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# **CONTROLLED RELEASE OF ANTIOXIDANTS FROM SILICA HYBRIDS**

By

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A doctoral thesis submitted  
in partial fulfilment of the requirements  
for the award of the degree of  
Doctor of Philosophy  
of  
Loughborough University

September 2005

Institute of Polymer Technology and Materials Engineering

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## Abstract

Ternary hybrids based on poly(ethylene oxide) (PEO) / silica ( $\text{SiO}_2$ ) / antioxidants (AO) were produced by the sol-gel method and evaluated as slow-release antidegradants for polyamide Nylon 6.

An amount of 3-glycidyloxypropyltrimethoxysilane (GOTMS) was used to compatibilise the binary combination PEO- $\text{SiO}_2$ . The antioxidants evaluated were chosen from commercial sources representing both phenolic and amine classes of molecules. In particular the antioxidants evaluated in some depth were 3,5-di-tert-butyl-4-hydroxytoluene (BHT, the lowest molecular weight hindered phenol antioxidant), octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate (Irganox 1076) (a higher molecular weight phenolic antioxidant), bis-(2,2,6,6-tetramethyl-4-piperidyl)-sebacate (Tinuvin 770) (a sterically hindered secondary aliphatic amine stabiliser HAS), N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD, an aromatic amine antioxidant). A silica bound antioxidant was also prepared by pre-reacting 2,6-di-tert-butyl-4-hydroxymethylphenol (DBHMP) with  $\gamma$ -triethoxysilyl propyl isocyanate (TESP-NCO) to form a bifunctional urethane, compatibilising the organic antioxidant component with the inorganic  $\text{SiO}_2$  component.

The miscibility and degree of interaction of the three components was assessed by visual observation and thermal analysis (DSC). The formation of transparent mixtures was taken as indicative of miscible systems whereas the depression of enthalpy and/or reduction of melting point of either AO or PEO components was taken as evidence for the strong interactions.

The relative efficacy of such systems for the protection of thermally unstable polymers, such as polyamide, was assessed by producing laminates of polymer films containing an interlayer of cast PEO- $\text{SiO}_2$ -AO hybrid. To follow the path length of the migration of the antioxidant the hybrid film was placed between stacks of Nylon films up to 10 layers and examined by looking at the IR absorptions of hydroperoxides intermediates and carbonyl containing species resulting from oxidation in an oven at 60°C. The amount of oxidation product was decreased compared to an unstabilised polymer in the same conditions, as evidence of diffusion of AO from the organic-inorganic hybrid.

## **Acknowledgements**

I would like to thank my supervisor Dr. Leno Mascia for all his contributions and ideas over these years. His assistance and guidance were invaluable.

I would also like to thank the colleagues, the academic and technical staff at ITPME for their help, advice and support in my project.

My deepest thanks go to my family, without whose support and encouragement during my studies I wouldn't be here today.

Finally, I want to express my gratitude and affection to Gintare.

Live long and prosper.

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# 1 INTRODUCTION

## ***1.1 Sol-Gel processing***

In recent years the so-called sol-gel reactions have been extensively studied in order to improve or modify the process of producing inorganic glasses and ceramics. The development of sol-gel processing has allowed radical changes in the way the materials are prepared and in terms of the temperatures employed. The high temperatures ( $>1400^{\circ}\text{C}$ ) used for the sintering procedure in the traditional processing can be reduced to heating a sol-gel product to lower temperatures, such as  $900^{\circ}\text{C}$ . The sol-gel technique has stimulated a lot of interest in industry because of the possibility to obtain some multi-component systems not obtainable by the conventional smelting and sintering processes and for the production of silica-glasses of high purity.

## ***1.2 Organic-Inorganic Hybrids***

By mixing the precursors of the sol-gel reaction with either an organic polymer solution or a polymerisable oligomer it is possible, with a careful choice of the experimental conditions, to obtain co-continuous networks of organic and inorganic material with domain size in the nanoscale range: the resulting material is called an organic-inorganic hybrid. Phase separation may occur at the gel point, if the inorganic phase is not “sufficiently compatibilised” with the organic polymer.

## ***1.3 Antioxidants for polymers***

Organic polymers used in commercial applications as plastics necessitate a number of additives blended in during the final processing, to ensure adequate processability or lifetime properties. Examples of such additives are lubricants, pigments, flame-retardants, antistatic agents, UV stabilisers and antioxidants.

Plastics products may be exposed to aggressive environments, high temperatures and air, all of which will cause chemical reactions that will, in time, change the structure and composition of the material, affecting the structural properties and lifetime of the product. Ageing would cause the polymer to change in colour,

develop reaction products that would change crystallinity and chemical resistance, eventually chain scission would occur, losing mechanical properties and causing the material to fail. To delay this ageing, process antioxidants are commonly added to the polymer in various amount (typically in the order of up to a few percent). A number of problems are encountered, however, in the mixing of high molecular weight polymers with relatively low molecular weight additives. A major problem is the loss of additive during ageing, by evaporation or leaching. The strategies to overcome this problem vary considerably from copolymerisation and grafting on to polymer chain, to incorporating high molecular weight antioxidants.

### **1.4 Aims of the study**

Synthesis of an organic-inorganic hybrid that encapsulates an antioxidant may allow an effective solution for the loss of stabilisation activity over time. A substantial amount of low molecular weight antioxidant can be entrapped in the organic-inorganic hybrid, and this added to the polymer as filler. Mobility through the polymer would still be possible and the constitution of the organic-inorganic hybrid can be tailored to control the rate of diffusion. The encapsulated antioxidant hybrids, when incorporated in a traditional polymer system in a low percentage, would act as a slow releaser and reservoir of antioxidants into the surrounding polymer. At the same time, the antioxidant within the organic-inorganic hybrid filler may be more resistant to extraction in water and to losses by evaporation. Because the concentration of the stabilisers in the polymer is kept low at all times, it may also be possible to use very large amounts of antioxidants, as these would not be expected to crystallise out as discrete large crystals.

The manner in which the controlled release of antioxidants is to be achieved is indicated below:

- i ) Using mixtures of compatibilised antioxidant and silica, produced by the sol-gel method.
- ii ) Using mixtures of antioxidant-silica-auxiliary polymer [polyethylene oxide (or PEO)] hybrids.

Two classes of antioxidants will be examined: hindered phenol and hindered amine stabilisers.

To determine whether the objectives are achieved, model studies will be made to examine the rate of diffusion of the antioxidant from the silica and silica-auxiliary polymer hybrids.

It is to be noted that PEO has been chosen as auxiliary polymer for the production of the hybrid to encapsulate the antioxidant for the following reasons:

- a) It is proven to be compatible with siloxane precursors for the production of silica-polymer hybrids.
- b) It has a low melting and therefore will allow the antioxidant to have a high mobility at temperatures used for processing of conventional polymers. It is also useful for applications at high temperatures, such as hot-water pipes and others.
- c) It is hydrophilic in nature, and, therefore, can be used to control (enhance) the rate of diffusion from the hybrid into the polymer in aqueous environments for textile fibres applications and hot-water pipes.

## 2 BACKGROUND AND LITERATURE SURVEY

### 2.1 Sol-Gel Process[1]

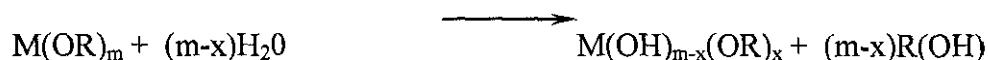
#### 2.1.1 Definitions and general principles

Revision of the terminology now offers a clear distinction between the natures of systems from the original precursor solution. The earlier terms *colloidal*, which referred to sols of dense charged oxide particles, and *polymeric*, which referred to suspensions of branched macromolecules, were found to be ambiguous, since the latter also consist of colloids. Therefore *colloidal* has been replaced by *particulate*, describing sols with a non-*polymeric* dispersed phase, formed in aqueous solutions. The use of the term *polymeric* is now preferred to describe silica sols formed solutions from the hydrolysis of metal alkoxides, not necessarily in aqueous media, with a particle size below the colloidal range limit of 1 nm [2, 3]. This limitation in size is not always applicable, especially in base-catalysed/high water content systems, but in this case the particles formed are not considered true colloidal [4].

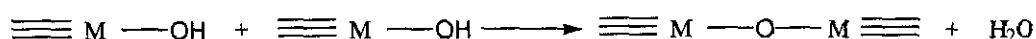
Aggregates of particles, particulate sols, under the influence of van der Waals forces, percolate in the presence of the liquid medium to form a *gel*. Base-catalysed polymeric systems with excess water, which consist of highly branched clusters that act like discrete particles, behave similarly. In contrast to these systems, acid-catalysed polymeric sols with low water contents do not form clusters but linear or branched polymers; these will entangle and cross link (with additional branching) at the gel point [2, 3]. Although these gels differ from each other because of the different types of bonding, they can all appropriately be described as substances of continuous solid skeleton enclosing a continuous liquid phase.

The chemical synthesis of oxides involves the transition of hydrolysable metal alkoxides from sol to gel. The general sol-gel reaction scheme is composed of a series of hydrolysis steps in conjunction with condensation steps.

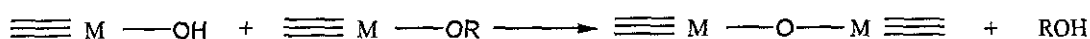
The hydrolysis reaction involves the stepwise replacement of alkoxy ligands with hydroxyl groups:



For network formation it is necessary that following the hydrolysis of the alkoxy groups, and their replacement with hydroxyls, the latter condense with each other eliminating water:



Ideally, the formation of M-OH bonds would be expected to be carried to completion before any condensation is initiated. In practice, the presence of partially hydrolysed molecules means that polymerisation reactions between  $\equiv MOH$  and  $ROM\equiv$  are also possible, releasing alcohol instead of water, according to the scheme:



Reaction intermediates formed by concurrent hydrolysis and condensation in the reaction mixture, such as dimers (i.e.  $(RO)_3M-O-M(OR)_3$ ) and trimers, are also liable to undergo further reaction.

A succession of events such as those described earlier leads to the formation of a polymeric sol, which eventually produces an inorganic oxide skeleton through a sol-gel transition. Along the skeleton can be found non-hydrolysed alkoxy and uncondensed hydroxyl groups. The concentrations of these groups in the gel depend on many variables: water content, reaction time, nature of the alkoxide, solvent, pH and thermal history. These variables are responsible for the resultant structure and the final properties of the glass produced.

### 2.1.2 Precursors

Metal alkoxides, the sol-gel process precursors, date back to the middle of last century, when Elbemen first synthesized TEOS (tetraethoxysilane or tetraethyl orthosilicate) by reacting silicon tetrachloride,  $SiCl_4$ , with ethanol. Soon after this, Mendeleyev discovered the ability of  $SiCl_4$  to form silicic acid, which subsequently was capable of condensation yielding high polysiloxanes [2].

The silicon alkoxides are the reagents of choice used in this process. There is a vast number of silicon alkoxides (alkoxysilanes) commercially available, but the most frequently used are TMOS (tetramethoxysilane) and TEOS. The latter, often the main source material for single silicon oxide systems, is a colourless liquid with a density of about  $0.9 \text{ g/cm}^3$  and is extremely pure when distilled [5].

The starting sol-gel mixtures of TEOS typically consist of the alkoxide, water and a solvent to allow complete miscibility. The latter is commonly an alcohol, often ethanol. To control the relative and absolute rates of hydrolysis and condensation reactions, a catalyst is also used. This is either an acid or a base. The reaction temperatures employed range from sub-zero to approximately  $90^\circ\text{C}$  [2].

In addition to tetralkoxysilanes, other components of sol-gel precursors include organofunctional alkoxysilanes. Alkyl-substituted alkoxysilanes or organoalkoxysilanes [2], are useful for modifying the polymer network because of the presence of the non-hydrolysable groups. They are also used when the introduction of organic matter within the network is required.

Also known as *coupling agents*, these silanes are primarily used as “connectors” between an organic resin matrix and mineral reinforcement (fibres and fillers) to improve the properties of composites [6]. The polymer-filler bond is achieved on one side via the alkoxy component, which attaches the molecule to the mineral surface through condensation with pendant silanes and, on the other side, through interactions of the organofunctional group with the polymer. The occurrence of copolymerisation reactions at the interphase leads also to the formation of *interpenetrating networks* (IPNs) [6, 7].

To enable the coupling agent to exert its function, the nature of the organofunctional group is varied according to the chemical nature of the matrix and the service conditions.

### 2.1.3 Hydrolysis and condensation mechanism

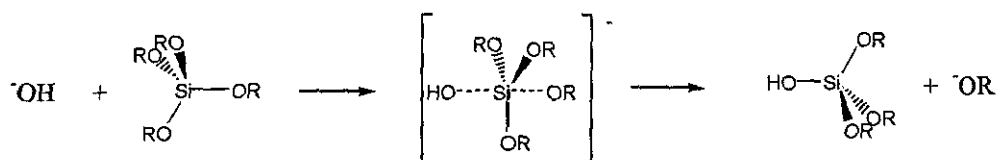
Alkoxysilanes undergo hydrolysis and condensation reactions in the presence of water; ultimately leading to the formation of silanes. However hydrolysis and condensation reactions are neither sequential nor they will always go to completion.

An alternative representation emphasises the existence of intermediate siloxane compounds and redistribution equilibria, where reaction by-products are consumed to produce a variety of species. This was proposed by Yoldas [8]. The suggested form of these species was  $\text{Si}_n\text{O}_{[2n-0.5(x+y)]}\text{OH}_x(\text{OR})_y$ , where  $n$  is the degree of polymerisation and,  $x$  and  $y$  are the respective numbers of terminal groups.

The hydrolysis reaction mechanisms presented here for tetraethoxysilane were suggested by Aelion *et al.* [9]. The mechanisms were later elaborated by Keefer [10], as shown below.

### i) Base-catalysed hydrolysis

The process involves nucleophilic substitution. The hydroxide nucleophile coordinates with the silicon, forming a transient intermediate trigonal-bipyramid; the alkoxide group positioned at the opposite site becomes the leaving group. The ethoxide ion is expected to react quickly with water to produce a new free

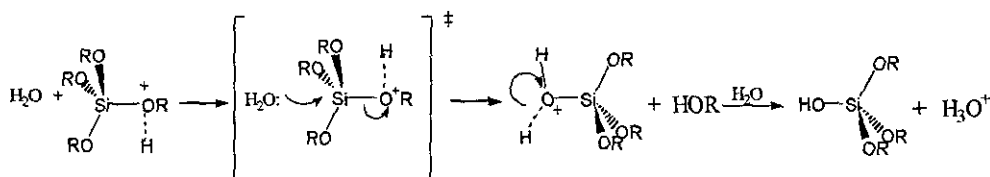


**Figure 2-1 Mechanism of base-catalysed hydrolysis by nucleophilic substitution;  $\text{R} = \text{H}, \text{Et}$  or  $\text{Si}(\text{OR})_3$  [after Iler]**

hydroxyl:

### ii) Acid-catalysed hydrolysis

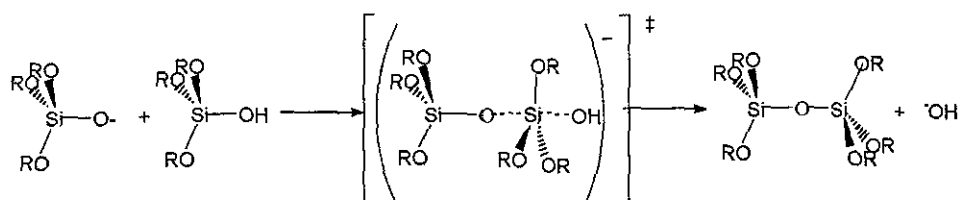
This takes place as an electrophilic reaction. The hydronium ion approaches the tetraethoxide molecule to form an activated complex.



**Figure 2-2 Mechanism of acid-catalysed hydrolysis by electrophilic reaction [after Iler]**

### iii ) Condensation catalysed in the pH range 3 - 12

Proposed by Iler [11], condensation in the pH range 3-12 is a nucleophilic substitution reaction, where a protonated silanol is attacked by a deprotonated silanol (the nucleophile), to form a  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  linkage, displacing a hydroxyl in the



**Figure 2-3 Mechanism of condensation by nucleophilic substitution [after Iler]** process.

### iv ) Condensation catalysed in acid conditions

In high acidic environments ( $\text{pH} < 3$ ), the mechanism of condensation changes from nucleophilic to electrophilic, where the least acidic unit available (i.e.,  $\text{Si}(\text{OH})_4$ ), is protonated to become the electrophile [10-12].



**Figure 2-4 Mechanism of condensation by electrophilic substitution. [after Iler]**

## 2.1.4 Factors affecting the hydrolytic polycondensation reactions

### i) Catalyst

The nature of the catalyst determines the relative rates of hydrolysis and condensation reactions. As is known [13], acid catalysts promote a fast hydrolysis, resulting in a rapid TEOS conversion, in contrast to the nucleophilic catalysis, which decreases the rate of hydrolysis and increases the rate of condensation; this results in less hydrolysed products.

Hence the degree of conversion of alkoxyasilanes, leading to the formation of Si-O-Si bonds, increases more quickly in basic than in acid environments.

Aelion *et al.* [9] concluded that the rate and extent of TEOS hydrolysis are greatly influenced by the dissociation constant and concentration of the acid or base catalyst. The condensation rate in the presence of HCl is proportional to the concentration of the acid. On the contrary, they found very low rates of reaction with weak acids. The same conclusions were also reached by Cihlar [14] who investigated strong acids such as HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, toluenesulphonic acid and weak acids such as formic and acetic. The weak acids were found not to be as efficient catalysts as the strong ones, but they did produce reasonable extents of hydrolysis in presence of 12,5 vol.% water.

Regarding the hydrolysis under basic conditions with NaOH catalyst, Aelion *et al.* have reported a first order kinetics with respect to TEOS in dilute solution, although at higher concentrations of monomer the reaction was complicated by the formation of insoluble polysilicates. Weaker bases such as NH<sub>4</sub>OH and pyridine were only effective as catalysts at higher concentrations. Also, in comparison to acid-catalysed hydrolysis, their results revealed a more pronounced dependence of the base-catalysed hydrolysis on solvent nature.

Mascia *et al.* [13] have studied the effects of catalysts belonging to three different classes of catalysts on the condensation of silanes: acid [TSA (p-toluenesulphonic acid monohydrate)], neutral [DBTDL (dibutyltindilaurate)] and basic [BDMA (benzyltrimethylamine)]. The catalysed TEOS polymeric structures were studied with SAXS. Basic catalysts lead to typical compact structures, while catalysis by

DBTDL (pH neutral) lead to more homogeneous structures and more optically transparent gels, similar to those produced under acid catalysis. This effect is a result of a relatively slower hydrolysis and monomer consumption with respect to the condensation. The monomer is available for condensation even at a late stage, in contrast to the acid catalysis where it is consumed very quickly.

## ii) pH of solution

In reactions under basic conditions the successive hydrolysis steps are faster, since the silanols replacing the alkoxy groups on the silicon are more acidic and that makes the molecule more prone to attack by hydroxide ions <sup>[10-12]</sup>. A slow hydrolysis generates silanols that are immediately used up by fast condensation, leaving no intermediates in the reaction medium. Therefore it is not surprising that a large proportion of the alkoxy groups remain unreacted up to the point of gelation [15].

Although the base-catalysed hydrolysis of TEOS is predicted to be a first order reaction, this is verified only when the catalyst-to-silica concentration ratio is high. This is because the acidic silanol groups, generated during the hydrolysis, tend to neutralise the base, thereby reducing the effective rate of reaction [10-12]. As Keefer [12] explains, at high pH, although condensation is fast, the rate of production of SiO<sub>2</sub> is slow. Owing to the high solubility of the intermediate species, there will be low level of super saturation, which produces only a small number of large silica nuclei. These nuclei are the preferred sites for further precipitation of reacted species leading to the formation of dense clusters. This type of growth process is known as *Ostwald ripening*.

Acid-catalysed hydrolysis produces weakly cross-linked or linear polymers. This is attributed to the high reactivity of species with a low degree of hydrolysis (due to their higher electron density) [10]. When these undergo condensation, a large number of unreacted sites remain in the newly formed network. In contrast to basic hydrolysis, acid hydrolysis is a heterogeneous reaction, with products being produced at different stages of the reaction [16], giving rise to a wide distribution of different degrees of condensation [15]. Assink *et al.* [15] support the general belief that the overall kinetics of the acid-catalysed reaction of TMOS is

determined by the slow condensation step, which is also responsible for the presence in the medium of a wide number of intermediates (detected by NMR).

It has been argued by Keefer [10] that there are ways of increasing the cross-linking density of the silicate network structure formed under acidic conditions. One is by reducing the pH to a limit of  $\sim 2$ , where hydrolysis is at its maximum rate. The effect of speeding up hydrolysis at the expense of condensation would be for more silicate to reach a more advanced state of hydrolysis, therefore acquiring a greater number of active sites capable of cross linking.

In acidic environments, an important issue is the reversibility of reaction. Under mild acidic conditions, and in the presence of excess solvent, re-alkoxylation is possible, converting silanols (especially the well-hydrolysed ones [16]) back to the alkoxy [10, 17] irrespective of the degree of condensation. If the pH is not sufficiently low, the silanols are neutral and become liable to attack. Re-alkoxylation is, therefore, the main reason for the higher amount of residual organic matter in acid-catalysed gels than in base-catalysed gels [10].

### iii) Water

Simple stoichiometry clearly show that the minimum ratio water/alkoxide ( $r$ ) required for hydrolysis to go to completion is 2, a conclusion supported by theoretical models [18]. According to Yoldas [19] at  $r = 4$  orthosilicic acid is formed, which has a very large intermolecular separation, and therefore is unable to polymerise. In contrast, the silicate network  $\text{Si}(\text{O}_4)_{1/2}$ , completely void of hydroxyl groups, is formed through polymerisation at  $r = 2$ .

In practical terms, excess of water ( $r > 2$ ) is expected to cause an increase in the rate of hydrolysis compared to condensation [20]. In acidic conditions, hydrolysis predominates [10] and goes to completion, leading to a decrease in the content of intermediates [21] and to the development of a more cross linked polymer [22, 23]. In high water/acidic conditions, Sakka *et al.* obtained spherical and highly cross-linked silicate particles, but not surprisingly, under low water conditions, the particles were transformed into *chain-like* aggregates.

A kinetic justification for these observations is that under low water conditions the condensation of hydrolysed monomer (whose product is water) is inhibited by a

shift of the equilibrium in favour of the reverse reaction, consequently encouraging further hydrolysis [23]. Despite the effect of water on relative rates, both hydrolysis and condensation are accelerated by higher water contents [14, 16].

The generalised effects of water in basic conditions are not dissimilar to those for acidic conditions. However, from observations by Klein *et al.* [4], it is clear that excess of water affects hydrolysis more than condensation, leading to solutions that kinetically resemble more closely acid-catalysed solutions rather than base-catalysed solutions with under-stoichiometric water content.

The water-to-alcohol concentration ratio plays an important role in acidic solutions as it dictates the probability of re-alkoxylation. During drying, the component present in higher concentrations inevitably remains in the sol-gel solution. Whereas water would continue to hydrolyse unreacted sites, alcohols tend to re-esterify silanols, hence driving the re-alkoxylation reactions to completion [10].

#### iv ) Solvent

An important factor in sol-gel reactions is the type of solvent used. It affects the rates of hydrolysis and condensation and, consequently, also the structural development of the silicate.

Alcohols, depending on the size of the alkoxy group, provide different solvent environments for the hydrolysis reactions. Yoldas [8] argues that the smaller the alkyl radical of the alcohol is, the higher the rates of both hydrolysis and condensation reactions, leading to more complete networks of higher silica contents[8, 19]. The effect of the alcohol molecule's size is diminished at higher monomer concentrations, where the relatively higher viscosity of the system reduces the diffusion capability.

Other types of solvents have been also used:

- (a) *polar protic*, such as H<sub>2</sub>O, methanol and formamide;
- (b) *polar aprotic*, such as DMF, THF and acetonitrile;
- (c) *non-polar aprotic*, such as dioxane;

According numerous authors [15, 17, 24, 25], the nature of the silicate network is determined by the level of affinity that the solvent has with the reactants during condensation. This depends on the dielectric constant of the solvent.

Polar aprotic solvents inhibit the condensation reactions by deactivating the nucleophile through H-bonding and by raising the activation energy through stabilisation of the nucleophile's negative charge. Polar aprotic solvents, as well, can decelerate condensation by solvating the reacting species (e.g.,  $\equiv\text{Si-O}^-$ ). Non-polar aprotic solvents, on the other hand, cannot impede the condensation process because they offer no possibilities of either H-bonding or solvation on the negatively charged ions.

Alcoholic solvents, such as ethanol (EtOH) and propanol (PrOH) form azeotropic mixtures with water. The azeotrope, which has a higher vapour pressure than each single component, evaporates first and leaves behind either water or alcohol (depending on their initial amount). If the alcohol is in excess, silanols re-esterify and the water produced is readily removed as part of the azeotrope, thus driving the reverse alkoxylation reaction to completion. Therefore, because the hydrolysis reaction is thermodynamically favourable, the composition of the sol-gel solution should be such that it ensures that water (and not the alcohol) evaporates last [10].

The effect of solvent concentration in acid-catalysed hydrolysis is not entirely clear. However, in the case of base-catalysed solutions, it is known that by increasing the amount of EtOH within specific limits, hydrolysis is favoured, since species stay in solution longer and early condensation is prevented [4, 19].

### v ) Alkoxide

Shorter distances between reacting species increase the probability of mutual collision and lead to structures of higher oxide content [19]. Therefore the concentration of the alkoxide in the sol-gel system is an important factor.

One of the earliest studies in this field was that of Aelion *et al.* [9]. They determined that the rate of hydrolysis decreases with the increasing of the length of the alkyl radical. Whether it is reduced diffusivity[8] or steric impediment due to the longer alkoxy group, the fact remains that molecular mobility is significantly impaired [2]. On the other hand, studies[26] involving -R groups ranging from methyl to butyl have revealed only a very weak effect of the size of these groups on hydrolysis.

Condensation is also affected by the nature of the alkyl radical, since the diffusivity of intermediate species having long non-hydrolysed groups attached to them, is reduced.

If one or more of the groups attached to the silicon is non-reactive, the network structure is modified. If, indeed, the number of these  $R^I$  groups is equal to 2 in structures such as  $R^I_2Si(OR)_2$  only linear polymers are formed,  $R^I_3SiOR$  being chain terminators [2, 8].

#### **vi ) Steric effect**

The effects of steric impedance associated with the chain length of the alkyl radical have been discussed in the previous section. Steric effects also account for the prevention of re-esterification during a base-catalysed reaction. Assuming that the  $S_N2$  mechanism is predominating, the inversion of the tetrahedron and the necessity for back-side attack are the factors that account for the difficulty in the occurrence of the reverse reaction[10, 12].

The probability of further reactions taking place after condensation of incompletely hydrolysed species is greater in the case of acid-catalysed reactions. Because of the absence of inversion, the low degree of cross-linking in an acid-catalysed solution constitutes a smaller obstacle to the continuation of reactions. Consequently, under equivalent conditions, where both basic and acidic catalysis favour condensation of non-hydrolysed species, acidic catalysis is the best effective way of allowing hydrolysis to go to completion[10].

#### **vii ) Aggregation and growth of polyalkoxysilanes**

In the reports of Keefer[10], the silicates formed under either basic or acid conditions, are described as fractal in nature. Fractals are structures resulting from random growth processes. They have dilational symmetry and because of this, their appearance remains unchanged after magnification. In mass fractals, the volume occupied grows faster than the mass that generates it. Surface fractals, on the other hand, are highly complex structures with a surface area that increases with mass at a faster rate than normal (Euclidean) objects.

