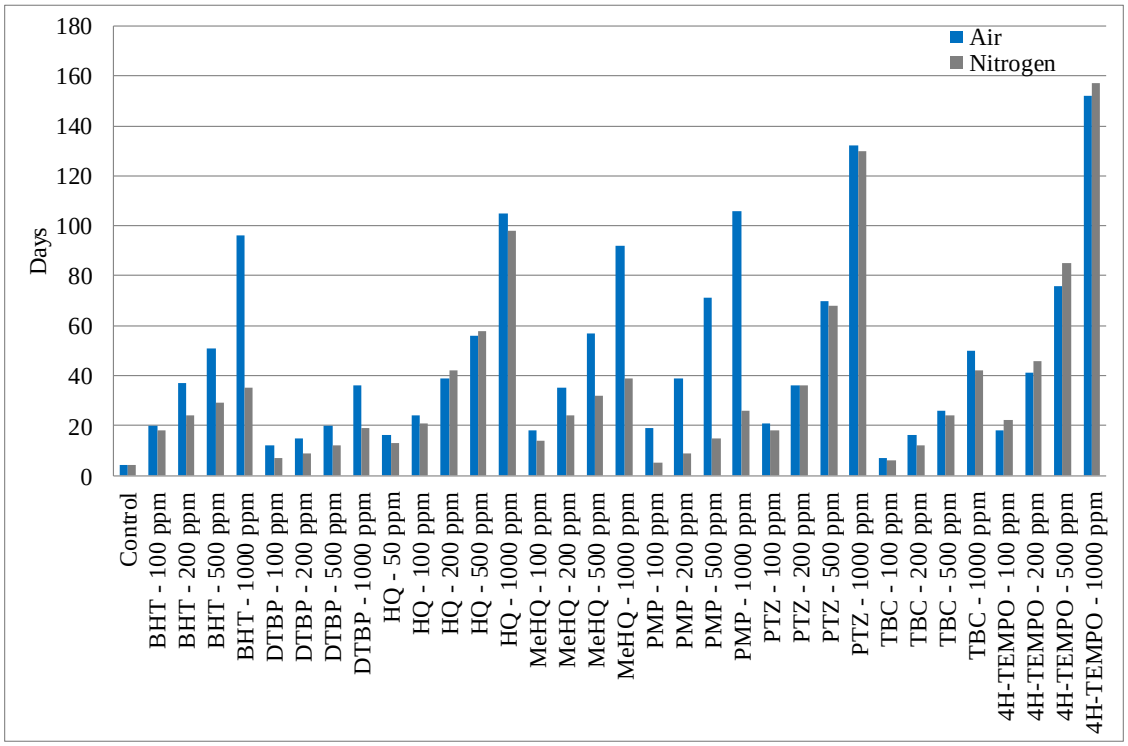

Chart A1.5.12 – HMDI-PEA Resin Stability @ 40°C

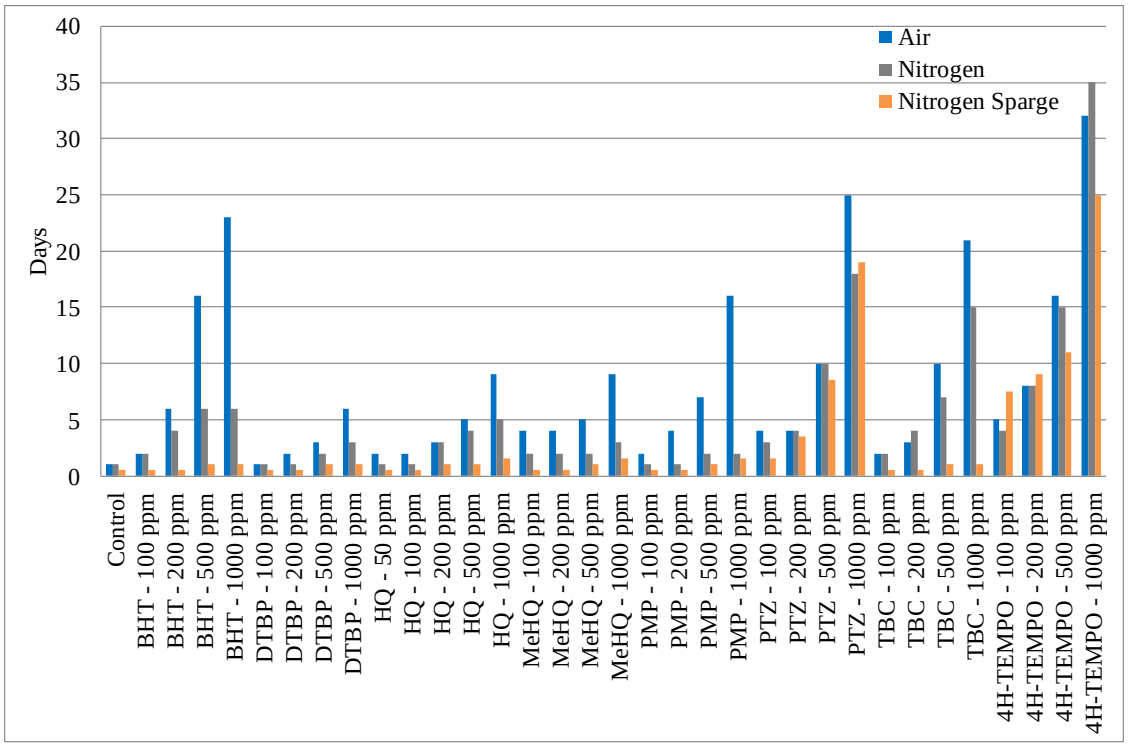

Chart A1.5.13 – HMDI-PEA Resin Stability @ 80°C

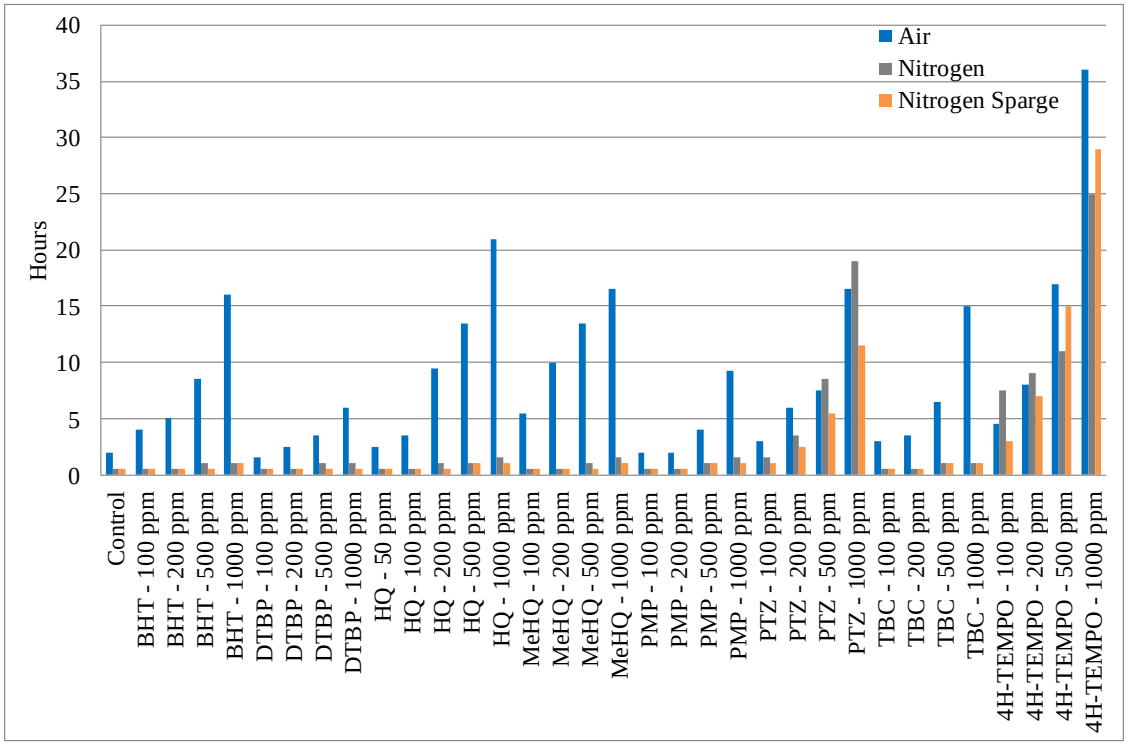

Chart A1.5.14 – HMDI-PEA Resin Stability @ 120°C

A1.6 – Polyethylene Urethane Methacrylate

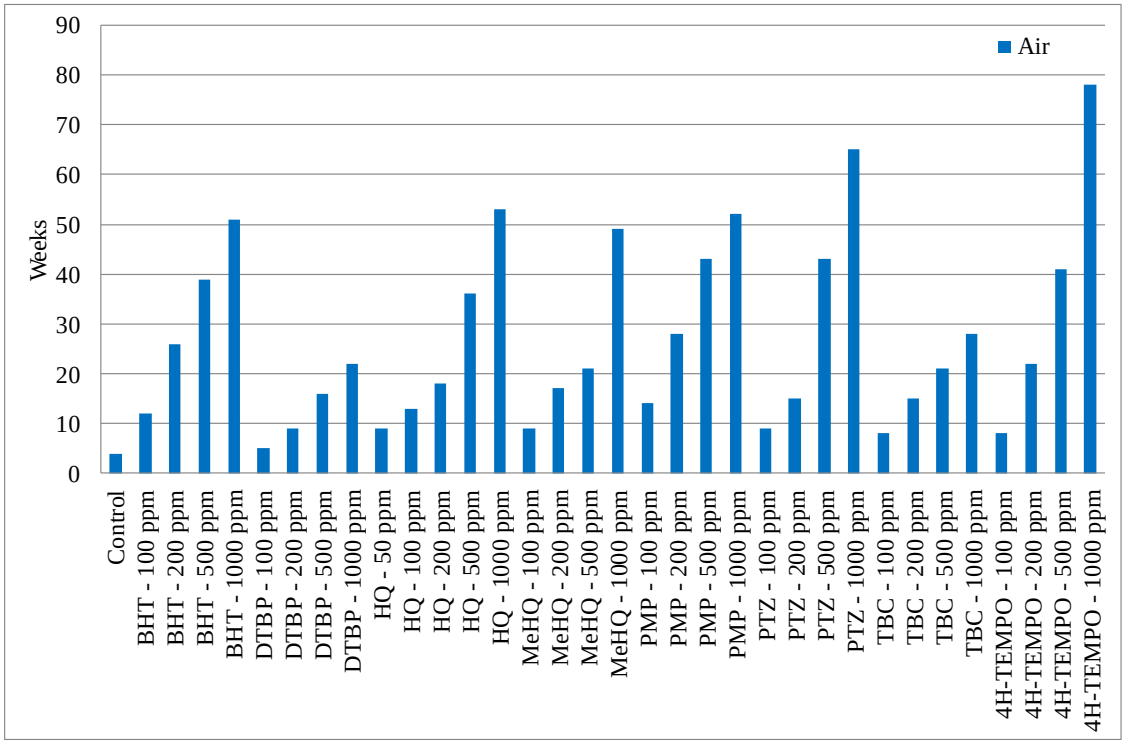

Chart A1.6.1 – MDI-PEM Resin Stability @ 20°C

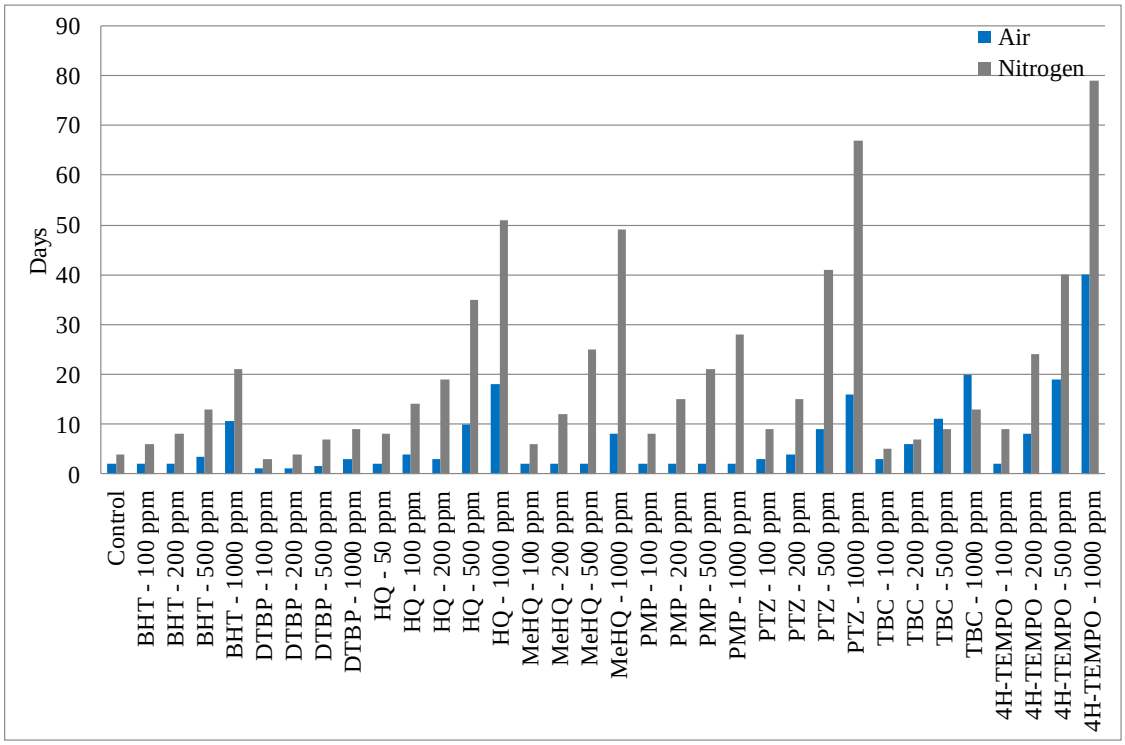

Chart A1.6.2 – MDI-PEM Resin Stability @ 40°C

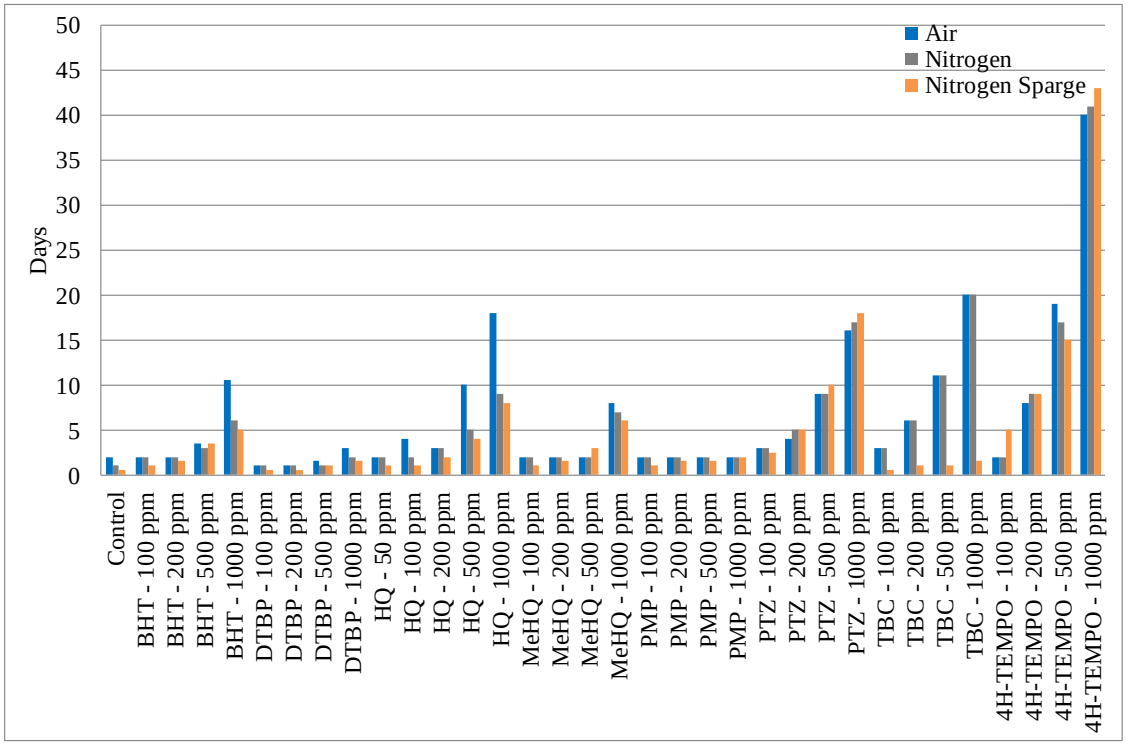

Chart A1.6.3 – MDI-PEM Resin Stability @ 80°C

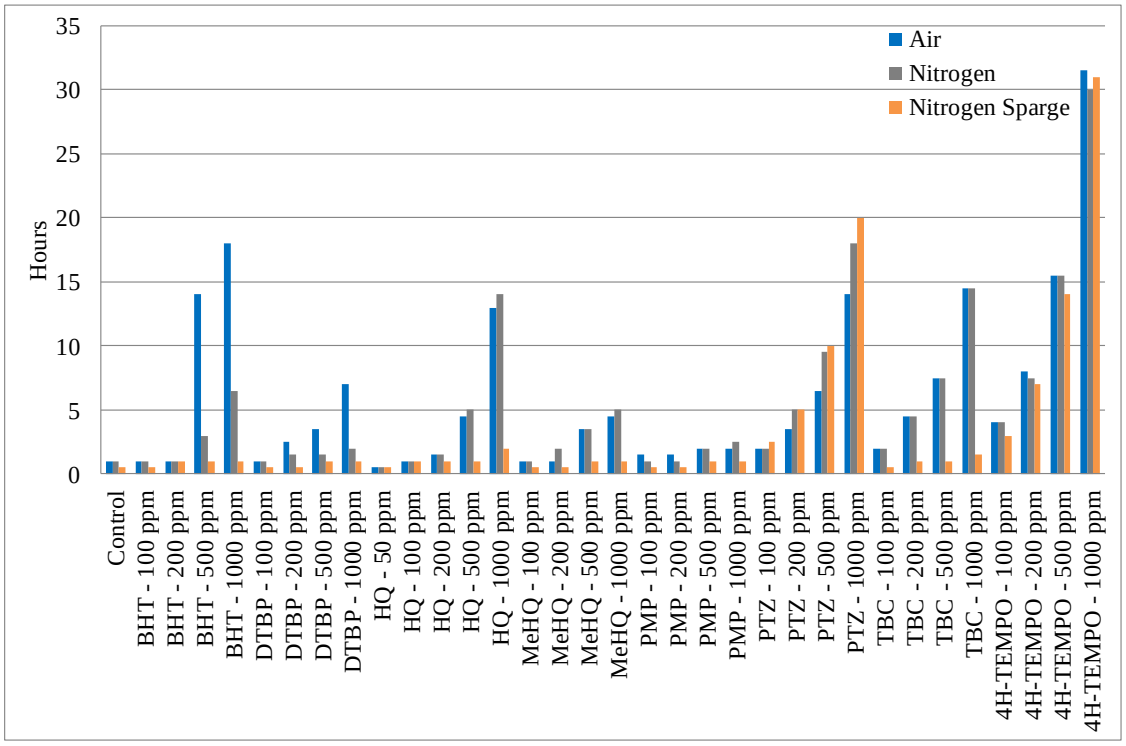

Chart A1.6.4 – MDI-PEM Resin Stability @ 120°C

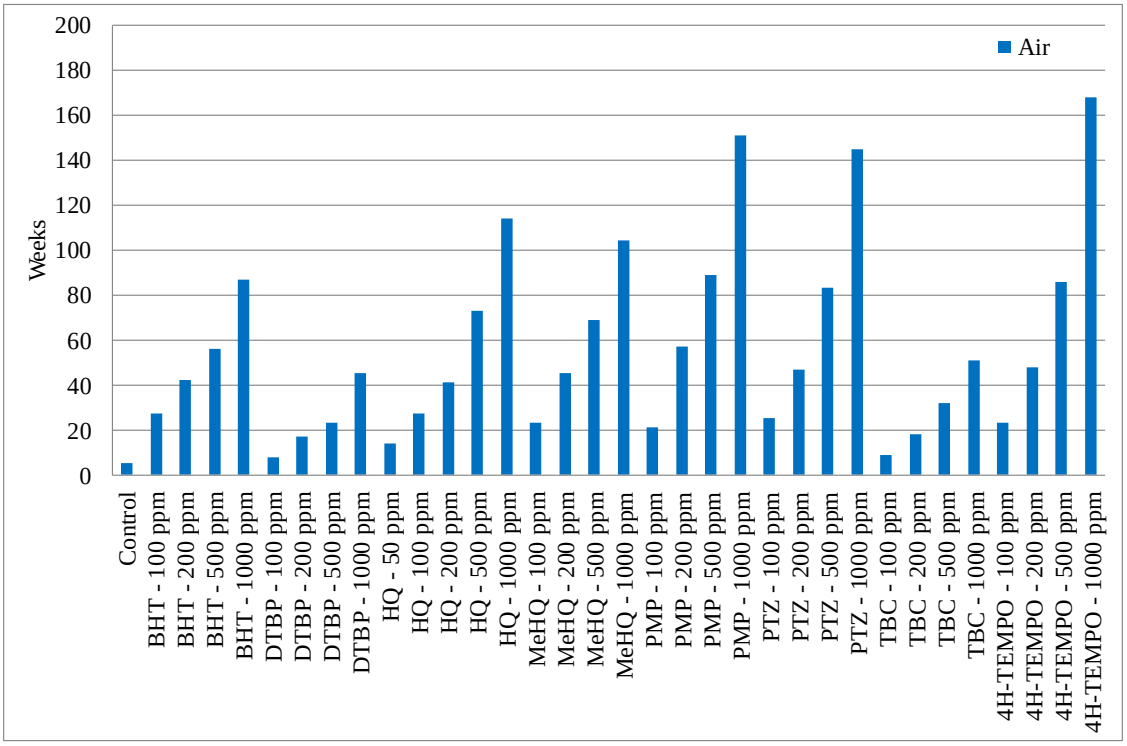

Chart A1.6.5 – IPDI-PEM Resin Stability @ 20°C

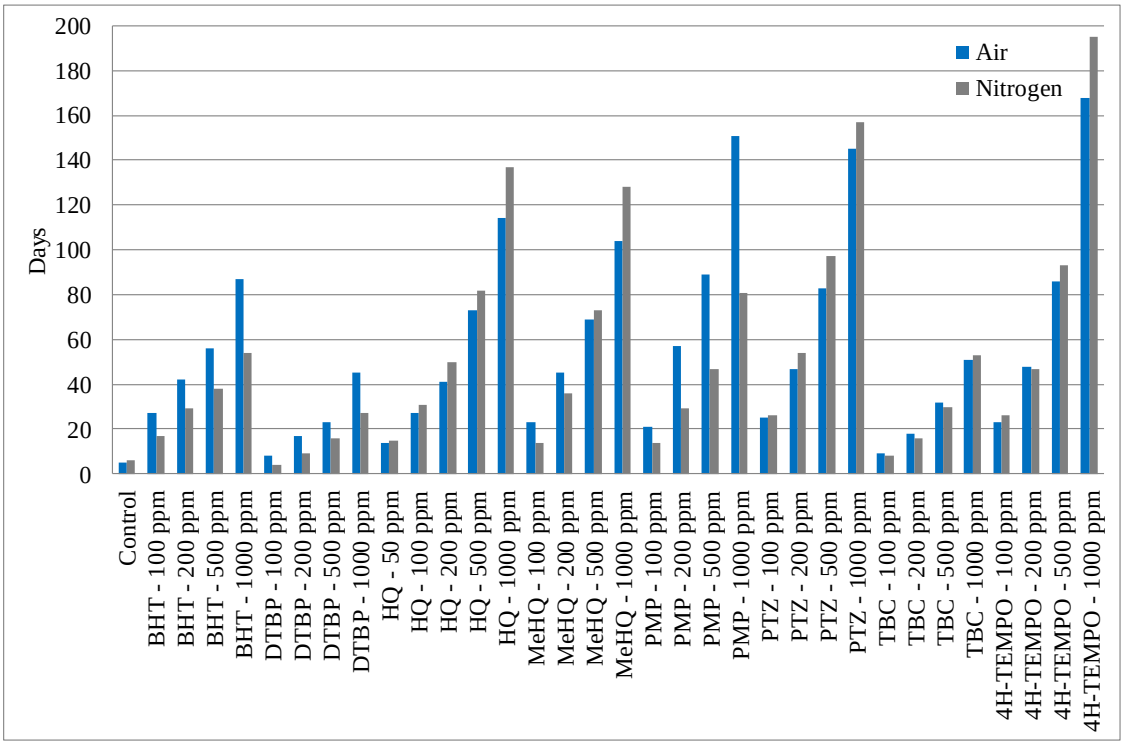

Chart A1.6.6 – IPDI-PEM Resin Stability @ 40°C

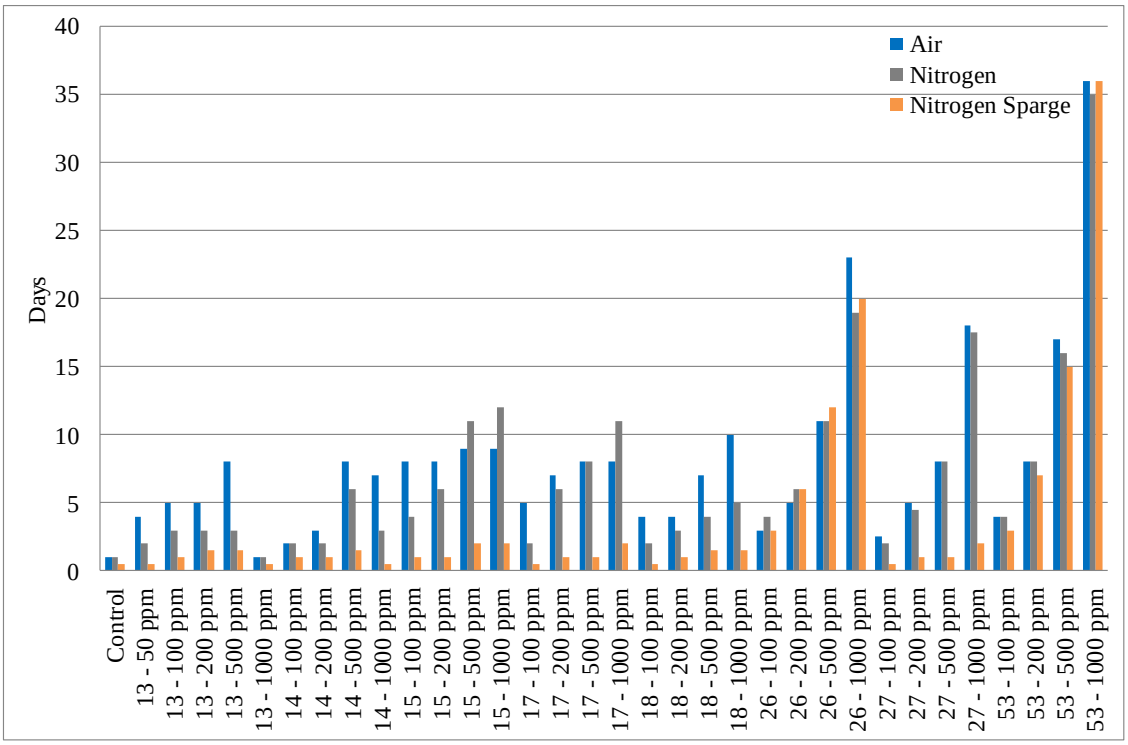

Chart A1.6.7 – IPDI-PEM Resin Stability @ 80°C

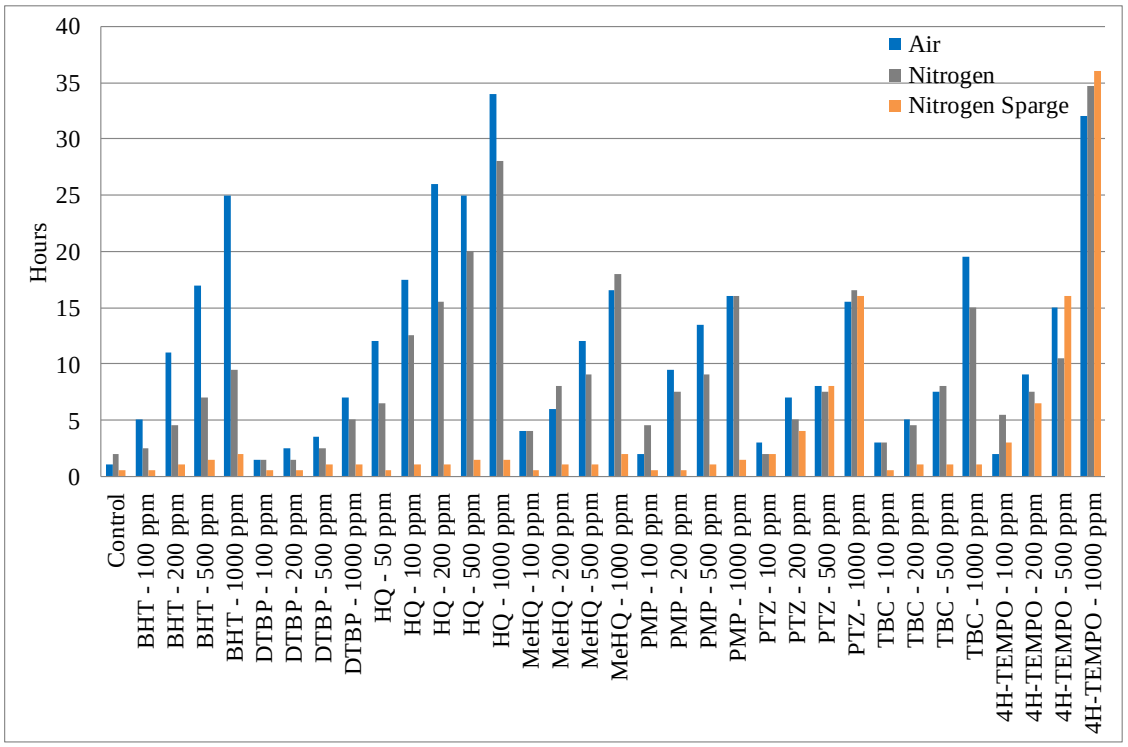

Chart A1.6.8 – IPDI-PEM Resin Stability @ 120°C

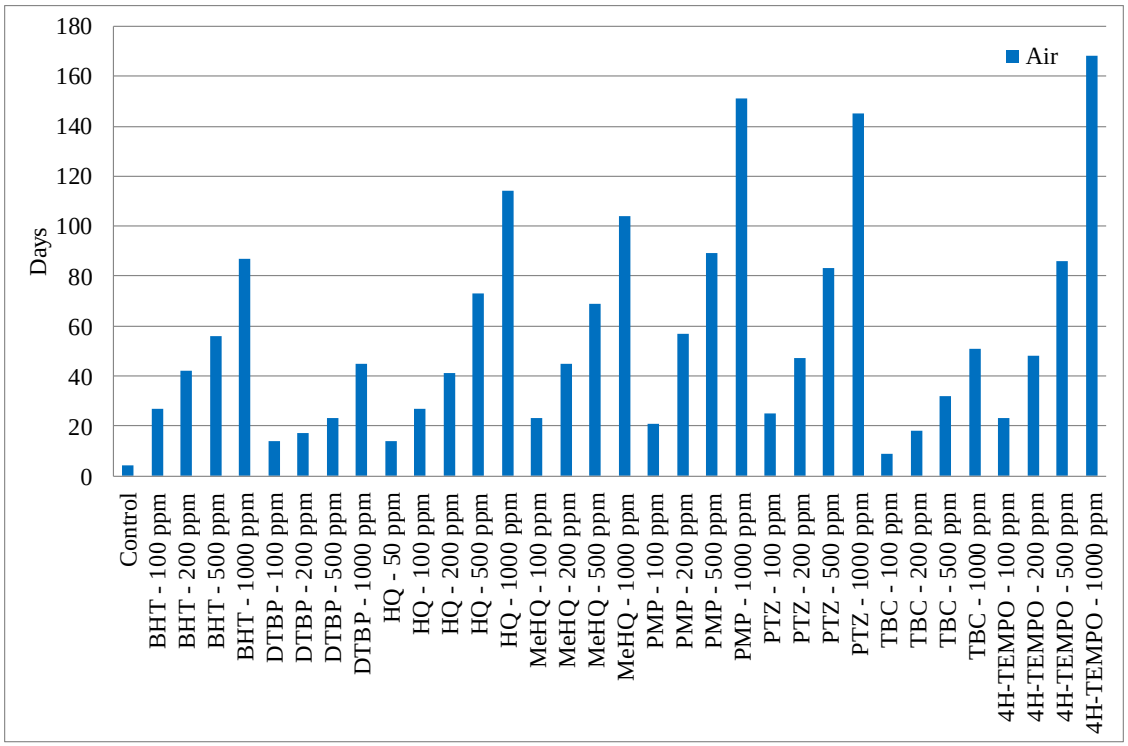

Chart A1.6.9 – HDMI-PEM Resin Stability @ 40°C

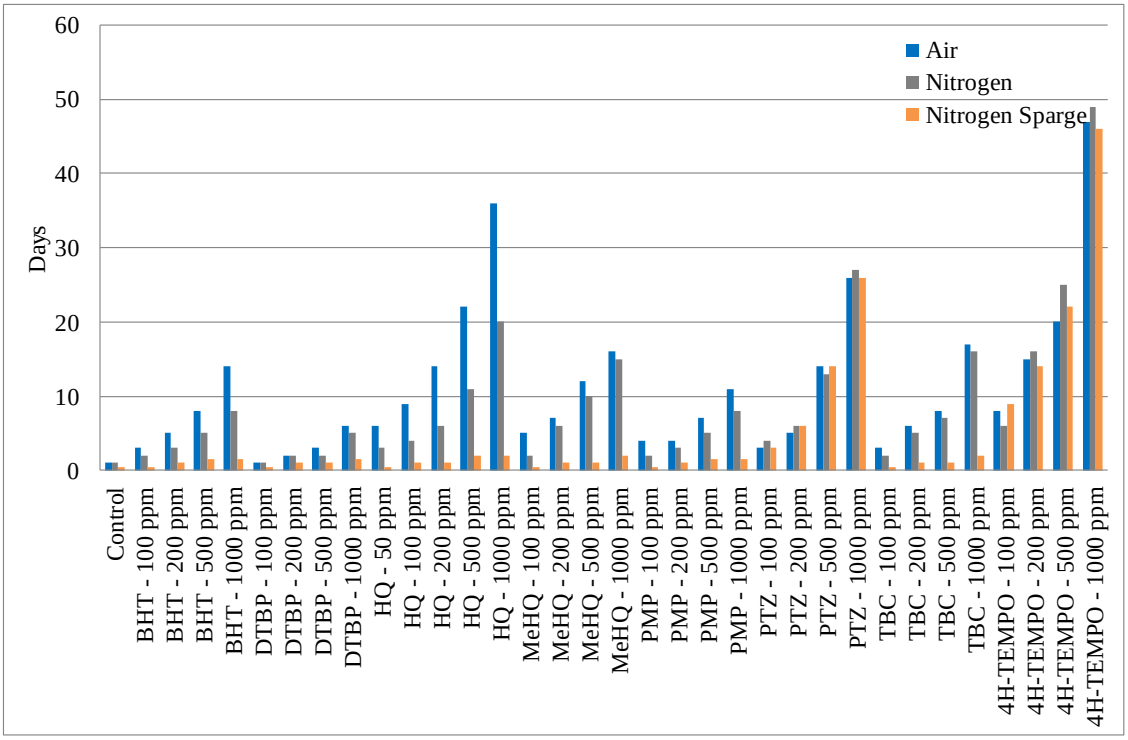

Chart A1.6.10 – HMDI-PEM Resin Stability @ 80°C

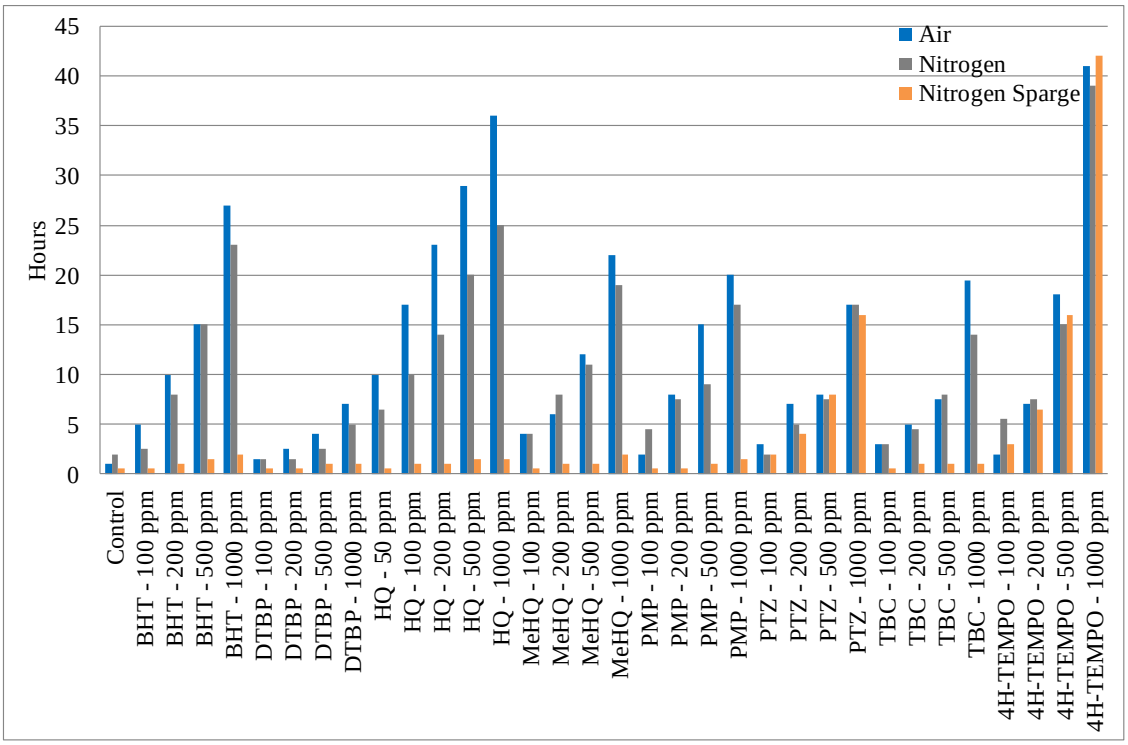

Chart A1.6.11 – HMDI-PEM Resin Stability @ 120°C

A1.7 – Polypropylene Glycol Urethane Acrylate & Methacrylate

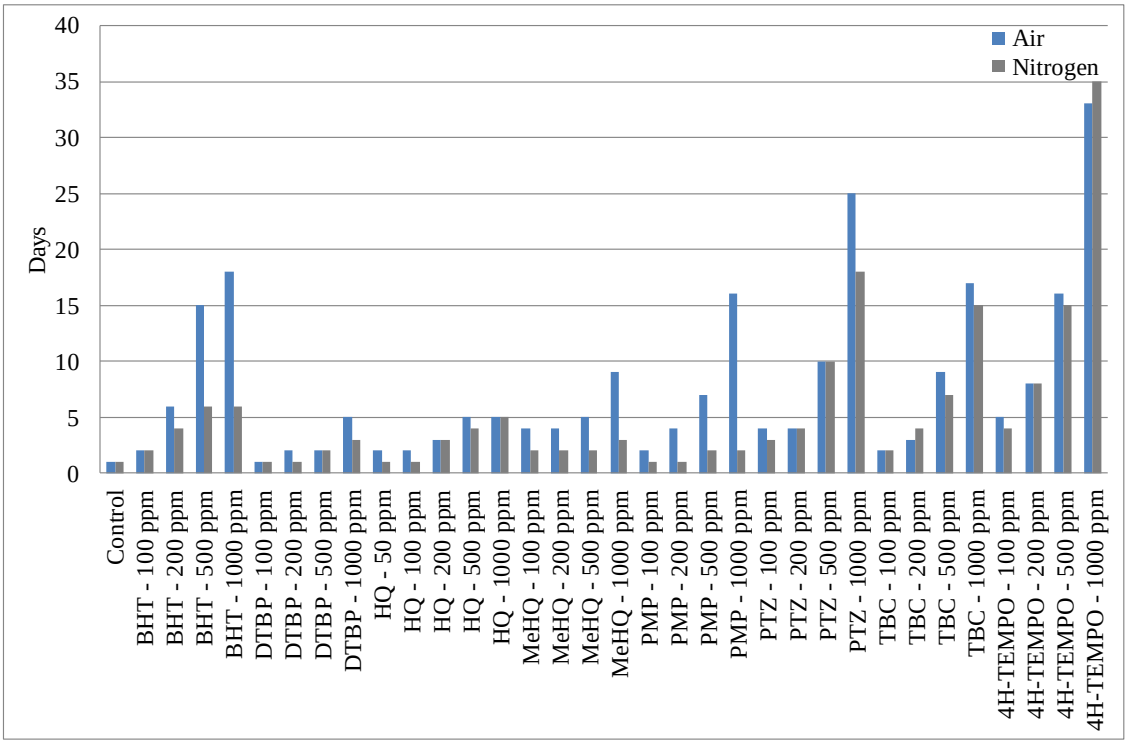

Chart A1.7.1 – IPDI-PPGA Resin Stability @ 80°C

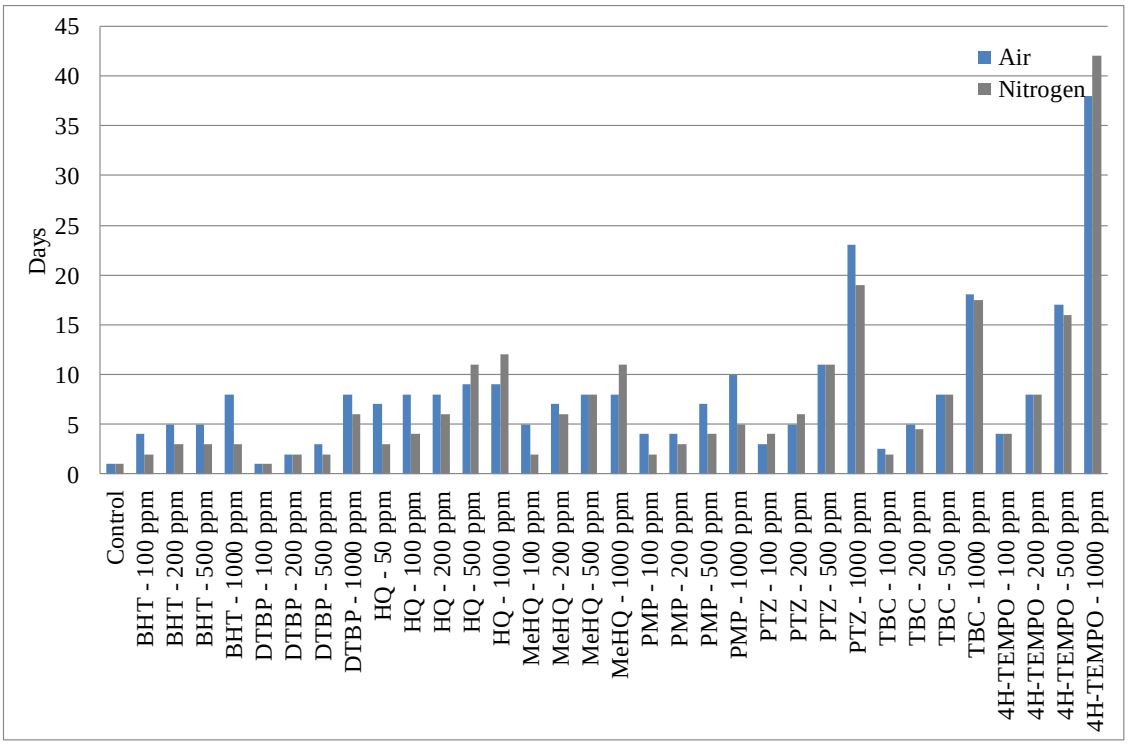

Chart A1.7.2 – IPDI-PPGMA Resin Stability @ 80°C

A1.8 – Water-Bourne Urethane Acrylate & Methacrylate

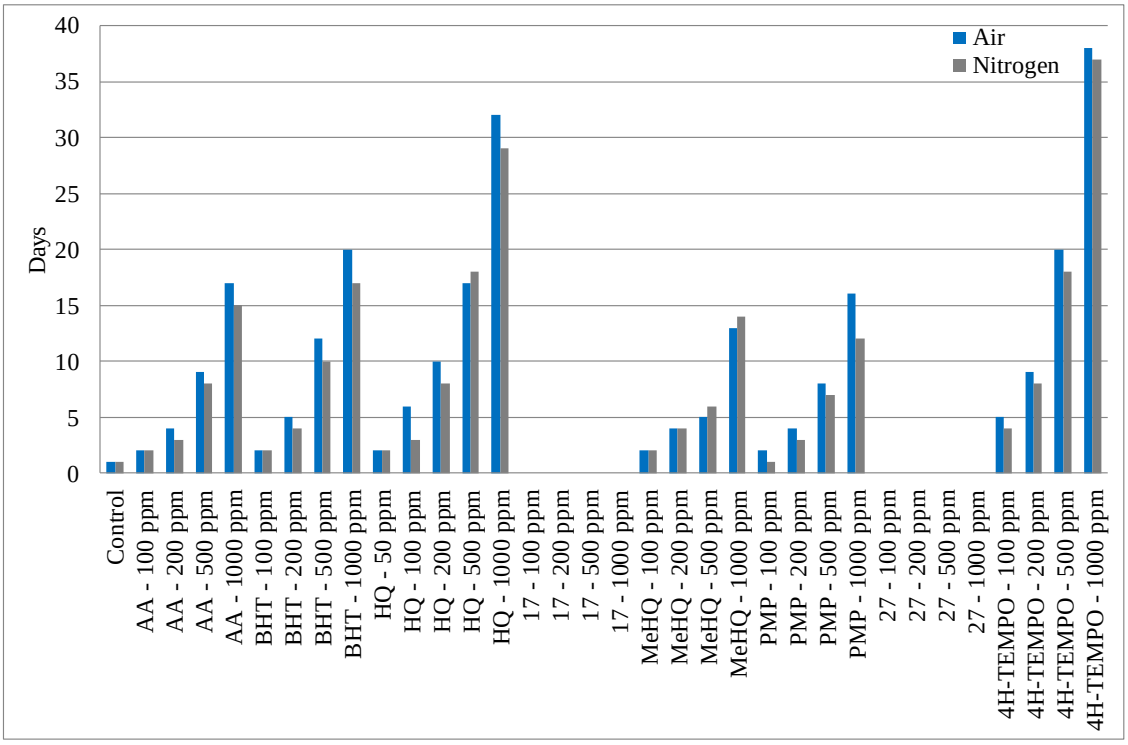

Chart A1.8.1 – HDT-PEGA Resin Stability @ 85°C

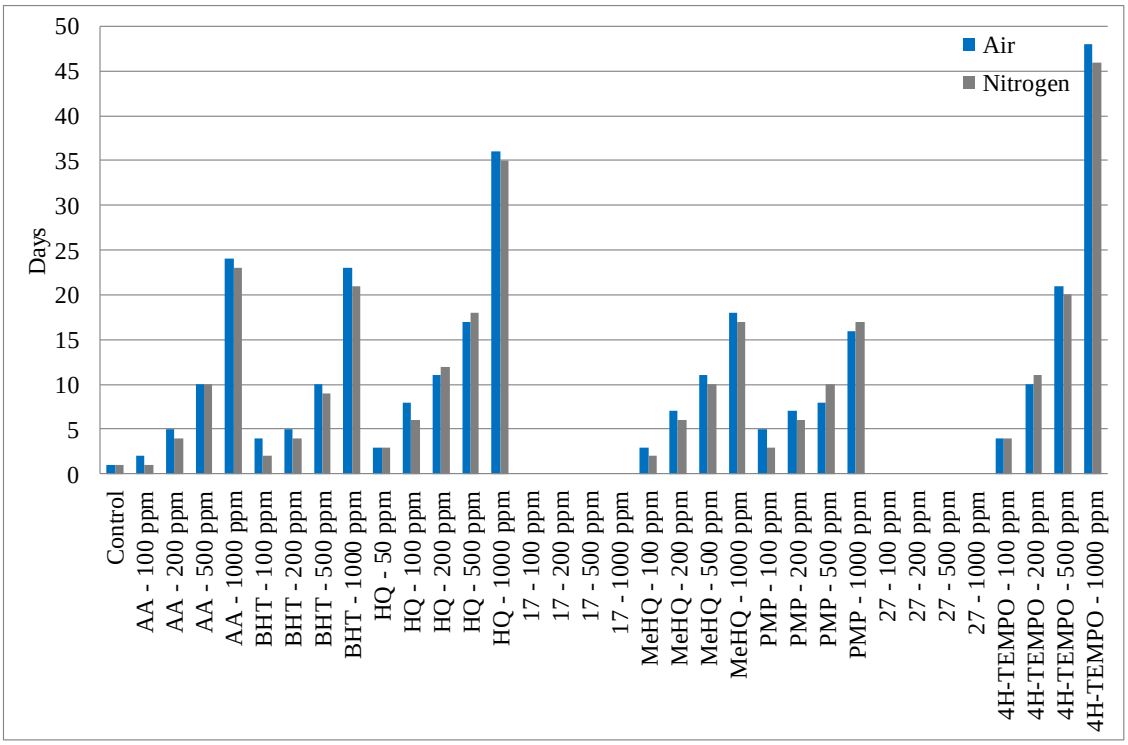

Chart A1.8.2 – HDT-PEGMA Resin Stability @ 85°C

A2.0 – Binary Inhibitor Stability Results

A2.1 – Epoxy Acrylate & Methacrylate

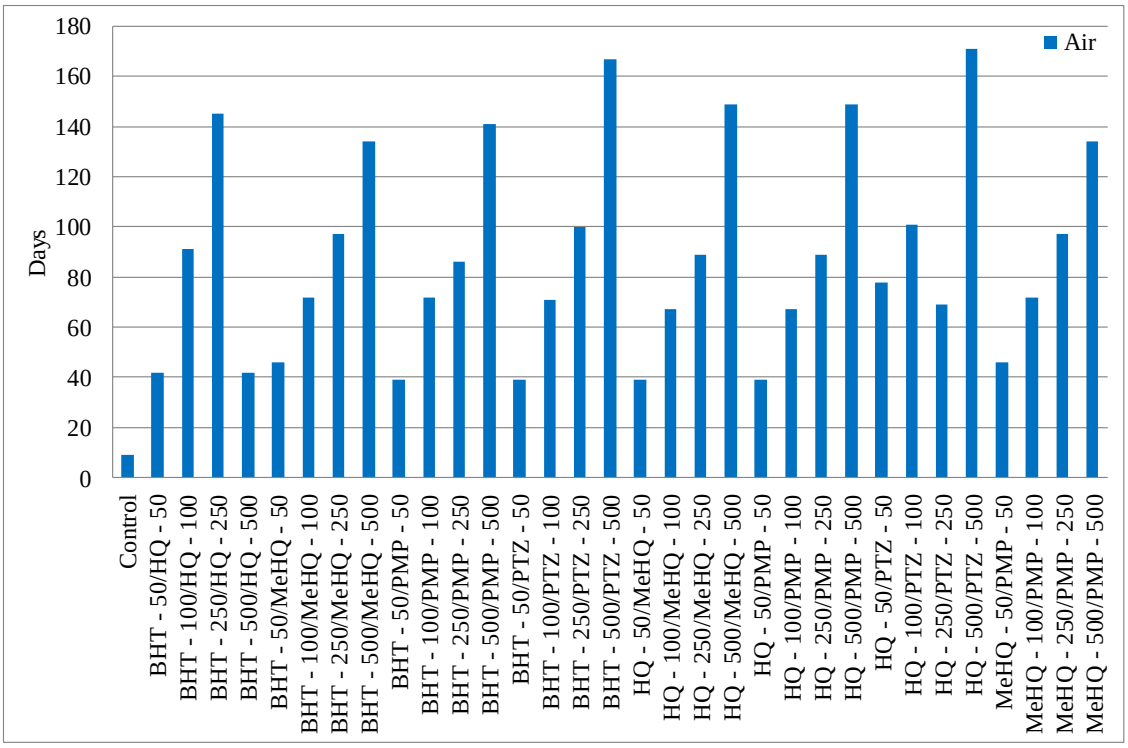

Chart A2.1.1 – BADGEDA Resin Stability @ 40°C

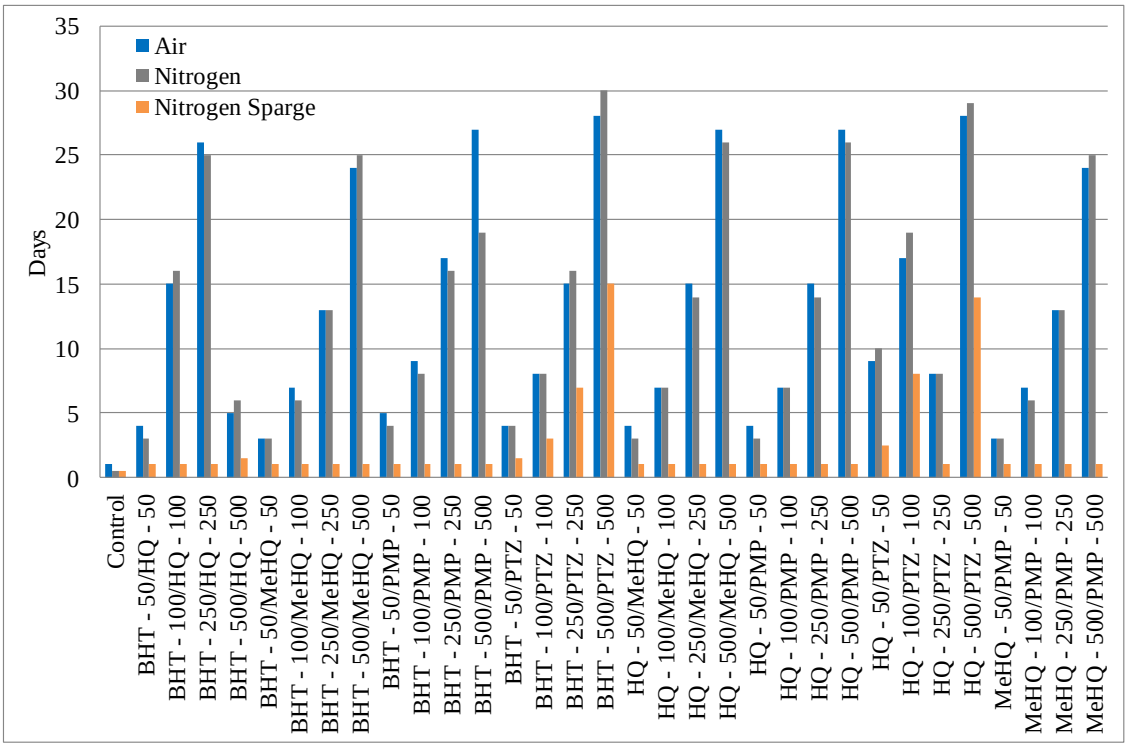

Chart A2.1.2 – BADGEDA Resin Stability @ 80°C

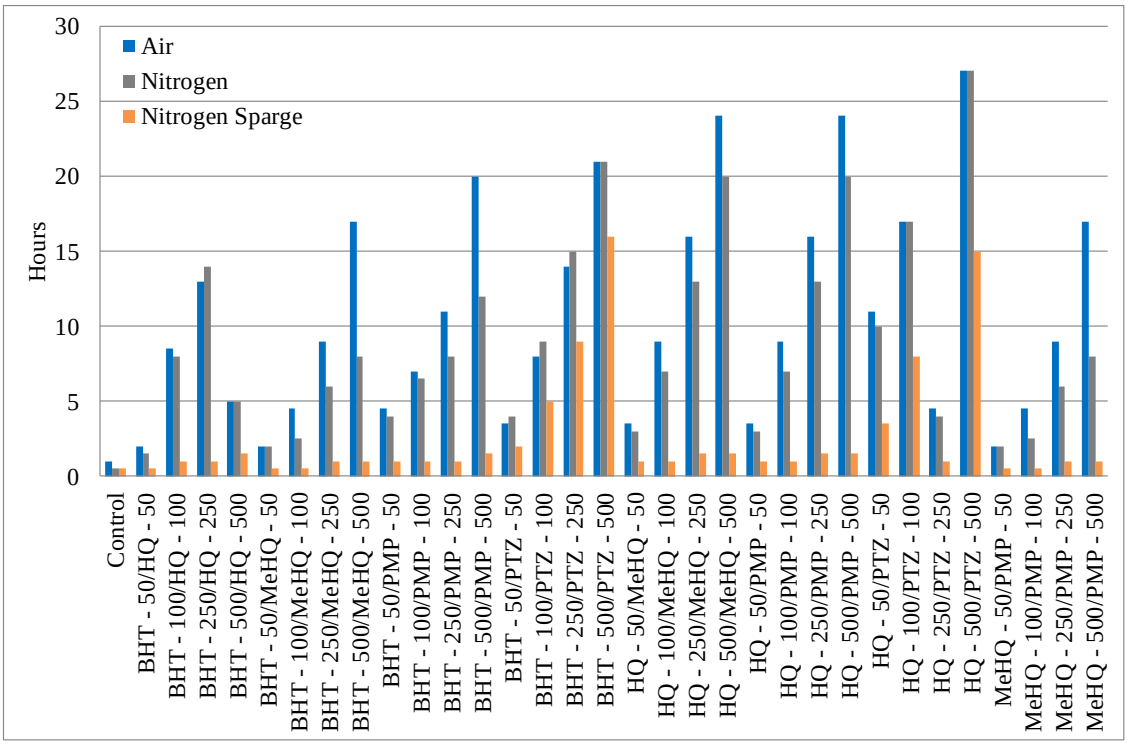

Chart A2.1.3 – BADGEDA Resin Stability @ 120°C

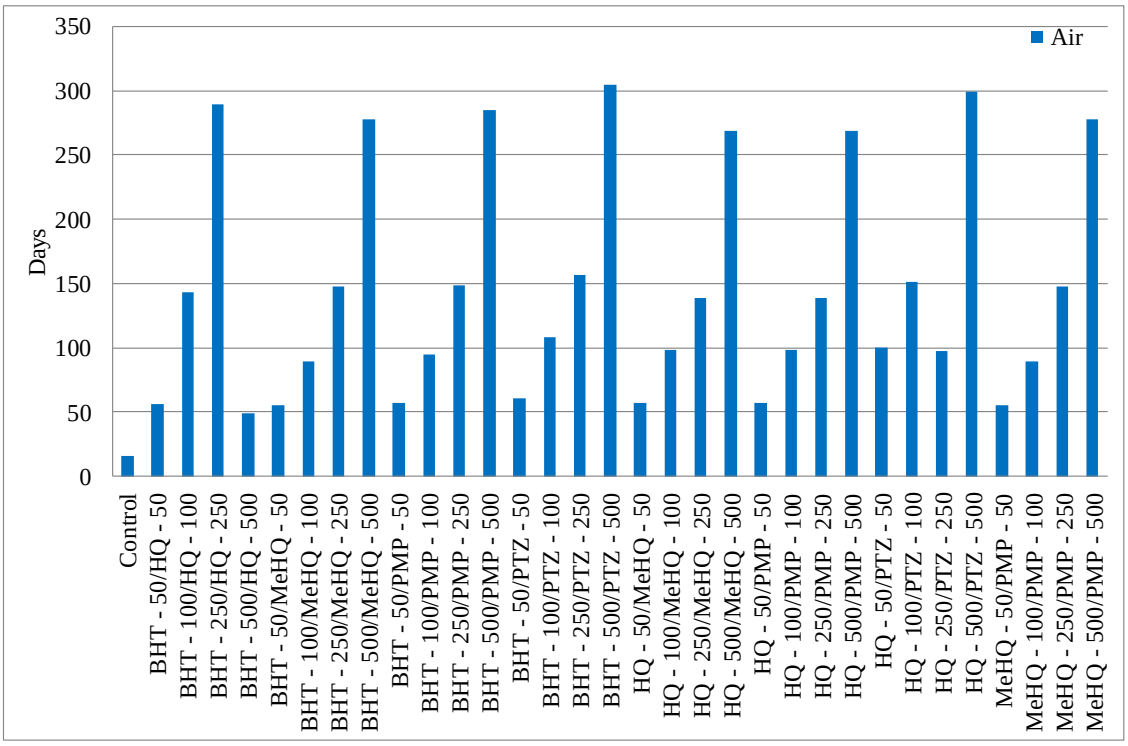

Chart A2.1.4 – BADGEDMA Resin Stability @ 40°C

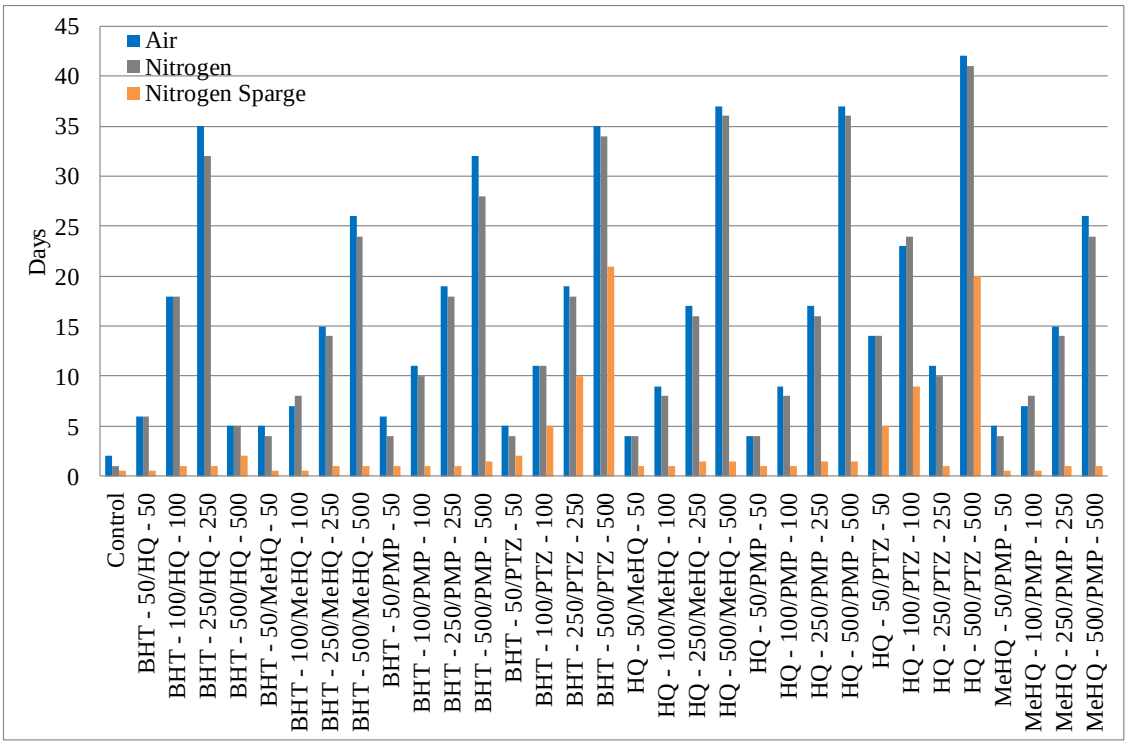

Chart A2.1.5 – BADGEDMA Resin Stability @ 80°C

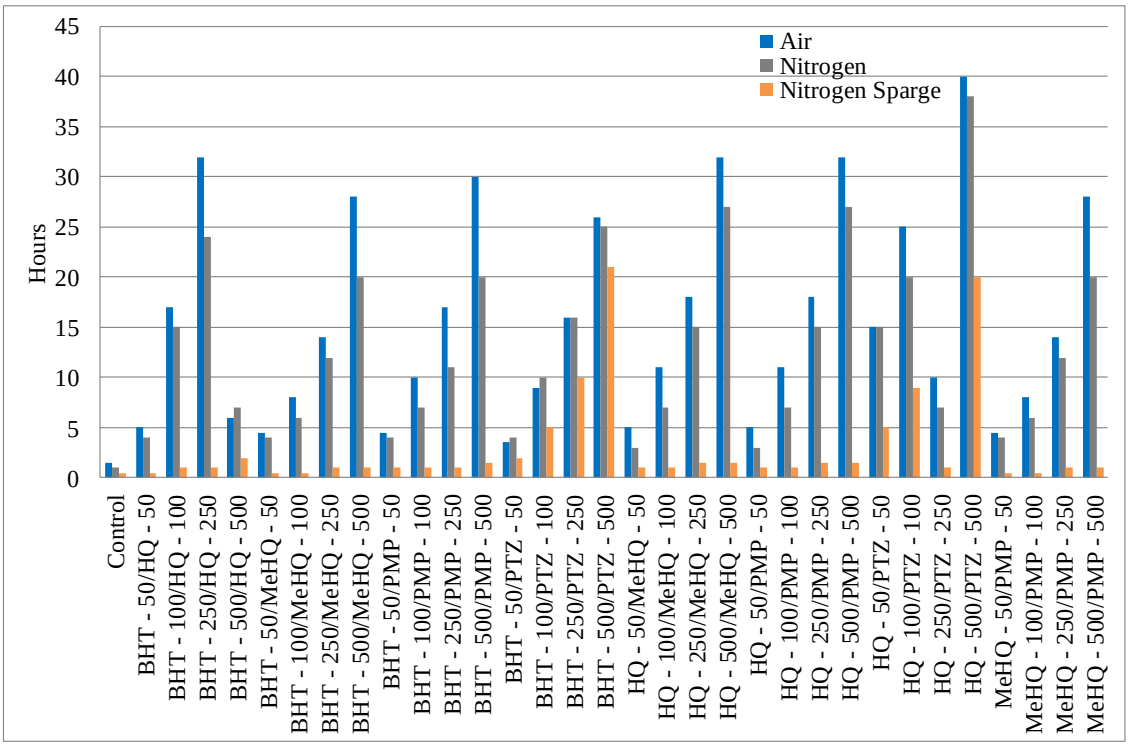

Chart A2.1.6 – BADGEDMA Resin Stability @ 120°C

A2.2 – Urethane Acrylate & Methacrylate

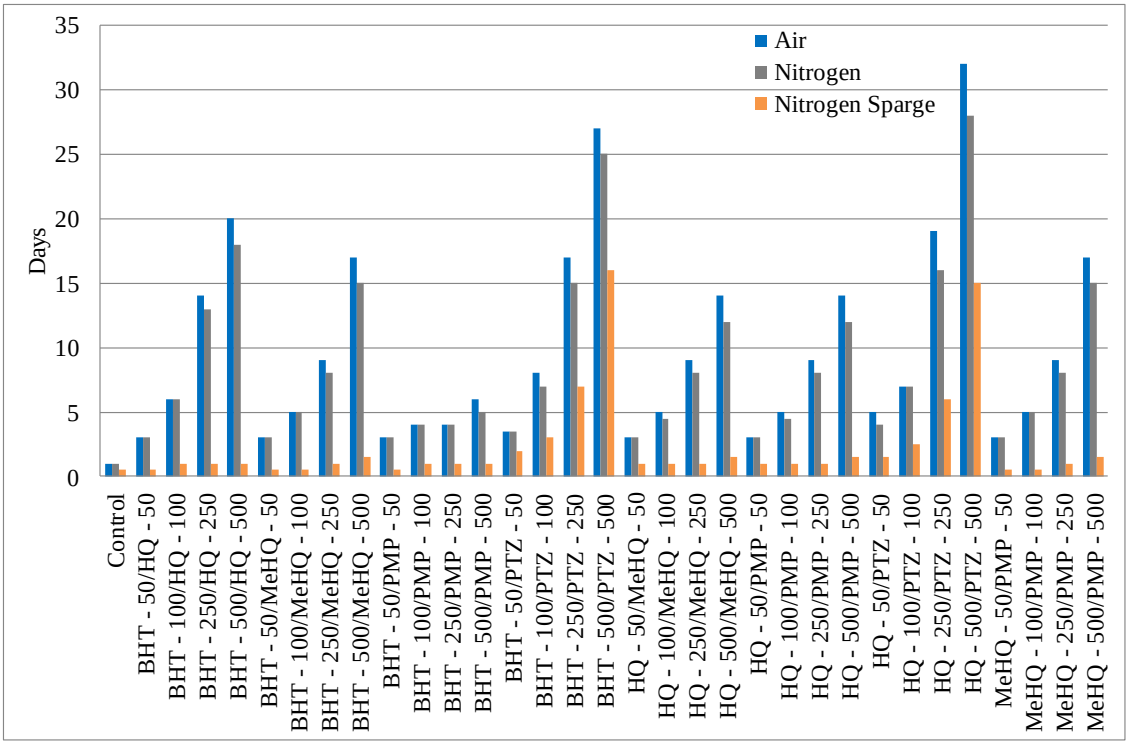

Chart A2.2.1 – MDI-PEA Resin Stability @ 80°C

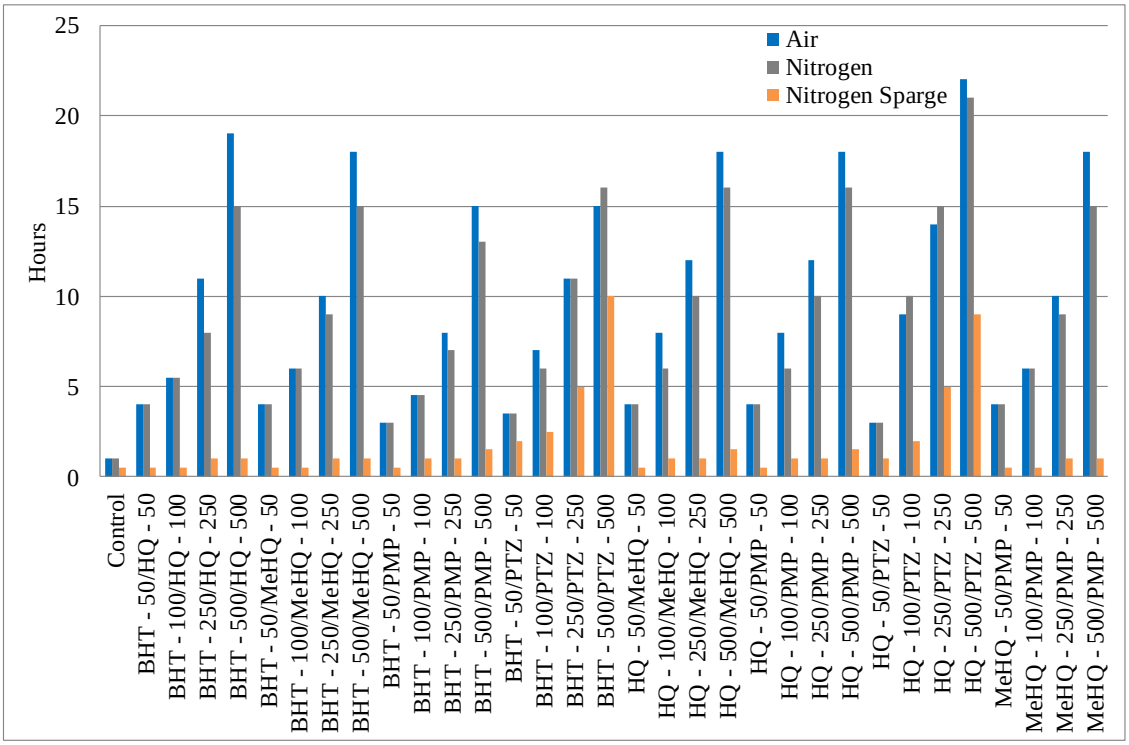

Chart A2.2.2 – MDI-PEA Resin Stability @ 120°C

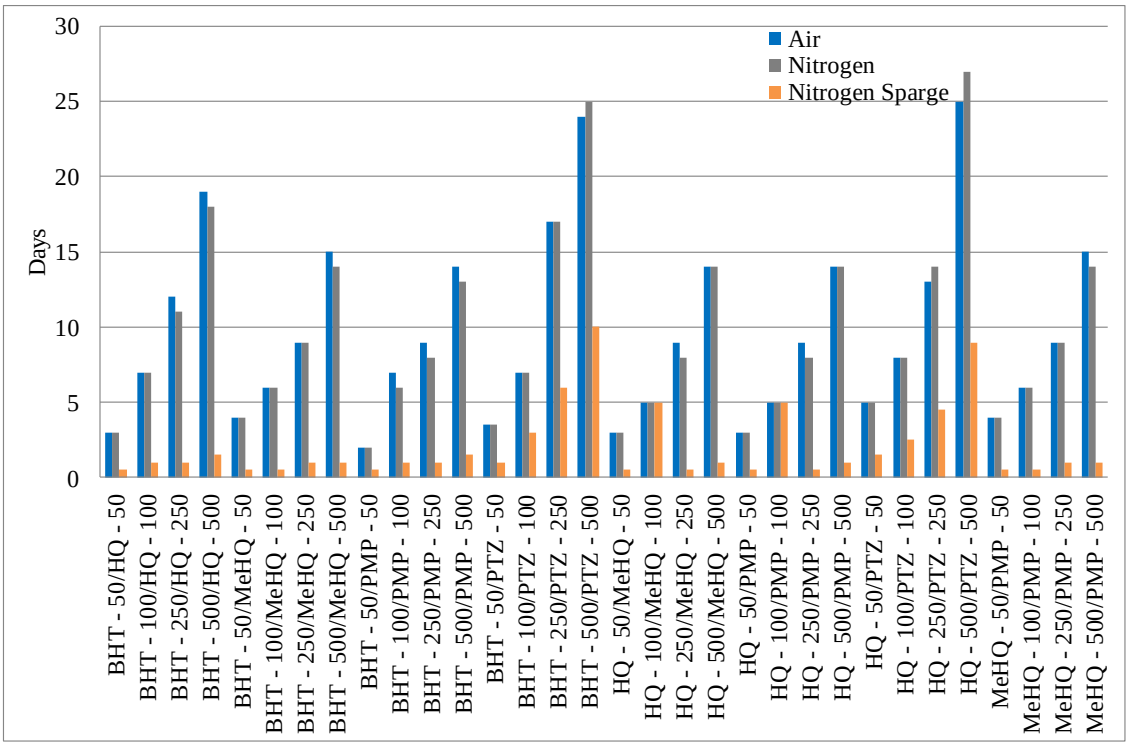

Chart A2.2.3 – IPDI-PEA Resin Stability @ 80°C

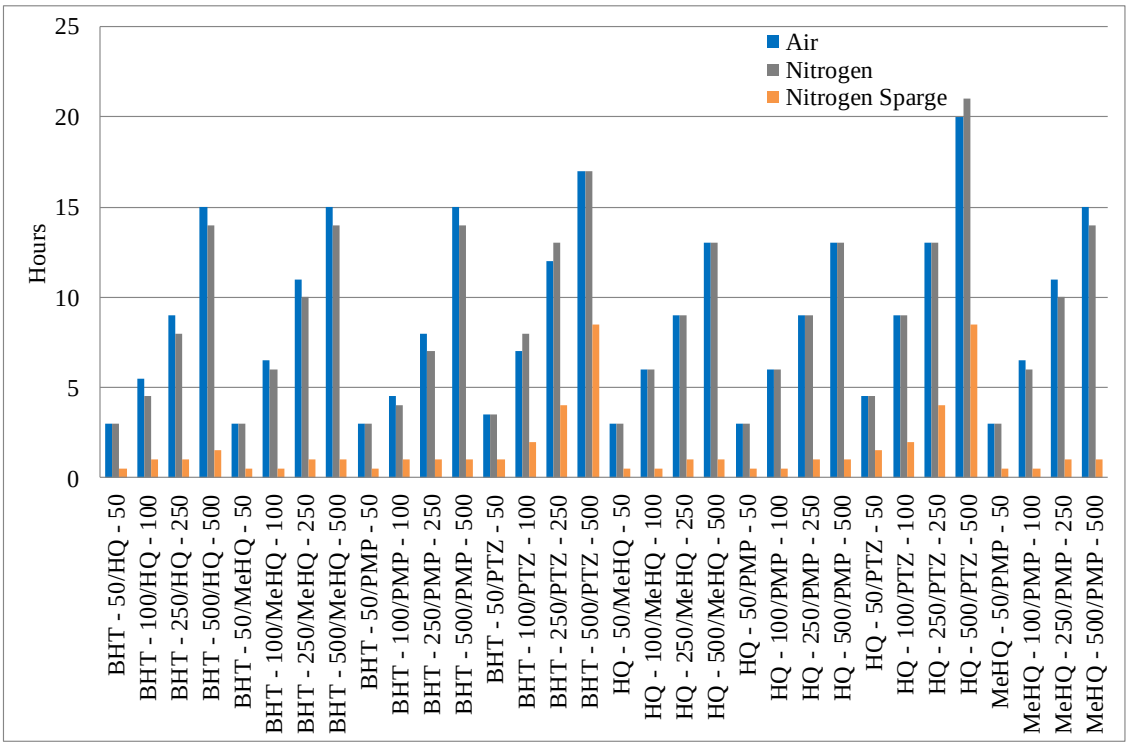

Chart A2.2.4 – IPDI-PEA Resin Stability @ 120°C

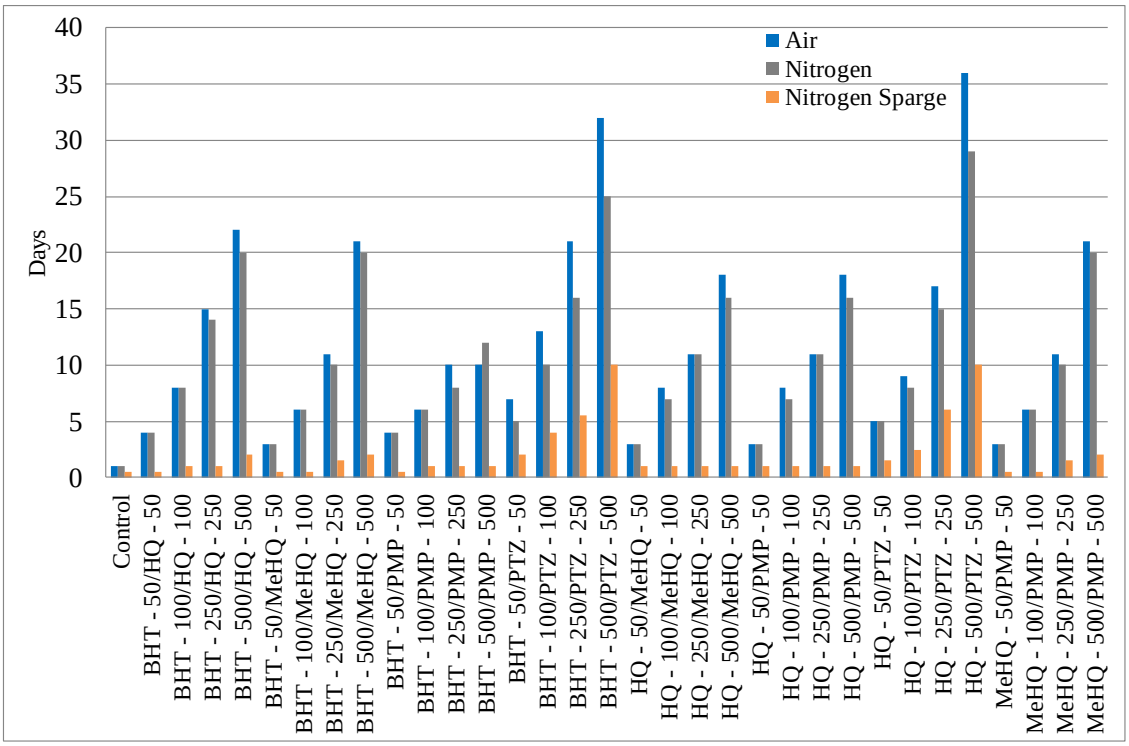

Chart A2.2.5 – MDI-PEM Resin Stability @ 80°C

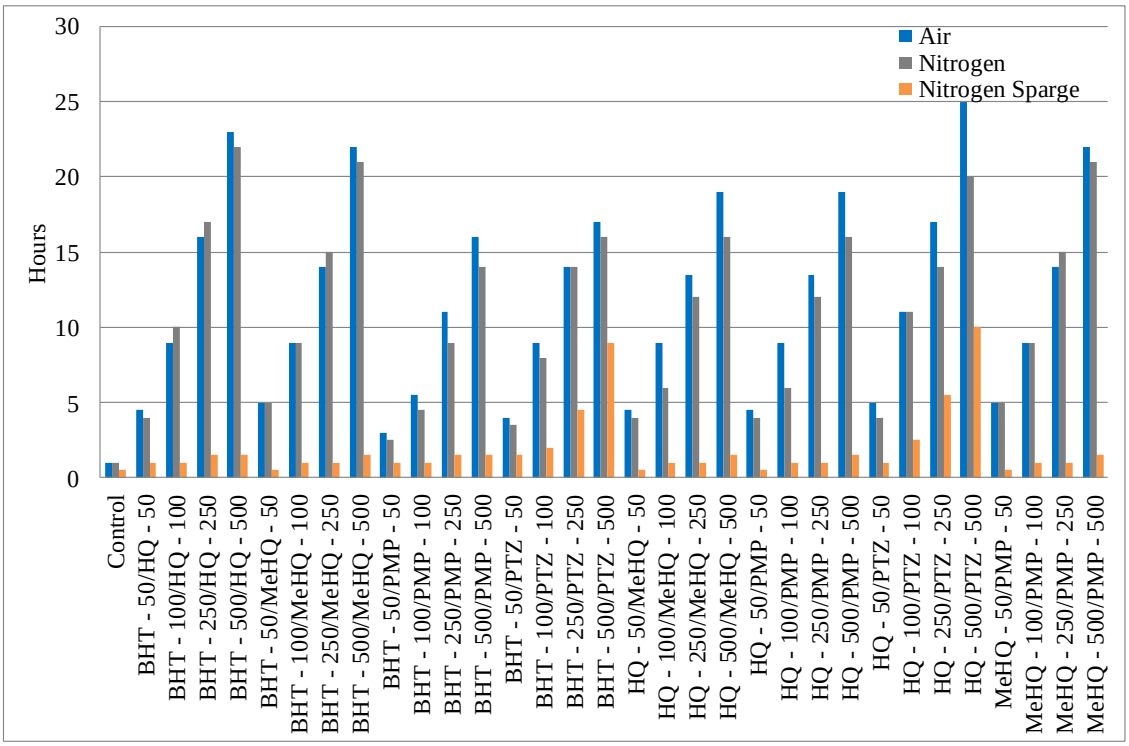

Chart A2.2.6 – MDI-PEM Resin Stability @ 120°C

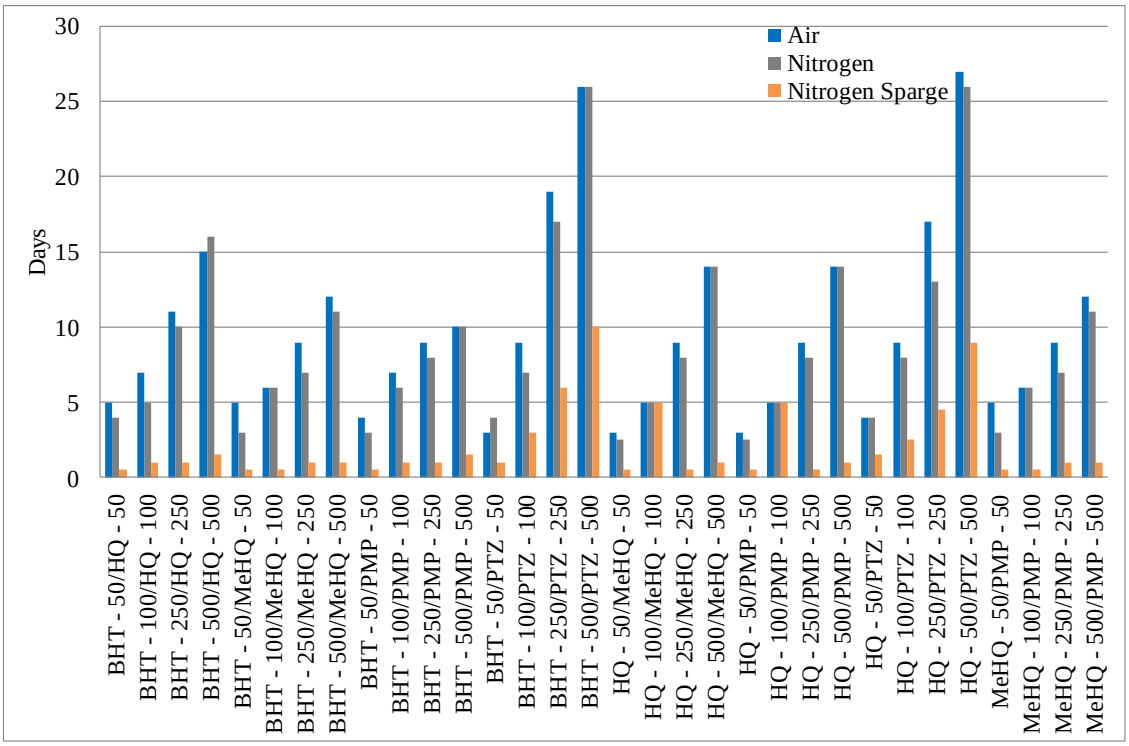

Chart A2.2.7 – IPDI-PEM Resin Stability @ 80°C

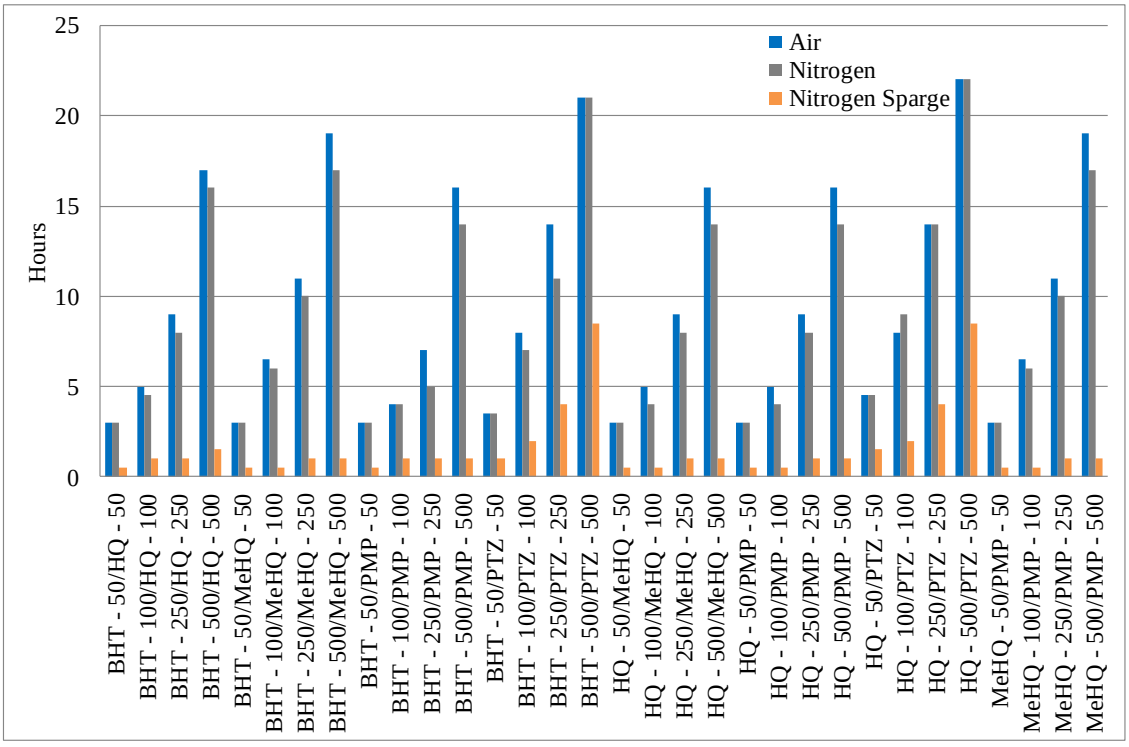

Chart A2.2.8 – IPDI-PEM Resin Stability @ 120°C

A3.0 – Line of Best Fit Data

Inhibitor	Air Headspace						Nitrogen Headspace					
	100ppm			1000ppm			100ppm			1000ppm		
	a	b	c	a	b	c	a	b	c	a	b	c
HQ	9.6604	9	0.0571	2.7457	10	0.0532	5.4572	10	0.0607	9.5160	9	0.0507
PMP	2.0078	10	0.0590	1.5595	12	0.0666	1.2171	10	0.0571	2.8158	13	0.0751