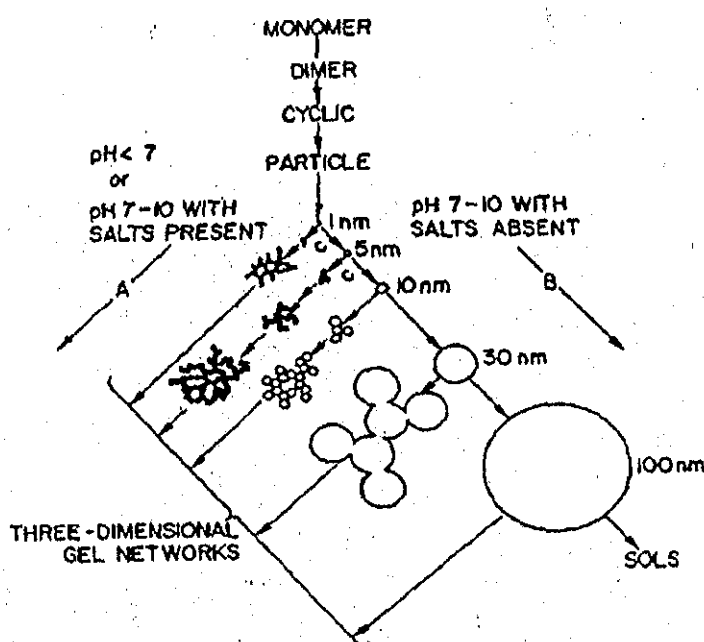
Fractal dimensions, in silicate systems, may be determined by x-ray, neutron or light scattering measurements, while the growth of domains can only be simulated

by computer models. Typically, fractal geometry describes silica structures on the basis of the relative rates of hydrolysis and condensation [10]. For base-catalysed reactions, using the *poisoned Eden* model (a reaction-limited monomer-cluster aggregation model), structures range from non-fractal (at high water concentrations), to colloidal (with fractal rough surfaces), to true fractal (polymeric) (at lower water concentrations). In acid-catalysed systems, where the small particles involved tend to form branched polymers that grow by polymer-polymer interactions, the resultant structures are shown to be true fractal by the *RLCA* (Reaction Limited Cluster-cluster Aggregation) model.

The idea that silicic acid monomer can polymerise into siloxane similarly to organic polymers, is rejected by Iler. His classical theory of polymerisation of silica [11] involves polymerisation of the monomer to first form particles, which then grow and coalesce with other particles to form weak-lace type of structures.

At concentrations above the solubility limit of silica (100-200 ppm),  $\text{Si}(\text{OH})_4$  polymerises by condensation at rates controlled by either the concentrations of  $\text{OH}^-$  or  $\text{H}^+$  ions in the way discussed previously. The tendency to form  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  bonds at the expense of silanol groups, leads to the formation of cyclic structures and their subsequent growth by addition of monomer into large three-dimensional polymers. These internal condensation reactions produce compact entities with pendant silanol groups for subsequent growth. Particle size at this point is important because it determines the radius of curvature of the surface that controls the solubility of the particle. Solubility is also determined by the degree of condensation within the particles. The largest and most condensed particles survive and continue to grow by the Ostwald ripening mechanism. At  $\text{pH} > 7$ , where silica dissolution and re-deposition rates are high, this activity leads to particles of colloidal dimensions. At high pH up to 10.5 and moderate solution concentrations, negative charges on particles cause mutual repulsion and growth without aggregation [9]. High temperature has a similar effect, since accelerated growth leads to a small number of larger-sized particles [11, 27]. Charges may be reduced by the addition of a coagulant (for example,  $\text{Na}^+$  ion of a salt such as  $\text{Na}_2\text{SO}_4$  or  $\text{NaCl}$ ) in which case aggregation can occur. At too high salt concentrations, precipitation is observed. At low pH, where the rate of polymerisation (and de-

polymerisation) is slow, particles are very small in size and further growth is discouraged. Under these conditions, the tendency to form networks rather than oversized particles is more pronounced. This effect is due to the low ionic charge on particle surfaces, which allows higher rates of inter-particle collisions. Therefore, at a 'high' concentration of  $\text{SiO}_2 > 1\%$ , aggregation of very small particles is possible. At pH levels ranging from 5 to 6, there is a rapid simultaneous formation and aggregation of particles [11]. The above processes and the effects of pH are shown in Figure 2-5.



**Figure 2-5 Polymerisation behaviour of silica [after Iler]**

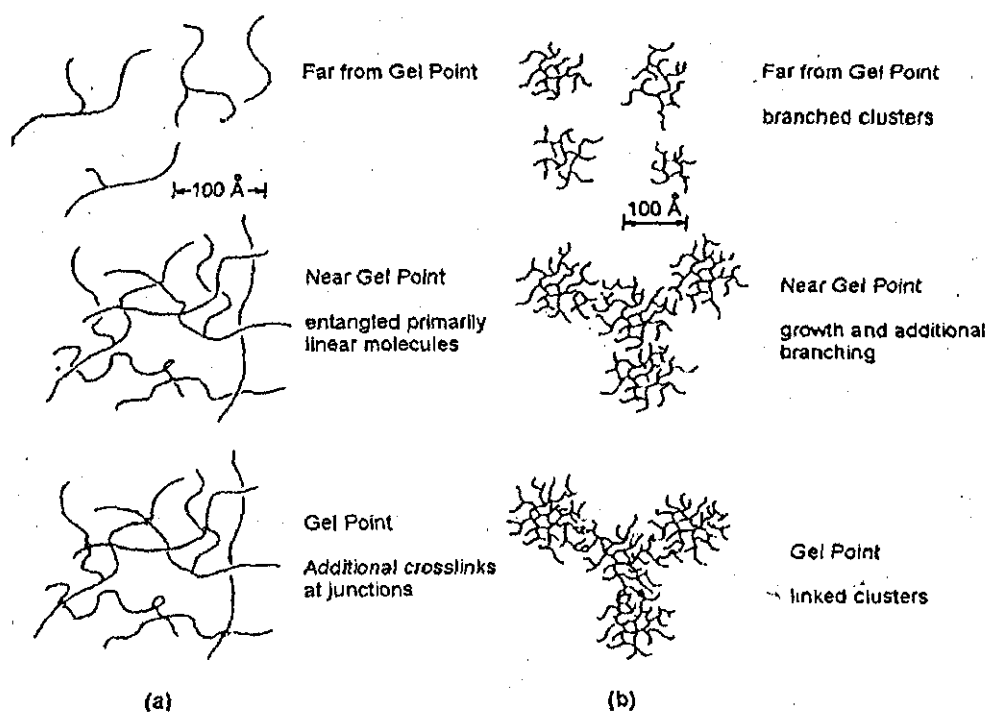
Aggregate particles attach to each other through siloxane bonds. These bonds result from the condensation of surface silanol groups and  $\text{Si-O}^-$  ions at the point of contact between the particles. The negative curvature at the point of inter-particle contact accounts for the very low local solubility. This pushes the process of further bonding through fast monomer deposition [11]. The hydrogen bond plays an important role because it's the link between silanol and siloxane groups of the

particle surfaces, directly or through water molecules. H-bonding will be present even up to advanced stages of aging and desiccation [28].

The process of chain and branch forming is only present in those systems that prevent excessive growth by keeping repulsive charges to low levels. At pH 2, the overall net charge is zero (due to the occurrence of the isoelectric point of silica), but the polymerisation is still possible. It is hypothesised by Iler [11] that the negative charge on Si-O<sup>-</sup> ions, presumably involved in the initial reactions between surface species, is counterbalanced by the positive charge on H<sup>+</sup> ions present in the polymerising medium.

### 2.1.5 Gelation

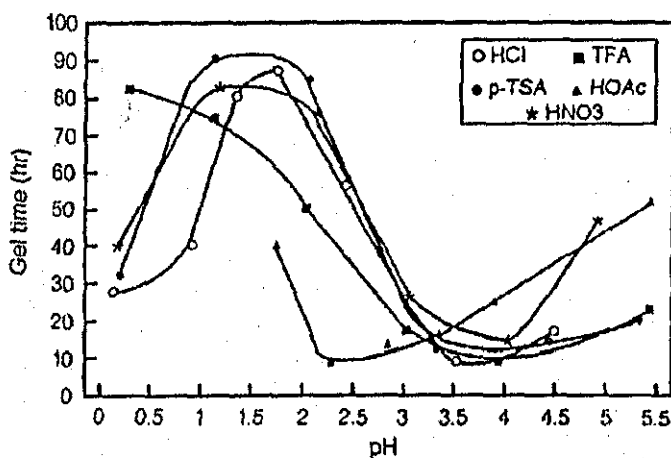
This process is possible where repulsive surface charges are low enough to allow aggregation and growth. This condition will exist below a certain pH level. As a result of polymerisation into three-dimensional networks, an increasing fraction of the sol becomes occupied by *micro gel* regions [11]. These regions, in contrast to precipitates, have the same refractive index and density as the surrounding sol, which explains the transparency of the system.



**Figure 2-6 Polymer growth and gel formation in a) acid b) basic – catalysed systems. [after Brinker and Scherer]**

Prior to gelation point and under acidic conditions, the precursor of the gel consists of linear or randomly branched polymers having a low fractal dimension, while under basic conditions this is made up of individual highly branched clusters. At the gelation point, linear chains become entangled as they maintain their fractal structure, while branched clusters impinge on each other [3]. The viscosity at this stage increases asymptotically and a transparent gel is formed.

The gel time depends exclusively on the pH of the medium, as shown below. It is possible to distinguish clearly three regions defined in terms of pH level, respectively: below 2, between 2 and 7 and above 7.



**Figure 2-7** Variation of gel time with pH, [after Brinker and Scherer].

The region below  $\text{pH} = 2$  corresponds to a maximum sol stability (i.e. long gel time), whereas the minimum, which corresponds to rapid gelation, occurs between  $\text{pH} 3$  and  $4$ .

The effect of the catalyst on the rate of gelation of silicon alkoxides follows the same trends as the rates of hydrolysis and condensation. Pope et al. [29] say that the dissociation constant of acids is not enough to explain their observed behaviour. They suggest that the nature of the acid anion ( $\text{Cr}^-$ ,  $\text{F}^-$ ,  $\text{CH}_3\text{-COO}^-$ ) has an important role. Taking the example of the acetic acid (HOAc), they suggested that the acetyl groups react during the sol-gel reaction to form ethyl acetate. Sakka et al. [23] also observed the difference in the gelation behaviour of HOAc from stronger acids. The former produces a gradual increase in viscosity, while the latter give an abrupt change in viscosity when reaching gelation.

The effect of HF catalyst observed at  $\text{pH} < 2$  has been explained by Iler. The  $\text{F}^-$  ion is smaller in size than  $\text{OH}^-$  (which is active at  $\text{pH} > 2$ ), so can act in its place to raise the coordination number of the silicon atom from 4 to 5 or 6. In this way it's possible to explain how the activated complex necessary for a nucleophilic reaction can be formed [29]. Acid catalysis, in the presence of the fluoride ion, accelerates both hydrolysis and condensation, hence the observed increase in gelation rate. A side effect of this reaction is that the fluoride ion, that can also partially substitute the oxygen in the structure of silica, reduces the amount of H-bonded water as well

as the number of silanols. These reductions keep silica more hydrophobic causing the gel to retain lower amounts of water during the expulsion of the liquid phase [30].

The increase of water content in alkoxide solutions usually promotes gelation [23]. Results by Bechtold *et al.* [31] show hyperbolic relationship between gel time and  $H_2O/TEOS$  ratio,  $r$ , confirming the validity of the previous statement. Sakka *et al.* explain [23] that a too high water content tends to produce a counter-effect of dilution, therefore gelation is impeded rather than promoted.

The findings of Boonstra *et al.* [32] provide indirect evidence of the effect of small additions of water above the stoichiometric amounts. In their two-step reactions with TEOS, a small excess of water added, either at the initial acidic step or at the subsequent basic step, produces an  $H_2O/EtOH$  ratio that favours the formation of  $OH$  groups in greater amounts than  $EtO^-$  terminal groups on the surface of the particles. Considering that the  $OH$  groups increase the growth rate, gelation under these conditions is reached faster.

An increase in the concentration of the alcoholic solvent leads to a decrease in the monomer concentration due to dilution. Therefore, the polymerisation rate decreases due to a decreased rate of intermolecular collisions, and gelation is delayed [2].

Polymerisation rate, and therefore gelation rate, falls with increasing alkyl group chain length, whether the group belongs to the alkoxide or the alcohol. Behind this effect there are steric reasons that follow the same logic as with the rates of hydrolysis and condensation. Enhancements in monomer mobility by transesterification with a smaller ligand from a lower alcohol can reduce the gel time.

### 2.1.6 Other considerations about the transition of sol to gel

Several approaches have been taken to define the gel point. Arbitrary parameters such as the *point of no fluidity* [11, 31], are useful measures of gel time, but are not very accurate, and therefore, they cannot give information about viscosity changes taking place. This information, on the other hand, can be provided by rheological measurements using cone, plate or coaxial cylinder rheometres.

Several authors have reported that the sol-gel transition of acid-catalysed TEOS solutions takes place in three stages [33, 34]. In steady shear experiments, Xu *et al.* [33] observed that during the first stage, the sol exhibits Newtonian behaviour, so that the viscosity is independent of the shear rate imposed by the measuring instrument. Although the monomer is polymerising, the formation of aggregate is not dominant and therefore the increase in viscosity is small. During the second stage, a steady increase in viscosity is observed due to the formation of linear polymers, and at the third stage, a more pronounced increase in viscosity occurs as a result of the formation of 3-D networks [33].

Sacks *et al.* [34], using dynamic viscometry measurements, have found that the loss modulus ( $G''$ ), grows at a higher rate than the elastic modulus ( $G'$ ) during the initial stage. This happens because the energy dissipation during flow (which contributes to  $G''$ ) is more significant than the weak polymer-polymer interactions (which contribute to  $G'$ ). As a result, the loss tangent ( $\tan \delta$ ), in this stage, also increases. In the second stage, the  $\tan \delta$  decreases as  $G'$  grows faster than  $G''$  due to a large-scale aggregation of hydrolysed monomer. The sol starts developing an elastic character and displays shear thinning in response to applied shear stresses. Thixotropic flow, accompanied by pronounced yielding and hysteresis effects, is observed at the last stage before the onset of gelation, where the loss tangent decreases even further and the extensive network gives rise to large  $G'$  and  $G''$ .

The definition of gel point in terms of rheological behaviour of solutions is essential if the phenomena that bring about the appropriate conditions for manufacturing techniques are to be understood. For example, Sakka and co-workers [35, 36] reported that the sol must have optimum spinability to enable fibre drawing and film casting. However, apart from recognition of the importance of the chemistry of the solution (low water acid-catalysed TEOS) and the requirement of linear polymeric chains, only arbitrary viscosity levels have been stipulated for the optimum consistency of the sol.

### 2.1.7 Ageing and drying of gels

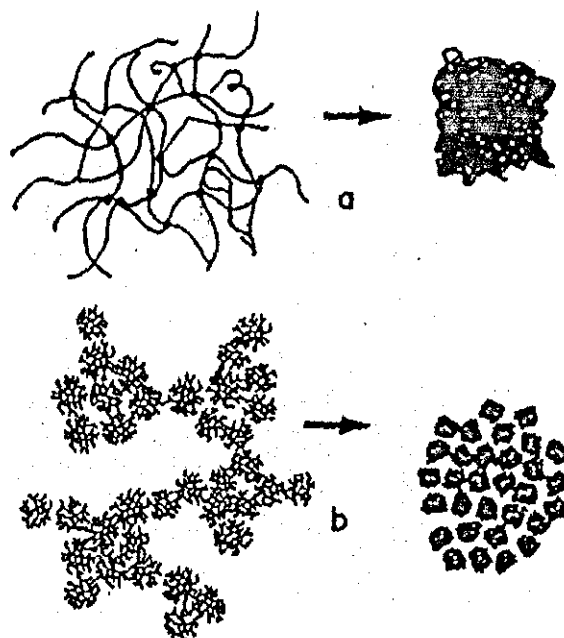
The effect of time on structure is known as ageing [19]. Since condensation reactions take place the properties of the gel can also change. The solubility of

silica decreases, and so does the specific surface by the loss of porosity. The accompanying increase in skeletal stiffness causes a marked increase in the modulus of aged gels [2].

The cause of the changes in gel structure originates from the early stages of its formation. Phase separation is possible either in the form of density fluctuations across regions of high and low cross-link density, or by creation of monomer-rich and monomer-poor areas by having high rates of depolymerisation under conditions of high solvent concentration [3]. Indeed, most parameters that control hydrolysis and condensation are very important to determine the nature of the resultant gel structure [2-4, 19].

In aerogels, the liquid solvent is replaced by a supercritical phase, eliminating the interfacial (liquid/gas) tension, capillary pressure and preventing fracture or warping. The result is a silica body of up to 95% fine porosity. Xerogels are sintered aerogels, but they are still porous. The theory of drying gels has been studied extensively [37, 38].

Conditions that lead to weak networks are constrained to result in high structural compaction because under the influence of capillary forces, coming from drying, flexible branches deform and collapse to a greater extent. Therefore, as a principle, low pH and low water contents produce dense gels whereas high pH (6 - 10) and high water contents produce gels of high porosity. See Figure 2-8.



**Figure 2-8 Representation of desiccation of a) acid b) basic – catalysed gels, [after Brinker and Scherer]**

Since large pores lead to lower surface extension and provide wider paths for the evaporation of volatile molecules, these systems develop lower drying stresses and are less susceptible to fracture [3, 29, 39]. Acidic systems can be made to behave similarly to the basic ones if treated in conditions that promote particle growth [40].

The function of substances such as DMF [23, 41] and formamide as drying control chemical additives is to regulate the relative rates of hydrolysis and condensation, so that larger particles of uniform size are formed. During ageing, a tight size distribution of large pores is achieved that facilitate the expulsion of volatiles, keeping capillary stresses at safe level [42].

## **2.2 Organic Inorganic Hybrids**

### **2.2.1 Introduction**

During the last 10 years a new technology has been developed for the production of heterogeneous nanostructured materials containing organic and inorganic

components. Such materials are normally known as organic-inorganic hybrids, ceramers or nanocomposites and are characterised by two interpenetrating domains having nano-scale dimensions. Organic-inorganic hybrids can be obtained by dissolving preformed polymers into a sol-gel precursor solution, consisting of a metal-alkoxide, a catalyst and, optionally, a coupling agent. The alkoxide components are allowed to hydrolyse and undergo condensation reactions to form glassy inorganic oxide domains in a polymer solution. Alternatively both the organic and the inorganic phases can be formed together through the simultaneous polymerisation of an organic monomer (or oligomer) and sol-gel reactions of the inorganic oxide precursors.

Hybrid materials have an immense potential for applications in a variety of advanced technologies, both as structural materials and as functional materials. The primary properties of structural materials include strength, stiffness and toughness, while secondary characteristics include protective barrier, thermal oxidative stability and absorption resistance. Functional nanocomposites, on the other hand, will have high order characteristics, such as tailored reflection characteristics, non linear optical effects [43], optical transparency, electrical and photo catalytic properties [44, 45], biological compatibility [46, 47] and many other desirable attributes such as tailored porosity [48].

The properties of a composite material depend not only upon the characteristics of the single components but also upon the composite's phase morphology and interfacial properties. One approach to increase the latter property is to blur the ordinarily sharp interfacial zone by synthesising materials, which show a high degree of interpenetration between the two organic and inorganic phases. The degree of phase separation in these materials can vary, but domain size is typically on the nanometer scale. As a result of this intimate mixing, these hybrids are highly transparent: a property that renders them valuable outside the boundaries of traditional composites. Traditional composites tend to be largely opaque because of light scattering by the particles within the continuous matrix. In addition to the domain size, the most important factors in determining the transparency of composites are the shapes of the domains and the relative difference between the refractive indices of the two phases. For discrete spherical particles embedded in a

matrix, the reduction of light intensity due to scattering is given by the equation below, where  $I_0$  is the intensity of transmitting light with no scattering,  $I$  is the intensity when scattering takes place,  $x$  is the optical path length,  $V_p$  is the volume fraction of particles,  $r$  is the particle radius,  $\lambda$  is the wavelength and,  $n_p$  and  $n_m$  are the refractive indices of the particles and the matrix [49].

$$\frac{I}{I_0} = \exp \left[ \frac{-3V_p x r^3}{4\lambda^4} \left( \frac{n_p}{n_m} - 1 \right) \right]$$

From the above equation is clear that when the refractive index of the matrix is equal to that of the particles becomes  $I=I_0$ , so there will be no scattering by the solution. On the other hand, when  $n_p \neq n_m$ , scattering losses will be minimised only when the particle's dimensions are much smaller than the wavelength of light ( $r^3 \ll \lambda^4$ ).

### 2.2.2 Types of organic-inorganic hybrids

In order to produce a classification of hybrid systems, Novak [50] divided them into five major classes based on their macromolecular structures and phase connectivities.

**Type I:** Soluble, preformed organic polymers embedded in an inorganic network.

This family of hybrids is the result of the most common route used to form organic-inorganic composite materials through the sol-gel process. It involves carrying out the inorganic hydrolysis and condensation of the inorganic phase precursors in the presence of a preformed organic polymer.

**Type II:** Embedded, preformed organic polymer covalently bonded to the inorganic network.

This class of composites, as the previous one consists of linear polymers dispersed in organic glass matrices but, plus the benefit of planned covalent links between the two phases.

**Type III:** Mutually interpenetrating organic-inorganic networks

This type of hybrid is the result of the efforts to solve some practical processing problems of the two previous classes of hybrids. The main feature of these hybrids

is that their formation involves the in situ formation of the organic polymer and the inorganic matrix.

Type IV: Mutually interpenetrating organic-inorganic networks with covalent bonds between the organic and the inorganic phases.

This type of hybrids has the same features than the previous one but this time the two phases are linked also by covalent bonds.

Type V: "Non Shrinking" sol-gel composite materials.

Novak introduced this class of hybrids in order to identify some of the hybrids produced by his group that had the idea to solve shrinking problems that usually characterise all the previous types of hybrids.

### **2.2.3 Simultaneous Formation of the Inorganic and Organic Networks**

Despite the excellent performance of many hybrid materials, type I and II, mentioned previously, the methods of forming composites by the incorporation of preformed polymers into sol-gel glasses is essentially limited by the fact that only a finite number of polymers are soluble in the sol-gel solution. Under the right conditions the polymer can be trapped in the inorganic system, or vice versa, before significant phase separation occurs. In this way, transparent organic-inorganic composite materials can be prepared which contain organic polymers that would normally be insoluble in typical sol-gel solutions.

The solution of this problem has been approached in many ways. One of these consists in modifying one or both the organic and the inorganic components of the composite, in order to render them compatible with each other. The modification consists of adding to either the organic or the inorganic component, functional groups similar in nature of the other constituent. Such modifiers are also known as coupling agents.

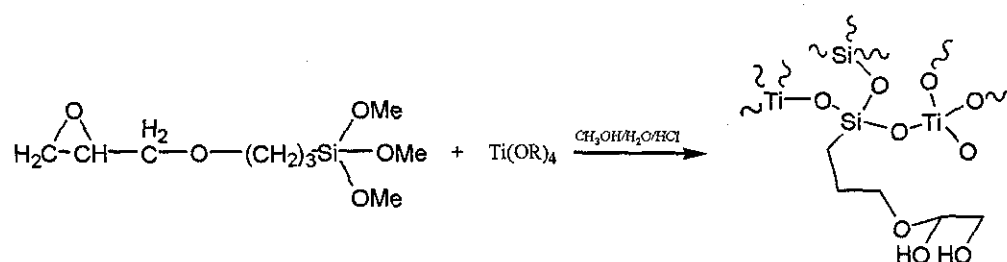
Mascia and Tang [51], for instance, successfully prepared hybrids of epoxy resin and silica through functionalisation of the organic polymer with mono and di-functional secondary amine trialkoxysilanes, such as Y-9669 (*n*-phenylamino propyltrimethoxysilane) and A1170 ( $\gamma$ -trimethoxysilylpropylamine).

Mascia and Kioul [13, 52-54], used GOTMS ( $\gamma$ -glycidoxypyrrol-trimethoxysilane) in their work with polyamic acid solutions in NMP and hydrolysed solutions of TEOS. Transparency in film cast in solutions with enough amounts of GOTMS was found to be a function of mixing time and temperature. The authors attributed the transition of the films from a cloudy to a transparent appearance to compatibilisation of the polymer and the developing siloxane by trimethoxyl functionalities grafted to the polyamic acid backbone by the coupling agent through the carboxylic acid groups present. These functionalities were expected to subsequently take place into the formation of the inorganic network.

Mark and co-workers [55, 56] have also reported a work where a coupling agent was used to increase compatibility in PMDA-ODA/SiO<sub>2</sub> hybrids. Aminophenyl trimethoxysilane reacted with the polyamic acid and later added to TMOS produced smaller SiO<sub>2</sub> clusters of better size distribution, possessing physical bonds with the surrounding matrix. In a parallel work, the same group premixed the coupling agent with the TMOS solution showing the potential for better transparency and higher thermal stability in films. It was postulated that the improvements in properties seen by the addition of aminophenyltrimethoxysilane, were due to the improved compatibility of the polyimide and the siloxane arising from interconnectivity through amino groups, from the coupling agent, and the large surface area created by the small size of the clusters [57].

Ober and Johnen [58] have also produced transparent hybrid films by incorporating a bonding site via a preliminary grafting reaction of the polyamic acid with  $\gamma$ -aminopropyltrimethoxysilane and via the incorporation of a PDMS segment whose scission by the reaction with water allowed attachment to the PMDA/ODA polyamic acid backbone.

Schmidt synthesised TiO<sub>2</sub>/SiO<sub>2</sub>-epoxyde composite materials displaying excellent transparency, hardness and wettability [59]. This was achieved by the sol-gel condensation of GOTMS ( $\gamma$ -glycidoxypyrrol-trimethoxysilane) with titanium alkoxides. The siloxane was used to provide wettability, thanks to the hydroxide groups formed by the epoxide ring opening, and the TiO<sub>2</sub> was introduced in order to produce a complete inorganic network. The reaction can be schematised as follows.



**Figure 2-9 Schematic representation of Schmidt condensation [after Schmidt]**

Reflecting their inorganic character these composite materials exhibited relatively low strength and were brittle. In order to increase the flexibility, an organic polymer poly-methylmethacrylate, commercially available as methacrylate monomer possessing alkoxyethyl functional groups, was added through an in-situ polymerisation.

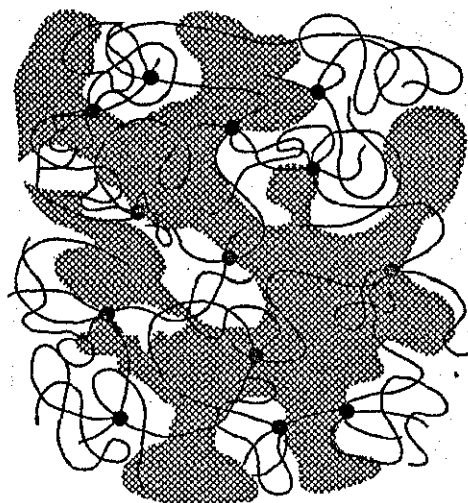
The advantages of SIPNs (Simultaneous Interpenetrating Networks) [50] approach over using preformed polymers to form sol-gel derived composites are various. First of all, by incorporating bifunctional monomers, the SIPN approach allows to cross-link the organic polymer, thereby locking-in the interpenetrating phase morphology. This approach allows the in-situ formation and thus the homogeneous incorporation of polymers, which normally wouldn't be miscible. Lastly, these materials typically display greater homogeneity and smaller domain size than comparable preformed materials.