MeHQ	6.2096	9	0.0553	7.4837	10	0.0567	5.0612	8	0.0484	8.7111	10	0.0565
TBC	1.2171	10	0.0571	2.5706	9	0.0475	5.4953	8	0.0484	4.1168	9	0.0484
BHT	3.7838	10	0.0607	6.5974	13	0.0778	9.6604	9	0.0571	1.9623	11	0.0603
4H-TEMPO	3.3886	10	0.0582	9.4573	10	0.0554	2.6222	10	0.0571	6.2417	10	0.0536
PTZ	5.9336	9	0.0543	7.5837	10	0.0560	9.3098	9	0.0548	6.6215	10	0.0550
DTBP	3.6004	8	0.0484	2.8205	9	0.0520	3.6004	8	0.0484	1.0377	10	0.0557

Table A3.1 – Data for Equation 4.1 for HDDA-MEA Resin

Inhibitor	Air Headspace						Nitrogen Headspace					
	100ppm			1000ppm			100ppm			1000ppm		
	a	b	c	a	b	c	a	b	c	a	b	c
HQ	1.2577	9	0.0512	1.5074	10	0.0517	4.3091	9	0.0535	1.4710	10	0.0512
PMP	4.0664	9	0.0548	3.2337	10	0.0584	1.7768	9	0.0520	5.2781	8	0.0443
MeHQ	1.2577	9	0.0512	1.1453	9	0.0448	8.3434	7	0.0433	2.6150	7	0.0341
TBC	5.1234	9	0.0548	7.5483	8	0.0439	1.7768	9	0.0520	3.2938	9	0.0477
BHT	4.0664	9	0.0548	1.1956	10	0.0561	3.6004	8	0.0484	8.1328	9	0.0548
4H-TEMPO	3.6503	10	0.0582	2.0829	11	0.0575	5.8858	9	0.0529	6.3302	10	0.0536
PTZ	2.8205	9	0.0520	4.0586	11	0.0608	1.7216	9	0.0501	1.8087	11	0.0581
DTBP	5.2560	7	0.0433	6.2905	8	0.0484	5.2560	7	0.0433	2.2115	8	0.0456

Table A3.2 - Data for Equation 4.1 for HDDMA-MEA Resin

Inhibitor	Air Headspace						Nitrogen Headspace					
	100ppm			1000ppm			100ppm			1000ppm		
	a	b	c	a	b	c	a	b	c	a	b	c
HQ	4.7871	11	0.0642	1.0271	13	0.0676	9.1241	11	0.0666	4.7679	12	0.0656
PMP	7.5559	11	0.0653	5.7026	12	0.0664	1.1407	12	0.0686	1.7636	12	0.0649
MeHQ	5.1742	11	0.0641	1.5110	13	0.0694	2.2815	12	0.0685	2.4079	13	0.0707
TBC	9.5092	11	0.0672	3.9010	12	0.0663	2.3243	12	0.0693	2.4232	12	0.0649
BHT	2.7456	11	0.0623	5.2964	12	0.0663	6.9188	11	0.0672	1.6203	12	0.0644
4H-TEMPO	5.1742	11	0.0641	1.5110	13	0.0694	2.2815	12	0.0685	2.4079	13	0.0707
PTZ	1.4724	12	0.0673	1.6354	13	0.0691	5.9772	12	0.0710	7.4937	12	0.0669
DTBP	4.5474	11	0.0650	8.4627	12	0.0693	8.9660	11	0.0697	7.2383	11	0.0657

Table A3.3 - Data for Equation 4.1 for HDDGEDA Resin

Inhibitor	Air Headspace						Nitrogen Headspace					
	100ppm			1000ppm			100ppm			1000ppm		
	a	b	c	a	b	c	a	b	c	a	b	c
HQ	1.1432	12	0.0667	6.7491	12	0.0660	4.0689	12	0.0698	2.4128	13	0.0692
PMP	1.0430	11	0.0594	4.8523	12	0.0656	1.7056	12	0.0701	4.3655	9	0.0500
MeHQ	6.7908	10	0.0585	8.0937	12	0.0670	1.4499	11	0.0617	8.8904	12	0.0673
TBC	8.6706	10	0.0593	5.6408	12	0.0664	7.7849	12	0.0715	1.8595	13	0.0693
BHT	4.7538	11	0.0638	5.2143	12	0.0658	8.0165	10	0.0621	6.2231	12	0.0690
4H-TEMPO	1.1378	12	0.0658	5.1284	13	0.0713	2.9083	12	0.0688	4.6359	13	0.0707
PTZ	9.4979	11	0.0658	1.7894	13	0.0690	1.9889	12	0.0679	1.1996	13	0.0677
DTBP	6.5874	10	0.0590	1.1299	12	0.0626	2.8161	12	0.0727	1.2284	13	0.0748

Table A3.4 - Data for Equation 4.1 for BADGEDA Resin

Inhibitor	Air Headspace						Nitrogen Headspace					
	100ppm			1000ppm			100ppm			1000ppm		
	a	b	c	a	b	c	a	b	c	a	b	c
HQ	4.9438	11	0.0647	3.6693	12	0.0652	4.6264	11	0.0648	2.2192	13	0.0700
PMP	5.1598	11	0.0650	1.1142	13	0.0688	3.9287	13	0.0788	1.3691	14	0.0771
MeHQ	4.5236	11	0.0646	1.5271	13	0.0699	9.1241	11	0.0666	6.7691	12	0.0676
TBC	2.4875	11	0.0634	2.2799	12	0.0648	3.9266	11	0.0646	1.5633	12	0.0637
BHT	7.6248	11	0.0660	8.0532	12	0.0679	9.4166	11	0.0685	7.3117	13	0.0753
4H-TEMPO	1.1827	12	0.0666	8.0308	13	0.0735	2.8759	12	0.0691	6.7552	13	0.0724
PTZ	3.3611	12	0.0703	1.3778	13	0.0689	1.6526	12	0.0681	6.0269	12	0.0665
DTBP	3.2241	11	0.0643	3.0745	12	0.0666	9.6407	12	0.0772	3.9623	12	0.0718