#### 2.2.4 Structure property relationship for hybrid materials

Typical advantages of organic polymers are low rigidity, low density, high toughness, and easy processing whereas ceramics have very high rigidity and strength including high surface hardness. Depending on composition they can also have a high refractive index. Combining polymers and ceramers effectively will produce a new class of high performance materials generally known as organic-inorganic hybrid materials. Because of the continuity of phases, their nanostructured and the interfacial interactions, the properties of these materials can exceed those predicted from conventional composites [51, 59-63]. Indeed,

materials at interface can constitute a separate phase known as “interphase” [51, 59, 61], which can contribute substantially to the overall properties of hybrid materials. The homogeneity or separation of phases in the developing hybrid have been studied extensively [64-70].

The variables affecting the structure and properties of hybrids have been discussed by Landry et al. [71], who have examined by SAXS two different samples of organic-inorganic silica composites, and proposed morphological models to describe them. EAS (triethoxysilane-end capped bisphenol-A epoxy resin) was reacted with TEOS under slightly basic conditions, and a random copolymer MMA-TMS (trimethoxysilane-methylmethacrylate) was reacted with TMOS (tetramethoxysilane) in acidic medium. It was concluded that the inorganic phase in the EAS-TEOS hybrid, exhibits particle like characteristics at length scale less than 250 Å, and the organic-inorganic components are co-continuous at larger distances. The MMA-TMS based hybrid, on the other hand, is better described by co-continuous organic and inorganic phases (IPNs) with a periodic fluctuation of about 40 Å. This difference in morphology can be probably examined in the following terms. In the acid catalysed MMA hybrid the TMOS is expected to form a branched polymer structure. Once most of the solvent is removed, phase separation is likely to occur to form a co-continuous interpenetrating network between the organic polymer and the inorganic polymer phases. A tentative of schematic representation of the morphology is shown in Figure 2-10.

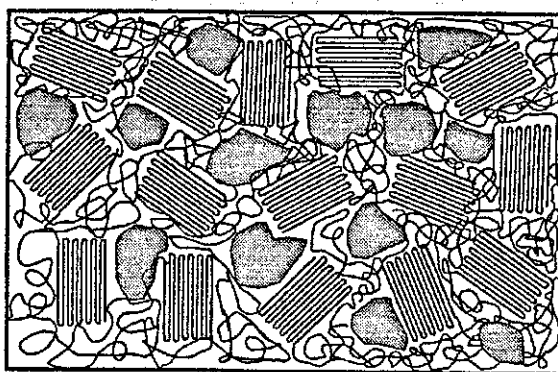


**Figure 2-10 Schematic representation of the morphology of an OIC hybrid based on the simulations results for SAXS profiles. It features co-continuous organic and inorganic phases. Microphase separation is proposed to occur by localisation of the inorganic phase in the mesh regions of the cross linked polymer. Some attachments of the inorganic alkoxides to the functional sites on the polymer are possible (black-filled circles) [after Landry and Coltrain]**

Much of the inorganic phase is preferentially positioned within the “polymer free” regions of the cross-linked polymer network. The idea of discrete inorganic domain morphology was suggested also by Wilkes and co-workers [72-74], where the inorganic domains are formed at the functional sites on the polymer, accompanied by chemical cross linking at the organic-inorganic interface.

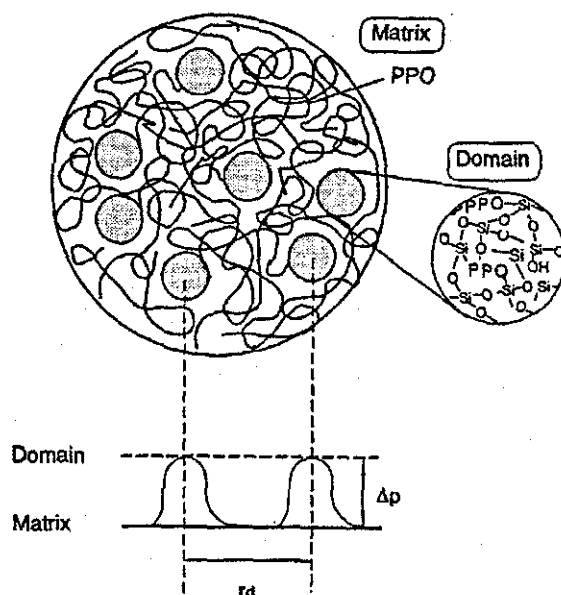
Yano et al. [75] prepared organic-inorganic silica hybrids following two different approaches. One method involved mixing the organic polymer HPC (hydroxypropyl-cellulose), PVA (poly-vinyl-alcohol) or PVDF (poly-vinylidene-fluoride) with TEOS. During the sol-gel process, in this way, the inorganic mineral is deposited in the organic matrix forming hydrogen bonding between inorganic phase and inorganic phase. In this case hydrogen bonding plays an important role in avoiding phase separation. The other route followed by these authors, was to introduce triethoxysilyl groups into the organic polymer prior to the sol gel reaction with TEOS involving covalent bonds between the two phases. This time the

polymers used were PPO (poly-propylene-oxide end-capped with triethoxysilane) and the copolymer Vac/VTES (vinyl-acetate/vinyl-triethoxysilane). The experiments conducted on the first type of composite showed that with the increasing amount of TEOS content there is an increase of dynamic modulus. But no change in  $\tan(\delta)$  was observed, apart from a decrease of the intensity of its peak, because the molecular motions of the organic polymer are not restricted by the deposited silica component. Shown below is a proposed hypothetical morphology for the PVDF/SiO<sub>2</sub> hybrid.



**Figure 2-11 Model of PVDF/SiO<sub>2</sub> hybrid morphology [after Yano et al.]. In the proposed model it is possible to distinguish well, zones where the PVDF chains are crystallised, others where such chains are disorganised and others occupied by the silica particles (black filled zones).**

The SAXS profiles of the covalent bonded polymers show a large sharp peak and it's height increases when increasing the TEOS content. This is perhaps due to micro phase separation between silica rich domains and the organic polymer matrix. This time the  $\tan(\delta)$  peak shifts to higher temperatures due to the molecular motions of the organic polymer being restricted by the silica rich domains. The small silica domains responsible for the low mobility of the organic polymer are visible in the morphology model proposed for the poly(propylene oxide)/silica (PPO/SiO<sub>2</sub>) hybrid shown in Figure 2-12.



**Figure 2-12 Morphology model of PPO/SiO<sub>2</sub> hybrid [after Yano *et al.*].** The model proposed shows a system where the silica domains are dispersed in the polymer matrix. The distance, measured from the centre, between each silica domain is expressed by  $rd$ .  $\rho$  is the density, in terms of silica, and it's fluctuation  $\Delta\rho$  between two domains goes from a maximum value (centre of the domain) to a minimum (polymer matrix)

A similar model is proposed for other triethoxysilane-terminated polymers such as PTMO [poly(tetramethylene oxide)] [72, 76, 77], PDMS [poly(dimethylsiloxane)] [78] and epoxy resins [71].

Wei *et al.* [79] have synthesised by the sol-gel method two different polymethacrylate-silica covalent-bonded hybrid materials. The polymers used were PMCM [poly(methyl methacrylate-co-3-trimethoxysilyl propyl methacrylate)] and PHEMA [poly(2-hydroxyethyl methacrylate)]. These results were comparable to those found by Yano *et al.* [75]. The rapid formation of covalent bonds between the polymer and the silica during the sol-gel reaction prevents phase separation. The storage modulus and the  $T_g$  of the PHEMA/SiO<sub>2</sub> composite, increase with the increasing amount of TEOS.

Wilkes *et al.* [80] studied PDMS (poly-dimethyl-siloxane)/TEOS hybrids. They were among the first to report the synthesis of hybrids based on PDMS (poly-

dimethyl siloxane) oligomers and silica from TEOS. The embedded inorganic phase conferred rigidity to these materials with a corresponding decrease in ductility. The properties were found to be substantially influenced by the amount of catalyst (HCl) added, leading to a better interdispersion of the two phases according to evidence from small angle x-ray scattering. The effect was attributed to kinetic factors, as the tendency for self-condensation of the oligomeric species through their silanol functionalities is retarded by co-condensation reactions, following the fast hydrolysis of TEOS [80]. Not surprisingly, the use of a larger amount of TEOS [80] and water, as well as additional thermal treatment [81], gave rise to a more highly cross-linked silica structure, leading to an increase in dynamic modulus. The molecular weight of the oligomeric species was also found to be important as far as it can influence the propensity of the condensing phases to segregate; not surprisingly, low molecular weight oligomers produce systems of a higher degree of homogeneity [80, 82]. Ning, Zhao and Mark [83] obtained similar results to Wilkes, using a system in which water for hydrolysis was generated in situ from the esterification reaction of acetic acid and ethanol.

In relation to homogeneity by virtue of the growth mechanisms and the resultant connectivity in hybrid systems, Black, Assink and co-workers [84] have demonstrated the influence of the strength of the catalyst in the reaction of silanol-terminated PDMS with TEOS by using dibutyltin dilaurate (DBTDL) and tin octoate (TO) as catalysts. The more reactive catalyst TO was found to affect growth in a way that gave rise to a more highly phase-separated microstructure featuring a larger number of isolated  $\text{SiO}_2$  domains. Their conclusions, obtained by varying the amount of TO in the formulations, can be correlated to those obtained by Wilkes and co-workers [80] using HCl as catalyst.

Hybrids utilising PTMO [poly(tetramethylene oxide)] oligomers have also been synthesised. The main difference of the PTMO-TEOS system, investigated by Wilkes *et al.* [82], to the PDMS-based system is the inclusion of triethoxysilyl terminal groups in the oligomers which increase the amount of linkages formed between the elastomeric and the rigid siloxane phases. The final materials showed improved mechanical strength and strain-to-break. The same team proposed a model based on SAXS data for the morphology of the hybrid from the PTMO-

TEOS system. The model resembles that of a segmented copolymer displaying discrete micro-domains. Further treatments [85], involving solubilisation and leaching-out of part of the silica from within hybrid films by immersion into 1M NaOH solution, caused the mobilisation of the oligomeric chains which led to more pronounced phase separation. These experiments provided the evidence for the structure of the proposed model consisting of the encapsulation of oligomer chains within the inorganic network. The use of an organic component of higher molecular weight than usual, in the form of PTMO-based polyurethane oligomers [72], has provided additional proof of the efficiency of increased functionalisation on structure-related properties.

Triethoxysilyl groups along the backbone chain of the PTMO chains led to an increase in the number of linkages between the oligomer chain and the siloxane network.

As a consequence of the greater connectivity of the phases, there was an increase in  $T_g$ , associated to an increase in modulus and strength and a respective decrease in strain-at-break. Furthermore, the SAXS observation of a decreased inter-domain distance with higher average number of pendant triethoxysilyl groups on the PTMO backbone indicated a higher interdispersion of the organic and the inorganic phases.

Chan and co-workers [86-88] synthesised poly(methyl methacrylate)] PMMA/silica hybrids via the sol-gel process, and observed that the glass transition behaviour depended on the heat treatment. Through Infra Red and Differential Scanning Calorimetric analysis they founded that heat treatment causes further condensation reactions, which consume silanol groups and diminish the hindrance effect from ethyl group of unreacted silanol, at the same time the quantity of domains composed of pure silica increase.

Hydrogen bonds can be formed from carbonyl groups and silanol groups of the organic and inorganic phases. With the higher interfacial interactions from hydrogen bonding, heat treated hybrid materials acquire higher miscibility. Hence, PMMA/TEOS hybrids exhibit, in DSC experiments, two glass transition temperatures. But After heat treatment at 180 °C for 24h such hybrids showed closer glass transition temperatures or, in certain cases, only a single  $T_g$ , meaning

that the phase separation between the organic and the inorganic components was reducing or in some cases disappearing.

Ochi and co-workers [89] synthesised Epoxy Silica hybrids containing up to 20% of silica from DGEBA (Epoxy resin Epikote 828) and GOTMS (glycidoxo-propyl-trimethoxysilane) or TMOS (tetramethoxysilane) by sol-gel process. TEM examinations showed a very inter-co-penetrated hybrid structure. The conclusion reached by Ochi *et al.* was that the fine silica particles visible at the TEM did not contain pure silica, but a mixture of silica and epoxy network. In the DGEBA/GPTMS hybrids the storage modulus in the rubbery region increased and the peak area of the  $\tan(\delta)$  curves in the glass transition region decreased with the hybridisation with silica. These results, combined with those from the TEM analysis, showed that the silica network was dispersed in epoxy network in a molecular order by covalent bonds so that the motion of the network chains is strongly restricted. This result was attributed to the suppression of the epoxy network constituent with the incorporation of a silica network containing a functional (epoxy) group, which can react with the organic component.

## **2.3 Poly(Ethylene Oxide) Systems**

### **2.3.1 Synthesis**

Poly(ethylene oxide) is produced by ring opening of ethylene oxide in a step reaction polymerisation.

The ring opening is obtained with a variety of ionic reagents. The developments in the use of coordinated anionic catalysts for the stereo-specific polymerisation of olefins have led to their application and modification for the production of PEOs.

The polymer is divided in two different classes with common names based on the molecular weight:

- 1) Poly(ethylene glycol) for  $M_n$  of the range 600~20,000.
- 2) Poly(ethylene oxide) for  $M_n$  100,000 up to 8,000,000.

PEGs and PEOs display good stability and hydrophilic power, so that they can be mixed with water to a wide range of viscosities. With the increase of molecular weight the melting point of PEGs increase and they change from viscous liquids to

soft solids to flexible/ductile solids. They exhibit very low toxicity and are not irritant to skin or eye [90].

The chemical structure of the polymer is  $\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{H}$ . The presence of ether linkages in a very short hydrocarbon chain gives a tough, ductile, highly crystalline thermoplastic that is also very soluble in water. SAXS data indicate that PEO forms relatively compact units in water rather than swollen random coils[91]. The polymer exhibits a monoclinic crystal structure with a unit cell consisting of two ethylene oxide polymer chains present in the form of parallel helices.

### 2.3.2 Hybrids of PEO with Silica

Studies have shown that silica and PEO have strong interaction, because the silanol groups ( $\text{Si}-\text{OH}$ ) of the surface of the hydrophilic silica interact with the ether group of PEO: the crystalline structure the polymer is disrupted and phase interpenetration occurs [92]. The silica surface and the PEO are interacting by hydrogen bridges throughout the polymer chain [93]. Many preparations of silica have been researched, both preformed [94, 95] and prepared in situ via the sol-gel method [91, 96]. When silica particles are exposed to a dissolved PEO chains, the hydrophilic and dipolar active hydrogen atoms on the silanols on the surface of the silica act as hydrogen-bond donating groups to the free electron pairs of the oxygen atoms of the PEO chains (hydrogen-bond accepting groups). When PEO is present in the silica alkoxide precursor solution it is considered to absorb on silanols of polymerising silica; this interaction makes the interface between the components unstable[97]. It was also observed that the change of mesopores in the silica structure during ageing, drying and heating was affected by the incorporation of PEO[96]. SAXS data indicate that the strong interaction between the organic and inorganic components arises relatively early in the condensation, when the silica oligomer growth is the size of several nanometres, which contain at least several tens monomers, and is probably accompanied by a disentanglement of the aggregated PEO chains and formation of aggregate complex silica oligomers-PEO. Due to the formation of hydrogen bonds between the silanols on silica and PEO, the number of free silanols sites should become less than the corresponding situation without PEO, leading to less branched silica network. Considering the

highly open structure of silica gel produced in acidic conditions, PEO chains are supported in the silica network in a quasi-interpenetrating structure after gelation. PEO chains within the network substantially inhibit the bond formation of Si-O-Si that occurs due to shrinkage during drying, leading to less fully condensed silica.

To prevent the occurrence of spinodal decomposition and phase separation at the gel point, a trialkoxysilanes compatibilisation agent may be used, which chemically binds with the growing silica phase and the OH terminal groups of the PEO and considerably accelerates the gelation[98, 99].

By varying the composition of the alkoxy silanes solution mixture and the mixing conditions different morphologies can be obtained, ranging from semi-interpenetrating networks of PEO within highly cross-linked silica domains, to finely dispersed nanostructured systems, exhibiting either co-continuous or particulate structures[100]. The degree of crystallinity of the PEO phase in the compatibilised hybrid system is drastically reduced and the surface area is much larger than the equivalent silica system produced under the same conditions, as further evidence of strong interaction at the interface between the organic and inorganic components.

### **2.3.3 Miscibility of PEO with Antioxidants**

Model studies of binary mixtures of PEO with phenolic compounds such as resorcinol shows the formation of bi-eutectic phase in the solid representing strong interactions between the phenolic OH group and the ether oxygen in the PEO. In such cases the small aromatic molecule forms both a pure component crystalline state and a stoichiometric crystalline complex with poly(ethylene oxide)[101]

## **2.4 Ageing of polymers**

Polymers are susceptible to ageing through oxidative degradation throughout their life cycle. The extent of degradation depends on both their inherent sensitivity to oxidation, as dictated by their chemical structure and the presence of impurities, and the nature and aggressiveness of the service environment. High temperature of manufacturing and of use, aggressive and corrosive gases, acids and alkaline

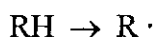
liquids, oxygen in the air are all factors that contribute to degradation and weathering of the polymer.

### 2.4.1 Mechanism of oxidation [102]

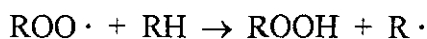
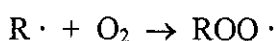
The reaction of organic compounds with molecular oxygen happens inevitably whenever organic materials are exposed to the atmosphere. This oxidation is characterised by two features: autocatalysis and inhibition by additives. These features are generally typical for radical reactions, which, in turn, are almost invariably chain reactions.

The general sequence consist of a starting reaction, generating free radicals ( $R\cdot$ ), propagating reactions, yielding reaction products ( $ROOH$ ) and in a series of termination reaction leading to radical destruction.

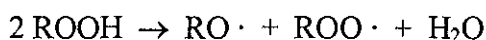
#### i) INITIATION



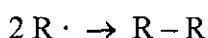
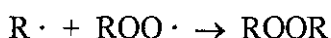
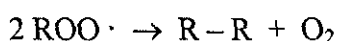
#### ii) PROPAGATION



#### iii) CHAIN BRANCHING



#### iv) TERMINATION

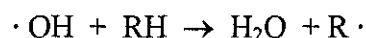
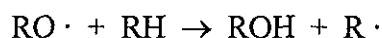


The oxidation initiating polymer radical  $R\cdot$  can form because of heat or light induced dissociation, mechanical stress or by reaction with radicals originating from foreign sources.

Considering the two basic reactions of propagation, the two radicals  $R\cdot$  and  $ROO\cdot$  (alkyl radicals and peroxy radicals) are the high-energy key intermediates. In the kinetic treatment of oxidation it is assumed that a stationary state is reached in

which the concentration of  $R \cdot$  and  $ROO \cdot$  are constant. The reaction of addition of molecular oxygen to an alkyl radical is very fast, therefore at reasonably high oxygen pressure the concentration of the peroxy radical is far greater than the concentration of the alkyl radicals. Consequently, the main termination reaction under such condition is the coupling of two peroxy radical with dissociation of molecular oxygen.

The key reactions of chain branching are both decay reactions of hydroperoxides. Such reactions are characterised by high activation energies. Consequently, they are becoming significant only at elevated temperatures, i.e. over 120 °C. The newly formed radicals  $RO \cdot$  and  $\cdot OH$  are capable to react with  $RH$  just as peroxy radicals, and thus can initiate new reaction chains:

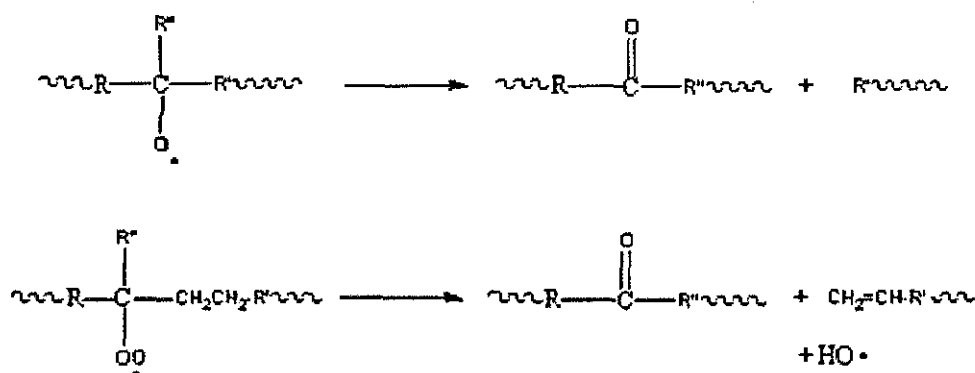


The autocatalytic character of this oxidation chain reaction is implied by such kinetic chain branching reactions. The decay of hydroperoxides is strongly catalysed by the presence of metal ion red-ox pairs, such as  $Fe^{+2}/Fe^{+3}$ ,  $Co^{+2}/Co^{+3}$ ,  $Mn^{+2}/Mn^{+3}$ , and  $Cu^{+}/Cu^{+2}$ .



The overall effect is formation of two new radicals able to continue the kinetic chain just explained.

The effect of this sequence of reaction on a polymer may be cross-linking or chain splitting. Cross-linking is the direct result of the termination reactions, while cleavage of the polymer chain is the result of reactions such as:

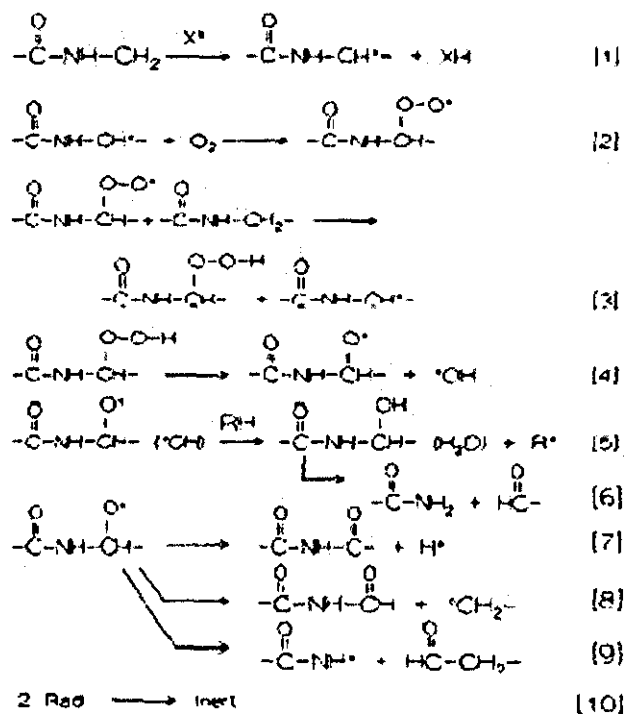


The experimental proofs and more detailed analysis of the oxidation chain reactions and the relative kinetics have been studied extensively[103-106], although not all aspects have been clarified [107-109].

## 2.4.2 Oxidation in polyamides

In the initiation step free radicals are generated. These radicals react with air oxygen and, in the propagation step, abstract the most labile hydrogen from the polymer chain, which results in an alkyl radical and a hydroperoxide. For amide-containing the reaction products found can be explained by assuming that the carbon-hydrogen bonds of the N-vicinal methylene group are the most labile ones. The hydroperoxides formed can decompose thermally into radicals. This reaction can be homolytic, although other decomposition reactions are also suggested. The alkoxy radical formed can abstract a hydrogen atom and form an unstable alcohol, which decomposes to a primary amide and an aldehyde or results in scission. The termination reaction can take place between any two radicals that can meet. However, because of the high reaction rate of alkyl radicals and oxygen and the short lifetime of most radicals, the reaction between two peroxy radicals is most plausible. The N-vicinal methylene group are easily oxidised, and that means that, chemically, polyethylene is more stable than aliphatic polyamides. Nevertheless the long-term stability of polyethylene is less than the stability of aliphatic polyamides[110]. This means that besides chemical factors, physical factors are important for the degradation rate of aliphatic polyamides. For the degradation rate of polymers it is shown that the morphology, for instance, can play an important

role[111] owing to different proportion of crystalline phase versus amorphous phase, where oxygen diffuses preferentially.



**Figure 2-13 Basic oxidation mechanism for aliphatic polyamides [after Gijsman *et al.*]**

Traditionally, aliphatic polyamides are stabilized with small amount of copper salts (up to 50ppm) in combination with halogen ions such as iodine and bromine[112, 113]. The efficiency of this stabilizer system is surprising, because copper ions are known to act as prodegradants in polyolefins. Phenolic antioxidants help to stabilize polyamides by improving initial colour after polycondensation. At elevated aging temperatures, e.g. Above 150 °C, the copper/iodide stabilizer systems show best performance, but at lower aging temperatures, the phenolic antioxidant alone or in combination with a phosphite secondary antioxidant is more effective. Discoloration after oven aging does not parallel the drop in mechanical properties. Discoloration is observed after only a short period of aging, while tensile strength and elongation are not affected until later[112].

Aliphatic polyamides find wide application as engineering plastics and fibre material, and during their normal use are exposed to sunlight. Photo aging is therefore a crucial mechanism of degradation, which acts in parallel with the solely

thermally activated process. The mechanisms of photo-oxidation were studied in great details with IR and UV spectroscopies, as well as chemical analysis [114], and new pathways of degradation are being investigated with the aid of new analytical methods, such as MALDI mass spectrometry[115].

### 2.4.3 Oxygen diffusion

Usually at moderate temperatures and normal usage conditions, the permeability of oxygen is sufficient to reach almost its equilibrium solubility over the whole thickness of the polymer [116]. In this case the majority of radicals are present as peroxy radicals. Oxygen diffusion-limited effects occur when the oxygen consumption is comparable to the supply by diffusion. This can be the case during processing, when the oxygen concentration is low, but also in accelerated ageing experiments. The mobility of oxygen in the polymer is a factor of considerable importance in the stabilization of the material; the polymer-oxygen interactions which govern the permeability and solubility of oxygen in the polymer are influenced not only by the chemical composition of the polymer and its additives but also by the physical state of the polymer: plastic deformation, orientation, stress, and ageing itself change the physical condition of the material. These deformations change the free volume present in the amorphous matrix of the polymer, and a correlation between the oxygen permeability and free volume has been presented[117]. The free volume theory is based on the assumption that molecular mobility is determined by the amount of empty space available for a diffusion jump; according to this model, diffusion is faster in more open structures having a higher free volume.

The oxygen uptake curves of polyamides typically show an auto retardant shape in contrast to the sigmoid shape commonly observed for polypropylene. For polypropylene, the amount of peroxides is related to the rate of oxygen uptake, whereas this is not the case for polyamides for which the role of hydroperoxides is less clear[118]. For polyolefins, the oxygen uptake curves are similar to those of liquid hydrocarbons and solid state oxidation has been almost exclusively interpreted in terms of homogeneous free-radical kinetics. However, for several reasons, oxidation of polymers in the solid state, especially semi-crystalline

polymers, must be heterogeneous in nature. Gugumus[104] suggested an alternative model explaining the observed increase in rate as a physical spreading of oxidation from localised regions of high oxidation rates due to a non-uniform distribution of initiation species in the virgin material[119].