Table A3.5 - Data for Equation 4.1 for BFDGEDA Resin

Inhibitor	Air Headspace						Nitrogen Headspace					
	100ppm			1000ppm			100ppm			1000ppm		
	a	b	c	a	b	c	a	b	c	a	b	c
HQ	1.5480	11	0.0603	4.0444	12	0.0641	4.3211	11	0.0632	4.5472	12	0.0646
PMP	2.6304	11	0.0621	1.9946	12	0.0626	1.4217	10	0.0554	1.1381	12	0.0629
MeHQ	1.6292	11	0.0608	2.8875	12	0.0639	2.6470	11	0.0621	4.2167	12	0.0647
TBC	6.5931	10	0.0581	1.9225	12	0.0628	4.8717	11	0.0640	2.0085	12	0.0627
BHT	7.3135	10	0.0570	2.7204	12	0.0637	1.2106	12	0.0668	6.6465	13	0.0739
4H-TEMPO	1.6292	11	0.0608	2.8875	12	0.0639	2.6470	11	0.0621	4.2167	12	0.0647
PTZ	1.5270	11	0.0601	8.6365	12	0.0666	1.0740	12	0.0655	9.3190	12	0.0668
DTBP	4.9228	10	0.0576	5.7333	11	0.0601	1.0091	11	0.0614	2.4577	10	0.0546

Table A3.6 - Data for Equation 4.1 for HDDGEDMA Resin

Inhibitor	Air Headspace						Nitrogen Headspace					
	100ppm			1000ppm			100ppm			1000ppm		
	a	b	c	a	b	c	a	b	c	a	b	c
HQ	4.9888	11	0.0640	5.0709	12	0.0651	9.2194	11	0.0657	1.3584	13	0.0681
PMP	8.8803	11	0.0657	7.1140	12	0.0685	1.0774	12	0.0676	2.0757	13	0.0650
MeHQ	1.0486	12	0.0663	1.0522	13	0.0679	5.0594	11	0.0644	1.4637	13	0.0685
TBC	3.6787	11	0.0631	5.6639	12	0.0663	4.1187	12	0.0699	3.6073	13	0.0710
BHT	3.3358	11	0.0625	8.8770	12	0.0672	1.0206	14	0.0793	1.5506	15	0.0828
4H-TEMPO	2.9119	12	0.0686	5.3979	13	0.0715	3.3087	11	0.0621	5.2057	13	0.0712
PTZ	8.5564	11	0.0652	2.5454	13	0.0700	8.7706	11	0.0654	3.8204	13	0.0709
DTBP	2.1637	11	0.0622	1.8338	12	0.0637	1.1011	14	0.0812	4.2185	13	0.0747

Table A3.7 - Data for Equation 4.1 for BADGEDMA Resin

Inhibitor	Air Headspace						Nitrogen Headspace					
	100ppm			1000ppm			100ppm			1000ppm		
	a	b	c	a	b	c	a	b	c	a	b	c
HQ	1.1432	12	0.0667	6.7491	12	0.0660	4.0689	12	0.0698	2.4128	13	0.0692
PMP	1.0430	11	0.0594	4.8523	12	0.0656	1.7056	12	0.0701	4.3655	9	0.0500
MeHQ	6.7908	10	0.0585	8.0937	12	0.0670	1.4499	11	0.0617	8.8904	12	0.0673
TBC	8.6706	10	0.0593	5.6408	12	0.0664	7.7849	12	0.0715	1.8595	13	0.0693
BHT	4.7538	11	0.0638	5.2143	12	0.0658	8.0165	10	0.0621	6.2231	12	0.0690
4H-TEMPO	6.7908	10	0.0585	8.0937	12	0.0670	1.4499	11	0.0617	8.8904	12	0.0673
PTZ	9.4979	11	0.0658	1.7894	13	0.0690	1.9889	12	0.06791	4.3655	13	0.0677
DTBP	6.5874	10	0.0590	1.1299	12	0.0626	2.8161	12	0.0727	1.2284	13	0.0748

Table A3.8 - Data for Equation 4.1 for BFDGEDMA Resin

Inhibitor	Air Headspace						Nitrogen Headspace					
	100ppm			1000ppm			100ppm			1000ppm		
	a	b	c	a	b	c	a	b	c	a	b	c
HQ	2.8808	11	0.0637	1.3276	12	0.0653	1.4635	10	0.0560	2.1843	10	0.0523
PMP	3.0392	11	0.0651	2.1535	14	0.0812	4.3314	10	0.0607	3.0648	12	0.0704
MeHQ	2.8472	10	0.0571	9.5733	11	0.0633	8.9625	7	0.0420	1.6583	10	0.0519
TBC	4.9441	11	0.0657	2.0199	11	0.0589	1.7341	9	0.0507	3.9175	8	0.0422
BHT	5.6318	10	0.0588	9.0417	11	0.0631	1.2577	9	0.0512	1.7454	10	0.0539
4H-TEMPO	5.5455	11	0.0651	8.7314	11	0.0609	4.5262	9	0.0524	2.4477	10	0.0513
PTZ	4.9487	11	0.0662	4.3258	12	0.0668	5.6465	9	0.0535	1.5365	11	0.0577
DTBP	3.9978	11	0.0672	4.1660	11	0.0629	1.8888	9	0.0535	1.0270	11	0.0607

Table A3.9 - Data for Equation 4.1 for MDI-PEA Resin

Inhibitor	Air Headspace						Nitrogen Headspace					
	100ppm			1000ppm			100ppm			1000ppm		
	a	b	c	a	b	c	a	b	c	a	b	c
HQ	1.5881	12	0.0691	1.6661	13	0.0713	1.1956	10	0.0561	2.1843	10	0.0523
PMP	1.8775	12	0.0699	1.7987	13	0.0713	2.4058	8	0.0461	3.0648	12	0.0704
MeHQ	7.0903	10	0.0589	4.2891	12	0.0671	2.3757	9	0.0519	1.6583	10	0.0519