#### 2.4.4 Additives diffusion

Generally the migration is considered a process where polymerisation residues or stabilisers can diffuse through the polymer matrix to the surface where they interrupt the radical chain of oxidation reactions. Some of the results for the studies on diffusion coefficients of additives in polymers are[120]:

- the diffusion coefficient is related to the temperature and an Arrhenius-type equation is valid for these systems;
- is dependent on the  $T_g$ , but a discontinuity can be observed at this transition temperature;
- is dependent on the polymer morphology, i.e. crystallinity, orientation, etc.
- is dependent on the molecular mass of the stabiliser.
- the diffusion processes are dependent upon the melting temperature of the stabiliser and a discontinuity can be observed at this transition temperature.

In 1974 Roe *et al.*[121] suggested an experimental method to study the diffusion concentration profile of a stabiliser assuming that a thick polymer film could be in principle considered as a stack of several thin polymer films maintained in strict contact. By this method, the stabiliser concentration in each thin film of the stack assembly can be monitored by some conventional and non-destructive analytical technique, such as FTIR or UV spectrophotometry.

#### 2.4.5 Measuring techniques

Accelerated tests on oven aged samples at elevated temperatures using mechanical and chemical characterisation at regular ageing time intervals have routinely been used to estimate the oxidative stability and useful life of polymers. An alternative approach to the study of oxidation is to use rate sensitive techniques such as oxygen uptake, and chemiluminescence (CL). Oxygen uptake has been referred to

as the most direct technique measuring the consumption of the reactant oxygen, whereas the CL techniques measure the luminescence caused by oxidation products such as peroxy radicals or other species formed during oxidation[119]. A relatively new technique for studying the oxidative stability of a polymer is to use isothermal microcalorimetry for measurement of the weak heat generation accompanying the oxidation[122].

The Carbonyl index is a measure of the change in concentration of the C=O stretch band in the infrared spectrum of the polymer. Because carbonyl is one of the products of the oxidation of the carbon backbone, it relates directly to the extent of degradation. The infrared spectrum can also be inspected for indications on the behaviour of antioxidants present in the material, i.e. leaching out, diffusion through, consumption, provided the absorption peaks of the additives do not overlap those of the matrix polymer, or difficulties in the deconvolution process would result in unreliable data[123].

Oxidation Induction Time (OIT) is performed with an isothermal DSC: the sample is heated rapidly to a standard temperature and then kept in a oxygen or air atmosphere; The time necessary to record the onset of a exothermal oxidation reaction of the material, compared with the unprotected polymer, is a measure of the protection level afforded by the additives.

## **2.5 Antioxidants for Polymers**

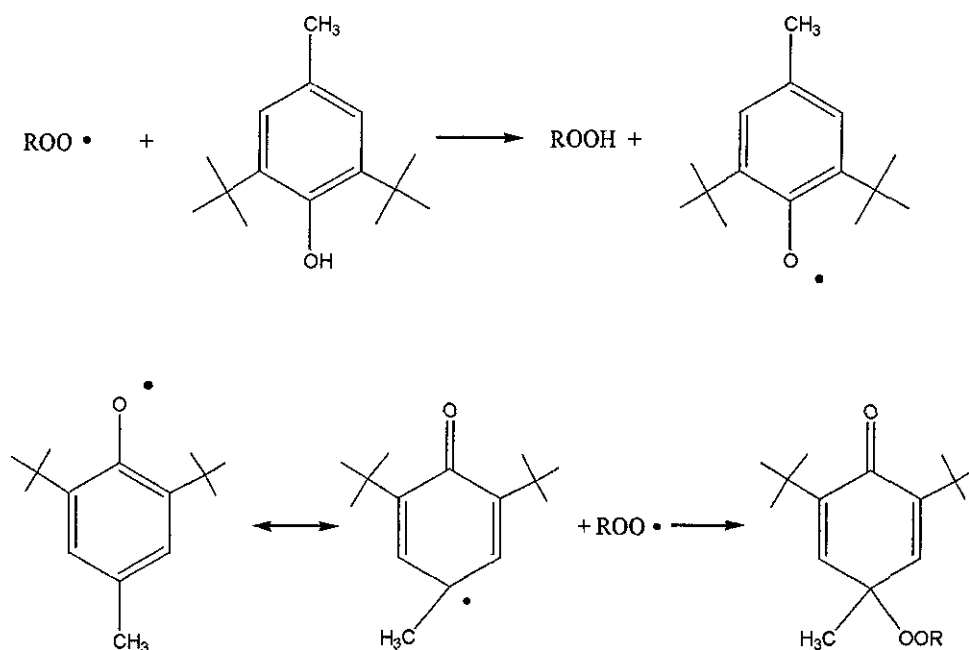
### **2.5.1 Inhibition of oxidation [102]**

The effectiveness of antioxidants is based on the fact that they are able to influence the previously described process of oxidation in different ways, dependent on their chemical structure. Two large basic groups of antioxidant are distinguished: chain terminating, or primary antioxidants, and hydroperoxide decomposers, or secondary antioxidants, frequently called synergists.

The majority of primary antioxidants are sterically hindered phenols or secondary aromatic amines. They are capable of undergoing fast reactions with peroxy radicals; therefore, they are frequently called radical scavengers. These will be the

focus of this investigation. The secondary antioxidants are essentially thioethers and esters of thiodipropionic acid or triesters of phosphorous acid, i.e. phosphites. Research continue to develop improved antioxidants [124] and develop new classes of stabilisers [125].

Stabilisation is based on the following reaction scheme competing with the second propagation step in the radical chain reaction:



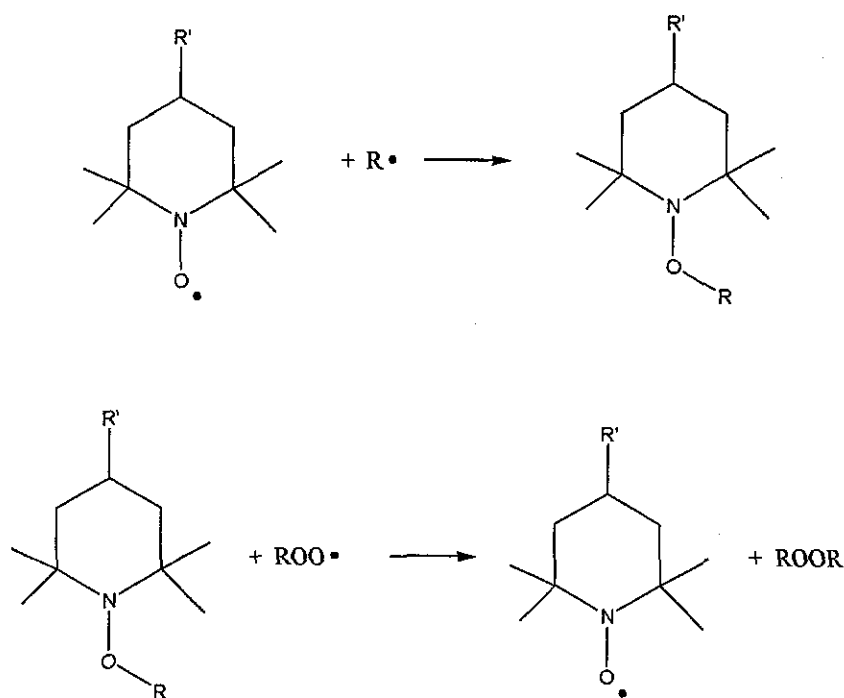
This transform the reactive peroxy radical into a phenoxyl radical, much less reactive because of resonance, which, in turn, is capable to react with a second peroxy radical according to the above scheme [126-128].

The thermal stability of the peroxy cyclohexadienones is limited: their decomposition leads to new reaction chains also at temperatures below 150 °C. The phenoxyl radicals do not initiate new radical chains at the normal temperatures of use and testing, however, this propagation reaction becomes possible at high temperatures. This means that the effectiveness of sterically hindered phenols is decreasing with increasing temperature.

### 2.5.2 Hindered amine light stabilisers[129]

In presence of UV radiation, another mechanism for the degradation of the organic material becomes accessible: free radicals are formed in polymers exposed to light, as a consequence of the excitation of light-absorbing functionalities in the polymer. In the presence of normal atmospheric oxygen the material will simultaneously oxidise (photo oxidation) following the chain reaction kinetic discussed above in 2.4.1, the only difference being the cause of the initiation step. It is difficult to distinguish the pure photochemical processes from the thermal oxidation processes, which are superimposed and occur simultaneously.

Mechanism of reducing the initiation rate, considered the most important step of UV stabilisation, include adding molecules that can act as UV absorbers, quenchers of excited states, hydroperoxide decomposers and free radical scavengers. Hindered secondary amines do not absorb light above wavelength of 250 nm and thus cannot be considered UV absorbers nor quenchers [130]. Researches have shown that, under photo oxidative conditions, sterically hindered amines are partly converted to the corresponding nitroxyl radicals, formed by reaction with molecular oxygen [131-134]. The mechanism is not yet completely understood; generally, it is now assumed that these nitroxyl radicals trap alkyl radicals appearing in the oxidation chain reaction to form N-alkoxy-amines, from which nitroxyl radicals are regenerated [135, 136]:



Because they act on different mechanisms of oxidations, often both types of antioxidants are added simultaneously to protect the polymer. Experiments to combine the hindered aminic and hindered phenolic moieties in the same molecule show promising results[137]. However hindered amine light stabilizers (HALS) are known to show synergism as well as antagonism with acidic compounds including phenolic antioxidants, in that a salt of both substrates accelerates the homolytic decomposition of hydroperoxides[138].

### 2.5.3 Physical and chemical requirements for antioxidants [102]

Besides its main function of inhibiting the oxidation of polymeric materials, an antioxidant must fulfil a whole series of important ancillary properties, which are usually determining factors in assessing the practicability of a compound. Apart from cost considerations, these properties may be divided into three groups: chemical, physical and toxicological. Toxicological properties are of crucial importance for selection of antioxidants in polymers destined for food packaging; information on the extent to which approval is granted in different plastics is provided by the additives manufacturers, and will not be discussed here.

## **Chemical ancillary properties**

### **i ) Discoloration**

An antioxidant has to be colourless and should contribute as little as possible to discoloration of the substrate during long term use. The colour caused by aromatic amines is the main reason for the fact that antioxidant of this type are less used in thermoplastics. Some yellowing may be observed also with sterically hindered phenols, caused by the formation of the oxidation products of the antioxidants [126-128]. Depending on the substrate polymer and the conditions of ageing, a yellowing effect may be caused mainly by the substrate or by the additive: polymers, such as polyurethanes, polycarbonates and styrenics, which change colour during the ageing, superimpose this effect to the yellowing of the additive itself. Antioxidant-caused discoloration during heat treatment in the processing is generally not very important; the effects are more complicated under conditions of artificial or outdoor weathering.

### **ii ) Thermal stability**

An antioxidant has to survive the conditions of manufacturing and processing. The commercially available materials all fulfil this requirement of short term heat stability at temperatures of up to 300 to 320 °C.

### **iii ) Hydrolytic stability**

Some commercial antioxidants are esters of carboxylic acids. Ester groups normally do not hydrolyse under conditions encountered by a polymer. Phosphites used as secondary antioxidants, on the other hand, are much more sensitive towards hydrolysis.

## **Physical ancillary properties**

### **i ) Handling**

Commercial antioxidants are usually free flowing powders with melting points of up to 250 °C or liquids of medium to low viscosity. To ensure storage and transportation stability, melting or softening points should not be below 50 °C. Dust-free preparations are preferred for health and industrial hygiene reasons.

ii ) Solubility and emulsifiability

Whenever the antioxidant is added during the manufacturing step of the polymer, it has to be introduced into the process in a suitable physical form. For some processes the antioxidant has to be soluble in the monomer or in the polymerisation solvent. In others, such as the ABS emulsion polymerisation process, the preferred method is to add the antioxidant as an emulsion.

iii ) Volatility

In the final stage of the polymer manufacture (drying, monomer devolatilisation), an added antioxidant should not be lost through volatilisation. Many antioxidants, mainly long term heat stabilisers, are added during processing of the polymer: they should not volatilise or cause unwanted odour. Most commercial antioxidants fulfil this requirement.

iv ) Extraction resistance

Resistance to extraction is generally a very important requirement: it is a condition for toxicological approval. Aggressive solvents environments can pose demanding requirements on the additives.

v ) Compatibility and migration

With some polymer it is occasionally observed that additives tend to bloom on the surface of the material: such processes usually require a few weeks or months. Blooming is observed when the additives form a supersaturated solution in the polymer and have sufficiently high diffusion rates to migrate to the surface. Antioxidants are generally less soluble in polymers than in lower molar mass liquids. Studies have shown that diffusion coefficients are dependent on the polymer (glass transition temperature), its morphology (crystallinity, orientation) and on the additive itself: quantitative measurements of diffusion coefficients of additives in polyolefins and polyurethane are the subject of numerous publications [139-143]. A rough relation states that the susceptibility for blooming is about 1 : 10 : 100 for polypropylene, high density polyethylene and low density polyethylene.

#### **2.5.4 Strategies for improvement of the retention properties of the antioxidant in the polymer**

The effectiveness of antioxidants depends not only on their intrinsic chemical activity, but also on their physical retention in the polymer. Loss of antioxidant through migration into the surrounding environment, by leaching out into contact food constituents or by extractive action of aggressive solvents, leads not only to premature failure of the polymer article, but also to problems associated with health hazards and toxicological effects. The effects of various physical factors (e.g. solubility, diffusion, volatility, leachability) on polymer oxidation, stabilisation and antioxidant behaviour, both during high-temperature processing and in service, have been described [144, 145].

In recent years, much research has been targeted at the different aspects of antioxidant permanence in an attempt to address the problem of their physical loss. To improve the extraction stability of additives different approaches have been followed [146]:

- i) Synthesis of antioxidants with increasing molecular weight: generally, the compatibility is improved when the antioxidant and the host polymer have similar characteristics. Compatibility of antioxidants in non-polar hydrocarbon polymers, therefore, decreases with increasing antioxidant polarity and increases with the number, length and branching of the inert alkyl substituents attached to the antioxidant function. Many commercial antioxidants with higher molecular masses have been developed and many have long inert (8-18 carbon atoms) alkyl chains;
- ii) Synthesis of oligomeric antioxidants with molecular weight of 3000 and above: further attempts have led to the development of oligomeric and macromolecular antioxidants, by co-polymerising the stabiliser group with a suitable co-monomer, in a variety of methods, e.g. free-radical, ring-opening and condensation polymerisations [147];
- iii) Chemical bonding of the antioxidant to the polymer backbone by a grafting process or incorporation of antioxidants by copolymerisation with a suitable monomer [148]: reactive antioxidants are compounds containing one or more antioxidant functions and one or more chemical functions capable of reacting

either with monomers or with already formed polymers; by being chemically bound to the polymer, the leaching problem is eliminated completely; however, the mobility necessary to be an effective antioxidant is severely impaired and the product is more expensive since new specialty polymers must be produced for each end use product.

- iv) Encapsulating the antioxidant in a controlled-release system, that is then blended in the processed material: the blend would allow prolonged stabilisation, while avoiding the problem of supersaturation.

### 2.5.5 Encapsulated antioxidant

Current research is inconclusive on the practical effectiveness of this approach [149-152]. Some positive results have been reported by Keen *et al.*[150] where BHT was encapsulated into cross-linked calcium alginate particles and was blended in a rubber; the oxidation induction time was increased from 5 minutes with BHT alone to up to 17 minutes using the same concentration of additive in encapsulated form. Other experiments by Allen *et al.*[151] show contrasting effects of the interaction of the antioxidants with silica filler, depending on their chemical structure, which lead to consider that not only entrapment but also an ability to desorb would control the activity of prebound additives. Modelling the encapsulation of polymer additives is complex, partly because of the many different encapsulating geometries possible, and partly because the rate of release into the surrounding polymer depends upon solubility and diffusion rates of the additive in both the encapsulant and the host polymer[149].

The rate of dissolution in water of a sparingly soluble model drug can be varied by hybridising it with silica nanoparticles produced via sol-gel; the rate can be controlled by letting the hydrolysis start before the drug is added to the solution, indicating that a part of the drug is chemically bound to the silica gel and is enclosed in the Si-O network so that not all the drug is available for release. The fraction of molecule bound weakly to the external surface of the agglomerates can dissolve and desorb so that the dissolution rate is correlated to the surface area of the silica[153].

### 2.5.6 Interaction of antioxidant with a silica filler

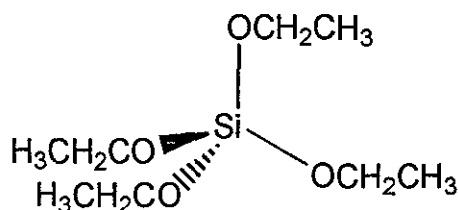
All polymeric materials are processed after the polymerisation, to improve the properties and finalise the product. In this stage heat and photo stabilisers and other process additives may be mixed in, different polymers may be blended, fillers and reinforcements added. Care has to be given to optimise the interactions between the different additives and the components of the finished material. Amorphous silica is widely used as an antiblocking agent for polymer films, or as inert charge to decrease the cost of the material without degrading the properties. Positive effects are represented by synergies between additives. Adverse effects may be adsorption of antioxidants by the filler, so that the effective concentration is actually lower [48, 154, 155]. In thermoplastics, this last effect is a recognized problem, which can be countered by using additives that sacrificially adsorb on to filler surfaces thereby blocking adsorption of the stabilisers. However this effect can be turned into what may be considered a reservoir of stabiliser [156], with the interaction between the additives and the silica surface ensuring that the additive is released slowly, thereby preventing leaching and volatilisation of the stabiliser, thus affording longer lasting protection of the polymer. From adsorption studies on amorphous silica, fillers with high surface area and active groups on the surface and more open pore structure are most likely to display controlled release and preferential adsorption effects.

### 3 EXPERIMENTAL

#### 3.1 Materials

##### 3.1.1 Alkoxysilanes precursor for the production of silica by the sol-gel method

The alkoxysilanes precursor used in these reactions is tetraethoxysilane (or tetraethylorthosilicate), abbreviated as TEOS, supplied by Fluka Chemie AG, 98% pure. This is a transparent liquid, with a relative density of 0.933 and boiling point in the range 163-167°C. The molecular weight of TEOS is 208.33 g·mol<sup>-1</sup>. The complete hydrolysis and condensation of TEOS with water yields SiO<sub>2</sub>. Note that the molecular weight of SiO<sub>2</sub> is 60.08 g·mol<sup>-1</sup>; hence the molecular weight ratio TEOS/SiO<sub>2</sub> is 3.47



Tetraethoxysilane (TEOS)

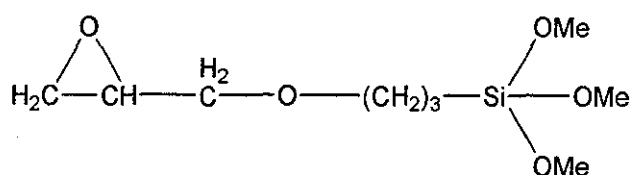
##### 3.1.2 Compatibilisers and coupling agents

Organic molecules of medium-to-high molecular weight have generally low miscibility with precursor solutions used to produce silica by the sol-gel route. The following coupling agents were therefore used with the view to produce the interactions between organic and inorganic components:

- i) 3-glycidyloxypropyltrimethoxysilane, abbreviated as GOTMS, supplied by Fluka Chemie AG; it is a transparent liquid with a boiling point of 260°C, a molecular weight of 236.34 g·mol<sup>-1</sup> (giving a molecular weight of

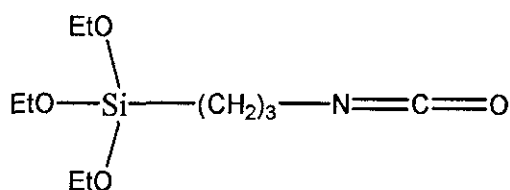
167.3 g·mol<sup>-1</sup> when fully co-condensed with the silica network). As explained in the literature survey, previous experimental evidence shows that GOTMS reacts with terminal hydroxyls in the PEO and co-condenses in the silica matrix, helping to prevent phase separation of the two polymers.

The structure of GOTMS is



GOTMS

- ii)  $\gamma$ -triethoxysilyl propyl isocyanate, abbreviated as TESP-NCO, obtained from Aldrich (purity >95%); it is a viscous liquid with molecular weight 247.37 g·mol<sup>-1</sup> (the molecular weight is 136.4 g·mol<sup>-1</sup> when fully co-condensed in the silica network). TESP-NCO was chosen for the isocyanate ability to react with the OH groups of the phenolic antioxidants or NH groups of the amine antioxidant investigated, while the  $\gamma$ -triethoxysilyl moiety would co-condense within the growing silica phase. This would have the effect of promoting adsorptions of further antioxidant molecules on the surface of the inorganic phase.

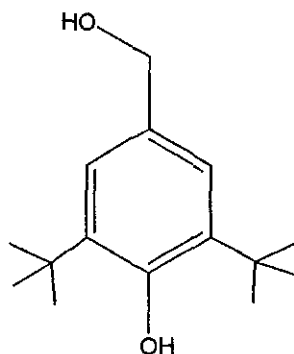


Isocyanate-Coupling agent (TESP-NCO)

The structure of TESP-NCO is

- iii) 2,6-di-tert-butyl-4-hydroxymethylphenol, abbreviated as DBHMP, supplied by TCI (Tokyo Kasei Organic Chemicals); it is a white powder with a purity >97% and a melting point of 141°C. This is a reactant was chosen for the

synthesis of a trialkoxysilane-based compatibiliser for the phenolic antioxidants. The aliphatic hydroxyl can react with the isocyanate in TESP-NCO much more readily than the aromatic hydroxyl normally present in phenolic antioxidant, and such adduct would co-condense in the inorganic phase. The formula of DBHMP is



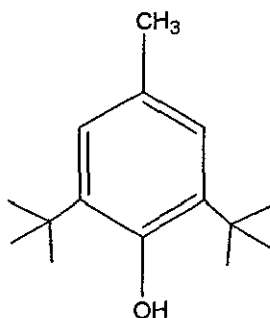
2,6-di-tertbutyl-4-hydroxymethylphenol (DBHMP)

### 3.1.3 Antioxidants

Two classes of antioxidant were considered in this study: phenolic antioxidants and hindered amine antioxidants. Refer to section 2.5 for a detailed discussion of the properties and requirements of antioxidants. A selection of commonly used commercial antioxidants was made, to represent the two classes of antidegradants. The lowest molecular weight of the hindered phenolic antioxidants (BHT) and two higher molecular weight alternatives (Irganox 1076 and Irganox 1010) are widely used in the stabilisation of polyolefins and other polymers against thermo-oxidation. The aromatic amine IPPD, used for example in the protection of synthetic rubber, and the hindered aliphatic amine Tinuvin 770 are routinely used in the industrial practice to protect against UV-activated oxidation.

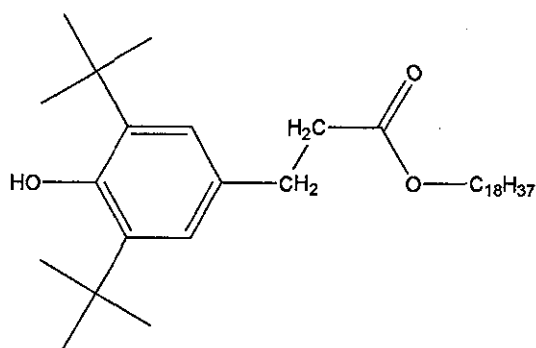
The antioxidants considered for the production of hybrids are

- i ) 3,5-di-tert-butyl-4-hydroxytoluene (2,6-di-tert-butyl-4-methylphenol) (BHT) was supplied by Aldrich; it is a white powder with a molecular weight of  $220 \text{ g}\cdot\text{mol}^{-1}$ . The formula of BHT is



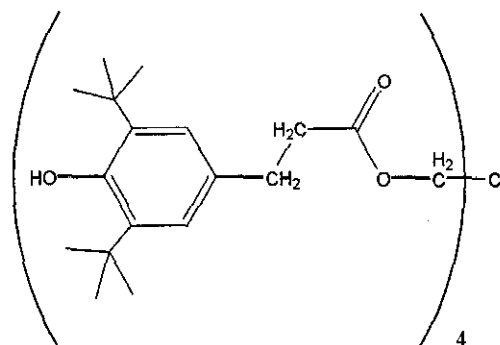
3,5-di-tert-butyl-4-hydroxytoluene (BHT)

- ii ) Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate. This was supplied by Ciba Specialty Chemicals with the trade name of Irganox 1076. It has a melting range of  $49\text{-}54^\circ\text{C}$  and a molecular weight of  $531 \text{ g}\cdot\text{mol}^{-1}$ . The formula of Irganox 1076 is



octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate  
Irganox 1076

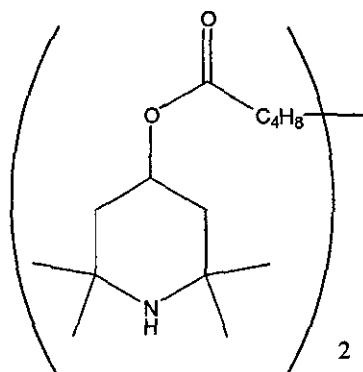
- iii ) Pentaerythrityl-tetrakis-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)]-propionate. This was supplied by Ciba Specialty Chemicals with the trade name of Irganox 1010. It has a molecular weight of  $1178 \text{ g}\cdot\text{mol}^{-1}$ , two crystalline forms and a melting range of  $110\text{-}125^\circ\text{C}$ . The formula of Irganox 1010 is



pentaerythritol-tetrakis-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate]

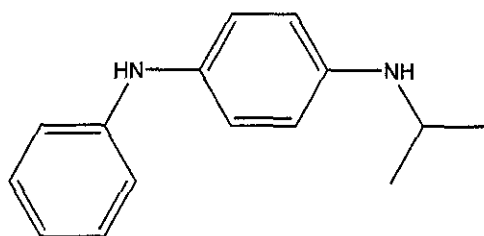
Irganox 1010

- iv) Bis-(2,2,6,6-tetramethyl-4-piperidyl)-sebacate. This was supplied by Ciba Specialty Chemicals with the trade name of Tinuvin 770. It has a purity >97%, molecular weight  $480 \text{ g}\cdot\text{mol}^{-1}$ , melting point  $84^\circ\text{C}$ . The formula is



Tinuvin 770

- v) N-isopropyl-N'-phenyl-p-phenylenediamine. This was supplied by Flexsys N.V./S.A. under the trade name of IPPD. It has a purity >97%, molecular weight  $226 \text{ g}\cdot\text{mol}^{-1}$ , melting point  $75^\circ\text{C}$ . The formula of IPPD is



N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD)

### 3.1.4 Organic polymer component of the hybrid

Poly(ethylene oxide) was selected as organic polymer component of the hybrid because its relatively high hydrophilicity would allow interaction with the reacting hydrated siloxane and the formation of nanoscale dispersed domains.

The polymer used was supplied in form of fine white powder by Union Carbide Corporation under the commercial name of Polyox resin WSRN-10. The number average molecular weight is in the region of 100,000. It has a melting range of 63-69 °C, and was dissolved in THF to a concentration of 10 %w/w, obtaining a viscous translucent solution. The general formula for PEO is:



### 3.1.5 Solvents and water

Ethanol was used as a miscibiliser for the alkoxysilane/water system. It is an azeotropic solution containing 5% of water. It was supplied by Fisher Chemicals. The water used was deionised in the laboratory. The THF used was supplied by Fisher Chemicals as analytical grade 99+.

### 3.1.6 Catalysts

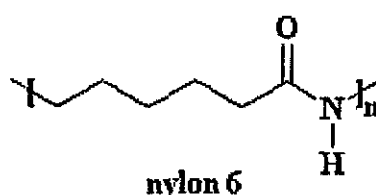
- i) In the production of alkoxysilane/water precursor solution hydrochloric acid (HCl) was used as catalyst for the hydrolysis/condensation reaction. It was supplied by Fluka Chemie AG as 32% w/w solution in water and was diluted to 2% w/w with demineralised water in the laboratory, in order to gain better control of the acidity of the reaction.
- ii) In the preparation of the compatibiliser involving condensation of TESP-NCO with DBHMP a drop of dibutyltindilaurate (DBTDL) was added to the reaction solution as catalyst according to the procedure described by Pan *et al.* [148]. DBTDL was an analytical grade solution supplied by Fisher Chemicals. The resulting concentration of the catalyst in the reaction mixture was 0.5% w/w.

### 3.1.7 Polyamide 6 film

Nylon 6 polyamide was used as model polymer for the diffusion study of antioxidants from the organic/inorganic hybrid because the polar amide group would favourably interact with the surface hydroxyl of the silica phase and the ether oxygen in the PEO chain, allowing for intimate contact and easier diffusion of the antioxidants through the surfaces. In temperate ambient conditions, up to 7% humidity is absorbed in Nylon, and such water molecules would not adversely affect the hydrophilic chain of PEO or the porous silica.

Poly(caprolactam) sheets of thickness 12  $\mu\text{m}$  were supplied by Snia S.p.A., and were used as supplied. The film is transparent and flexible, with a melting point of 220  $^{\circ}\text{C}$  and a glass transition temperature of 40  $^{\circ}\text{C}$ . The film was stored at room temperature before being used in the experiments.

The chemical structure of Nylon 6 is:



## 3.2 Preparation of the Sol-Gel hybrids

### 3.2.1 Notation

In order to simplify the reference to a particular sample, table 3-1 shows an abbreviated notation that can be employed, comprising of an abbreviated name identifying the components and two digits specifying the relative quantities (in weight-by-weight percentage).

**Table 3-1 Codes used for hybrids**

| Code  | Antioxidant | Molecular Weight<br>$M_w$ [g·mol <sup>-1</sup> ] |
|-------|-------------|--------------------------------------------------|
| BHT   | BHT         | 220                                              |
| I1076 | Irganox1076 | 531                                              |
| I1010 | Irganox1010 | 1178                                             |
| T770  | Tinuvin770  | 480                                              |
| IPPD  | IPPD        | 226                                              |

Table 3-2 summarises the molecular weights of the species present that are capable of reacting by hydrolysis/condensation (TEOS, GOTMS, TESP) of silicon moieties and by addition of the isocyanate group. Hydrolysis/condensation changes the formula weight associated with each condensed species, and that is being shown in the third column of table 3-2. FW (solid) is the formula molecular weight without the alkyl radicals in the alkoxysilane groups. The FW corresponds to the MW of the units that enter the silica network for compatibilisation. Therefore silica content in the compositions discussed in the results chapter is calculated by assuming that TEOS is fully hydrolysed and condensed to SiO<sub>2</sub> and likewise that the triethoxysilyl group reacts to SiO<sub>3/2</sub>.

**Table 3-2 Silicon-containing precursors for hybrids**

| Precursor    | $M_w$ | FW<br>(solid) |
|--------------|-------|---------------|
| TESP-U-DBHMP | 483   | 372           |
| TESP-NCO     | 247   | 136           |
| TESP-U-Et    | 293   | 188           |
| GOTMS        | 236   | 167           |
| TEOS         | 208   | 60            |

### 3.2.2 Dissolution of solid components

Where some of the reactants were solids, they were pre-dissolved in the minimum quantity of appropriate solvent. Ethanol was the solvent of choice and the quantity has been included in the formulation. When a different or additional solvent was used it is specified.

### 3.2.3 Preparation of TESP-U-DBHMP compatibilisers

A preliminary screening of different compatibilisers suitable for the sol-gel reactions was carried out using four different compatibiliser systems. These were:

1. Reaction of TESP-NCO and DBHMP. Two solvent systems were tried:  $\text{CHCl}_3$  and Toluene / Tetrahydrofuran (THF) mixture at 8:1 weight ratio. DBHMP was dissolved at room temperature to give a 17% w/w solution. TESP-NCO was then added in a stoichiometric ratio 1:1.
2. Reaction of TESP-NCO with Irganox 1076. The antioxidant in powder form was dissolved in THF to a concentration of 20 %w/w and then TESP-NCO was added to obtain the required stoichiometric ratio. DBTDL was added and the mixture stirred at 80°C for 1 week.
3. Reaction of TESP-NCO with Tinuvin 770. The amine antioxidant was dissolved in THF to a concentration of 20%w/w and then TESP-NCO was added with the required stoichiometry.
4. Reaction of GOTMS. GOTMS was not pre-treated, and was added to the sol-gel mixture as it was supplied.

### 3.2.4 Preparation of precursors for antioxidant-silica hybrids

A closed cylindrical glass tube (diameter circa 25mm) was used as the reaction vessel. A paraffin oil bath on a hot plate provided the temperature control and a magnetic stirrer provided for the homogeneity of the mixture. The order of addition of the component was TEOS, compatibilisers, ethanol, water and HCl (in a diluted solution), to achieve better pH control. The mixture was stirred for 10 minutes before the antioxidant was added in the form of alcoholic solution at 20%w/w concentration. After the incorporation of the antioxidant, the solution was stirred in a closed vessel for one hour or until the onset of gelation, if this occurred sooner.

The temperature of the reaction bath was kept at 60-70°C. The ratio H<sub>2</sub>O/TEOS was always adjusted at 1 mole of H<sub>2</sub>O per mole of alkoxy group in the system.

### **3.2.5 Preparation of polymer-silica-antioxidant hybrids**

A measured quantity of polyethylene oxide was dissolved in THF to a concentration of 10%w/w and kept at 60 °C under stirring. The antioxidant was dissolved separately in THF to a concentration of 10%w/w. A sol-gel precursor was prepared as described above and let to react for 10 minutes. In the IPPD containing series of experiments, the GOTMS content was kept constant at a 1 : 0.15 molar ratio with respect to TEOS (1 : 0.01 weight ratio). The 3 solutions were then mixed together and stirred for one hour in a closed vessel at 60 °C. The viscous solution was cast as a film and the solvent was evaporated overnight at room temperature (22 ± 2 °C)

### **3.2.6 Gel time**

The gelation time T<sub>g</sub> for the bulk solution was determined by visual observation as the magnetic stirrer encountered solid lumps instead of viscous solution.

## **3.3 Preparation of samples for ageing**

### **3.3.1 Preparation of the sandwich samples for ageing**

The prepared hybrid was allowed to dry at room temperature for a minimum of 2 days. The hybrid material was crushed with a mortar and pestle to achieve uniform powder granularity.

### **3.3.2 Hot press**

A thin layer of powder (2mm) was spread between two films of Nylon 6 of thickness 12 µm. Two protective sheets of PET were used to separate from metal sheets and the whole setup hot pressed in a Moore Hydraulics press under 95 bar of pressure. The temperature of the upper and lower hot plates was set at 160 °C. The temperature was applied for 10 minutes, and then the setup was moved to a cold

press, where it was allowed to cool down while kept under pressure. Then the silica hybrid sample was peeled off and stored.

### 3.3.3 Setup after Roe

Following the setup used by Roe *et al.*[121], circular discs 2cm in diameter were cut out from the hot pressed silica hybrids and from 12  $\mu\text{m}$  thick Nylon 6 films. A stack was formed with this structure: 10 nylon layers, silica hybrid, and 10 nylon layers. The stack was sandwiched between 2 films of PET and secured in position with an aluminium frame. See Figure 3-1, to the left is a stack of 10 nylon 6 films over the metal frame; to the right the other 10 films stack with the silica hybrid on top. (A small piece broke as it was being handled).

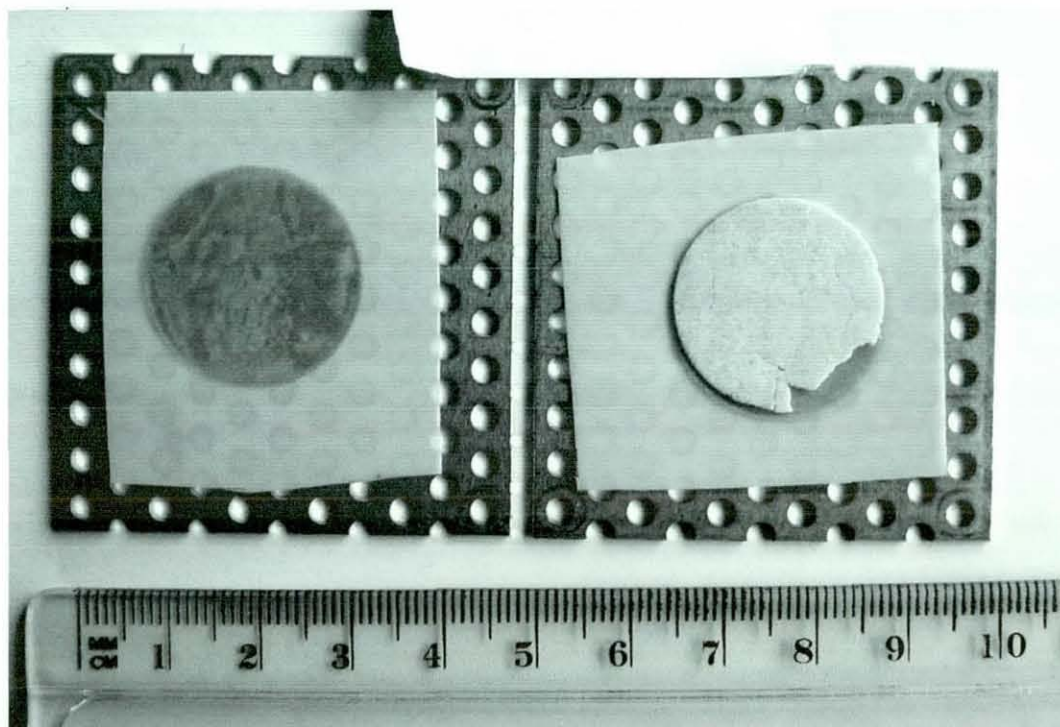


Figure 3-1 Roe setup for oven aging of Nylon 6 film stacks with hybrid

### 3.3.4 Oven ageing

The samples were placed in a Carbolite Eurotherm oven for ageing. Ambient air was allowed to circulate and the temperature was set at 60 °C. After each period, the rig was taken out of the oven and opened. The films were carefully separated with tweezers and analysed, then the set-up was reassembled and replaced in the

oven for further aging. The experiment was run for over 520 days (more than 17 months).

### **3.4 Characterisation Techniques**

#### **3.4.1 Infrared Spectroscopy**

Irradiation of infrared light on a thin liquid film or crystals diluted in an IR-transparent medium results in an absorbance patterns characteristic of different functional groups and molecules. Infrared frequencies in the wavelength range of 1-50  $\mu\text{m}$  are associated with molecular vibrations and vibration-rotation spectra. The mid-IR range of frequency is of particular use in organic structure analysis, because this is where the observed stretching vibrations occur, and can be correlated to molecular structural features. Identification of organic molecules by infrared has become routine, as it is possible to assign specific absorptions to particular groups. The advent of Fourier Transform methods has meant that modern IR equipments able to obtain quickly a spectral scan from a single excitation. Done repeatedly, the scans can be averaged to produce an accurate spectrum of the sample. Infrared frequency is most commonly measured in wave numbers, the reciprocal of wavelength in centimetres.

A MATTSON 3000 FTIR Spectrometer was used: employing a single beam of radiation in transmittance mode, the instrument performed 64 scans with a resolution of 4  $\text{cm}^{-1}$ . The mode of the obtained spectra was subsequently converted to absorbance. Preparation of the sample involved spreading a thin film of the liquid sample between two NaCl disks as supports or pulverizing about 1mg of solid sample with KBr powder as medium and then pressing the powder into a transparent pellet. Alternatively, when a thin film of polymer was analysed, it was directly held in place and the beam shone through it. This technique allowed measuring the extent of reactions of condensation of isocyanate with various reactants, and estimating the degree of protection of Nylon by the antioxidant in the diffusion experiment.

### 3.4.2 Differential Scanning Calorimetry

The thermal properties of various experiments were examined by Differential Scanning Calorimetry (DSC). This technique allowed estimating the degree of compatibilisation of different antioxidant and different phases in various compositions in the hybrids by observing the presence of melting endotherms of the antioxidant and its actual melting temperature. Samples of small pieces were weighted about 10 to 15 mg and placed in a small aluminium pan with a lid, together with the reference cell. A Dupont Instruments 910 Differential Scanning Calorimeter was used. The dried hybrid would be heated up from room temperature to a temperature of 110- 150 °C at a rate of 10°C/minute, held at temperature for one minute then cooled at the same rate until room temperature or slightly below; this was normally followed by another heating ramp at the same rate. At 110- 150°C the antioxidants and PEO would be melted, while the silica phase would not begin sintering. The measurements were carried out in nitrogen flow ( $\sim 50 \text{ cm}^3/\text{min}$ ).

Oxygen Induction Time measurement (OIT) were also carried out by DSC. In an OIT experiment, a small sample was placed in an open pan in the DSC cell, which was then heated to the selected temperature in nitrogen atmosphere. When isothermal conditions were achieved, the gas flow was rapidly changed to atmospheric air ( $\sim 50 \text{ cm}^3/\text{min}$ ) and the exothermal peak of oxidation measured, if observed at all. The OIT quoted would be the time passed between the changes of gas and the onset of oxidation peak.

### 3.4.3 Scanning Electron Microscopy

In the scanning electron microscopy (SEM), the radiation that interacts with the specimen is a beam of high-energy electrons, produced from a filament and accelerated by a high voltage. Three imaging signals can be used [157], back scattered electrons, secondary electrons and x-rays. Characteristic x-rays have well-defined energies for different atoms. Thus, analytical information can be obtained from an x-ray spectrum [158]. Back-scattered electrons are primary beam electrons that have been elastically scattered by the nuclei in the sample and escape from the surface. Thus they can be used to obtain compositional contrast in the sample.

Secondary electrons are emitted with low energy from the top few nanometres of the materials. This technique yields topographic images of the sample surface. Due to its great depth of field, SEM images have an almost three-dimensional appearance, and have a much higher resolution.

Damage to the polymer by the electron beam is one of the principal shortcomings of electron microscopy. Three effects, namely loss of crystallinity or mass, contrast artefacts and distortion, can lead to great changes in the image formed in the microscope [159]. In order to minimise this, the surface of the specimen is coated with an electrically conductive thin layer of gold or gold/palladium alloy.

Information regarding the homogeneity of the hybrid phases, and dispersion or crystallisation of the antioxidants was obtained through SEM micrographs of the surface of synthesised hybrid.

Small specimens of hybrids were glued to a stub and a thin layer of gold was sputtered on to ensure conductivity; a Leica Cambridge Instruments Ltd. Stereoscan 360 equipment was used for the observation at different magnification levels.

#### **3.4.4 Visual observations**

Crystals and in-homogeneities of dimension comparable to the wavelength of visible light (400-800 nm) cause light scattering, causing a material to appear cloudy and opaque. Silica obtained via the sol-gel route is a homogeneous, amorphous material that does not absorb nor scatter the visible light.

By visual observation and comparison with these materials, the compatibility and homogeneity of the antioxidant-containing hybrids can be qualitatively assessed.

The product of the sol-gel reaction was a transparent gel, which cracked under the stress developed during the drying process. The hybrid produced via sol-gel with only TEOS, GOTMS and PEO was a transparent gel that dried without cracking when cast as a film. The domains of crystalline PEO are of small dimensions and light scattering does not occur [98].

## 4 RESULTS AND DISCUSSION

The sol gel method of synthesis was used to prepare organic inorganic hybrids composed of modified silica, poly(ethylene oxide) and commercial antioxidants.

A number of intermediates was synthesised by isocyanate addition to hydroxyl groups, and the extent of reaction evaluated by FT-IR (see section 4.3); these and other coupling agents (see section 4.4) were then co-condensed in the sol-gel synthesis of modified silica.

A series of binary (see section 4.6 and 4.7) and ternary (silica-PEO-antioxidant see section 4.8) hybrids were synthesised and characterised by visual inspection (see section 4.5), by measuring the time to gel (section 4.2), and by Fourier Transform Infra Red spectroscopy, Differential Scanning Calorimetry and Scanning Electron Microscopy (all discussed in sections 4.6 to 4.8).

Ternary hybrid containing the commercial antioxidant BHT was used as model for a functionalised filler delivery system for antioxidant protection in polymer: a study of the diffusion of BHT out of the hybrid and into a surrounding Nylon 6 film was carried out by Oxygen Induction Time (see section 4.9) and FT-IR analysis (see section 4.10).

### 4.1 *Effects of the acidity of the precursor solution*

The conditions change drastically when moving from hindered phenols (weak acids) to secondary hindered amines (medium strength bases). As discussed in the literature review, very different silica morphologies are obtained from acid or basic conditions, as well as different gelation rates.

The pH of the precursor alkoxide solution was set at pH~3 with a solution of HCl 2% w/w in water. The pH was not monitored after the addition of PEO or antioxidant.

When the ammonium salt of the hindered amine Tinuvin 770 was made with HCl prior to its incorporation in the reaction mixture, a homogeneous solution could not be obtained, and therefore this route was not pursued.

When the free amine was added as an alcoholic solution to the hydrolysing acid mixture, it caused an abrupt rise of pH and almost immediate gelation.

## **4.2 Observations on gelation behaviour**

### **4.2.1 General Considerations**

Gel time varied widely between different solutions, as can be expected by the large number of variables involved, such as compatibiliser content and type, nature of the antioxidant,  $pK_a$ , amount of solvent. For this reason gel time was not considered as a parameter unless it was so short that it prevented the mixture from achieving the required homogeneity. If, after one hour of stirring, the solution was not gelled, it was poured over a sheet of hydrophobic paper and the solvent evaporated to produce films of about 0.7 mm thickness.

### **4.2.2 Effect of amine antioxidants**

Samples containing the amine antioxidant Tinuvin 770 gelled very quickly after the amine solution was added to the alkoxide precursors. This prevents the completing of hydrolysis of the alkoxide, thereby preventing the formation of an open silica structure.

In samples 1 and 2 (see table 4-1) the salt of the amine was formed with hydrochloric acid in the ethanol solution, prior to mixing with the alkoxide precursor. Gel time increased considerably, but upon drying of the film, phase separation was noted: the antioxidant salt formed white needle crystals distinct from the bulk of the silica phase.

In samples 3 to 7, silica with various amine content were synthesized, always obtaining a clear transparent solution that evolved into a clear transparent gel within 5 minutes of mixing. After drying the resulting solid always shrank considerably and cracked.

| Sample | Tinuvin770 % | Temperature of reaction (°C) | Gel time<br>T <sub>G</sub> (min) | Appearance of gel                |
|--------|--------------|------------------------------|----------------------------------|----------------------------------|
| T770-1 | 4 (salt)     | 57                           | 30                               | Opaque, white crystals separated |
| T770-2 | 10 (salt)    | 57                           | 18                               | Opaque, white crystals separated |
| T770-3 | 4            | 53                           | 5                                | Clear, transparent gel           |
| T770-4 | 8            | 53                           | 4                                | Clear, transparent gel           |
| T770-5 | 17           | 56                           | 3                                | Clear, transparent gel           |
| T770-6 | 17           | 70                           | 3                                | Clear, transparent gel           |
| T770-7 | 29           | 50                           | 5                                | Clear, transparent gel           |

**Table 4-1 Gel time of sol-gel silica with Tinuvin 770**

### 4.2.3 Effect of phenolic antioxidant

Samples containing the phenolic antioxidants BHT or Irganox 1076 were stirred at temperature around 60 °C until loss of flowing ability, to determine the gel time. See table 4-2 for samples containing BHT and table 4-3 for samples containing Irganox 1076, shown graphically in Figure 4-1.

| Sample | BHT (%) | Temperature of reaction (°C) | Gel time<br>T <sub>G</sub> (min) | Appearance of gel             |
|--------|---------|------------------------------|----------------------------------|-------------------------------|
| BHT-1  | 0.2     | 63                           | 50                               | Clear, transparent gel        |
| BHT -2 | 2.5     | 65                           | 40                               | Opaque soln., translucent gel |
| BHT -3 | 5       | 63                           | 70                               | Phase separation              |
| BHT -4 | 6       | 63                           | 60                               | Phase separation              |
| BHT -5 | 11      | 62                           | 70                               | Phase separation              |

**Table 4-2 Gel time of sol-gel silica with BHT**

Solutions containing BHT gelled considerably faster than solution containing Irganox 1076, the former gelling in around 1 hour, while the latter in over 2 hours. Increasing antioxidant concentration results in an increase in gel time. This is probably to be attributed to the dilution effect of the non-reacting antioxidant among the polymerising silica sol.

| Sample  | Irganox 1076 (%) | Temperature of reaction (°C)) | Gel time T <sub>G</sub> (min) | Appearance of gel             |
|---------|------------------|-------------------------------|-------------------------------|-------------------------------|
| I1076-1 | 0.1              | 63                            | 130                           | Clear, transparent gel        |
| I1076-2 | 0.1              | 67                            | 120                           | Clear, transparent gel        |
| I1076-3 | 0.2              | 65                            | 115                           | Clear, transparent gel        |
| I1076-4 | 0.5              | 62                            | 140                           | Opaque soln., translucent gel |
| I1076-5 | 1                | 58                            | 150                           | Opaque soln., translucent gel |
| I1076-6 | 2                | 61                            | 155                           | Phase separation              |
| I1076-7 | 5                | 60                            | 160                           | Phase separation              |
| I1076-8 | 10               | 62                            | 170                           | Phase separation              |

Table 4-3 Gel time of sol-gel silica with Irganox 1076

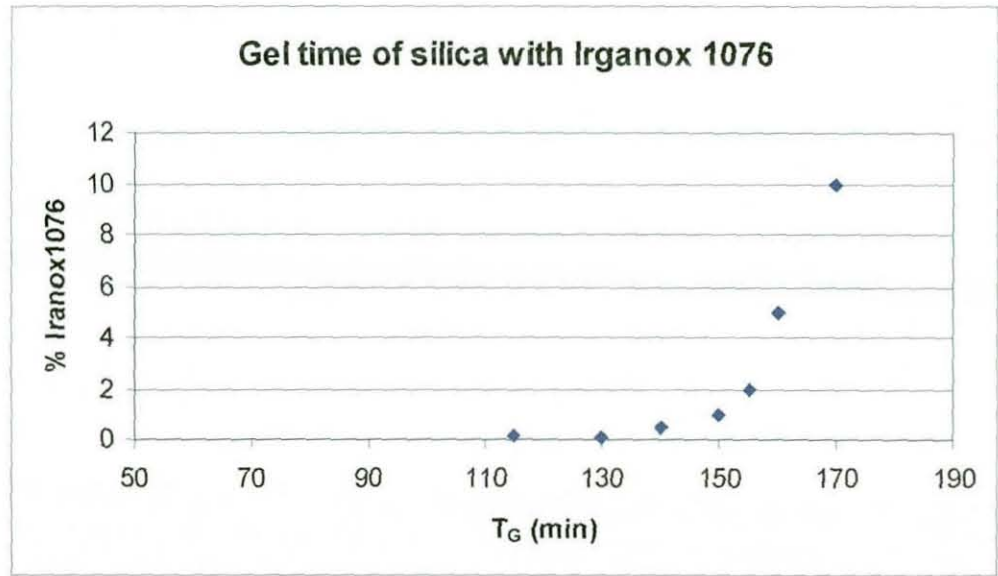


Figure 4-1 Gel time of sol-gel silica with Irganox 1076 (60 °C)

Even small concentration of phenolic antioxidant were sufficient to cause phase separation in the dry gel, causing the solid to be opaque and, at concentrations above 5% (for BHT) or 2% (for Irganox 1076), exhibiting clear crystalline domains of antioxidant separated from the silica.

### **4.3 Analysis of the reaction products of TESP-NCO**

TESP-NCO is a bi-functional molecule, containing both the alkoxysilane group and the isocyanate group. The former is able to hydrolyse under acidic or basic condition and self-condense or co-condense with TEOS in a typical sol-gel reaction. The latter is a very reactive centre, subject to addition by any nucleophilic species that also contains labile hydrogen, such as alcohol and amine. Such additions yield carbamate or urea linkages, more polar groups, which are also donor and acceptor of hydrogen bonds.

#### **4.3.1 Reaction of TESP-NCO with DBHMP**

The aliphatic isocyanate group can react either with the phenolic or hydroxymethyl function to form a urethane bond. This adduct should be able to incorporate in the silica matrix and form van der Waals interactions with the rings of the hindered phenols, thereby enhancing the miscibility with the inorganic phase. Since there is no chemical bond, molecular mobility is not prevented, and therefore the organic compounds can still act as effective antioxidants. The literature [148] confirms that the hydroxymethyl group is much more reactive than the phenolic –OH so that the reaction is expected to occur at the aliphatic hydroxyl group.

The isocyanate and the alcohol were dissolved together in a mixture of xylene and TFH (8:1). Infrared spectra of the two components and the mixture right after dissolution are in Figure 7-1 to 7-3. Then 0.1 ml of dibutyltin dilaurate (DBTDL) solution in benzene is added; DBTDL is a known catalyst for urethane formation reactions.

Within 2 hours the reaction goes to completion. This is indicated by the disappearance of the stretching of the conjugated  $\text{N}=\text{C}=\text{O}$  at  $2272\text{ cm}^{-1}$  (see Fig. 7-2 and 7-3), while the stretching of carbonyl in the urethane appears at  $1708\text{ cm}^{-1}$  (Fig. 7-4).

#### **4.3.2 Reaction of TESP-NCO with Irganox 1076**

The isocyanate was presumed to be able to form a urethane bond by reacting with the phenolic group. If this occurred the antioxidant would be chemically bound to

the silica matrix. In any case the urethane functions formed in this way are known to be thermally labile, so that if the reaction occurred the organic molecule could be released over time during the processing of the polymer. The steric hindrance of two tert-butyl groups in ortho position to the phenol are expected to inhibit the reaction and, therefore, may require a vast excess of phenol and long reaction times. Phenol excess of 200% and 300% were investigated with reaction times of up to 2 weeks. Temperature was kept below 90 °C to avoid thermal dissociation of the addition. FT-IR spectra were recorded to evaluate the extent of reaction of the condensation TESP-NCO with the aliphatic OH group of DBHMP and the aromatic OH group of Irganox 1076 (figures 7-5, 7-1, 7-2, 7-6, 7-7). TESP-NCO reacts with DBHMP within 1 day to 100% conversion, while Irganox 1076 is much less reactive, giving only 50% yield (1:1 TESP-NCO : Irganox molar ratio) in 1 week. The latter product is not useful because all the unreacted isocyanate is attacked by the water and decomposes to amine and CO<sub>2</sub>. The NCO peak at 2270 cm<sup>-1</sup> never disappears, indicating a lack of reactivity. As an additional attempt, TESP-NCO was stirred with BHT for one week at 50°C, but again only a yield below 50% was observed. (See Figure 7-8 for the FTIR spectrum of BHT) In both these cases the only functional group available for reaction with the isocyanate is a sterically highly hindered aromatic alcohol, a reaction that is known to be unfavoured and easily decomposed by heating. This makes it unsuitable to be used as compatibiliser for the organic-inorganic hybrid.

#### 4.3.3 Reaction of TESP-NCO with Tinuvin 770

An amine is a much stronger nucleophile than an alcohol; hence it reacts faster with the isocyanate group. No catalyst was necessary, even at room temperature. Although Tinuvin 770 contains a hindered amine group, this reaction is more favourable than the one with the hindered phenol of Irganox 1076, and therefore the reaction is expected to occur much quicker. (Figure 7-9) In this case the urea linkage formed is non-reversible, hence the amine is expected to be locked in the silica matrix and may not act as antioxidant for the polymer due to the loss of mobility.