TBC	1.8857	11	0.0632	2.0199	11	0.0589	1.5149	9	0.0507	3.9175	8	0.0422
BHT	3.2528	11	0.0641	9.0417	11	0.0631	1.3235	11	0.0621	1.7454	10	0.0539
4H-TEMPO	9.2455	11	0.0659	8.7314	11	0.0609	1.0290	10	0.0532	2.4477	10	0.0513
PTZ	9.6924	11	0.0668	6.7929	12	0.0673	3.1872	11	0.0644	1.5365	11	0.0577
DTBP	2.5377	12	0.0719	4.2873	12	0.0697	1.0496	11	0.0640	1.0271	11	0.0607

Table A3.10 - Data for Equation 4.1 for IPDI-PEA Resin

Inhibitor	Air Headspace						Nitrogen Headspace					
	100ppm			1000ppm			100ppm			1000ppm		
	a	b	c	a	b	c	a	b	c	a	b	c
HQ	4.1574	13	0.0805	8.7447	12	0.0689	4.2124	12	0.0744	5.7148	10	0.0559
PMP	4.2068	12	0.0726	2.2613	15	0.0887	2.4922	11	0.0657	2.2666	12	0.0699
MeHQ	3.9895	12	0.0732	1.4406	14	0.0788	6.3630	10	0.0621	2.8987	12	0.0683
TBC	6.4326	11	0.0669	3.1838	11	0.0599	1.8139	9	0.0512	9.8441	7	0.0384
BHT	5.3930	12	0.0739	1.5836	12	0.0643	6.3628	10	0.0621	1.6933	10	0.0544
4H-TEMPO	8.3960	11	0.0669	1.3463	12	0.0612	1.5256	9	0.0499	3.3753	10	0.0518
PTZ	1.3133	12	0.0688	9.7865	12	0.0692	2.9518	10	0.0585	9.2524	10	0.0562
DTBP	1.8865	12	0.0719	1.3148	12	0.0666	1.8822	9	0.0535	2.5786	10	0.0585

Table A3.11 - Data for Equation 4.1 for MDI-PEM Resin

Inhibitor	Air Headspace						Nitrogen Headspace					
	100ppm			1000ppm			100ppm			1000ppm		
	a	b	c	a	b	c	a	b	c	a	b	c
HQ	4.0394	9	0.0495	2.9752	12	0.0650	2.7220	9	0.0502	4.0492	11	0.0596
PMP	2.3677	12	0.0699	1.2233	13	0.0697	7.6813	9	0.0539	2.4483	11	0.0500
MeHQ	1.9835	11	0.0618	1.1818	13	0.0700	1.2419	10	0.0554	1.7276	12	0.0624
TBC	2.7032	11	0.0645	3.9414	11	0.0600	2.8205	9	0.0520	6.4613	10	0.0555
BHT	1.2979	11	0.0606	1.7699	12	0.0642	2.1228	11	0.0637	2.5277	11	0.0614
4H-TEMPO	2.4289	13	0.0761	1.0612	13	0.0672	8.0570	10	0.0591	1.3686	12	0.0613
PTZ	2.2591	12	0.0693	2.2518	13	0.0707	4.9921	12	0.0718	7.7916	12	0.0679
DTBP	1.2830	12	0.0702	2.4106	12	0.0672	1.4102	9	0.0520	1.6274	11	0.0608

Table A3.12 - Data for Equation 4.1 for IPDI-PEM Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	2.5395	10	0.0554	0.9110	1.5828	10	0.0540	0.8483
PMP	1.9260	11	0.0626	0.9737	1.3676	12	0.0682	0.9604
MeHQ	5.5375	10	0.0578	0.9276	2.6868	10	0.0553	0.8925
TBC	2.2900	9	0.0491	0.9148	2.7026	9	0.0492	0.9049
BHT	5.7701	12	0.0723	0.9218	8.9549	10	0.0601	0.9522
4H-TEMPO	8.7707	10	0.0573	0.8853	3.3643	10	0.0541	0.8483
PTZ	3.7814	10	0.0561	0.9685	2.8920	10	0.0547	0.9673
DTBP	1.4919	9	0.0513	0.9336	2.2631	9	0.0524	0.9541

Table A3.13 – Data for Equation 4.1 for a Calculated Mean for HDDA-MEA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	6.7388	9	0.0518	0.9732	1.6245	10	0.0537	0.9380
PMP	1.9260	10	0.0578	0.9725	1.1678	9	0.0484	0.8792
MeHQ	1.1060	9	0.0466	0.8838	8.7325	7	0.0371	0.7797
TBC	8.4929	8	0.0462	0.8815	1.8321	9	0.0480	0.9082
BHT	1.7905	10	0.0582	0.9985	1.3764	9	0.0507	0.9678
4H-TEMPO	1.5374	11	0.0589	0.8847	3.5385	10	0.0542	0.8704
PTZ	1.6011	11	0.0603	0.9483	8.6485	10	0.0580	0.9215
DTBP	3.5366	8	0.0475	0.8441	6.5867	7	0.0430	0.8775

Table A3.14 – Data for Equation 4.1 for a Calculated Mean for HDDMA-MEA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	4.0804	12	0.0671	0.9846	2.6767	12	0.0660	0.9782
PMP	3.2040	12	0.0665	0.9903	2.0619	12	0.0672	0.9759
MeHQ	6.6856	12	0.0688	0.9933	1.0229	13	0.0700	0.9886
TBC	1.9646	12	0.0661	0.9891	2.7428	12	0.0669	0.9836
BHT	2.3423	12	0.0657	0.9858	9.0762	11	0.0647	0.9648
4H-TEMPO	6.0472	13	0.0746	0.9951	4.2194	13	0.0733	0.9933
PTZ	6.001	12	0.0681	0.9922	4.2863	12	0.0671	0.9846
DTBP	2.6128	12	0.0675	0.9885	1.2171	12	0.0684	0.9913

Table A3.15 – Data for Equation 4.1 for a Calculated Mean for HDDGEDA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	1.6902	12	0.0651	0.9842	1.5325	12	0.0648	0.9744
PMP	2.1120	12	0.0658	0.9861	3.3008	12	0.0687	0.9850
MeHQ	3.6693	12	0.0676	0.9927	6.5482	12	0.0691	0.9900
TBC	2.0671	12	0.0666	0.9894	1.2902	12	0.0652	0.9770
BHT	1.8113	12	0.0655	0.9885	1.1987	11	0.0597	0.9455
4H-TEMPO	3.4531	13	0.0735	0.9958	1.8349	13	0.0714	0.9884
PTZ	3.9429	12	0.0673	0.9928	3.2535	12	0.0665	0.9899
DTBP	2.8056	12	0.0681	0.9892	2.8466	12	0.0709	0.9952

Table A3.16 – Data for Equation 4.1 for a Calculated Mean for BADGEDA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	1.9456	12	0.0653	0.9851	6.1556	12	0.0684	0.9753
PMP	3.7706	12	0.0675	0.9933	1.1151	14	0.0780	0.9749
MeHQ	5.9380	12	0.0691	0.9941	4.9819	12	0.0686	0.9933
TBC	1.1513	12	0.0647	0.9894	1.3336	12	0.0651	0.9807
BHT	2.0252	12	0.0656	0.9920	2.0561	13	0.0735	0.9751
4H-TEMPO	2.8752	13	0.0727	0.9976	3.3945	12	0.0726	0.9863
PTZ	6.6804	12	0.0688	0.9887	2.8567	12	0.0662	0.9836
DTBP	1.4207	12	0.0660	0.9923	5.3698	12	0.0739	0.9901

Table A13.17 – Data for Equation 4.1 for a Calculated Mean for BFDGEDA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	1.1033	12	0.0625	0.9821	9.4778	11	0.0622	0.9656
PMP	6.2732	11	0.0611	0.9830	3.9073	11	0.0617	0.9845
MeHQ	1.5096	12	0.0640	0.9914	1.7130	12	0.0640	0.9869
TBC	4.9215	11	0.0609	0.9817	7.1501	11	0.0617	0.9854
BHT	6.3661	11	0.0661	0.9945	1.3551	13	0.0710	0.9726
4H-TEMPO	5.4918	12	0.0667	0.9839	3.0098	12	0.0647	0.9797
PTZ	2.1669	12	0.0646	0.9920	2.4390	12	0.0647	0.9864
DTBP	1.9498	11	0.0588	0.9876	4.8046	10	0.0575	0.9996

Table A3.18 – Data for Equation 4.1 for a Calculated Mean for HDDGEDMA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	2.0446	12	0.0646	0.9884	3.2014	12	0.0660	0.9796
PMP	2.0928	12	0.0648	0.9922	1.4182	12	0.0657	0.9932
MeHQ	4.3633	12	0.0673	0.9965	4.3464	12	0.0670	0.9946
TBC	1.7808	12	0.0648	0.9911	1.0604	13	0.0694	0.9985
BHT	1.9056	12	0.0646	0.9965	3.0901	14	0.0798	0.9938
4H-TEMPO	1.2860	13	0.0694	0.9913	6.6951	12	0.0674	0.9869
PTZ	6.1813	12	0.0678	0.9966	8.0166	12	0.0683	0.9892
DTBP	6.9383	11	0.0627	0.9932	3.7428	13	0.0757	0.9767

Table A3.19 – Data for Equation 4.1 for a Calculated Mean for BADGEDMA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	6.1556	12	0.0684	0.9753	2.4572	12	0.0651	0.9917
PMP	1.1151	14	0.0780	0.9749	1.6548	12	0.0643	0.9943
MeHQ	4.9819	12	0.0686	0.9933	2.8925	12	0.0660	0.9921
TBC	1.3336	12	0.0651	0.9807	1.2919	12	0.0641	0.9915
BHT	2.0561	13	0.0735	0.9751	1.9039	12	0.0647	0.9973
4H-TEMPO	3.3945	13	0.0726	0.9863	1.2015	13	0.0692	0.9923
PTZ	2.8567	12	0.0662	0.9836	6.9261	12	0.0682	0.9945
DTBP	5.3698	12	0.0739	0.9901	3.6003	11	0.0611	0.9909

Table A3.20 – Data for Equation 4.1 for a Calculated Mean for BFDGEDMA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	5.3574	11	0.0625	0.9289	9.9598	9	0.0518	0.9473
PMP	2.1413	13	0.0753	0.9866	1.1162	12	0.0687	0.9861
MeHQ	3.0018	11	0.0616	0.9390	3.5137	9	0.0493	0.9752
TBC	3.2315	11	0.0619	0.9107	5.4366	8	0.0448	0.7709
BHT	5.2315	11	0.0630	0.9676	9.5409	9	0.0538	0.9805
4H-TEMPO	5.8691	11	0.0617	0.9259	1.4202	10	0.0518	0.9180
PTZ	2.2826	12	0.0670	0.9360	7.6212	10	0.0576	0.9043
DTBP	4.8076	11	0.0650	0.9375	5.7959	10	0.0605	0.9129

Table A3.21– Data for Equation 4.1 for a Calculated Mean for MDI-PEA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	5.8516	12	0.0699	0.9776	2.6878	11	0.0620	0.9942
PMP	7.5674	11	0.0632	0.9807	1.1791	10	0.0556	0.9999
MeHQ	2.7014	12	0.0676	0.9763	2.8030	9	0.0493	0.9774
TBC	6.5970	11	0.0638	0.9523	1.3175	10	0.0535	0.9270
BHT	1.8047	12	0.0660	0.9767	7.6513	10	0.0588	0.9802
4H-TEMPO	3.1807	12	0.0664	0.9727	5.3714	11	0.0613	0.9620
PTZ	2.8663	11	0.0594	0.9513	1.1996	12	0.0648	0.9824
DTBP	3.5823	12	0.0708	0.9821	1.4911	11	0.0636	0.9749

Table A3.22 – Data for Equation 4.1 for a Calculated Mean for IPDI-PEA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	1.9581	13	0.0739	0.9436	1.8215	11	0.0616	0.9763
PMP	2.6744	14	0.0833	0.9922	1.6139	12	0.0698	0.9851
MeHQ	4.4521	13	0.0775	0.9712	5.9241	11	0.0657	0.9787
TBC	3.7665	11	0.0622	0.9099	1.8874	8	0.0419	0.7137
BHT	1.5042	12	0.0662	0.9720	2.7021	10	0.0575	0.9412
4H-TEMPO	1.0758	12	0.0632	0.9186	1.6345	10	0.0520	0.8864
PTZ	5.6348	12	0.0697	0.9568	5.1242	10	0.0565	0.9494
DTBP	1.4081	12	0.0686	0.9619	8.5031	9	0.0565	0.9660

Table A3.13 – Data for Equation 4.1 for a Calculated Mean for MDI-PEM Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	4.3101	11	0.0607	0.9667	7.3986	10	0.0565	0.9995
PMP	3.2653	12	0.0675	0.9987	9.7899	10	0.0589	0.9987
MeHQ	2.7496	12	0.0671	0.9918	6.0760	11	0.0630	0.9956
TBC	4.7171	11	0.0625	0.9531	3.0647	10	0.0554	0.9353
BHT	6.6065	11	0.0629	0.9857	2.0801	11	0.0619	0.9998
4H-TEMPO	6.4735	12	0.0682	0.9784	9.1492	11	0.0625	0.9620
PTZ	9.1076	12	0.0701	0.9862	6.8557	12	0.0694	0.9818
DTBP	2.1188	12	0.0687	0.9826	7.6984	10	0.0607	0.9651

Table A3.24 – Data for Equation 4.1 for a Calculated Mean for IPDI-PEM Resin

A4.0 – Derived Inhibitor Equations

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	$1.8733x10^{7}$	$1.1003x10^{10}$	0.0554	0.8356	$-4.7428x10^{7}$	$5.1538x10^{10}$	0.0607	0.8527
PMP	$1.7104x10^{9}$	$-3.5002x10^{11}$	0.0626	0.8329	$3.1274x10^{10}$	$-7.3544x10^{12}$	0.0571	0.7860
MeHQ	$7.6252x10^{7}$	$1.5349x10^{9}$	0.0578	0.9413	$9.6228x10^{7}$	$-1.4764x10^{10}$	0.0484	0.9514
TBC	$-1.0667x10^{7}$	$1.1544x10^{10}$	0.0491	0.7281	$3.9636x10^{6}$	$2.7633x10^{8}$	0.0492	0.9859
BHT	$7.3263x10^{7}$	$-1.6367x10^{13}$	0.0723	0.8147	$2.0730x10^{8}$	$-1.5534x10^{10}$	0.0571	0.9932
4H-TEMPO	$6.7430x10^{7}$	$3.4969x10^{10}$	0.0573	0.8336	$4.0216x10^{7}$	$1.8642x10^{10}$	0.0571	0.8904
PTZ	$2.1150x10^{6}$	$1.6032x10^{10}$	0.0561	0.2833	$6.3228x10^{7}$	$3.9302x10^{7}$	0.0548	0.9688
DTBP	$2.7338x10^{6}$	$5.3874x10^{7}$	0.0513	0.9979	$1.1130x10^{7}$	$-1.7881x10^{9}$	0.0484	0.8864

Table A4.1 - Data for Equation 4.2 for HDDA-MEA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	$1.4543x10^{7}$	$5.4914x10^{7}$	0.0518	0.9860	$1.0948x10^{7}$	$6.0069x10^{9}$	0.0537	0.6414
PMP	$3.1411x10^{7}$	$1.2781x10^{9}$	0.0578	0.9981	$-1.3878x10^{6}$	$1.92074x10^{9}$	0.0484	0.9998
MeHQ	$-1.2486x10^{5}$	$1.2383x10^{9}$	0.0466	0.5095	$-6.3649x10^{4}$	$8.3976x10^{7}$	0.0371	0.8897
TBC	$-4.8539x10^{6}$	$4.9122x10^{9}$	0.0462	0.7662	$1.6855x10^{6}$	$1.3738x10^{9}$	0.0480	0.7773
BHT	$8.7657x10^{6}$	$6.4880x10^{93}$	0.0582	0.3229	$8.6364x10^{8}$	$-1.4603x10^{9}$	0.0507	0.8462
4H-TEMPO	$1.9087x10^{8}$	$2.7863x10^{10}$	0.0588	0.9575	$6.3796x10^{7}$	$-2.3037x10^{8}$	0.0542	0.9997
PTZ	$4.4782x10^{8}$	$-5.6704x10^{10}$	0.0603	0.9842	$1.9906x10^{8}$	$-1.9788x10^{10}$	0.0580	0.9990
DTBP	$6.4055x10^{5}$	$-7.2104x10^{6}$	0.0475	0.9993	$1.8732x105^{7}$	$1.0166x10^{7}$	0.0430	0.8088

Table A4.2 - Data for Equation 4.2 for HDDMA-MEA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	$1.0307x10^{10}$	$-4.6808x10^{11}$	0.0671	0.9772	$4.0584x10^{9}$	$6.5500x10^{110}$	0.0660	0.9976
PMP	$6.3354x10^{9}$	$-5.1533x10^{11}$	0.0665	0.9949	$6.9211x10^{8}$	$1.2748x10^{12}$	0.0672	0.4391
MeHQ	$1.6215x10^{10}$	$-1.4802x10^{12}$	0.0688	0.9921	$2.4220x10^{10}$	$-1.1245x10^{12}$	0.0670	0.9761
TBC	$3.2778x10^{9}$	$4.6935x10^{11}$	0.0661	0.9684	$1.0986x10^{8}$	$2.4363x10^{12}$	0.0669	0.5109
BHT	$5.5799x10^{9}$	$-4.3116x10^{11}$	0.0657	0.9897	$1.0316x10^{9}$	$5.0588x10^{11}$	0.0647	0.9128
4H-TEMPO	$2.1316x10^{11}$	$-3.1156x10^{13}$	0.0746	0.9492	$7.8890x10^{10}$	$-4.6774x10^{11}$	0.0733	0.9997
PTZ	$1.6535x10^{10}$	$-1.1522x10^{12}$	0.0681	0.9514	$1.6851x10^{9}$	$4.99232x10^{12}$	0.0671	0.2233
DTBP	$8.8977x10^{9}$	$-1.0503x10^{12}$	0.0675	0.9338	$-1.9197x10^{7}$	$1.0514x10^{12}$	0.0684	0.1191

Table A4.3 - Data for Equation 4.2 for HDDGEDA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	$2.3279x10^{9}$	$4.4711x10^{11}$	0.06514	0.9997	$6.0587x10^{8}$	$1.3558x10^{12}$	0.06487	0.8467
PMP	$4.8382x10^{9}$	$-1.9088x10^{11}$	0.0658	0.9801	$2.9467x10^{9}$	$8.2482x10^{11}$	0.0687	0.7622
MeHQ	$1.0602x10^{10}$	$-1.1205x10^{12}$	0.0676	0.9655	$1.6086x10^{10}$	$-9.1624x10^{11}$	0.0691	0.9733
TBC	$2.9169x10^{9}$	$6.9042x10^{11}$	0.0666	0.9779	$-8.1486x10^{8}$	$1.6439x10^{12}$	0.0652	0.9527
BHT	$4.8599x10^{9}$	$-4.5113x10^{11}$	0.0655	0.9478	$-1.2202x10^{8}$	$2.6462x10^{11}$	0.0597	0.4000
4H-TEMPO	$1.1971x10^{11}$	$-1.6702x10^{13}$	0.0735	0.9478	$2.4959x10^{10}$	$3.1821x10^{12}$	0.0714	0.9878
PTZ	$1.2259x10^{10}$	$-1.0183x10^{12}$	0.0673	0.9275	$1.0846x10^{9}$	$2.4591x10^{12}$	0.0665	0.8902
DTBP	$8.8886x10^{9}$	$-8.7633x10^{11}$	0.0681	0.9361	$-1.5385x10^{10}$	$1.4998x10^{13}$	0.0709	0.8244

Table A4.4 - Data for Equation 4.2 for BADGEDA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	$3.3421x10^{9}$	$2.8485x10^{11}$	0.0653	0.9975	$2.2873x10^{10}$	$-2.4050x10^{12}$	0.0685	0.9298
PMP	$1.1807x10^{10}$	$-1.3509x10^{12}$	0.0675	0.9523	$1.0847x10^{11}$	$3.6244x10^{13}$	0.0780	0.9288
MeHQ	$1.6466x10^{10}$	$-1.8355x10^{12}$	0.0691	0.9780	$6.5074x10^{9}$	$6.4205x10^{11}$	0.0686	0.9518
TBC	$2.2568x10^{9}$	$-1.4623x10^{10}$	0.0647	0.9959	$1.3008x10^{9}$	$3.8111x10^{11}$	0.0651	0.8905
BHT	$8.1008x10^{9}$	$-8.4182x10^{11}$	0.0656	0.8754	$8.0195x10^{10}$	$-1.2567x10^{13}$	0.0735	0.9351
4H-TEMPO	$8.7917x10^{10}$	$-1.1607x10^{13}$	0.0727	0.9703	$7.1863x10^{10}$	$-4.7333x10^{12}$	0.0726	0.9995
PTZ	$1.1574x10^{10}$	$1.5740x10^{12}$	0.0688	0.9580	$4.8603x10^{9}$	$8.3886x10^{11}$	0.0662	0.9369
DTBP	$3.0578x10^{9}$	$-7.5961x10^{10}$	0.0660	0.9866	$-6.3094x10^{9}$	$9.7944x10^{12}$	0.0739	0.9219

Table A4.5 - Data for Equation 4.2 for BFDGEDA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	$4.0943x10^{9}$	$-3.8202x10^{11}$	0.0625	0.9196	$4.3317x10^{9}$	$-2.9844x10^{11}$	0.0622	0.8423
PMP	$1.9240x10^{9}$	$-9.6521x10^{11}$	0.0611	0.8994	$1.2487x10^{9}$	$-1.7246x10^{11}$	0.0617	0.9650
MeHQ	$3.0273x10^{9}$	$-1.4500x10^{11}$	0.0639	0.9999	$4.3911x10^{9}$	$-3.5030x10^{11}$	0.0640	0.9768
TBC	$2.0659x10^{9}$	$-3.0847x10^{11}$	0.0609	0.9110	$1.6903x10^{9}$	$1.4053x10^{11}$	0.0617	0.8594
BHT	$2.9414x10^{9}$	$-4.7439x10^{11}$	0.0661	0.9010	$7.2505x10^{10}$	$-1.2802x10^{13}$	0.0710	0.8858
4H-TEMPO	$2.3790x10^{10}$	$-3.5691x10^{12}$	0.0667	0.9042	$2.1182x10^{10}$	$-4.1751x10^{12}$	0.0647	0.8587
PTZ	$9.4265x10^{9}$	$-1.5325x10^{12}$	0.0646	0.9158	$9.1611x10^{9}$	$-7.6128x10^{11}$	0.0647	0.8702
DTBP	$5.8234x10^{8}$	$-4.7772x10^{10}$	0.0588	0.9384	$-8.4809x10^{7}$	$1.0449x10^{11}$	0.0575	0.9529

Table A4.6 - Data for Equation 4.2 for HDDDGEDMA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	$4.8211x10^{9}$	$9.7199x10^{9}$	0.0646	0.9660	$1.3329x10^{10}$	$-1.0951x10^{12}$	0.0660	0.8799
PMP	$6.9178x10^{9}$	$-4.3984x10^{11}$	0.0650	0.8887	$1.1092x10^{9}$	$9.1372x10^{11}$	0.0657	0.9676
MeHQ	$1.0526x10^{10}$	$-4.7788x10^{11}$	0.0673	0.9708	$1.5701x10^{10}$	$-2.1392x10^{12}$	0.0670	0.9351
TBC	$5.8845x10^{9}$	$-6.3226x10^{11}$	0.0648	0.9324	$3.5504x10^{10}$	$-2.5957x10^{12}$	0.0694	0.8947
BHT	$9.4921x10^{9}$	$-1.5155x10^{12}$	0.0646	0.8825	$1.6095x10^{12}$	$-2.3132x10^{14}$	0.0798	0.9932
4H-TEMPO	$5.6742x10^{10}$	$-7.9576x10^{12}$	0.0694	0.8895	$5.7474x10^{10}$	$-1.1916x10^{13}$	0.0674	0.8407
PTZ	$2.7332x10^{10}$	$-4.2021x10^{12}$	0.0678	0.9032	$4.1475x10^{10}$	$-7.1118x10^{12}$	0.0683	0.8872
DTBP	$1.7971x10^{9}$	$-7.3761x10^{10}$	0.0626	0.9470	$-7.5477x10^{10}$	$1.0475x10^{14}$	0.0757	0.6977

Table A4.7 - Data for Equation 4.2 for BADGEDMA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	$5.9009x10^{9}$	$3.5188x10^{11}$	0.0651	0.9140	$2.1115x10^{10}$	$8.0044x10^{11}$	0.0679	0.8726
PMP	$5.2755x10^{9}$	$-6.9774x10^{11}$	0.0643	0.9614	$-1.8902x19^{10}$	$1.6170x10^{12}$	0.0560	0.7579
MeHQ	$8.9176x10^{9}$	$-1.2199x10^{12}$	0.0660	0.9716	$9.7171x10^{9}$	$-1.0684x10^{12}$	0.0670	0.9909
TBC	$6.1712x10^{9}$	$-1.0544x10^{12}$	0.0641	0.9035	$1.2011x10^{10}$	$5.1553x10^{12}$	0.0691	0.8267
BHT	$5.2654x10^{9}$	$-3.6481x10^{11}$	0.0647	0.9501	$6.8255x10^{9}$	$-2.8806x10^{11}$	0.0696	0.9695
4H-TEMPO	$5.5718x10^{10}$	$-9.1661x10^{12}$	0.0692	0.9035	$4.8279x10^{10}$	$-5.6760x10^{12}$	0.0693	0.9177
PTZ	$1.8827x10^{10}$	$-1.7648x10^{12}$	0.0682	0.9719	$1.1119x10^{10}$	$1.0685x10^{11}$	0.0670	0.9688
DTBP	$1.1823x10^{9}$	$-1.3164x10^{11}$	0.0611	0.9375	$1.0519x10^{10}$	$2.3398x10^{12}$	0.0749	0.9575

Table A4.8 - Data for Equation 4.2 for BFDGEDMA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	$1.0942x10^{9}$	$1.4268x10^{11}$	0.0625	0.9163	$7.5878x10^{6}$	$1.1496x10^{10}$	0.0560	0.3625
PMP	$2.3894x10^{11}$	$-5.2394x10^{13}$	0.0753	0.8228	$3.3572x10^{9}$	$-4.3833x10^{11}$	0.0607	0.9728
MeHQ	$1.0321x10^{9}$	$-1.3897x10^{11}$	0.0616	0.9457	$1.8326x10^{7}$	$-3.3505x10^{9}$	0.0420	0.8977
TBC	$-3.2491x10^{8}$	$5.1855x10^{11}$	0.0619	0.9903	$-1.4915x10^{6}$	$1.7102x10^{9}$	0.0507	0.8337
BHT	$9.4206x10^{8}$	$-2.3586x10^{10}$	0.0630	0.9966	$1.7996x10^{7}$	$-4.8028x10^{8}$	0.0512	0.9998
4H-TEMPO	$3.5398x10^{8}$	$4.7684x10^{11}$	0.0617	0.8253	$2.2168x10^{7}$	$2.2095x10^{9}$	0.0524	0.9997
PTZ	$4.2566x10^{9}$	$2.6621x10^{10}$	0.0670	0.9985	$1.6445x10^{8}$	$-1.1943x10^{10}$	0.0535	0.9993
DTBP	$8.5354x10^{7}$	$3.6544x10^{11}$	0.0650	0.2961	$1.1203x10^{8}$	$-7.4331x10^{9}$	0.0535	0.9958

Table A4.9 - Data for Equation 4.2 for MDI-PEA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	1.5866×10^{10}	-2.9620×10^{11}	0.0699	0.9409	-4.7428×10^{7}	5.1538×10^{10}	0.0607	0.8527
PMP	1.7900×10^{10}	-2.9711×10^{12}	0.0632	0.6906	3.1274×10^{10}	-7.3544×10^{12}	0.0571	0.7860
MeHQ	4.6869×10^{9}	-2.2398×10^{11}	0.0676	0.9800	9.6228×10^{7}	-1.4764×10^{10}	0.0484	0.9514
TBC	2.0348×10^{8}	1.8160×10^{11}	0.0638	0.7696	3.9636×10^{6}	2.7633×10^{8}	0.0492	0.9859
BHT	6.4321×10^{8}	6.5761×10^{11}	0.0660	0.1507	2.0730×10^{8}	-1.5534×10^{10}	0.0571	0.9932
4H-TEMPO	-5.7122×10^{7}	1.6909×10^{12}	0.0663	0.3381	4.0216×10^{7}	1.8642×10^{10}	0.0571	0.8904
PTZ	6.4708×10^{9}	-8.7599×10^{11}	0.0594	0.6632	6.3228×10^{7}	3.9302×10^{7}	0.0548	0.9688
DTBP	1.9440×10^{9}	2.3999×10^{12}	0.0708	0.9876	1.1130×10^{7}	-1.7881×10^{9}	0.0484	0.8864

Table A4.10 - Data for Equation 4.2 for IPDI-PEA Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	-3.4557×10^{10}	4.1442×10^{13}	0.0738	0.9629	-4.3740×10^{9}	3.7802×10^{12}	0.0616	0.7725
PMP	2.5079×10^{12}	-5.3502×10^{14}	0.0833	0.8361	2.2415×10^{9}	1.4373×10^{11}	0.0698	0.9601
MeHQ	1.5602×10^{11}	-2.1504×10^{13}	0.0775	0.9438	3.1500×10^{9}	-5.4762×10^{11}	0.0657	0.8842
TBC	-3.6098×10^{8}	6.4464×10^{11}	0.0622	0.8794	-1.9060×10^{6}	1.7487×10^{9}	0.0419	0.7894
BHT	-4.2326×10^{9}	5.1548×10^{12}	0.0662	0.8794	-5.1883×10^{7}	6.4396×10^{10}	0.0575	0.9029
4H-TEMPO	5.6299×10^{8}	7.7757×10^{11}	0.0632	0.9985	3.5809×10^{7}	-2.4869×10^{9}	0.0520	0.9979
PTZ	9.4147×10^{9}	4.0012×10^{11}	0.0697	0.9999	7.0006×10^{7}	1.9258×10^{10}	0.0565	0.9689
DTBP	-6.3523×10^{8}	1.8858×10^{12}	0.0686	0.8686	2.6560×10^{7}	-2.5509×10^{9}	0.0565	0.9378

Table A4.11 - Data for Equation 4.2 for MDI-PEM Resin

Inhibitor	Air Headspace				Nitrogen Headspace			
	a	b	c	R^2	a	b	c	R^2
HQ	$3.1275x10^{9}$	$-5.0520x10^{11}$	0.0607	0.8552	$4.2337x10^{8}$	$-6.1725x10^{10}$	0.0565	0.8780
PMP	$1.0962x10^{10}$	$-7.3492x10^{10}$	0.0675	0.8176	$2.6349x10^{8}$	$-2.8120x10^{10}$	0.0589	0.9813
MeHQ	$1.2910x10^{10}$	$-2.1788x10^{12}$	0.0671	0.9051	$1.9058x10^{9}$	$-2.6564x10^{11}$	0.0630	0.9697
TBC	$1.3759x10^{8}$	$3.0305x10^{11}$	0.0629	0.3715	$6.8659x10^{7}$	$-5.0687x10^{9}$	0.0554	0.9967
BHT	$1.8223x10^{9}$	$-1.4884x10^{11}$	0.0629	0.9602	$4.4984x10^{7}$	$1.9961x10^{11}$	0.0619	0.6717
4H-TEMPO	$-1.5197x10^{10}$	$2.2150x10^{13}$	0.0682	0.5380	$1.4311x10^{9}$	$9.0854x10^{8}$	0.0625	0.9717
PTZ	$2.2510x10^{10}$	$-1.0857x10^{12}$	0.0701	0.9662	$3.1106x10^{9}$	$4.8357x10^{12}$	0.0694	0.9647
DTBP	$1.2529x10^{9}$	$1.2484x10^{12}$	0.0687	0.9280	$1.7926x10^{8}$	$-1.8213x10^{10}$	0.0607	0.9987