#### **4.4 Effect of systems containing GOTMS coupling agent**

In an acidic environment, the epoxide group will open and react either with water to form a vicinal diol, or with the amine groups in the antioxidant, such as Tinuvin 770, forming a  $\alpha$ -hydroxyl tertiary amine. In the presence of PEO, the epoxide may also be able to bind with the OH group present at the end of the polyether chain, thus binding the organic phase to the growing, polymerising inorganic phase [98]. The phenolic groups in the antioxidants are not expected to react but will be able to form hydrogen bonds with the –OH groups formed from the opening of the epoxy group.

Some sol-gel silica samples were prepared at low content of BHT (0.2%w), and GOTMS contents of 3, 10 and 15% w/w, to assess the effect of such compatibilisation. The appearance of such gels is tabulated in Table 4-4.

| Sample  | % GOTMS | Appearance of gel |
|---------|---------|-------------------|
| GOTMS-1 | 3       | Clear, brittle    |
| GOTMS-2 | 10      | Clear, brittle    |
| GOTMS-3 | 15      | Clear, tough      |

**Table 4-4 Effect sol-gel silica of varying GOTMS content**

#### **4.5 Assessment of degree of compatibilisation of the antioxidant in sol-gel silica systems**

The techniques used to assess the degree of compatibilisation were:

##### **4.5.1 Visual inspection.**

By observing the presence of opaque formations in an otherwise clear and transparent film, it is possible to note spinodal decomposition during the casting of the film. Such was the case for the experiments with an Irganox 1076 content higher than 2%w/w. By comparison, the gels containing Tinuvin 770 were clear and transparent with antioxidant content as high as 70%w/w.

#### 4.5.2 DSC

All DSC thermograms are included in Appendix. Between  $-30^{\circ}\text{C}$  and  $200^{\circ}\text{C}$  the silica network does not undergo any transition. As discussed in the literature survey, sintering of sol-gel silica occurs at higher temperature. See figure 7-10: when the first heating ramp presents a endothermic slope which has no correspondent in the cooling ramp or in the second heating ramp, it is an indication that it was due to remaining reaction solvent from the synthesis. Hence the endo- or exothermal peaks observed in the binary and ternary compositions are due to melting or crystallisation of an organic phase within the inorganic matrix. In the absence of compatibilisation the enthalpy of fusion of the antioxidant would be directly proportional to the mass content of organic phase. The discrepancies that arise in the measure of values are attributed to antioxidant entrapped in the amorphous network or adsorbed on the surface of the pore structure, and unable to crystallise.

#### 4.6 Thermal Analysis of silica-antioxidant sol-gel systems

Binary hybrids of sol-gel silica and different antioxidants were synthesised and characterised by DSC. The amount of antioxidant that forms an independent and separated phase was investigated. In some samples traces of solvent will remain and require a prolonged treatment at high temperatures for its removal. This may affect the morphology and crystallinity of the additive/silica system, and it shows in the DSC traces as endothermic slope of the first heating curve.

##### 4.6.1 Silica

Silica derived from the sol-gel route does not undergo any reaction at the moderate temperature considered in this study, and so there are no peaks represented in the DSC scan. In some samples there is residual water present in the material, which will then slowly evaporate from the heating oven, and the thermogram will show a shallow endothermic drift on the first heating ramp, such as in Fig 7-10. This was disregarded in the subsequent analysis.

### 4.6.2 Silica-IPPD

The melting point of IPPD alone was determined by DSC to be 81.8 °C (Figure 7-11).

The precursors (as discussed in section 3.2.4) were stirred together and reacted for 30 min before being cast into an open container to gel and dry.

| Sample                | SiO <sub>2</sub> | IPPD | T <sub>m</sub> | Measured $\Delta H_f$      | Theoretical $\Delta H_f$<br>(Expected) | Difference<br>$\Delta H_f$ | % Non-crystallised<br>AO | Ratio<br>AO entrapped /<br>1g of hybrid |
|-----------------------|------------------|------|----------------|----------------------------|----------------------------------------|----------------------------|--------------------------|-----------------------------------------|
|                       | %                | %    | °C             | J/g (AO+SiO <sub>2</sub> ) | J/g (AO)                               | J/g (AO)                   | g/g (AO)                 | g (AO) /<br>g (SiO <sub>2</sub> )       |
| pure SiO <sub>2</sub> | 1                | 0    | N/A            | 0                          | 0                                      | 0                          | 0                        | 0                                       |
| IPPD(20)              | 80               | 20   | N/A            | 0                          | 24.6                                   | 24.6                       | 100                      | 0.25                                    |
| IPPD(30)              | 70               | 30   | 75.4           | 2.6                        | 36.9                                   | 34.3                       | 93                       | 0.40                                    |
| IPPD(40)              | 60               | 40   | 80.1           | 11.4                       | 49.2                                   | 37.8                       | 77                       | 0.51                                    |
| IPPD(60)              | 40               | 60   | 79.1           | 46.1                       | 73.9                                   | 27.8                       | 38                       | 0.56                                    |
| Pure IPPD             | 0                | 100  | 81.8           | 123.1                      | 123.1                                  |                            |                          |                                         |

**Table 4-5 Melting enthalpies of some sol-gel systems with IPPD antioxidant.**

Table 4-5 summarises the thermal data shown in figures 7-10, and 7-12 to 7-15. The composition of the samples, as ratio of IPPD to Silica, corresponds to concentrations of IPPD equal to 20, 30, 40 and 60 % of the total mass). The melting temperature and enthalpy of the antioxidant melting are given in the 4<sup>th</sup> and 5<sup>th</sup> column respectively. A value for the enthalpy calculated from the pure IPPD is given in the 6<sup>th</sup> column (in proportion to the total weight of the sample, i.e. the sample containing 30% of IPPD should show an enthalpy of fusion of  $123.1 \times 0.30 = 36.9$  J/g), and the difference with the experimental is in the next column (i.e. for the same sample  $36.9 - 2.6 = 34.3$  J/g). This represents the amount of antioxidant that is not able to crystallise/melt and is bound in the amorphous Silica. Based on these amounts, calculations are made of the ratios of bound IPPD to total IPPD (i.e. 34.3 J/g is 93% of 36.9 J/g) and bound IPPD to mass of Hybrid (i.e. in

the same example there are 0.42 g of IPPD in 1 g of hybrid, and 93% if this is bound in the matrix, which means there is 0.4 g of bound IPPD per gram of hybrid).

Since the melting point of the antioxidant remains invariant, the unbound IPPD crystallises as a separated phase from the silica matrix. The sample with IPPD content of 0.25g / 1g of Silica (Sol-gel SiO<sub>2</sub> (80) / IPPD (20) see figure 7-12) shows no melting peak, and therefore it indicates that it is completely entrapped in the inorganic phase.

#### **4.6.3 Silica-Tinuvin 770**

The analysis of sol-gel silica containing Tinuvin 770 in concentrations varying from 8% to 76% has revealed no well-defined crystallisation endothermic peak. The DSC scan of pure Tinuvin 770 show a clearly defined melting peak at 86 °C.(fig.7-16) Some spectra showed a large endothermic “well”, spanning almost the entire temperature range, which could either be sign of strongly bound solvent or that crystallisation is so hindered that the corresponding melting transitions is very blurred. Figures 7-16 to 7-21.

#### **4.6.4 Silica-BHT**

As mentioned in section 4.2.3, the composition of Silica-BHT with BHT content over 3% exhibits a visual phase separation, with progressive increasing content showing evidence of crystals visible to the naked eye. DSC scans of even higher BHT proportions show correspondingly a melting endothermic peak at around 70 °C

#### **4.6.5 Silica-Irganox 1076**

Sol-gel derived silica with Irganox 1076 exhibit melting endotherms corresponding to the antioxidant (T~60°C) at all concentrations, (see figures 7-22 to 7-24) pointing to the fact that adsorption of Irganox inside the amorphous silica network is labile and subject to separation upon heating. This suggested that the

intermolecular forces that keep the organic compound well distributed in the nanoscale, as evidenced by the transparency of the sample obtained as thin film via the sol-gel route, are not strong enough to keep the antioxidant permanently entrapped into the pores.

## 4.7 Assessment of solubility of antioxidant in PEO

### 4.7.1 PEO - IPPD

The samples were prepared by dissolving PEO and IPPD in THF to a concentration of 10%w/w and then casting as film. The DSC scan was then recorded (see figures 7-11 for IPPD, 7-25 for PEO reference, and 7-26 to 7-28) and summarized in table 4-6.

| Sample    | PEO | IPPD | Melting<br>Peak<br>(PEO) | $T_m$<br>IPPD | Measured<br>$\Delta H_f$ | Theoretical<br>$\Delta H_f$<br>(PEO) | Theoretical<br>$\Delta H_f$<br>(IPPD) | Sum of<br>theoretical<br>$\Delta H_f$ | Discrepancy $\Delta H_f$<br>[measured -<br>(calc. PEO)] | Discrepancy $\Delta H_f$<br>[measured -<br>(PEO+IPPD)] |
|-----------|-----|------|--------------------------|---------------|--------------------------|--------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------------------------|--------------------------------------------------------|
|           | %   | %    | °C                       |               | J/g                      | J/g                                  | J/g                                   | J/g                                   | J/g                                                     | J/g                                                    |
| Pure PEO  | 100 | 0    | 64.8                     |               | 153.2                    | 153.2                                | 0                                     | 153.2                                 |                                                         |                                                        |
| IPPD(20)  | 80  | 20   | 59.6                     |               | 118                      | 122.6                                | 24.6                                  | 147.2                                 | -4.6                                                    | -29.2                                                  |
| IPPD(40)  | 60  | 40   | 52.2                     |               | 121                      | 91.9                                 | 49.2                                  | 141.1                                 | 29.1                                                    | -20.1                                                  |
| IPPD(60)  | 40  | 60   | 49.5                     | 70.7          | 103.6                    | 61.3                                 | 73.9                                  | 135.2                                 | 42.3                                                    | -31.6                                                  |
| Pure IPPD | 0   | 100  |                          | 81.8          | 123.1                    | 0                                    | 123.1                                 | 123.1                                 |                                                         |                                                        |

**Table 4-6 Melting enthalpies of PEO/IPPD mixtures.**

The mixtures produced are compared to pure PEO dissolved and cast in the same way and to a pure IPPD powder. Melting peaks in °C are indicated in the 4<sup>th</sup> column and the corresponding measured enthalpies of fusion in the 6<sup>th</sup>. The melting temperatures are increasingly lower than the  $T_m$  of pure PEO, indicating less ordered crystals. Only one mixture showed evidence of a crystalline IPPD melting peak (see figure 7-28: PEO (40) / IPPD (60)). In this sample the two endothermic transitions are partially overlapping, so that distinct enthalpies cannot be calculated. The 7<sup>th</sup>, 8<sup>th</sup> and 9<sup>th</sup> (Theoretical) columns give the calculated values of

melting enthalpy of a physical ideal mixture of the same proportions. In other words, the melting enthalpy of each pure substance is multiplied by the weight fraction, so that the proportion of enthalpy due to each component can be compared to the experimental value. The last two columns calculate the difference between the calculated and the experimental values; if only the value calculated from PEO is taken into account, the experimental measure shows a depression of enthalpy for the 20%w/w PEO, which would indicate complete mixing of IPPD in the polymer phase, so that it does not contribute to the enthalpy released. (the 4.6 J/g difference is within the experimental error for the measured of the peak area). However, at higher proportions of IPPD, the energy due to the polymer phase (in weight proportion) is not sufficient to account for the enthalpies measured: a contribution of IPPD enthalpy must be included in the enthalpy released in these transitions (last column). The antioxidant, therefore, interacts strongly with the crystallisation of PEO and absorbs some heat at temperatures much lower than its crystalline melting temperature.

In Figure 4-2 the blue line tabulates the melting temperature of the PEO phase and the red line the melting peak of IPPD.

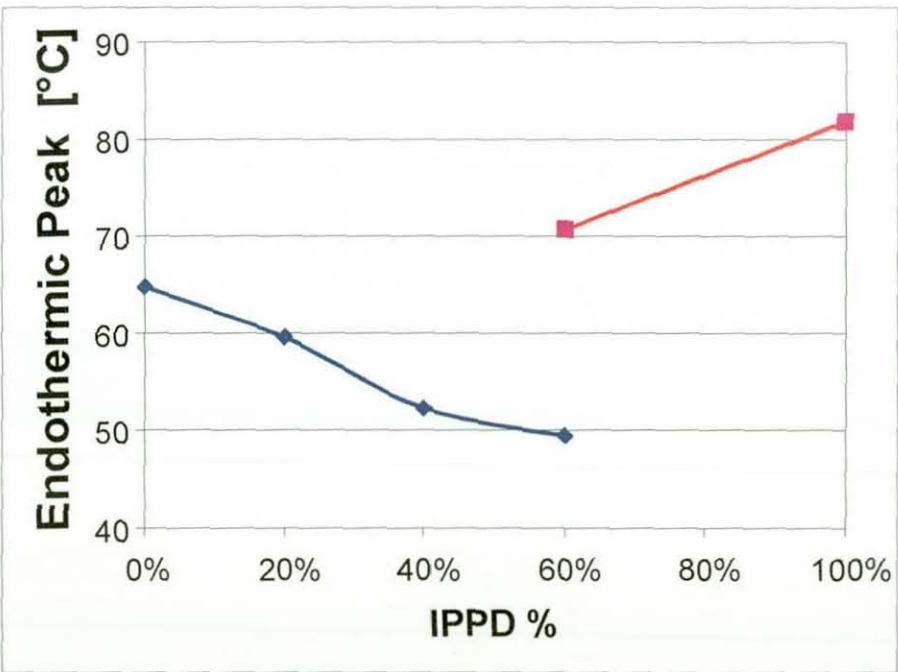


Figure 4-2 Effect of IPPD and PEO mixtures on crystallization

### 4.7.2 PEO - Irganox 1076

One sample was prepared by dissolving PEO and Irganox 1076 in THF to a concentration of 10%w/w and then casting as film. The DSC scan was then recorded: see figures 7-29 for Irganox 1076 reference, 7-25 for PEO, 7-30 for PEO (90)/I1076 (10), and the results are summarized in table 4-7.

| Sample                | PEO | Irganox 1076 | $T_m$ | Measured $\Delta H_f$ | Theoretical PEO $\Delta H_f$ | Discrepancy $\Delta H_f$ [measured - calculated PEO] |
|-----------------------|-----|--------------|-------|-----------------------|------------------------------|------------------------------------------------------|
|                       | %   | %            | °C    | J/g                   | J/g                          | J/g                                                  |
| Pure PEO              | 100 | 0            | 64.8  | 153.2                 |                              |                                                      |
| PEO (90) - I1076 (10) | 90  | 10           | 60.4  | 111.3                 | 137.9                        | -26.6                                                |
| Pure I1076            | 0   | 100          | 52.7  | 80.6                  |                              |                                                      |

**Table 4-7 Melting enthalpies of PEO/Irganox 1076 mixtures**

As observed with the PEO / IPPD mixtures, in the PEO / Irganox 1076 mixture there is also a depression of the observed melting enthalpy relative to the calculated value from the weight of PEO present. Also the melting temperature is lowered from that of pure PEO, indicating that the Irganox is interacting with the PEO crystals and does not crystallise separately. A calculation analogous to the one used in table 4-6 including the enthalpy contribution of Irganox 1076 (calculated as 10% of pure  $\Delta H_f$  (Irganox1076), that is 8.1 J/g) to the melting peak would yield a total calculated enthalpy of 145.9 J/g and, giving a discrepancy of 34.6 J/g.

## 4.8 Compatibilisation of PEO-SiO<sub>2</sub>-Antioxidant hybrids

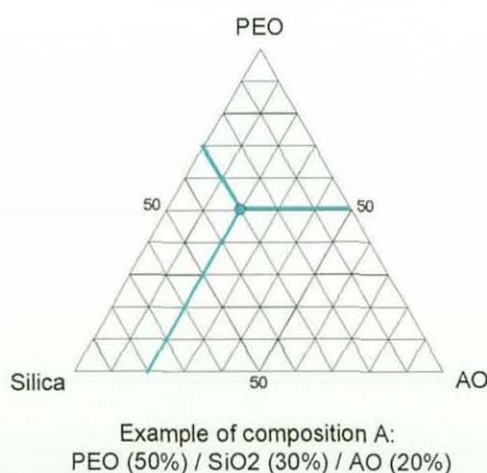
### 4.8.1 DSC of PEO-SiO<sub>2</sub>-Irganox 1076 hybrids

Many compositions were prepared with different proportions of PEO, Silica and Irganox 1076. A selection of DSC thermograms from these materials is presented for analysis and discussion in Figures 7-31 to 7-35. DSC spectra indicate that there is increasing amorphous phase of the PEO component with the addition of the phenolic antioxidant. This is noted by the presence of a much increased glass

transition in the region of  $-36\text{ }^{\circ}\text{C}$ . (see figure 7-33). The sample composed of PEO (40) /  $\text{SiO}_2$  (40) / I1076 (20) (figure 7-35) shows two overlapping melting peaks, attributed to the Irganox 1076 separately crystallising from the PEO. This is not observed in many other hybrids, at lower antioxidant concentration.

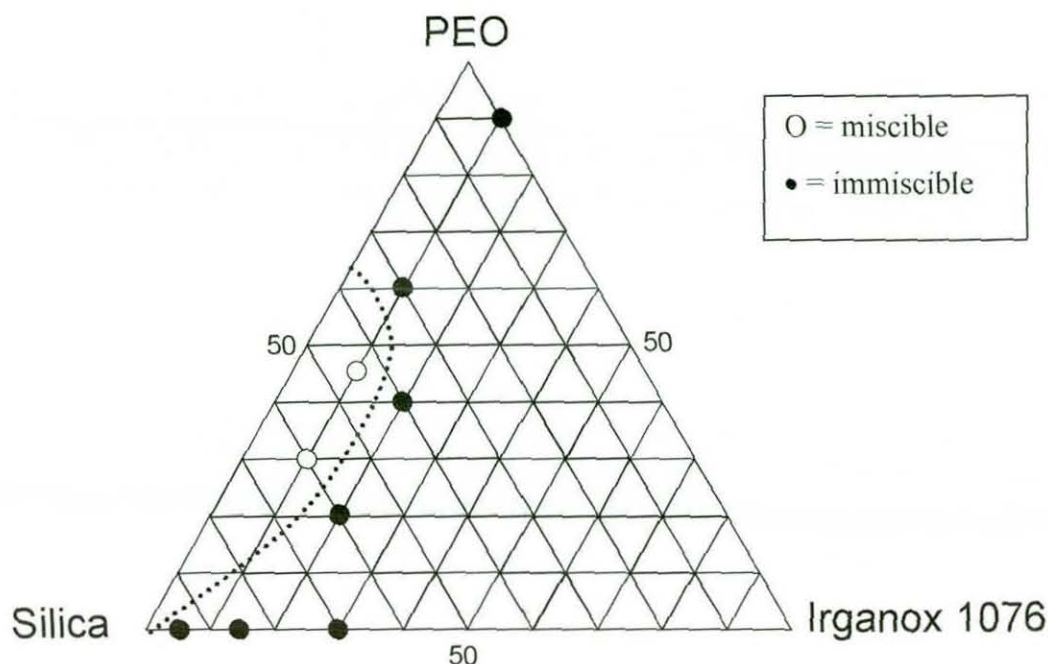
#### 4.8.2 Compatibilisation diagram of PEO- $\text{SiO}_2$ -Irganox 1076 hybrids

Different compositions and proportions of PEO- $\text{SiO}_2$ -Irganox 1076 hybrids were prepared and analysed. In collating these experiments, it is useful to visualise the results into a ternary composition diagram, such as the one in Figure 4-3. The equilateral triangle represents the whole range of compositions possible with three components. Each apex represents 100% of a component, and the sides of the triangle represent the three sets of binary mixtures possible. Points inside the triangle represent ternary compositions. The concentration, expressed in percentage, of each of the three components of a given formulation **A** can be read from the diagram following this method: from the point inside the diagram three lines are drawn parallel to the sides of the triangle; the amount of each component is proportional to the length of the line drawn to the side opposite its named apex. The sum total of the three lines is 100%. To aid the reader, a grid of small triangles has been drawn, each side of such triangles representing 10% increments. In the example given, the composition of formulation **A** is 50% of PEO, 30% of Silica and 20% of Antioxidant.



**Figure 4-3** Example of ternary diagram

The hybrids containing Irganox 1076 are presented in Figure 4-4. The compositions that exhibit phase separations, as evidenced by a separate antioxidant melting peak or at least a distinctive and noticeable shoulder on the PEO melting peak in the DSC, are marked with a black dot, and those compositions that do not present dishomogeneities or heterogeneous melting phases are marked with a white dot. Some of the corresponding DSC scan are presented for analysis in fig. 7-30 to 7-35 and 7-22 to 7-24.



**Figure 4-4 Ternary composition diagram for PEO-SiO<sub>2</sub>-Irganox 1076 hybrids**

From the scans of samples containing only silica and antioxidant it is possible to discuss the behaviour of the antioxidant. Irganox presents a distinct peak of fusion at around 50 °C even at low concentration, pointing to the fact that it is not molecularly entrapped in the amorphous silica matrix. The samples are nonetheless transparent, which means the dimension of the phases present is in the nanometre range. As the works of Liauw *et al.*[48] have shown, the pores of the amorphous silica are able to adsorb significant quantities of antioxidants, and as these results show are also able to release it when heated, so that an endothermic peak of melting is visible on the DSC scans. Adding the third phase of PEO markedly complicates the situation, because now the antioxidant can dissolve in the organic

phase, as well as being adsorbed on the surface of the inorganic silica pores. In the cases of Hybrid PEO (30) / SiO<sub>2</sub> (60) / Irganox 1076 (10) (fig 7-31) and hybrid PEO (45) / SiO<sub>2</sub> (45) / Irganox 1076 (10) (Figure 7-32), the melting peak of Irganox 1076 is completely suppressed, while in hybrid PEO (60) / SiO<sub>2</sub> (30) / Irganox 1076 (10) (Figure 7-34) the shoulder on the lower range of the PEO melting curve is clearly visible ( $T \sim 50$  °C). This means that the disappearance of the melting curve of Irganox 1076 isn't an artefact caused by PEO obscuring the melting of the minor phase, but a real physical effect, of complete compatibilisation of the antioxidant in both organic and inorganic matrix phases. The melting of Irganox as a shoulder on the PEO melting curve is even more pronounced as the proportion of antioxidant increases to 20% (see Figure 7-35)

#### 4.8.3 SEM of PEO-SiO<sub>2</sub>-Irganox 1076 hybrids

SEM images (see figures 7-64 to 7-69) show a predominance of PEO features on the surface, with the PEO spherulites clearly visible at lower magnifications (figures 7-66 and 7-67). Comparing greater magnifications in the two hybrids shows (for example figure 7-65 and 7-68) an increase of small crystallites in the PEO (40) / SiO<sub>2</sub> (40) / I1076 (20) relative to the lower concentration hybrid, confirming the indications of DSC that a greater quantity of Irganox 1076 is not dissolved in the organic phase, or adsorbed onto the silica pores.

#### 4.8.4 DSC of PEO-SiO<sub>2</sub>-IPPD hybrids

(See figures 7-36 to 7-42) The three components of the hybrids interact strongly so that complete compatibilisation is achieved at lower IPPD concentration. In some cases such as PEO (40) / SiO<sub>2</sub> (40) / IPPD (20) (see figure 7-37), the melting of both PEO and IPPD components is completely inhibited. Other hybrids yield more complex results: increasing the quantity of IPPD results in phase separation, as observed in the melting peaks of the IPPD crystals (figure 7-39 to 7-42) (IPPD content 40% to 60%) and of the PEO with IPPD entrapped (figures 7-36, 7-38 and

7-41 to 7-42), as observed in the cases previously discussed of PEO / IPPD and  $\text{SiO}_2$  / IPPD.

#### 4.8.5 Compatibilisation diagram of PEO- $\text{SiO}_2$ -IPPD hybrids

Different compositions and proportions of PEO- $\text{SiO}_2$ -IPPD hybrids were prepared and analysed. Some of those samples were discussed previously. In collating these experiments, it is useful to visualise the results into a ternary composition diagram, marking with a full dot those compositions that exhibit phase separations as evidenced by a separate antioxidant melting peak in the DSC, and marking with a white dot those compositions that do not present dishomogeneities or heterogeneous melting phases. The diagram is presented in Figure 4-5. The dotted line marks the region of compositions that presents clearly defined peaks of fusion of IPPD, distinct from the PEO.

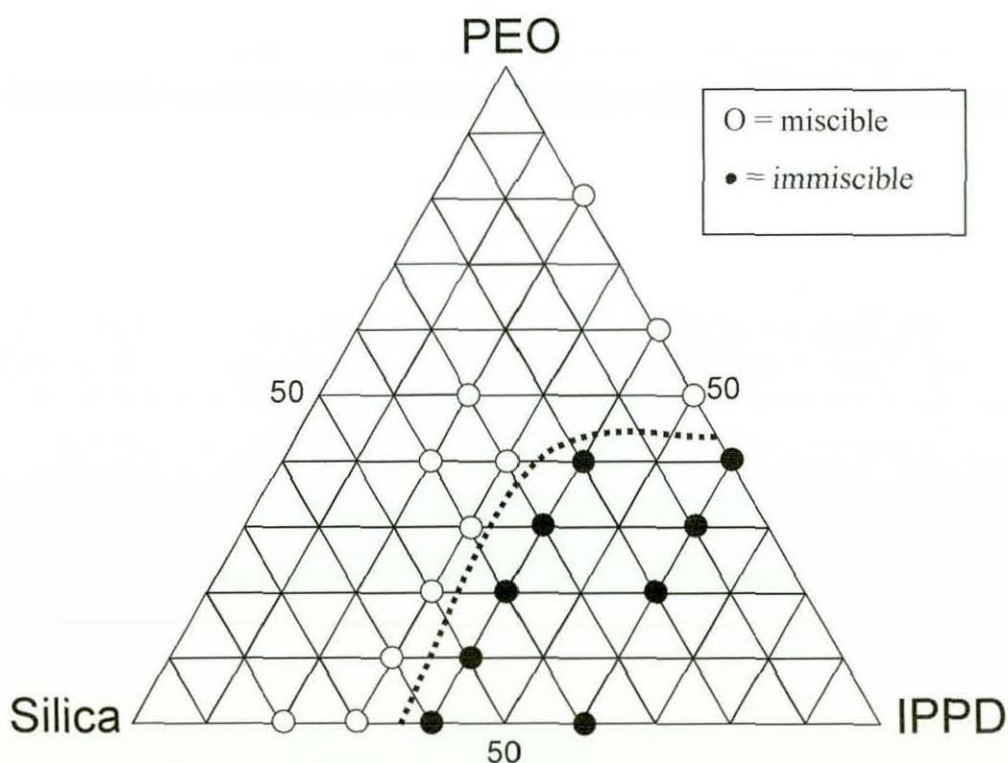


Figure 4-5 Ternary composition diagram for PEO- $\text{SiO}_2$ -IPPD hybrids

#### 4.8.6 SEM of PEO-SiO<sub>2</sub>-IPPD hybrids

SEM images show very distinct surfaces for the hybrid PEO (40) / Silica (20) / IPPD (40) (figure 7-70, 7-71) and hybrid PEO (30) / Silica (30) / IPPD (40) (figure 7-72, 7-73). The former shows a smooth and compact surface with very little surface crystals. The PEO characteristic morphology is not visible, as in the latter images, where the porosity and surface roughness, typical of PEO crystals, are much higher. Comparing the DSC scans of these two hybrids shows two very different melting peaks: a broad peak around 48 °C indicative of PEO impure crystals, for the hybrid PEO (40) / Silica (20) / IPPD (40) (figure 7-38), and a sharp peak at 80 °C of IPPD, for the hybrid PEO (30) / Silica (30) / IPPD (40) (figure 7-39)

#### 4.8.7 DSC of PEO-SiO<sub>2</sub>-BHT hybrids

In Figures 7-43 to 7-59 are presented some DSC thermograms for the different compositions of PEO/silica hybrid with BHT. The data shows that the three components interact strongly with each other over a wide range of compositions. The melting point of the pure (crystalline) antioxidant is 73 °C, the  $T_m$  of PEO crystallized from solution is around 65 °C. For many hybrids the melting point of these components differ appreciably from those values, and often the  $T_m$  of PEO and/or BHT are completely absent (e.g. Fig 7-50 related to hybrid PEO (50) / Silica (20) / BHT (30) ) where the PEO melting point is depressed to 55 °C and the  $T_m$  for BHT is not visible, despite being present at 30%w of the sample. Strong hydrogen bonding and dipolar interaction between the phenolic species and the organic ether chain can be attributed with interfering with the closed packing necessary to form polymer crystals, and therefore the structure is less ordered and melts more easily at lower temperatures and with much lower energy.