Table A4.12 - Data for Equation 4.2 for IPDI-PEM Resin

A5.0 – Resin Curing

A5.1 – UV Curing

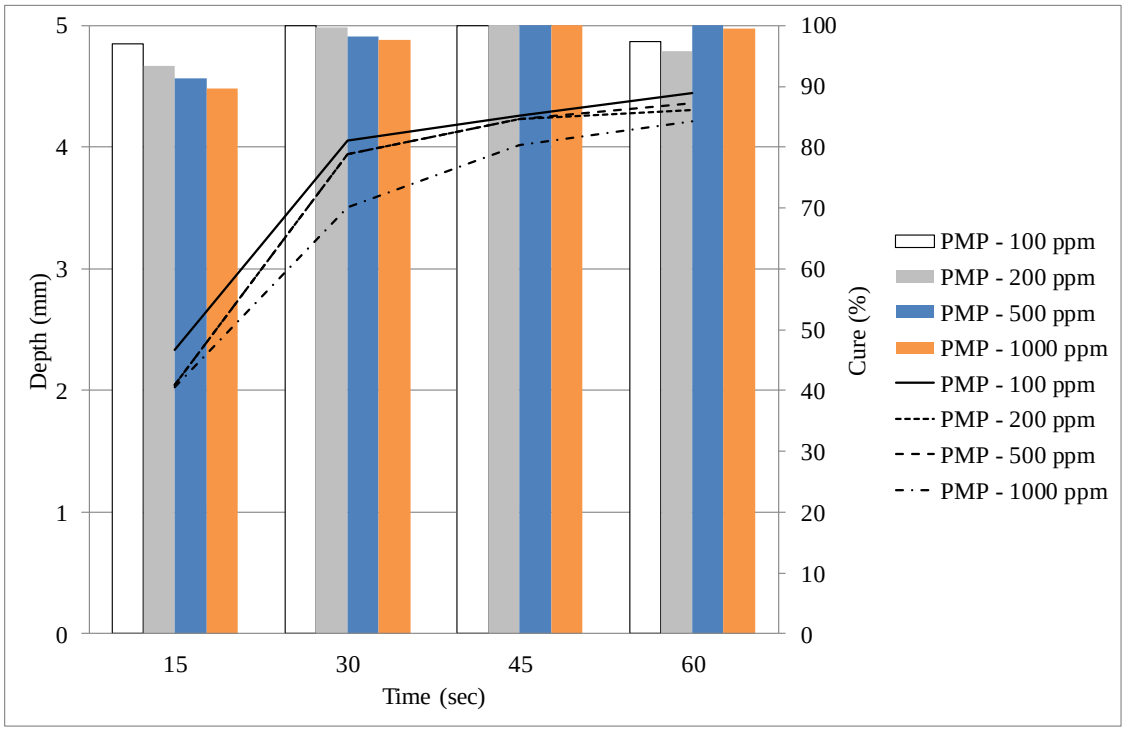

Chart A5.1.1 – BADGEDA Resin and PMP Inhibitor With 1% DMHA @ 20°C

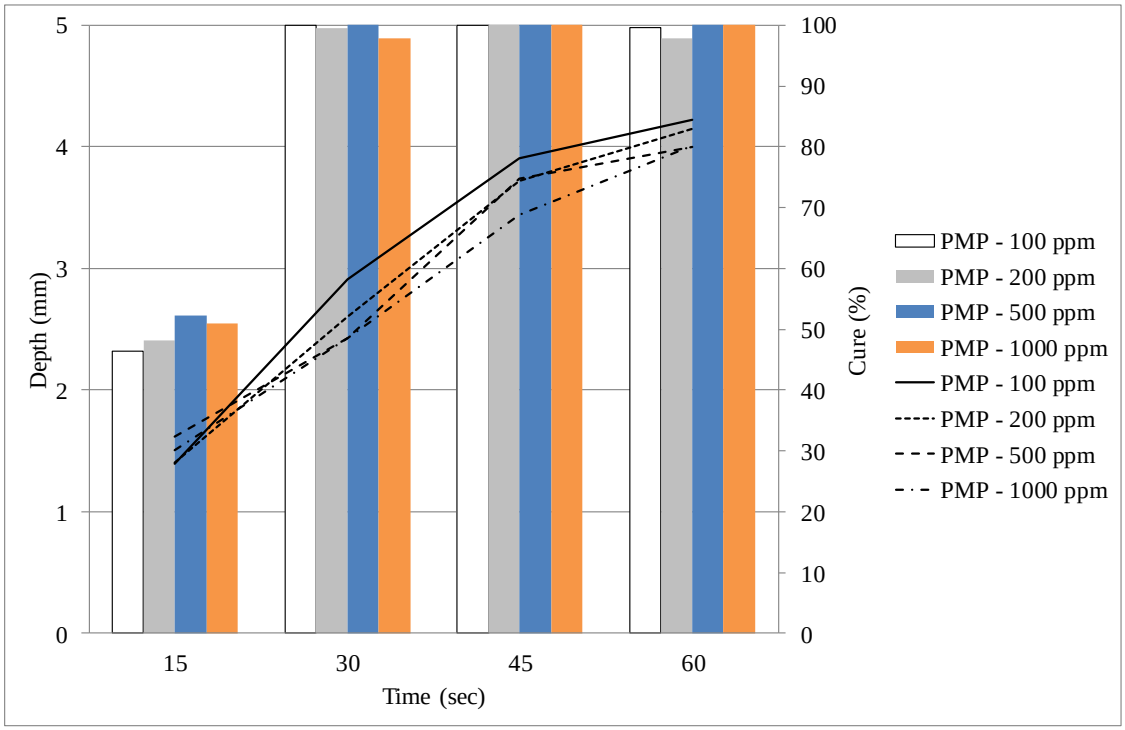

Chart A5.1.2 – BADGEDA Resin and PMP Inhibitor With 1% BP @ 20°C

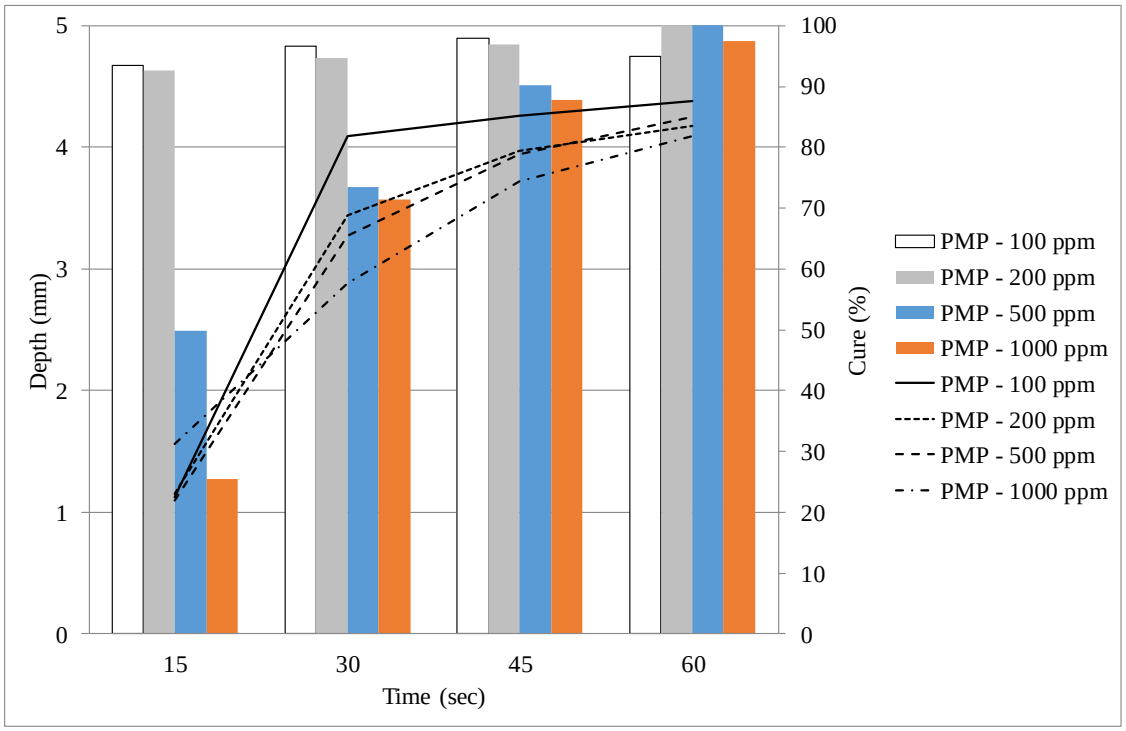

Chart A5.1.3 – BADGEDA Resin and PMP Inhibitor With 1% TPO @ 20°C

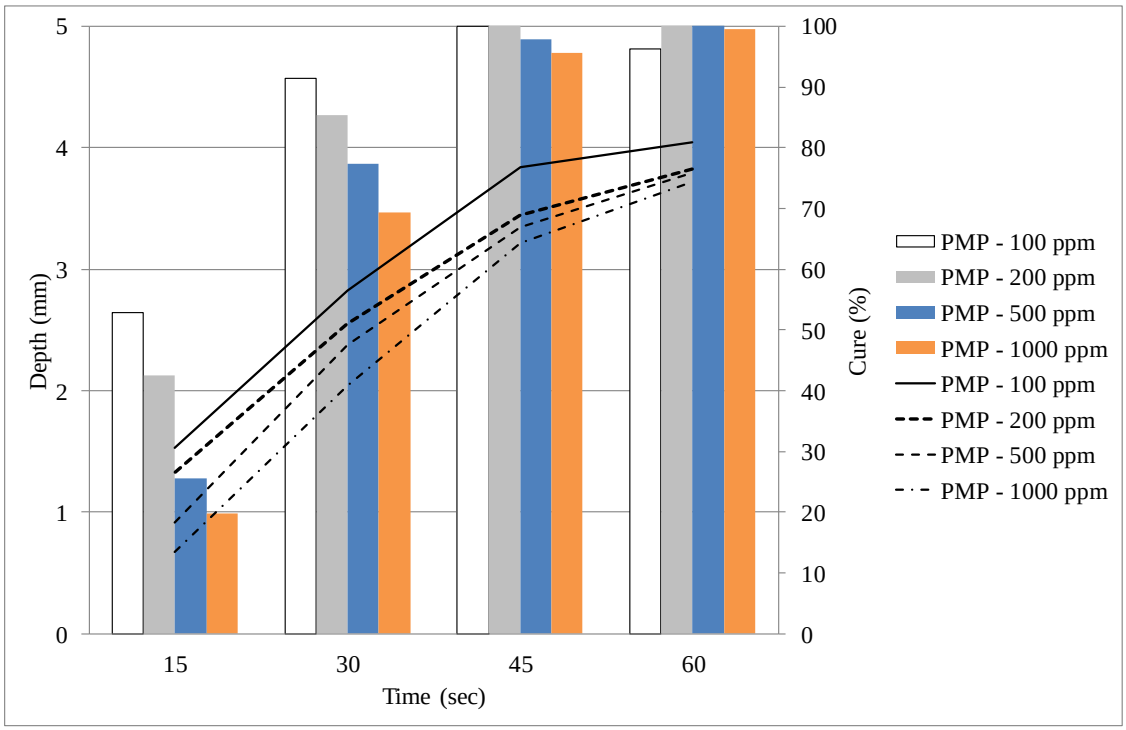

Chart A5.1.4 – BADGEDA Resin and PMP Inhibitor With 1% BAPO @ 20°C

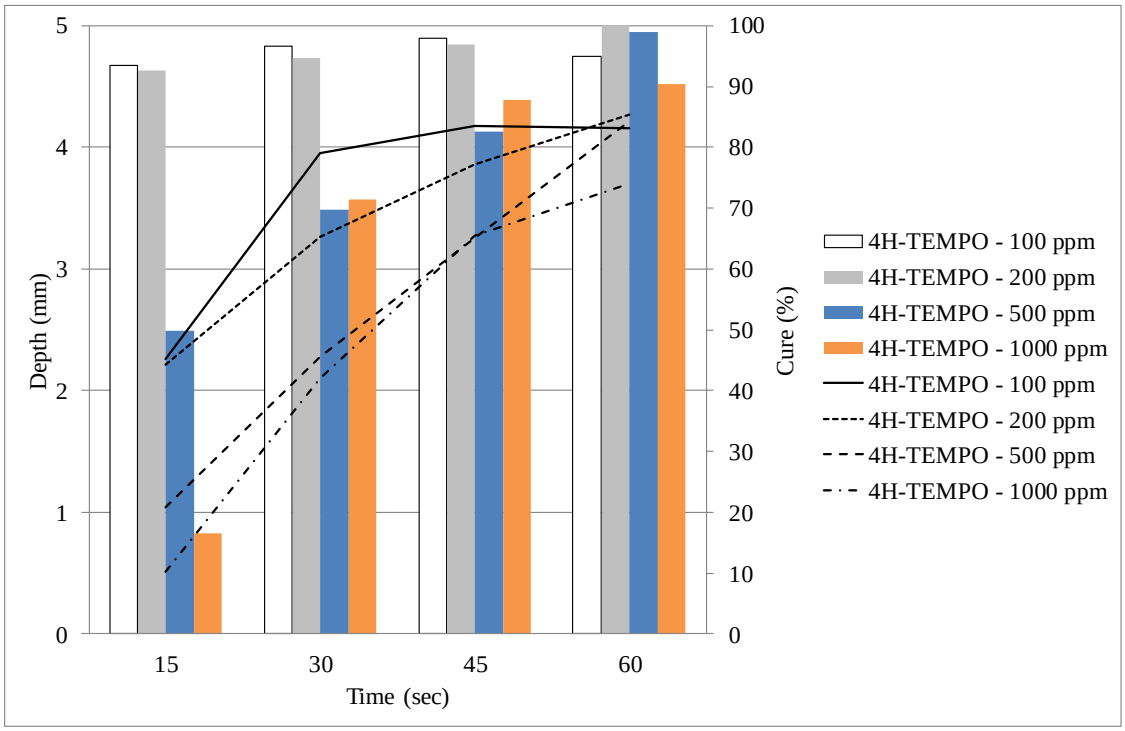

Chart A5.1.5 – IPDI-PEA Resin and 4H-TEMPO Inhibitor With 1% DMHA @ 20°C

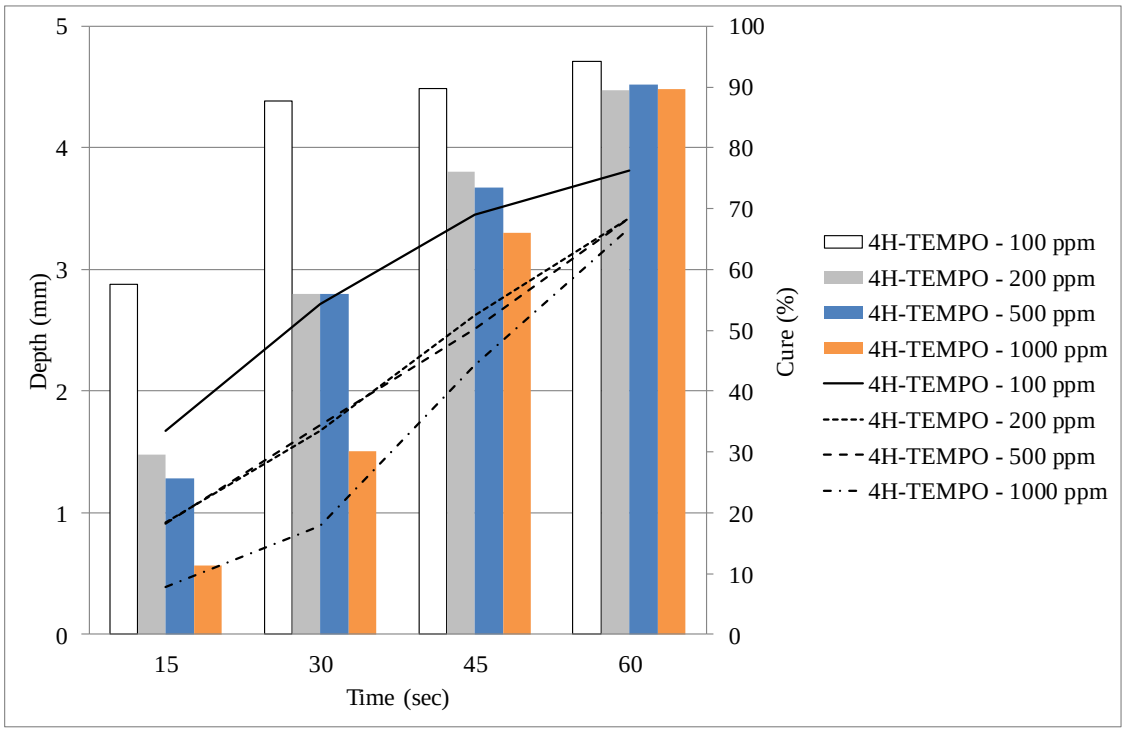

Chart A5.1.6 – IPDI-PEA Resin and 4H-TEMPO Inhibitor With 1% BP @ 20°C

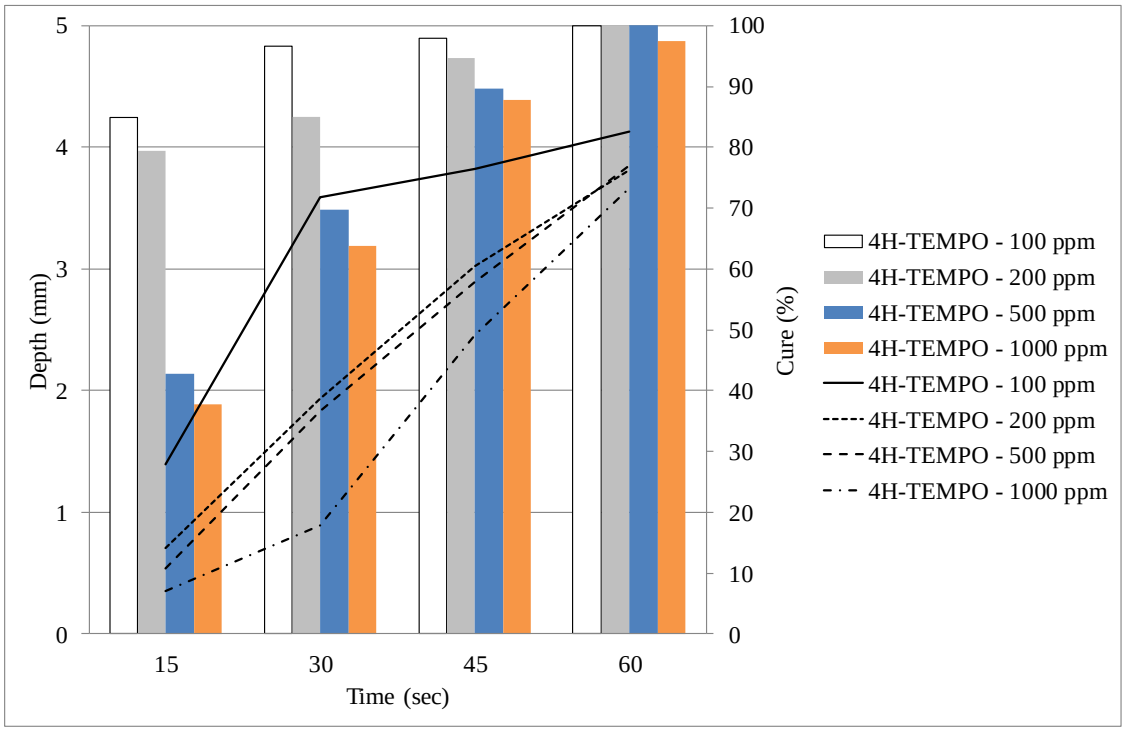

Chart A5.1.7 – IPDI-PEA Resin and 4H-TEMPO Inhibitor With 1% TPO @ 20°C

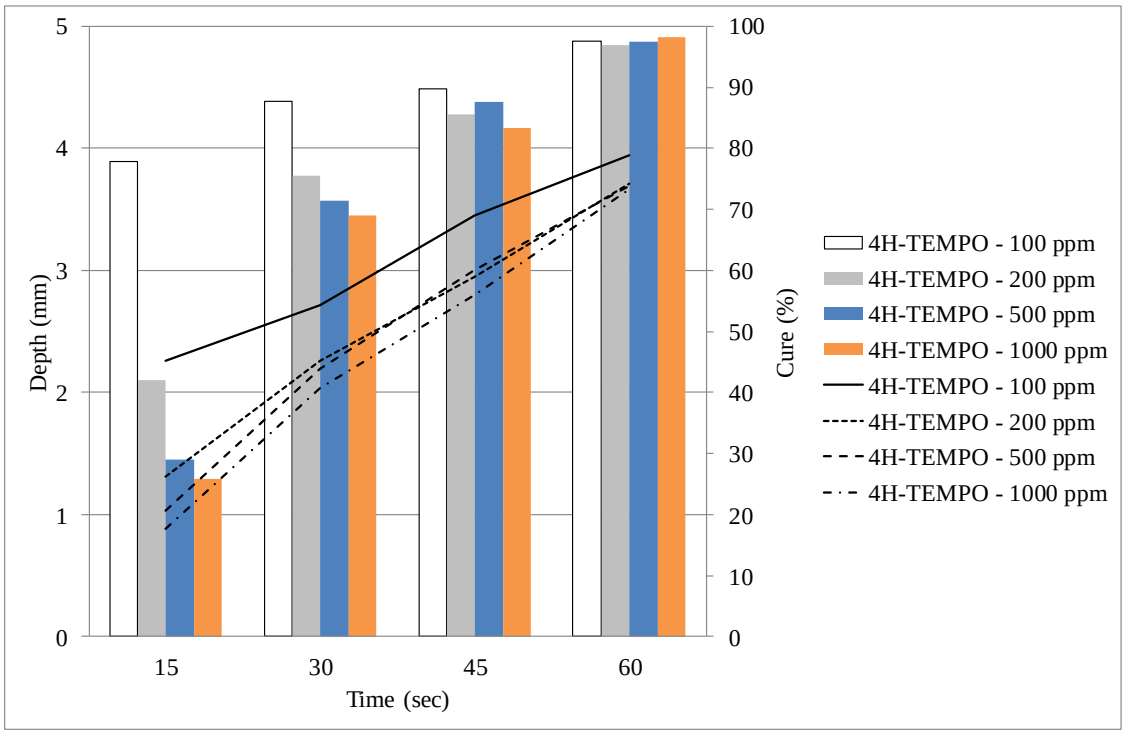

Chart A5.1.8 – IPDI-PEA Resin and 4H-TEMPO Inhibitor With 1% BAPO @ 20°C

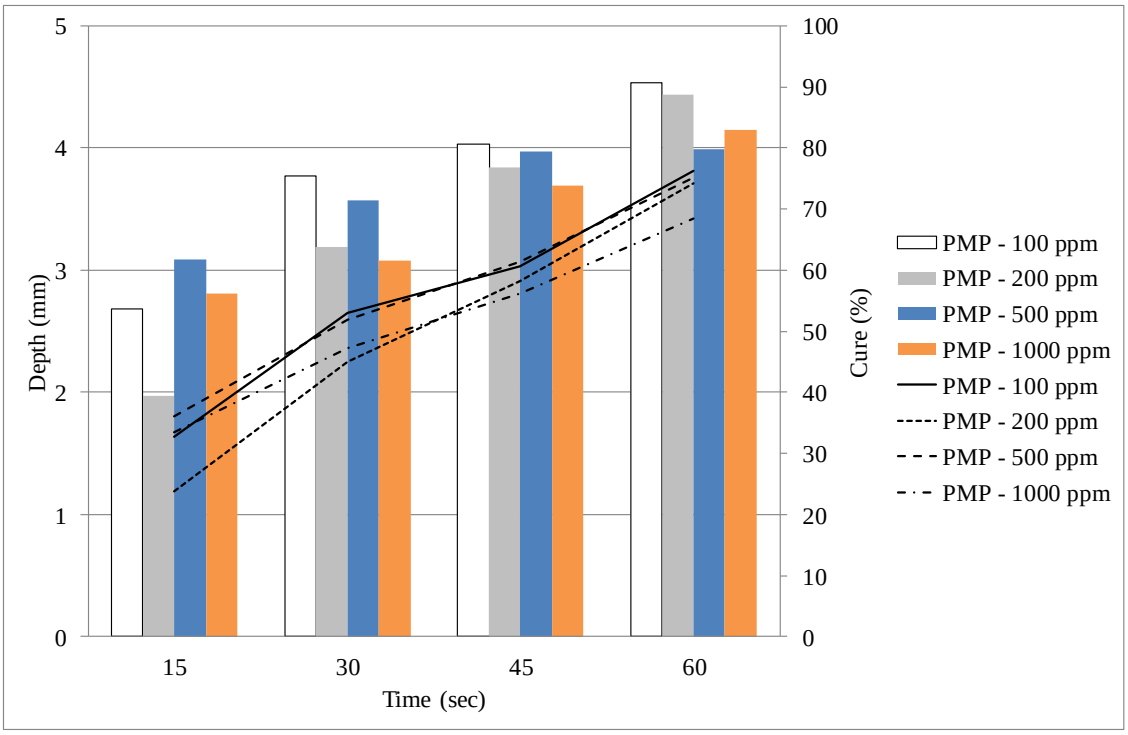

Chart A5.1.9 – IPDI-PEM Resin and PMP Inhibitor With 1% DHMA @ 20°C

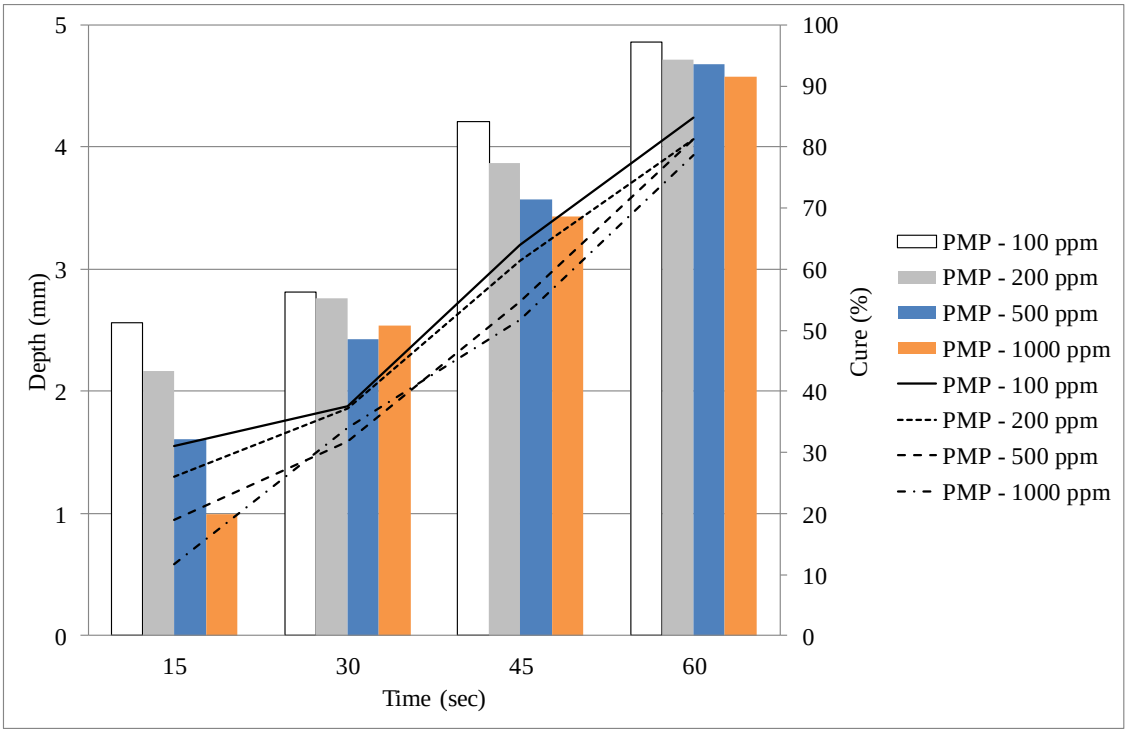

Chart A5.1.10 – IPDI-PEM Resin and PMP Inhibitor With 1% BP @ 20°C

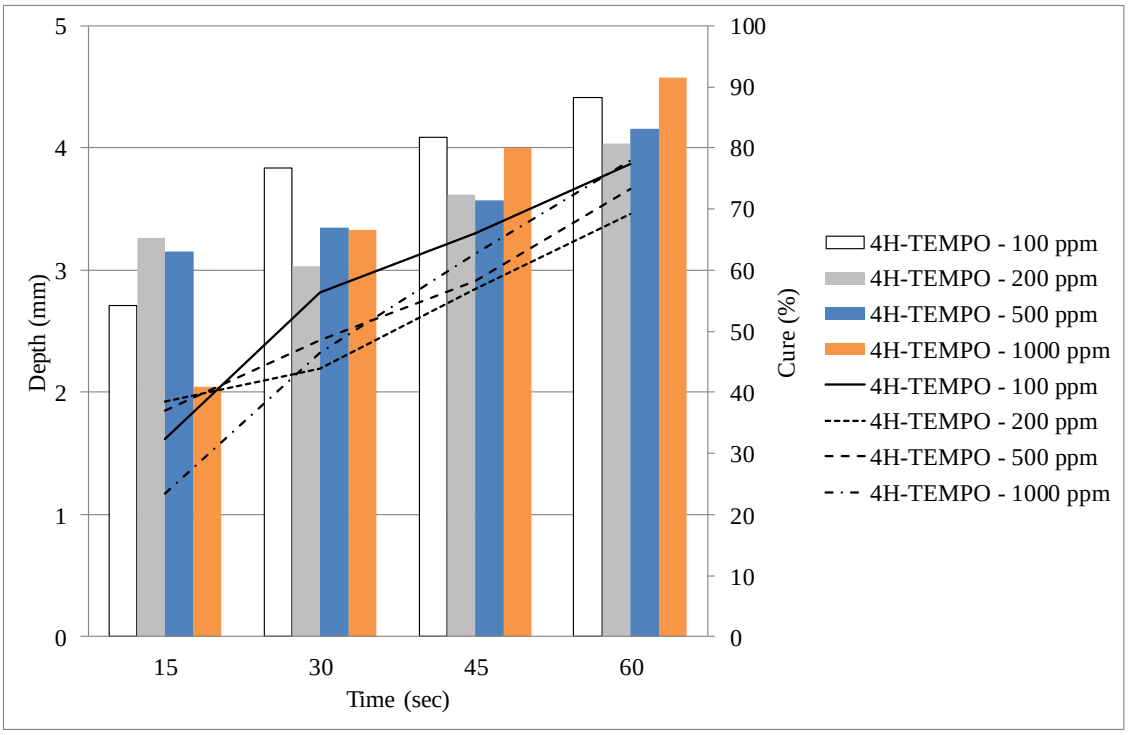

Chart A5.1.11 – IPDI-PEM Resin and PMP Inhibitor With 1% TPO @ 20°C

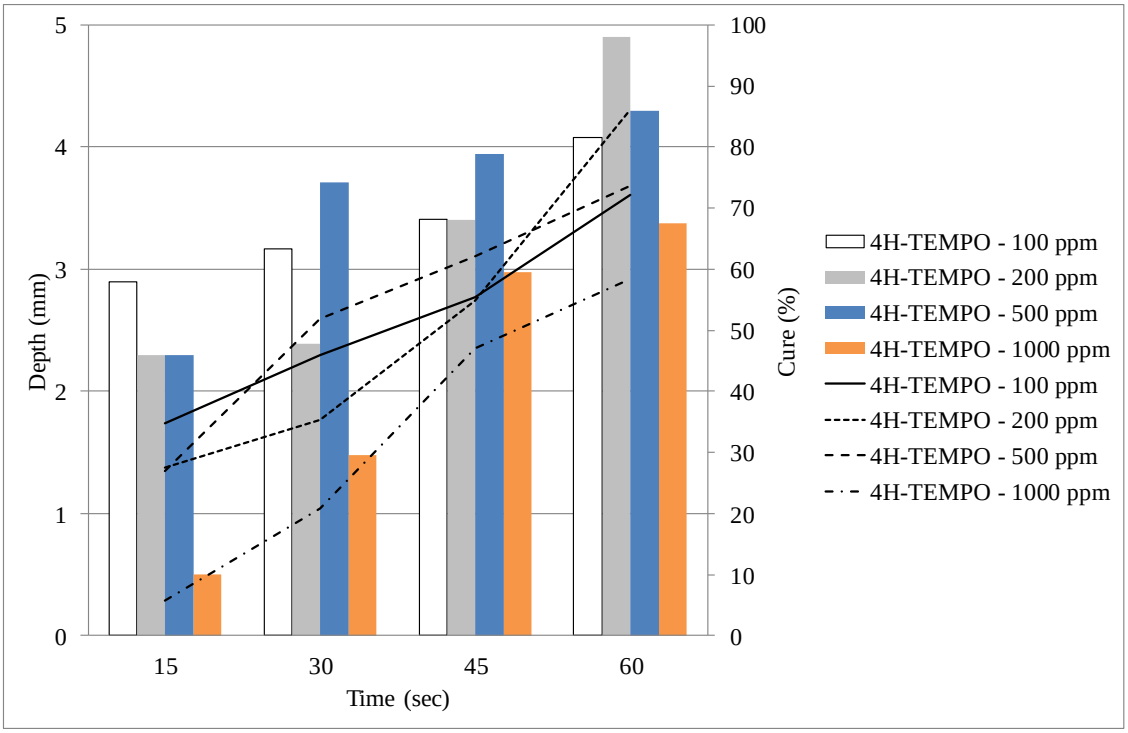

Chart A5.1.12 – IPDI-PEM Resin and PMP Inhibitor With 1% BAPO @ 20°C

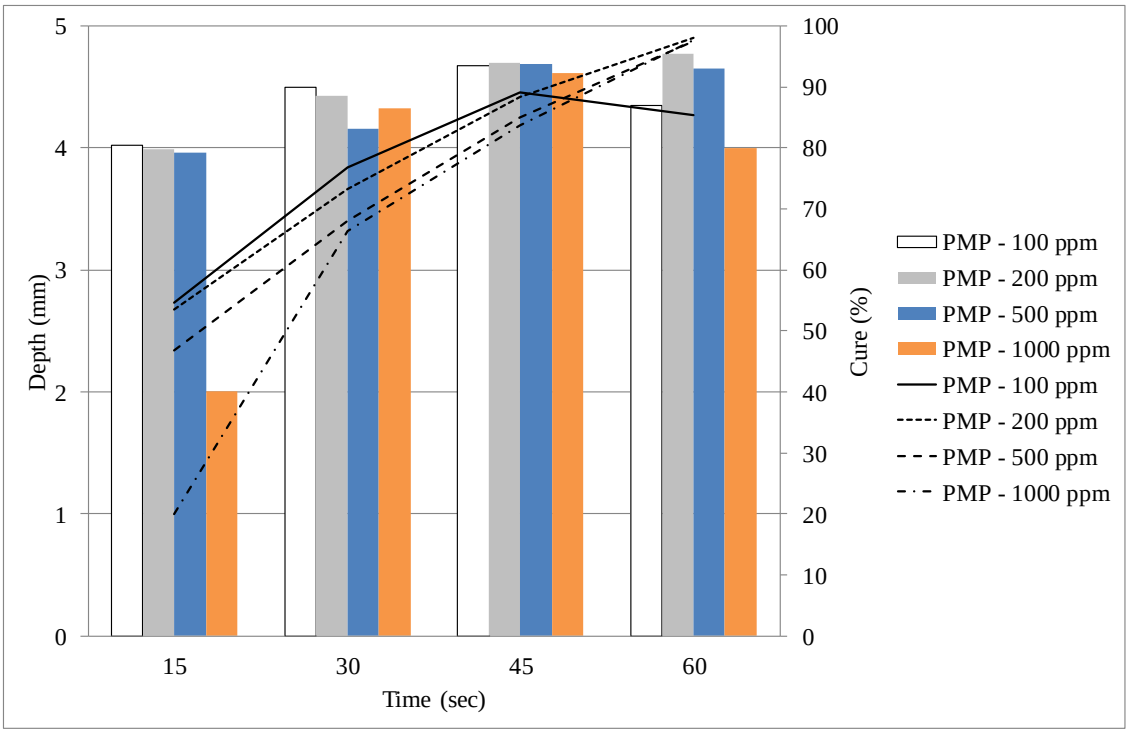

Chart A5.1.13 – BADGEDA Resin and PMP Inhibitor With 1% DHMA @ 20°C

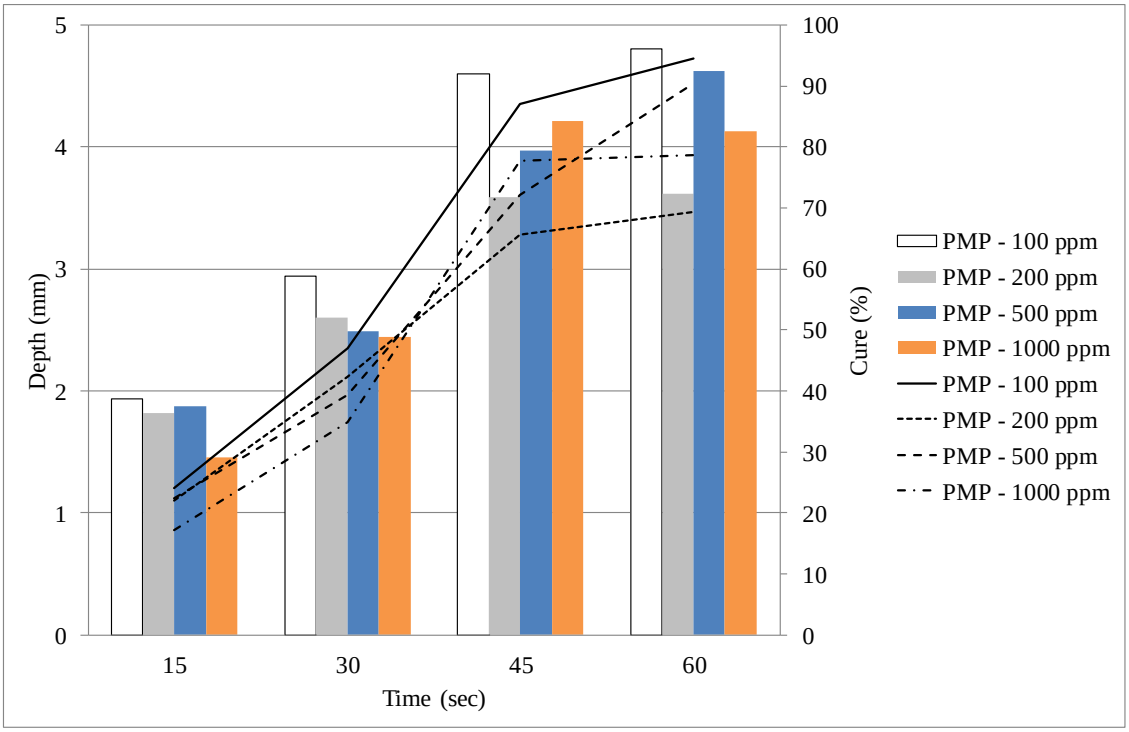

Chart A5.1.14 – BADGEDA Resin and PMP Inhibitor With 1% BP @ 20°C

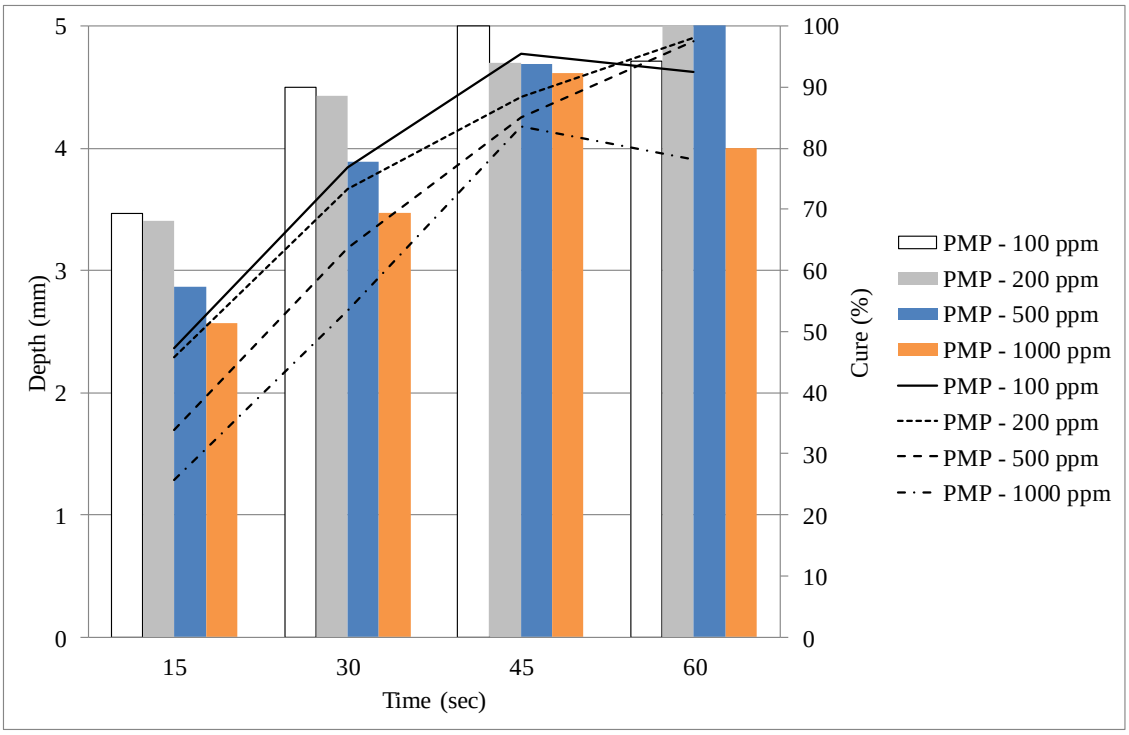

Chart A5.1.15 – BADGEDA Resin and PMP Inhibitor With 1% TPO @ 20°C

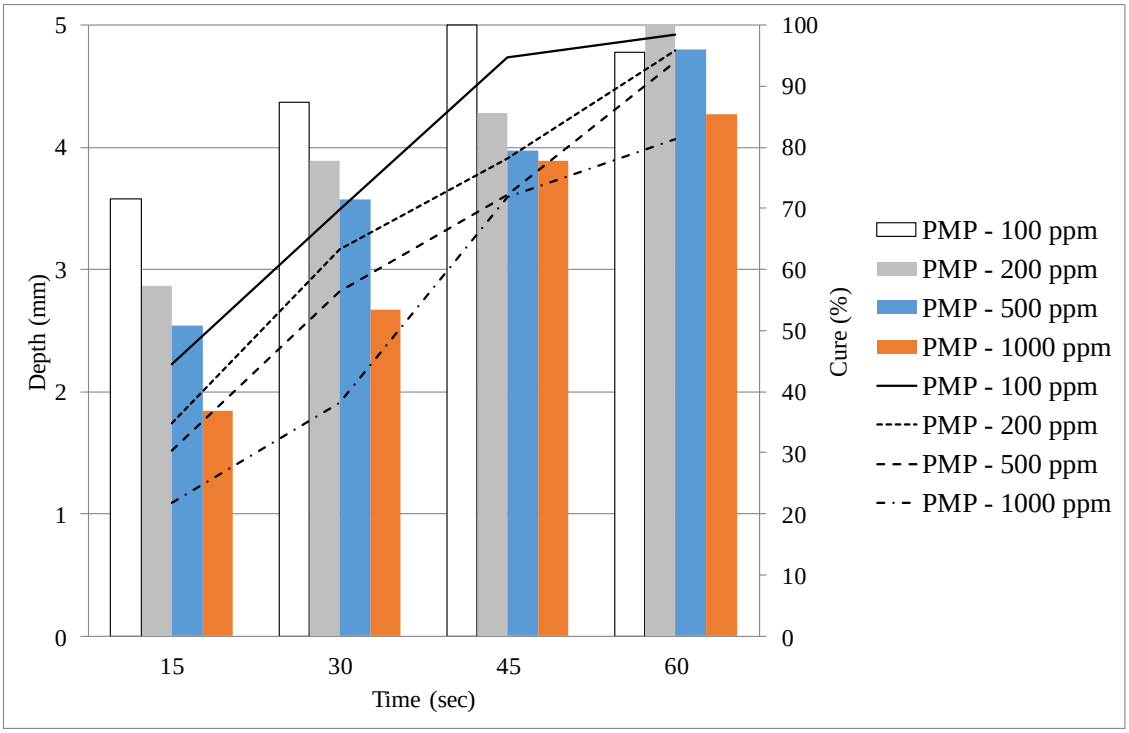

Chart A5.1.16 – BADGEDA Resin and PMP Inhibitor With 1% BAPO @ 20°C

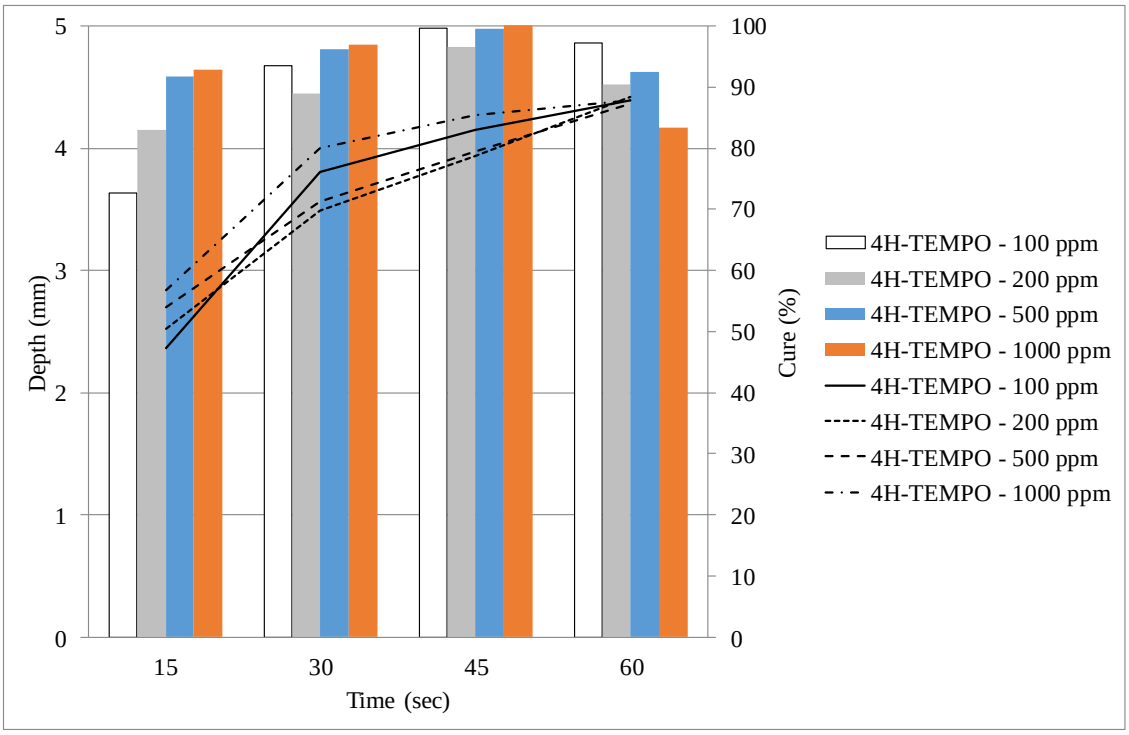

Chart A5.1.17 – BADGEDA Resin and 4H-TEMPO Inhibitor With 1% DHMA @ 20°C

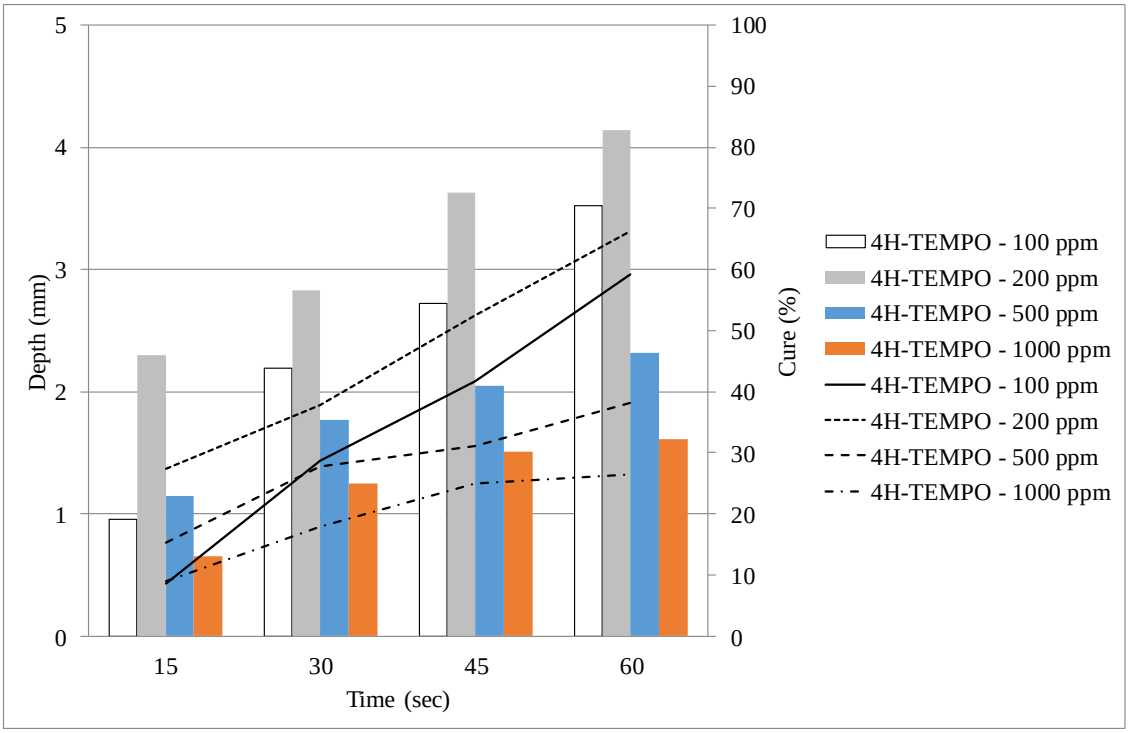

Chart A5.1.18 – BADGEDA Resin and 4H-TEMPO Inhibitor With 1% BP @ 20°C

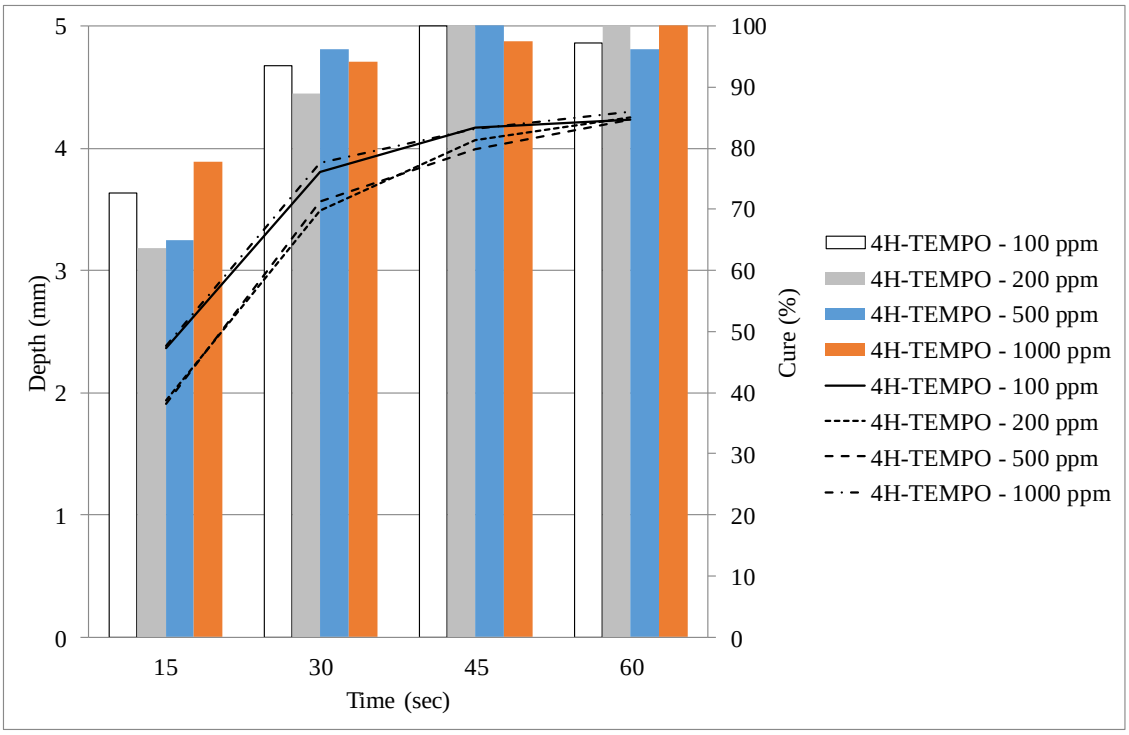

Chart A5.1.19 – BADGEDA Resin and 4H-TEMPO Inhibitor With 1% TPO @ 20°C

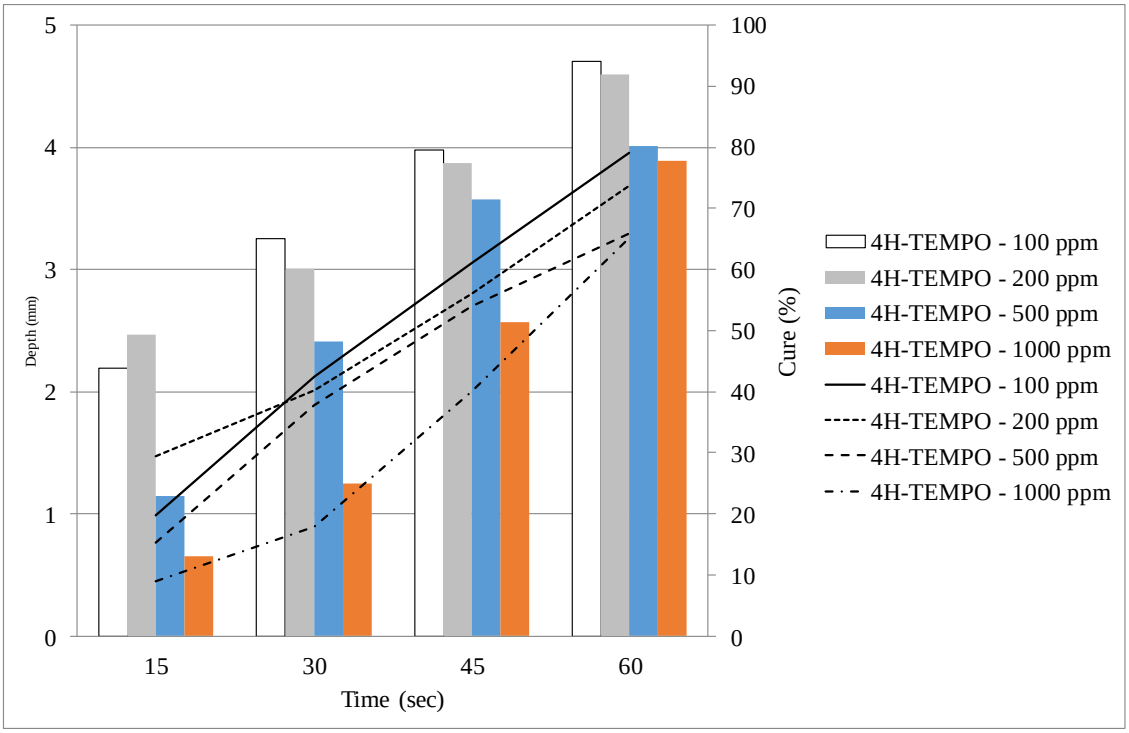

Chart A5.1.20 – BADGEDA Resin and 4H-TEMPO Inhibitor With 1% BAPO @ 20°C