The processing conditions are of great importance, as exemplified the experiment presented in figures 7-48 a) and b) [Hybrid PEO (40) / Silica (40) / BHT (20)] In this case, changing the conditions in the drying stage from (a) a loosely covered vial placed in a 60°C oven to (b) an open box at room temperature has caused a significant portion of the 20%w BHT to crystallize separately from the

organic/inorganic network. The slower rate of reaction of crosslinking in the inorganic network at room temperature has possibly triggered spinodal decomposition, which has caused microscopic phase segregation, and a lower compatibility threshold, compared with the material that was left to react at higher temperature but lower evaporation rate.

By comparison, another formulation with the same amount of BHT (see Figure 7-44) [Hybrid PEO (30) / Silica (50) / BHT (20)] has both PEO and BHT melting completely suppressed.

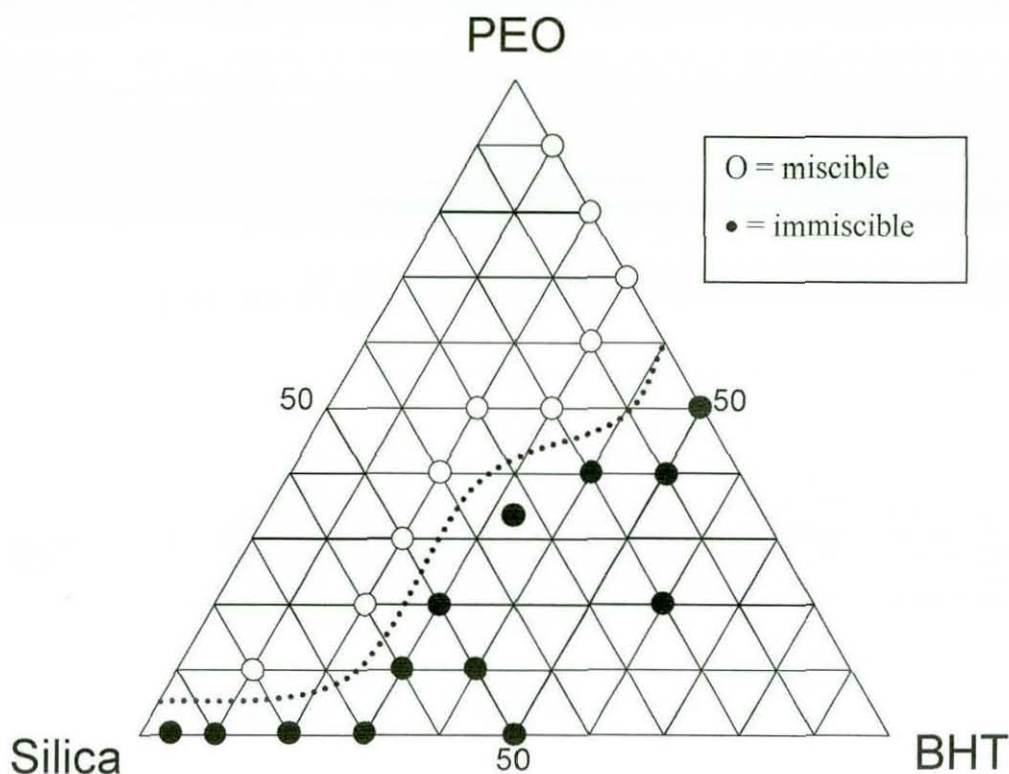
#### 4.8.8 Compatibilisation diagram of PEO-SiO<sub>2</sub>-BHT hybrids

The ternary diagram for some of the compositions of PEO-SiO<sub>2</sub>-BHT hybrids is presented in Figure 4-6. The black dots represent those compositions where a separate peak of melting of BHT was clearly present. To be recognized as BHT melting, the peak was considered if it was clearly distinguishable from the PEO melting curve (around 50 to 60 °C), although the temperature was in some composition significantly lower than that of pure BHT crystals (see fig 7-45 regarding hybrid PEO (40) / Silica (10) / BHT (50): the melting of PEO at 51 °C is followed by a partially overlapping melting curve at 67 °C, that can be attributed to imperfectly packed crystals of BHT). A composition laying on the threshold value for the complete compatibility of BHT in the organic-inorganic hybrid is PEO (20) / Silica (50) / BHT (30) (shown in Figure 7-47): following the melting curve at 60 °C there is an extremely small but clear peak of melting around 70 °C that can be attributed as the incipient melting of BHT; any composition containing similar proportions of silica and PEO components and increased BHT shows a much bigger melting peak (see figures 7-54 and 7-55 for compositions PEO (00) / Silica (50) / BHT (50) and PEO (10) / Silica (50) / BHT (40) respectively).

The range of compositions exhibiting compatibility, as represented by the white dots on the ternary composition diagram, is greater than in the case of Irganox 1076. This can be explained by considering the sterical hindrance that the octadecyl propionate ester chain presents in the Irganox, compared with the small methyl group in the corresponding position in BHT. This in turn allows a less effective

hydrogen bond interaction of the phenol with the ethyl ether chains in the PEO and a bigger volume occupied in the pores of the silica amorphous network.

Hybrids containing BHT exhibit a smaller range of compatible compositions than the case of IPPD. Comparison between different classes of molecules are inappropriate, because the chemical reactivity of the antioxidant and its acidity/basicity has a profound effect on the aggregation behaviour and morphology of the silica network, and that means the pore size distribution of the amorphous silica will vary. If it is hypothesised that the antioxidant is adsorbed on the surface of the pore structure of silica, this in turn modifies the behaviour of  $\text{SiO}_2$  towards the PEO chains present and the corresponding nanostructure of the mixture at gelation. In effect the antioxidant BHT is in a metastable phase within the organic/inorganic network, even when it appears fully compatibilised, as evidenced by the ease with which a seemingly miscible composition can produce segregated BHT crystals, when processed in a different way [see figures 7-48 a) and b)]. This is further indication that the small organic molecule of antioxidant would possess the necessary mobility to diffuse out of the hybrid organic/inorganic matrix and into a host polymer, thus acting as a slow release protective agent.



**Figure 4-6 Ternary composition diagram for PEO-SiO<sub>2</sub>-BHT hybrids**

Some samples that included in the formulation the TESP-U-DBHMP silica-urethane-phenol compatibiliser were also synthesized. The resulting ternary composition diagram is presented in fig. 4-7. The compatibiliser weight was included in the SiO<sub>2</sub> component for the purpose of the calculation of the composition. The region of complete compatibility of antioxidant in the hybrid system is considerably enlarged, including compositions of up to 40 % by weight of BHT. This leads to the conclusion that the synthesized urethane compatibiliser acts significantly in depressing the formation of a separated BHT phase, and aid the adsorption of antioxidant on the modified surface of the silica. PEO must also interact with this organically-functionalised surface, as the enthalpy of melting exhibited is often significantly depressed.

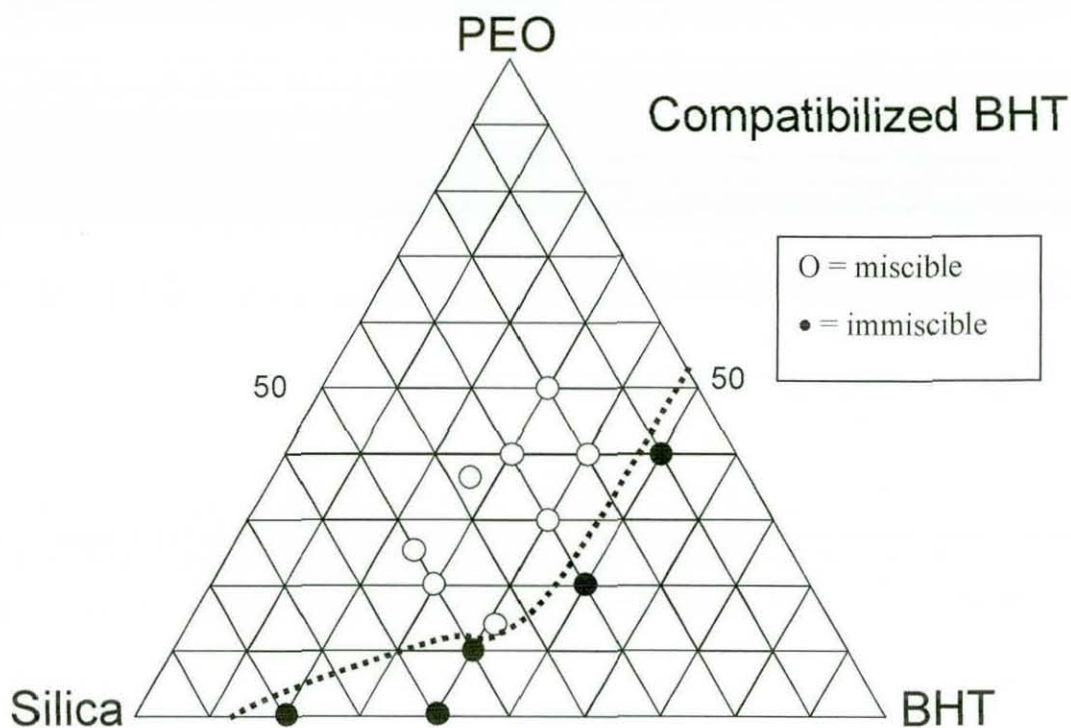


Figure 4-7 Ternary composition diagram for PEO-SiO<sub>2</sub>-compatibilised BHT hybrids

#### 4.8.9 SEM of PEO-SiO<sub>2</sub>-BHT hybrids

Figures 7-74 a) and 7-74 b) present the SEM micrographs of hybrid PEO (40) / Silica (40) / BHT (20) (see DSC in Figures 7-48a and 7-48b respectively). The surface of the hybrid material appears smooth and compact in Figure 7-48a) while there are numerous and evident small crystals segregating from the surface of Figure 7-48b). This confirms the indications of the DSC thermograms, that phase separation and independent crystallization of BHT had occurred in the material dried at room temperature.

Figure 7-44 present the DSC of hybrid PEO (30) / Silica (50) / BHT (20); the corresponding SEM surface micrograph is presented in figure 7-75. The melting endotherms of both PEO and BHT are completely suppressed, and the surface appearance is smooth and compact, with no evidence of crystals or surface porosity.

## **4.9 Oxygen Induction Time test of Nylon 6**

A preliminary screening of the suitability of the Oxygen Induction Time (OIT), as analytical parameter for the determination of degree of protection afforded by the diffused antioxidant into the Nylon 6 films, was conducted on unstabilised Nylon 6 films of 12  $\mu\text{m}$  and 40  $\mu\text{m}$  thickness. At temperatures in the region of 180 °C or lower there was no distinguishable exothermic curve for the oxidation reaction for 3 hours. After this time the cell was cooled and opened and it was found that the polymer had completely oxidized and browned. Increasing the oxidation temperature above 180 °C had the effect of obtaining an immediate oxidation exotherm, causing the error in the determination of onset time to be of the same scale as the measurement itself. In Figures 7-60 to 7-63 are presented the OIT thermograms relative to temperatures 150, 180, 200 and 220 °C for the 12  $\mu\text{m}$  film. The time marked  $t(0)$  on the graphs is the time of exchange of gas, from inert nitrogen to atmospheric air. This result confirms the prediction found in literature, that OIT is really limited to polyolefins systems [112].

## **4.10 Diffusion study of antioxidants in Nylon 6**

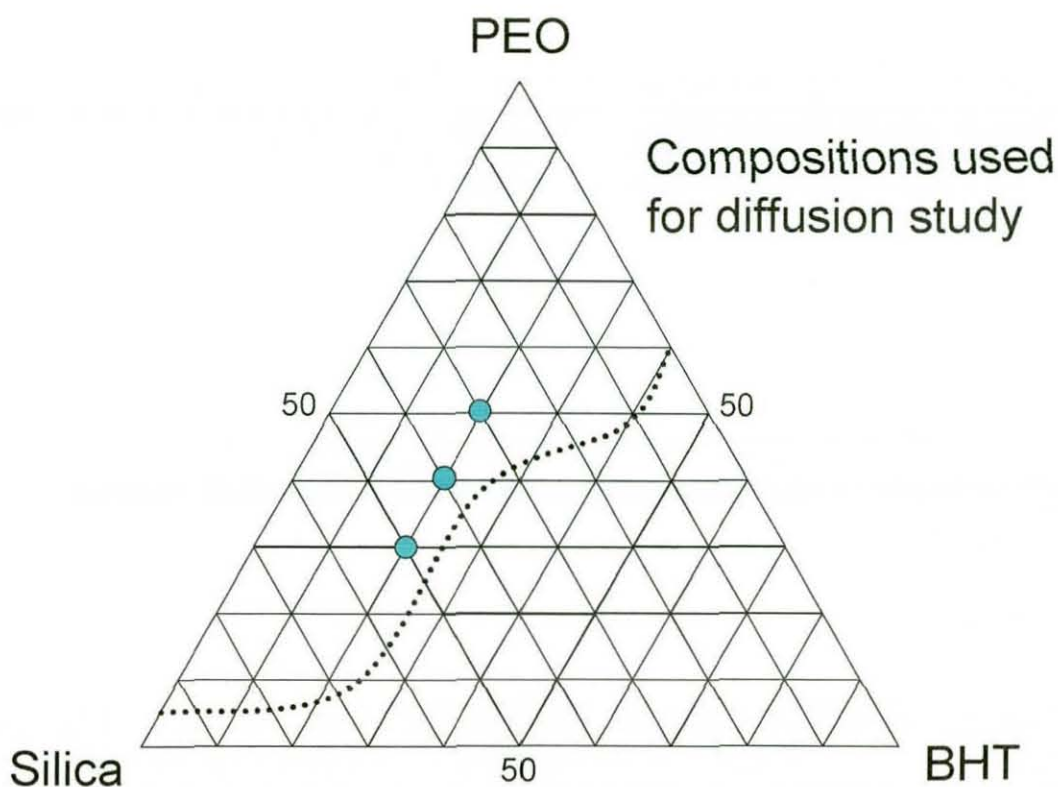
### **4.10.1 Setup for diffusion study**

The setup for the experiments on diffusion is described in section 3.3.3 and the samples were aged in oven at 60 °C for different times as described in section 3.3.4.

Three hybrids were oven aged, and table 4-8 presents the weight compositions; the corresponding ternary composition diagram is presented in fig 4-8: the dotted line represent a reminder of the region of compositions of BHT that are fully compatibilised within the organic-inorganic hybrid. All three compositions chosen have 20%w of BHT and are all within the range of full miscibility with both organic and inorganic phases. This means that there is no segregated, free melting antioxidant. The diffusion of BHT, therefore, proceeds from the mixture within the PEO and the molecules physically bound to the surface of the silica pores.

| Sample | PEO | Silica | BHT |
|--------|-----|--------|-----|
| 1      | 40  | 40     | 20  |
| 2      | 30  | 50     | 20  |
| 3      | 50  | 30     | 20  |

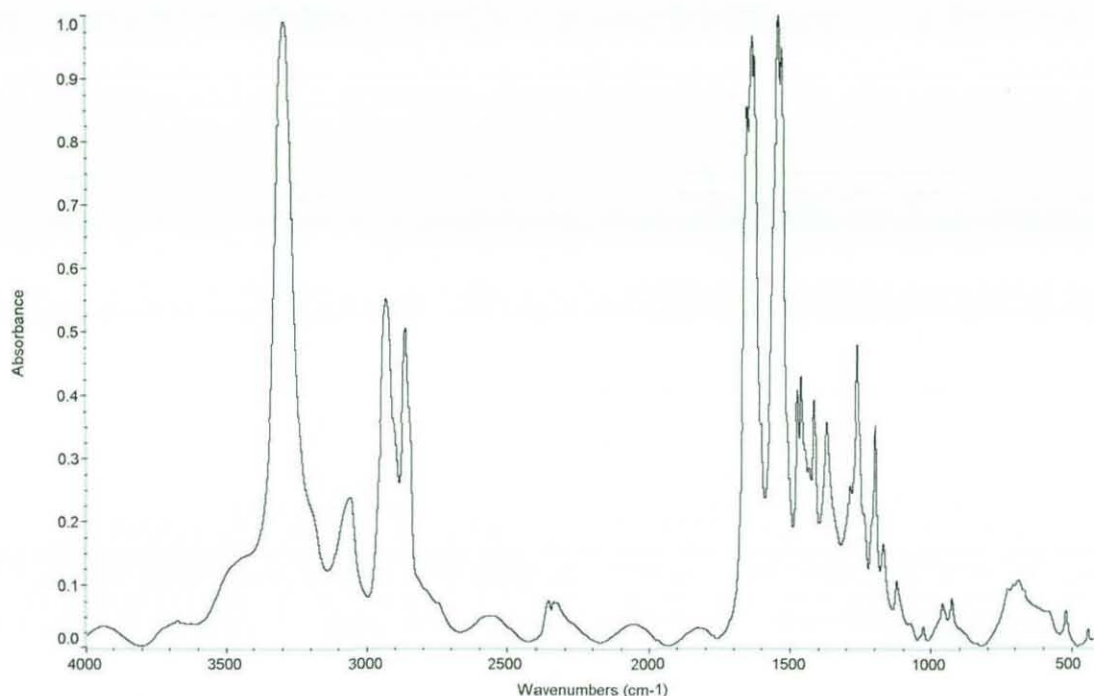
**Table 4-8 Compositions of hybrids used for oven ageing experiments**



**Figure 4-8 Ternary composition diagram for PEO-SiO<sub>2</sub>-BHT hybrids used in the Roe setup**

#### 4.10.2 IR of Nylon film

The FT-IR reference spectrum of the Nylon 6 film used is presented in Figure 4-9, and the reference spectrum of antioxidant BHT in figure 7-8. The main spectroscopy features in the Nylon spectrum are the NH peak at  $3304\text{ cm}^{-1}$ , the CH<sub>2</sub> bands at  $2932$  and  $2867\text{ cm}^{-1}$ , and the two bands of primary amide at  $1640$  and  $1550\text{ cm}^{-1}$ .



**Figure 4-9 IR spectrum of Nylon 6 film (12 $\mu$ m thick)**

#### **4.10.3 Spectra of different hybrid compositions**

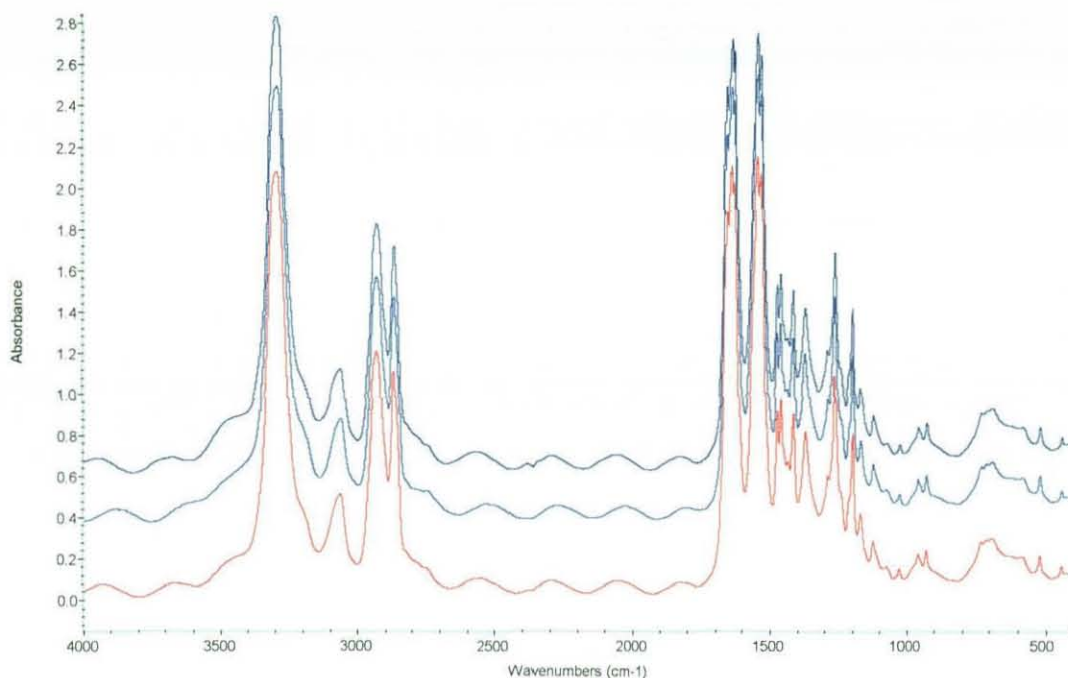
The FT-IR spectra of Nylon 6 films stacked with the three different hybrid compositions are very similar in appearance over the time of the oven ageing. Typical spectra are presented in figure 4-10.

In the subsequent FT-IR spectra of the ageing Nylon 6 it is not possible to discern any peak of BHT through the many absorptions of Nylon, as an evidence for the low concentrations of BHT in the polymer at all times. This is a desired effect, in so far as higher concentration of antioxidant can leach out of the polymer matrix.

Because a reference standard of known and invariable concentration and clearly identifiable absorbance peak is lacking from all these spectra, a quantitative analysis of the diffusion is not possible. A semi quantitative analysis is possible of the effects of antioxidants diffusion from the hybrids into the Nylon 6 layers as the thermally activated diffusion occurs over the course of the oven ageing experiments.

Because the behaviour of the Nylon 6 films aged with the three compositions is very similar, the effects of the diffusion of the antioxidant and protection from

thermal oxidations for all three samples will be discussed together using sample 1 as representative [composition PEO (40) / Silica (40) / BHT (20)].



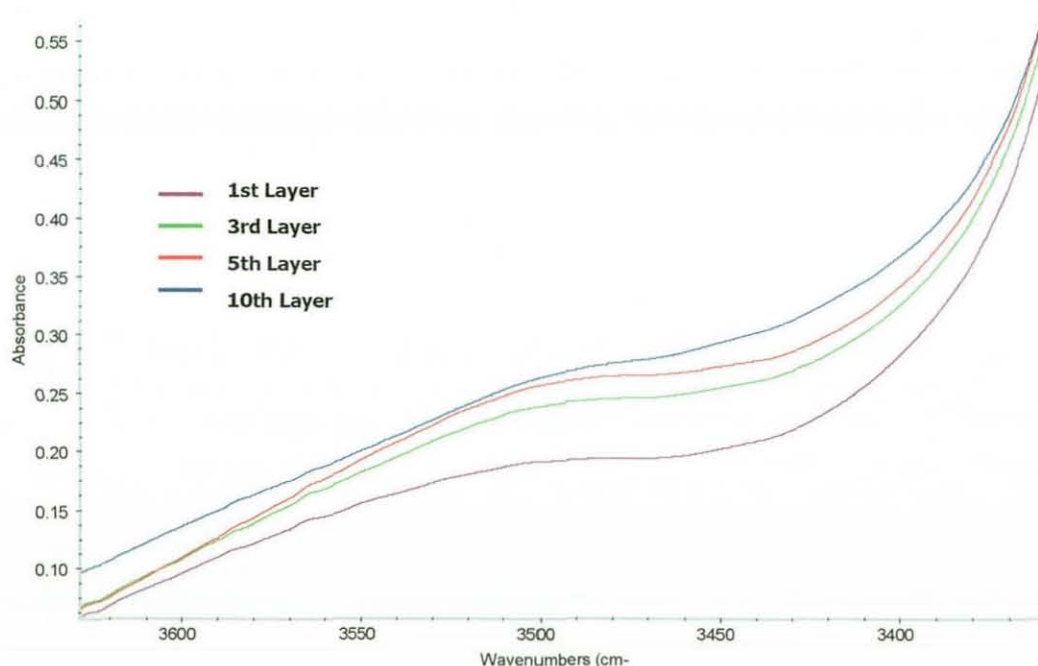
**Figure 4-10 IR spectra of Nylon 6 oven aged stacked with different hybrid compositions (see table 4-8): bottom sample 1, middle sample 2, top sample 3**

The analysis considers only areas of the spectra that may show indications of thermal degradation. As was discussed in the literature review (see section 2.4.2) atmospheric oxygen reacts with  $\text{CH}_2$  vicinal to an amide nitrogen, to form unstable hydroperoxides, which then degrade through many possible radical and ionic pathways, to form unsaturations in the backbone polymer chain, carbonyl and carboxyl groups (mainly imides, aldehydes and other unsaturated carbonyl). This eventually leads to chain scission, with the deterioration of mechanical properties and yellowing.

In particular, the frequency of hydroperoxide absorption has been reported near  $3400\text{ cm}^{-1}$ , and the region of carbonyl absorption as  $1690\text{--}1780\text{ cm}^{-1}$  [114].

#### 4.10.4 Change in hydroxyl region of IR spectrum

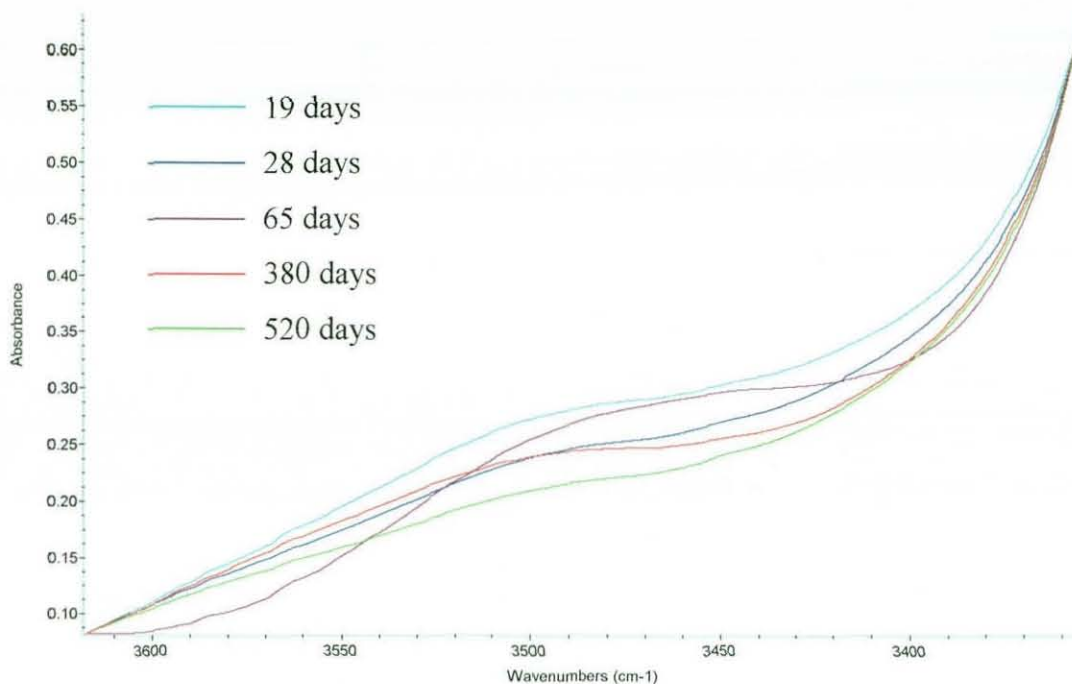
Hydroxyl and hydroperoxide group absorptions ( $3350\text{--}3550\text{cm}^{-1}$ ) appear as a broad shoulder on the NH band of the Nylon 6. The spectrum was rescaled so the peak of NH band had absorbance 1, so considering the amount of amide constant, as the early stages of oxidation are being investigated. Figure 4-11 presents the change in the hydroxyl region taking place as the layers further from the hybrid reservoir are progressively less affected by the diffusion of antioxidant, at a given ageing time. Layers are numbered starting with layer 1 being the closest film to the hybrid and layer 10 being the most external and farthest from the hybrid. IR absorbance in the hydroxyl region is greater the farther the layer is from the silica hybrid. Hydroxyl and hydroperoxide groups are the unstable intermediates of final thermal oxidative products, which are being formed and vanished continuously during the thermal treatment. The role of the antioxidant is to intercept the radical chain of reactions occurring as a result of hydroperoxide formation.