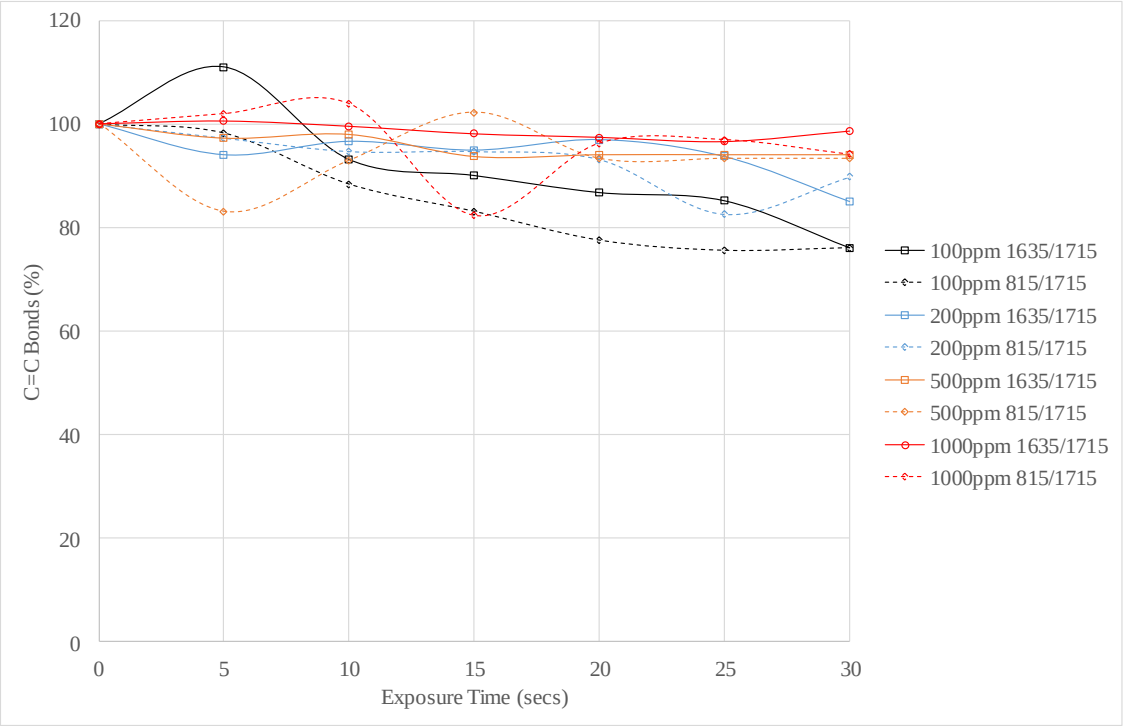

Chart A5.1.21 – UV Curing Progression of IPDI-PEA Resin and PMP Inhibitor With 1% DMHA @ 20°C

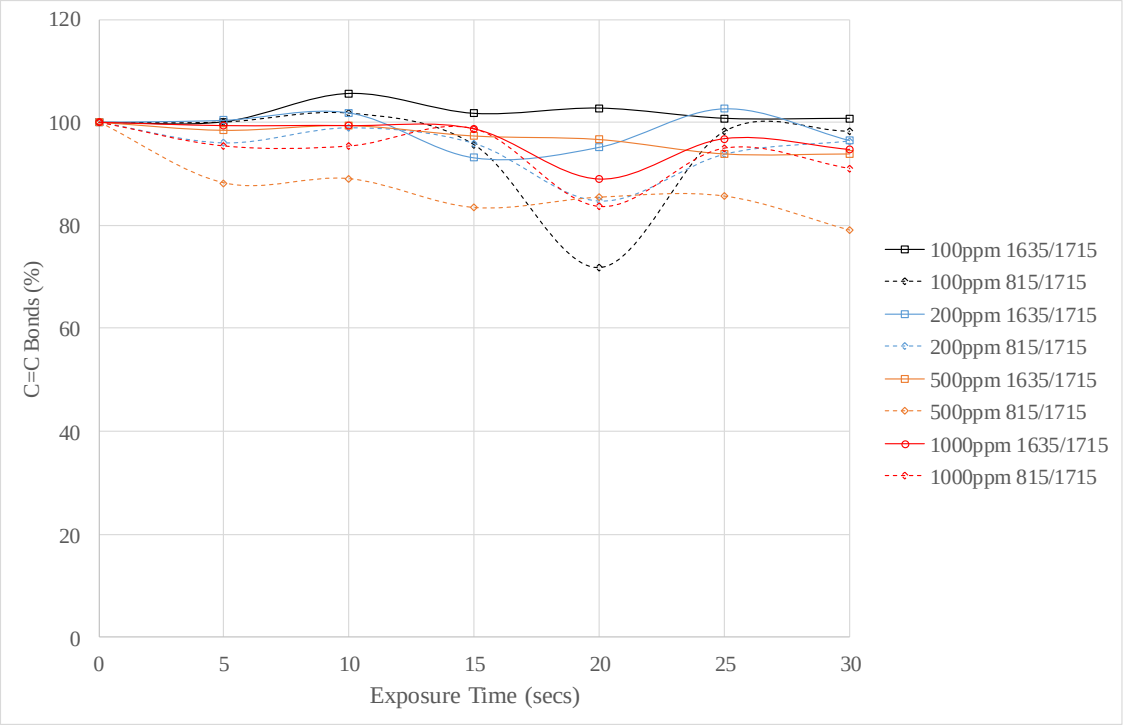

Chart A5.1.22 – UV Curing Progression of IPDI-PEA Resin and PMP Inhibitor With 1% BP @ 20°C

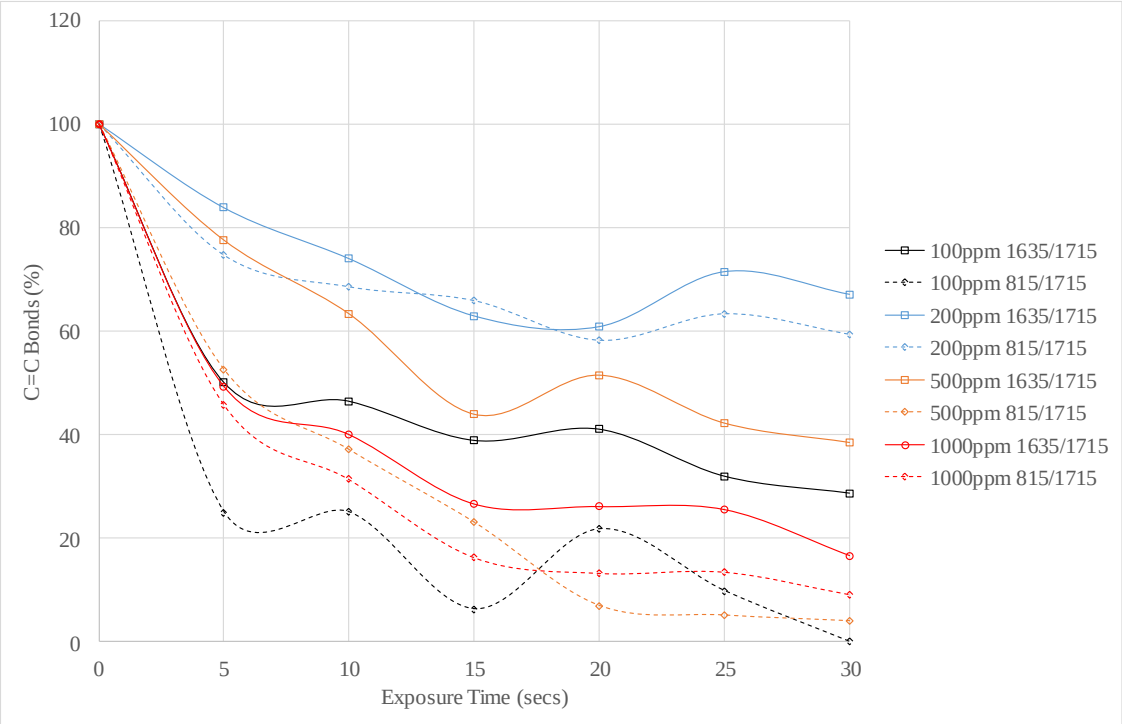

Chart A5.1.23 – UV Curing Progression of IPDI-PEA Resin and PMP Inhibitor With 1% TPO @ 20°C

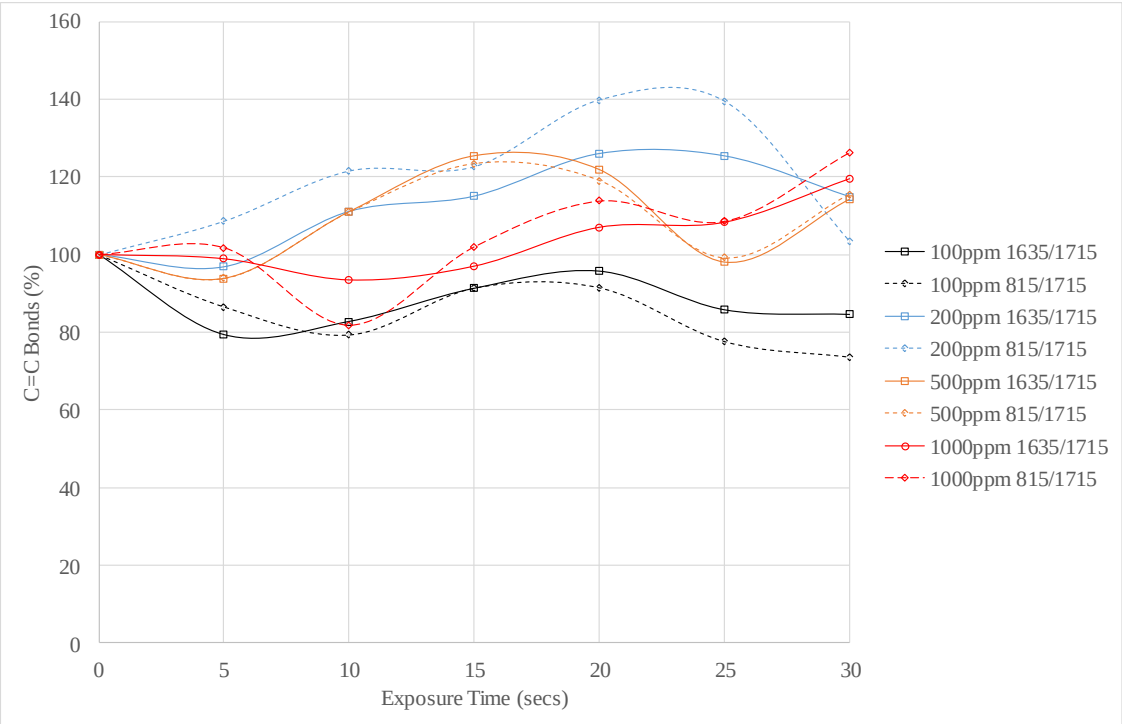

Chart A5.1.24 – UV Curing Progression of IPDI-PEA Resin and PMP Inhibitor With 1% BAPO @ 20°C

A5.2 – Peroxide Curing

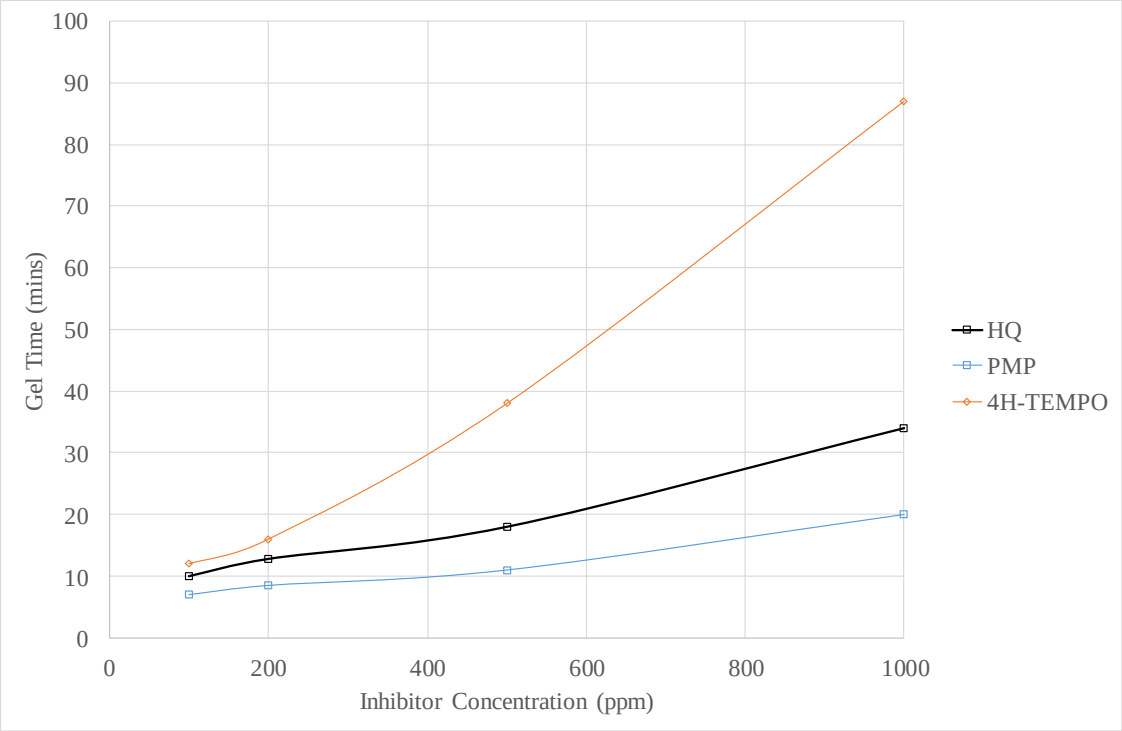

Chart A5.2.1 – Curing of IPDI-PEA Resin with 1% BPO @ 20°C – Fresh

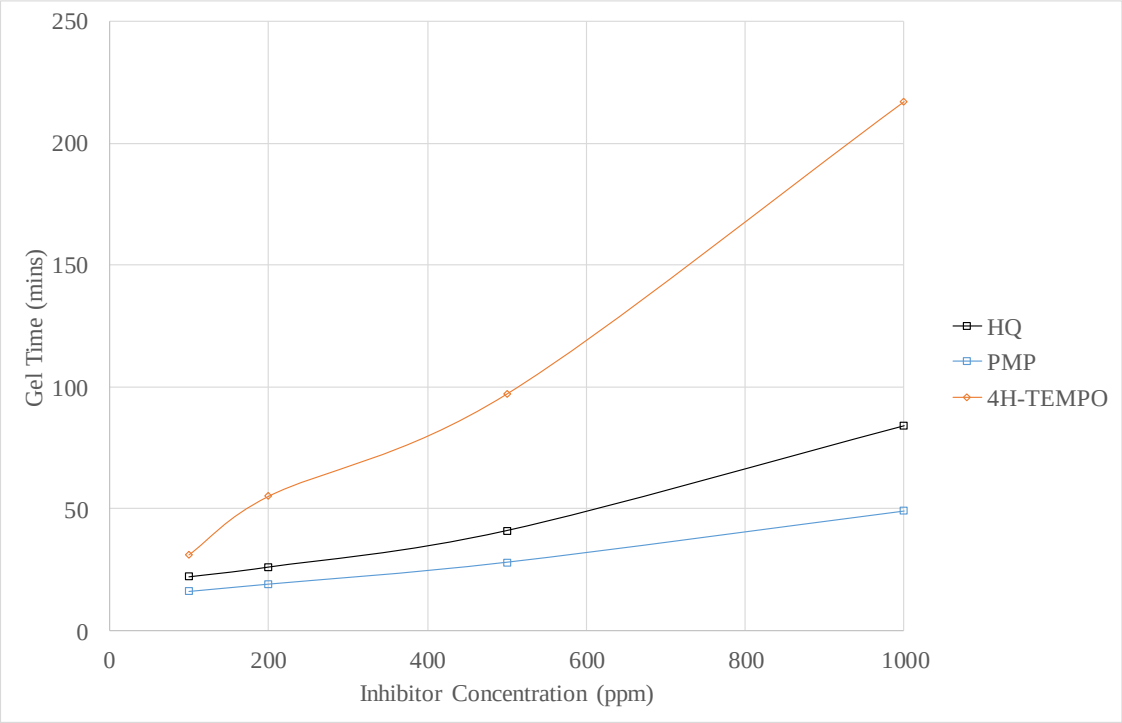

Chart A5.2.2 – Curing of IPDI-PEM Resin With 1% BPO @ 20°C - Fresh

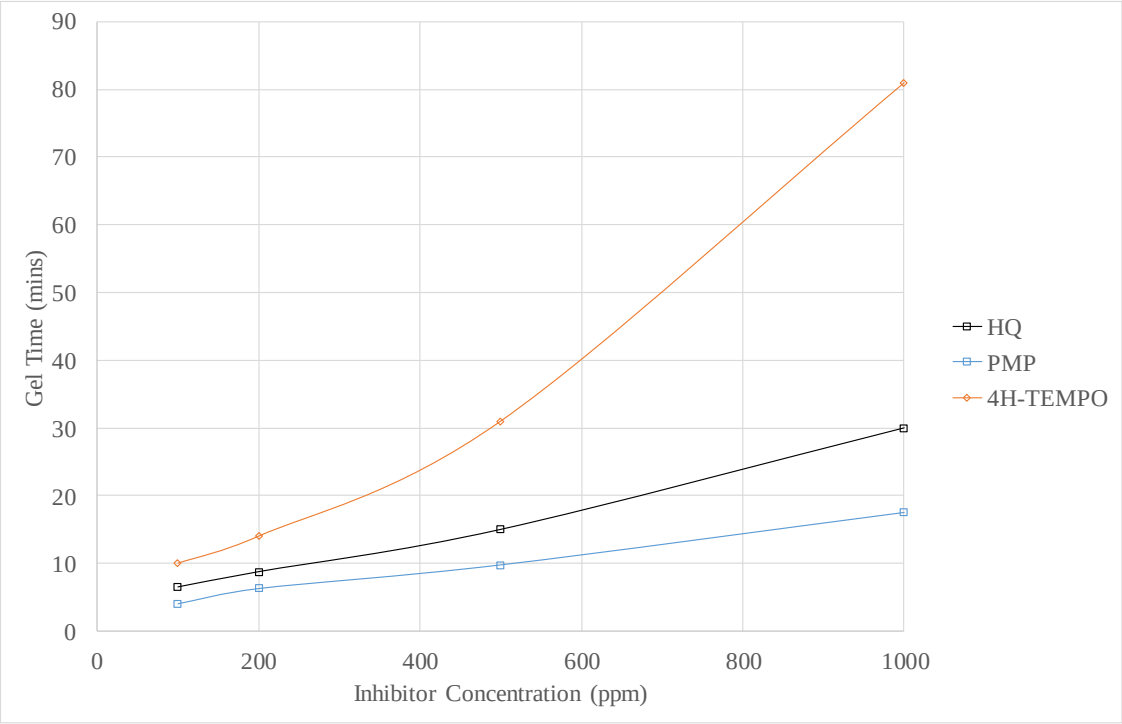

Chart A5.2.3 – Curing of IPDI-PEA Resin With 1% BPO @ 20°C – 12 Months Old

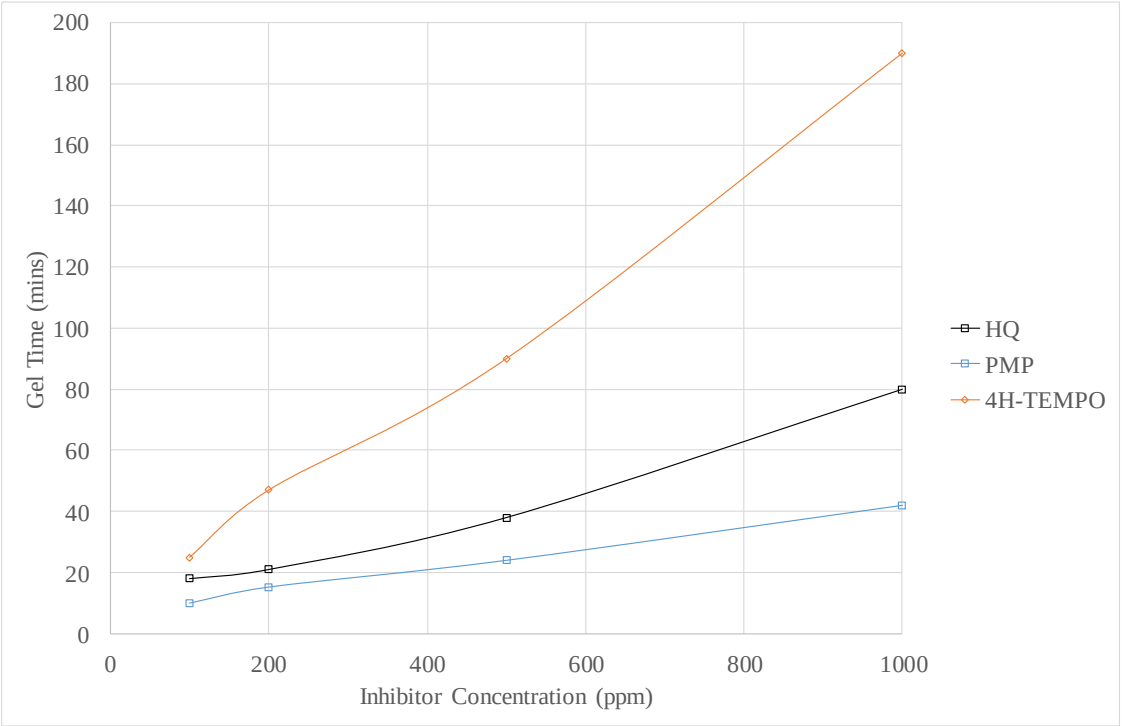

Chart A5.2.4 – Curing of IPDI-PEM Resin With 1% BPO @ 20°C – 12 Months Old

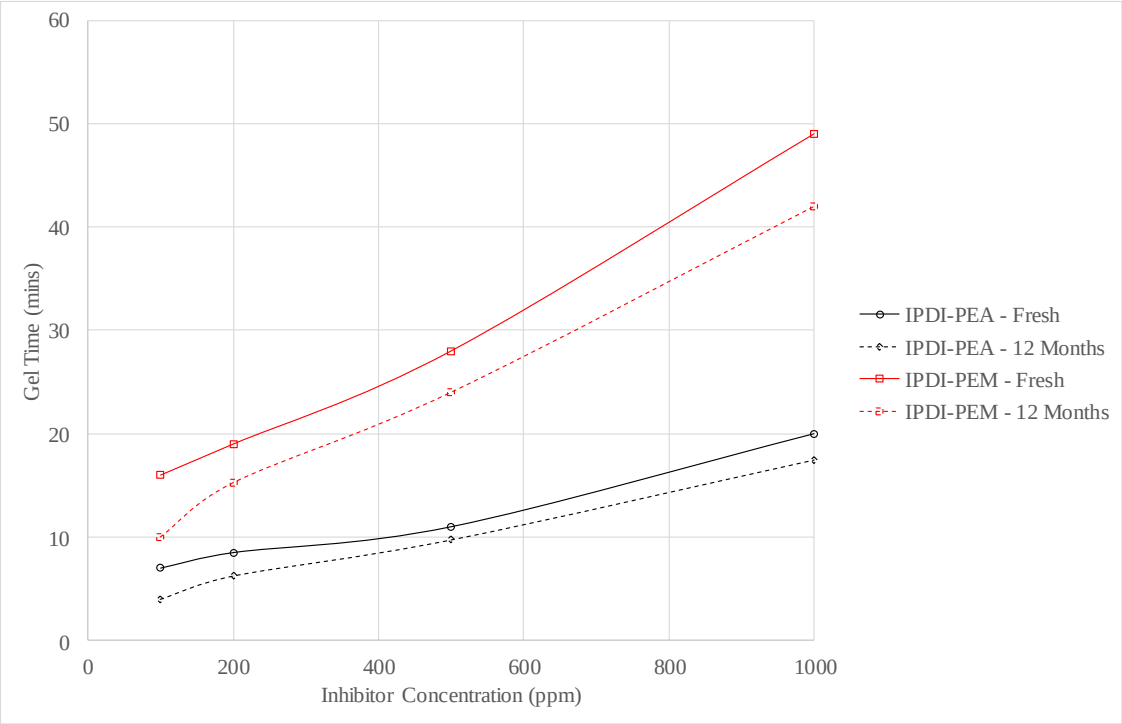

Chart A5.2.5 – Comparison between IPDI-PEA and IPDI-PEM Resins with PMP Inhibitor When Cured With 1% BPO @ 20°C