**Figure 4-11 Change in hydroxyl region of IR spectra of Nylon 6 during thermal ageing at 60°C, for 380 days.**

Figure 4-12 presents the change in the hydroxyl region of Nylon 6 as a given layer (e.g. layer 5) is subjected to longer oven ageing times. The hydroxyl absorbance

band decreases with ageing time, as the presence of a higher amount of antioxidant would indicate.



**Figure 4-12 Change in hydroxyl region of IR spectra of layer 5 of Nylon 6 at different times during thermal ageing at 60°C.**

In Figure 4-13 the variation in content of the hydroperoxide intermediate species was calculated for various ageing times of the sample at 60 °C. The Absorbance at  $3400\text{ cm}^{-1}$  of a reference Nylon 6 film, aged in the same conditions as the sample, was taken as 1 and the relative absorbances of the various layers rescaled to compare in the graph. It is possible to note how the hydroperoxide species increases along the layers, indicating a lower antioxidant content, as the distance from the hybrid reservoir increases.

Hydroperoxide groups in aliphatic polyamides are also reported to undergo decomposition at about 60 °C[114], however in a steady state process such as long term oxidation in abundance of oxygen, the amount of decomposing hydroperoxide is constantly replenished by new reactions starting.

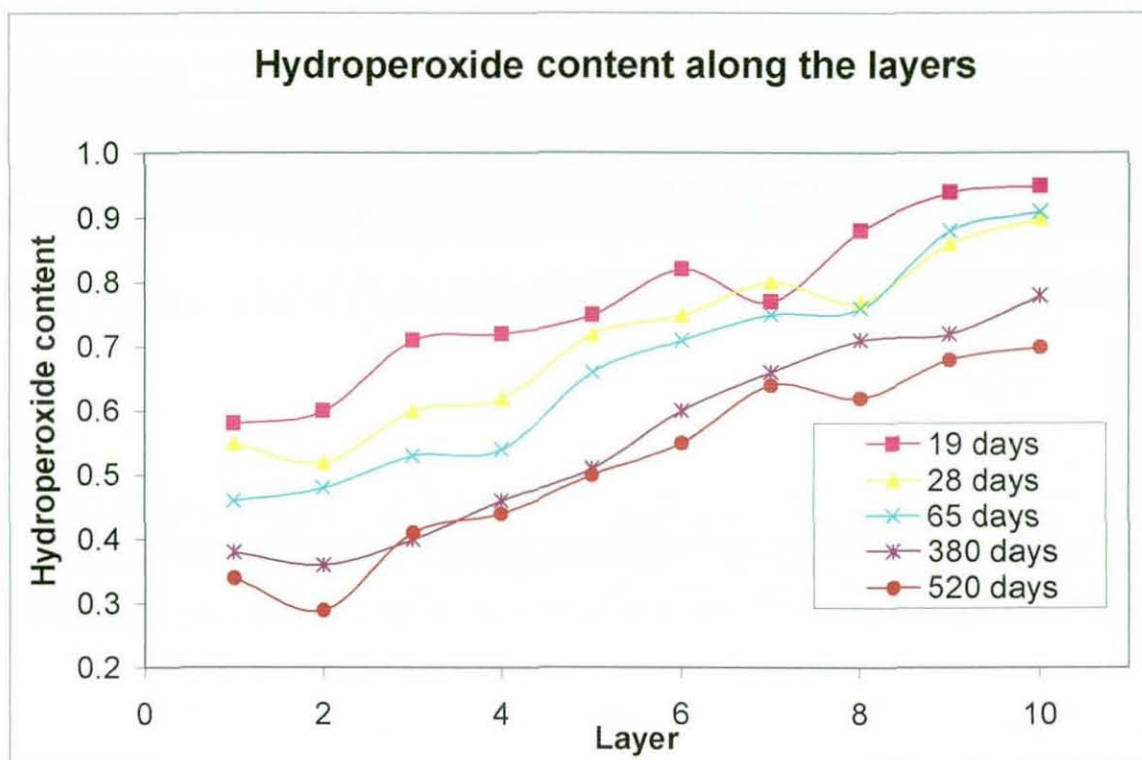


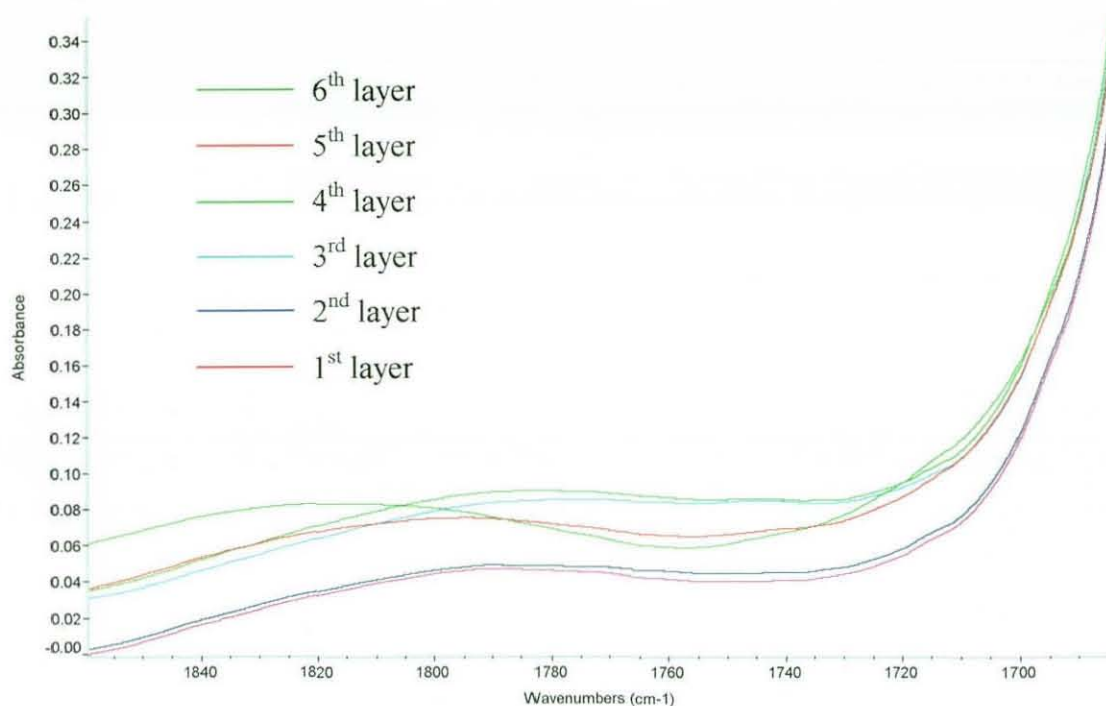
Figure 4-13 Change in hydroperoxide content from IR spectra of nylon 6 along the layers, during thermal ageing at 60°C, for different ageing times

#### 4.10.5 Change in carbonyl region of IR spectrum

Carbonyl species are the results of hydroxyl and hydroperoxides degradative decomposition, and are therefore products of thermal oxidations. There are many possible reaction products stemming from these reactions, most of which absorb IR radiation in the frequency range of 1700 to 1800  $\text{cm}^{-1}$ . Measuring the carbonyl band increase is, therefore, a good way of evaluating both the degree of degradation occurring and the extent of protection.

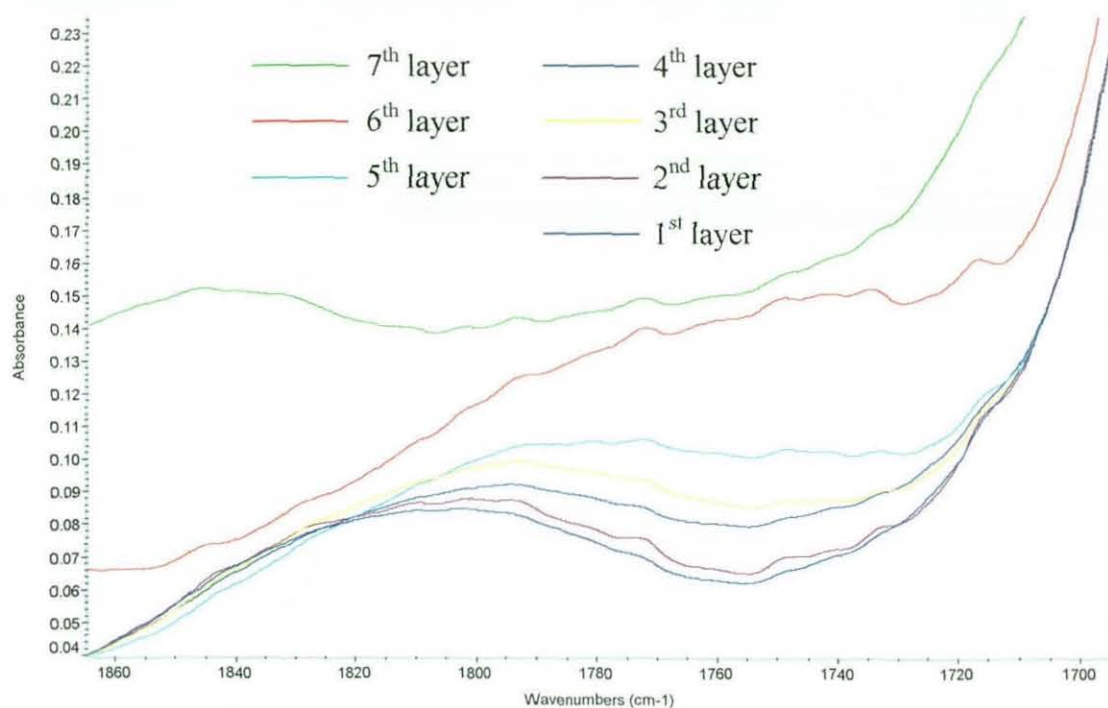
Figure 4-14 shows the absorbance change in the carbonyl region of IR for the different layers at 65 days of oven ageing at 60 °C. Because the oven temperature is only 60 °C the time scale of oxidation is considerably longer than published results for oxidation of Nylons, but more readily comparable to real terms of usage. This temperature was selected because is below the  $T_m$  of BHT. The carbonyl band

region is barely noticeable as an enlarged broad shoulder of the amide band absorption around  $1640\text{ cm}^{-1}$ .

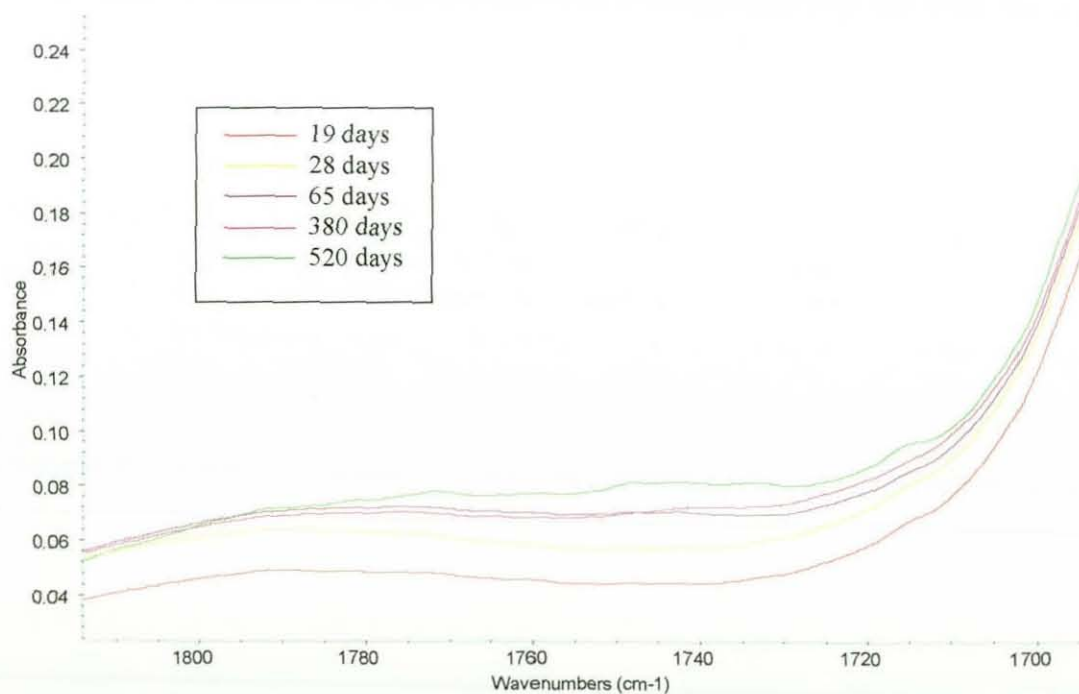


**Figure 4-14 Change in carbonyl region of IR spectra of Nylon 6 after 65 days of thermal ageing at  $60^{\circ}\text{C}$**

Figure 4-15 shows the carbonyl IR spectra of Nylon 6 at the much longer oven ageing time of 520 days. The region shows several overlapping bands. The peak at  $1735\text{ cm}^{-1}$  has been related to the presence of cyclopentanone derivatives[160]. Imides present a characteristic absorption peak at  $1735\text{ cm}^{-1}$  [113] Consequently, the peak observed at this frequency could result by the overlapping contributions from both cyclic ketones, whose content decreases over ageing, and imides, which remain constant after some time. It is possible that carboxylic acids formed within polymer bulk can exist as isolated species in equilibrium with dimeric acids (which absorb at  $1710\text{ cm}^{-1}$ ) due to their low mobility. This band is also due to the overlap of single species absorption, such as saturated aldehydes (at  $1725\text{ cm}^{-1}$ ), dimeric carboxylic acids (at  $1710\text{ cm}^{-1}$ ), and  $\alpha,\beta$ -unsaturated carbonyls (at  $1700\text{ cm}^{-1}$ )[113]. Carbonyl absorption is continuously increased with ageing time (see figure 4-16), as is inevitable with slow but continuous thermo-oxidation.



**Figure 4-15** Change in carbonyl region of IR spectra of Nylon 6 after 520 days of thermal ageing at 60°C



**Figure 4- 16** Change in carbonyl region of IR spectra of layer 5 of Nylon 6 film for ageing times from 19 days to 520 days, during thermal ageing at 60°C

## 5 CONCLUSIONS

### 5.1 *Compatibility of antioxidants with PEO*

DSC scans of PEO dissolved and mixed with IPPD show a marked decrease in the melting enthalpy of the PEO component, whereas IPPD shows a melting peak only at very high concentrations, pointing to a strong interaction of this amine antioxidant with the polymer. At the same time, the measured total enthalpy is higher than the values calculated from the PEO quantities present in the system. This indicates that IPPD co-crystallises with the PEO. The dissolved polymer and the amine antioxidant form two phases; one consisting of crystalline IPPD (with invariant melting point, with respect to the pure IPPD) and one consisting of PEO co-crystallised with IPPD, with a melting point lower than for pure PEO. The melting enthalpies of these two phases do not account for all the material present in the sample, resulting from an amount of PEO not crystallising. Increasing IPPD content gives an increase in the amorphous PEO phase, containing part of the antioxidant, which goes undetected by DSC scan. The remaining crystalline PEO phase, though, increases in amine concentration, resulting in less ordered crystals, shown by a progressively lower  $T_m$ .

### 5.2 *Miscibility of coupling agents in silica*

- i) GOTMS: Screening tests have shown that the use of GOTMS does not prevent crystallisation of the antioxidants. In the case of Tinuvin 770, the material is completely homogeneous even without GOTMS. Previous works have shown the function of GOTMS as coupling agent between silica and PEO in hybrids [98].
- ii) TESP-NCO reacted with Irganox 1076: It is clear that this product is unstable and the adduct may decompose during the sol-gel processing of the mixtures.
- iii) TESP-NCO reacted with Tinuvin 770: The addition is complete and the product can be entrapped within the silica network.

- iv) TESP-U-DBHMP is able to co-condense in the silica network and assist the dispersion of the hindered phenol antioxidant, i.e. it acts as a compatibiliser. High content ( $\sim 25\%w/w$  relative to  $SiO_2$ ) are necessary to have a significant effect on compatibility within the sol-gel film.
- v) IPPD, an amine antioxidant, is prevented from crystallising when present in concentration even as high as  $20\%w/w$ . Above this level a melting peak is evident, but a substantial amount of amine becomes bound to the silica.

### 5.3 Miscibility of antioxidants in PEO-SiO<sub>2</sub> hybrids

- i) There is a strong interaction between PEO and the amine stabiliser IPPD, as seen in the simple mixture and in the hybrids. There is interaction between PEO and the phenolic antioxidant Irganox 1076.
- ii) The presence of PEO in the materials with high content of silica is reducing the amount of crystallising IPPD, thus stabilising the entrapment of the antioxidant. Quantitative analysis of the effects is complex due to the presence of three components, which interact strongly.
- iii) The SEM images suggest dramatic changes in the appearance of the surface at the changing of proportions of the hybrids. All the surfaces were left free to evaporate at room pressure and temperature. The hybrid PEO (40) / Silica (20) / IPPD (40) (see Figures 7-70, 7-71) yielded a compact uniform surface, with sparse islands, attributable to the few crystallites of IPPD. DSC data of this sample shows a wide melting region at a temperature lower than that of PEO. The melting peak of IPPD is very small ( $\Delta H_f$  45.6 J/g,  $T_m$  47.4 °C) but not shifted from the corresponding transition temperature in the pure antioxidant.

Hybrid PEO (30) / Silica (30) / IPPD (40) (see figures 7-72, 7-73) presents a rugged porous surface, analogous to that of porous sol-gel derived silica. DSC of this sample shows a very small PEO melting peak ( $\Delta H_f$  1.1 J/g,  $T_m$  47.0 °C) and a clear IPPD melting endotherm ( $\Delta H_f$  33.5 J/g,  $T_m$  80.0 °C). Comparison of this latter enthalpy with the calculated value of 49.2 J/g for a non-interactive physical mixture of IPPD (40 / 60) yields a 68% un-bound

crystalline IPPD. This is therefore different from the former hybrid system where the IPPD also interacts and co-crystallise with the PEO.

- iv) *The thermal history strongly influences the morphology of the complex material:* DSC shows that the second heating scan, after heating and cooling ramps, is markedly different and the melting peaks are smaller, pointing to less ordered crystals or increased amorphous phase.
- v) Among the phenolic antioxidants considered, BHT has the highest degree of compatibility with the organic/inorganic hybrid, with concentrations of 20% by weight fully compatibilised between the organic PEO chain and amorphous silica pores. The compatibilised content increases to 40% by weight when the functionalised urethane-silane coupling agent is included in the formulation of the silica phase.

#### **5.4 Diffusion of antioxidant**

There is strong indication that BHT diffuses out of organic/inorganic hybrids made with sol-gel derived silica and PEO. Compositions with 20% by weight of BHT antioxidant and different proportions of PEO to silica were studied. A temperature as low as 60 °C was investigated in oven ageing experiments, and a degree of protection was afforded to Nylon 6 films 12 µm thick. The amount of hydroperoxide species, which represent the intermediate stage of thermal oxidation, was reduced. The appearance of carbonyl containing species, which are the first products of oxidations, was considerably delayed compared with non-protected polyamides. At the same time the overall concentration of antioxidant within the polymer remains low, so that there is reduced possibility of the additive leaching and blooming out of the polymer matrix.

#### **5.5 Suggestions for further work**

There is considerable scope for further work investigating these hybrid systems for delivery of antioxidants.

The range of additives used can be expanded to other classes of antioxidants, such as phosphites, and to mixtures of primary and secondary antioxidants, such as those commonly used in industrial practice, to establish the extent of preferred adsorption

and desorption of a type of additive versus another in such complex ternary hybrids.

The hybrids can be further characterised by small angle X-ray spectroscopy, to accurately determine the size of nanodomains.

Other compositions can be investigated in the diffusion study, especially investigating compositions that exhibit separated crystallised antioxidant, to investigate the effect of readily available antioxidant for short term and processing protection followed by desorbed antioxidant for long term protection through slow release.

The temperature of oven ageing can be varied to obtain a measure of the activation energy of desorption of antioxidant from the hybrid matrix. Temperatures below 60 °C would continue in the study of solid-state diffusion mechanisms, but would mean very long ageing times. Temperatures above the melting range of PEO would significantly change the morphology of the hybrid and therefore the mechanisms and rate of diffusion of the antioxidants.

The diffusion model can further refined by compounding the antioxidant-containing hybrid with the chosen polymer, thereby using it as functional filler. The protected compound can then be fully characterised in its mechanical, thermal and optical properties, as well as ageing behaviour. The long term ageing experiments can be carried out on the protected compound (direct protection) or using the Roe experiment by having a layer of protected polymer centred between layers of unprotected compound.

In addition to Nylon 6, a whole range of other polymers for delivery of antioxidants can be investigated. Polar polymers such as polyurethanes would offer a higher degree of interaction with the interface of the hybrid, compared with apolar polymers like polyolefins: the effects on the diffusion rate of antioxidants would be an interesting subject of further study.

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## 7 APPENDIX

### 7.1 IR Spectra

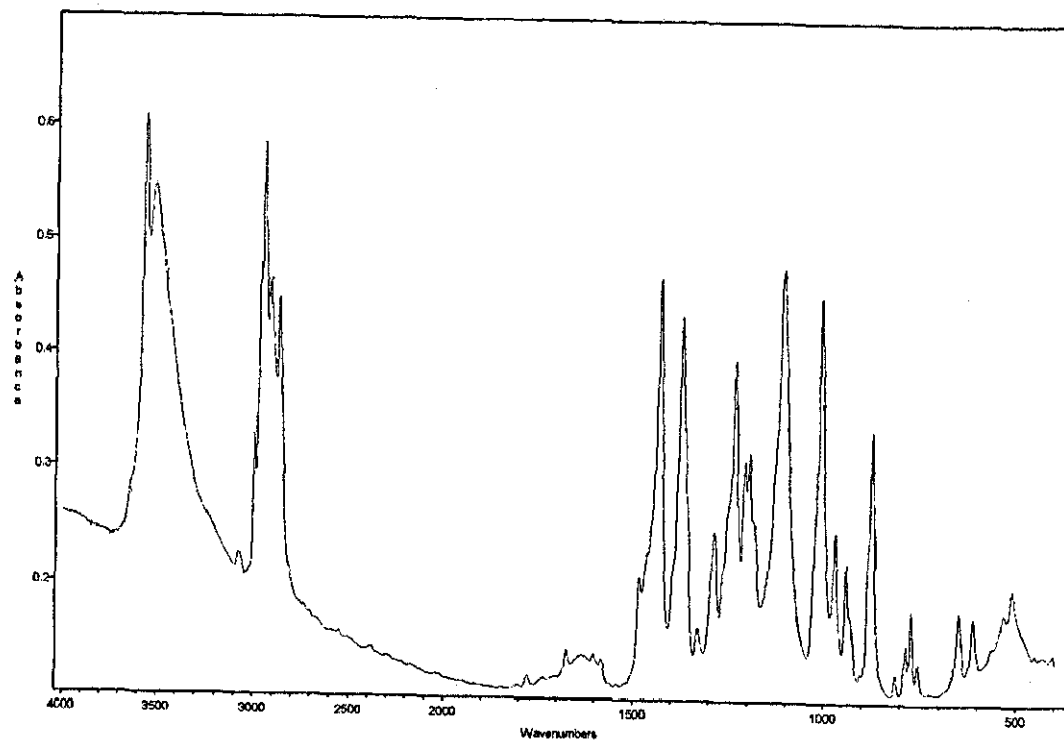


Figure 7-1 IR spectrum of 2,6-di-tertbutyl-4-hydroxymethylphenol (DBHMP)

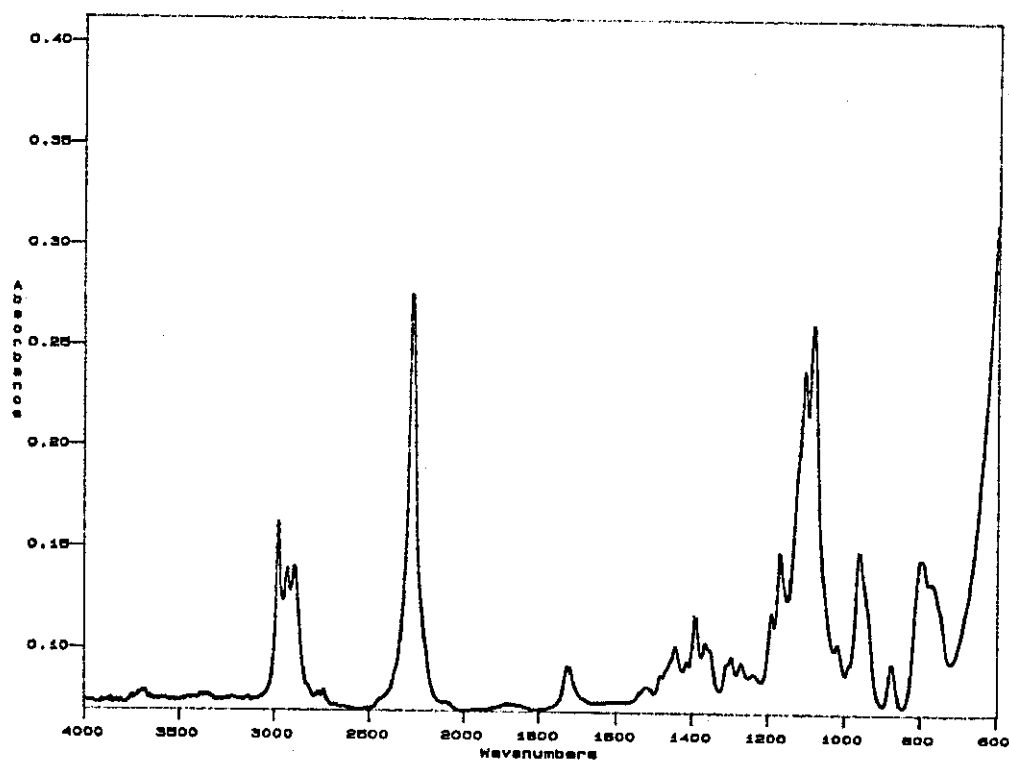


Figure 7-2 IR spectrum of  $\gamma$ -triethoxysilyl propyl isocyanate (TESP-NCO)

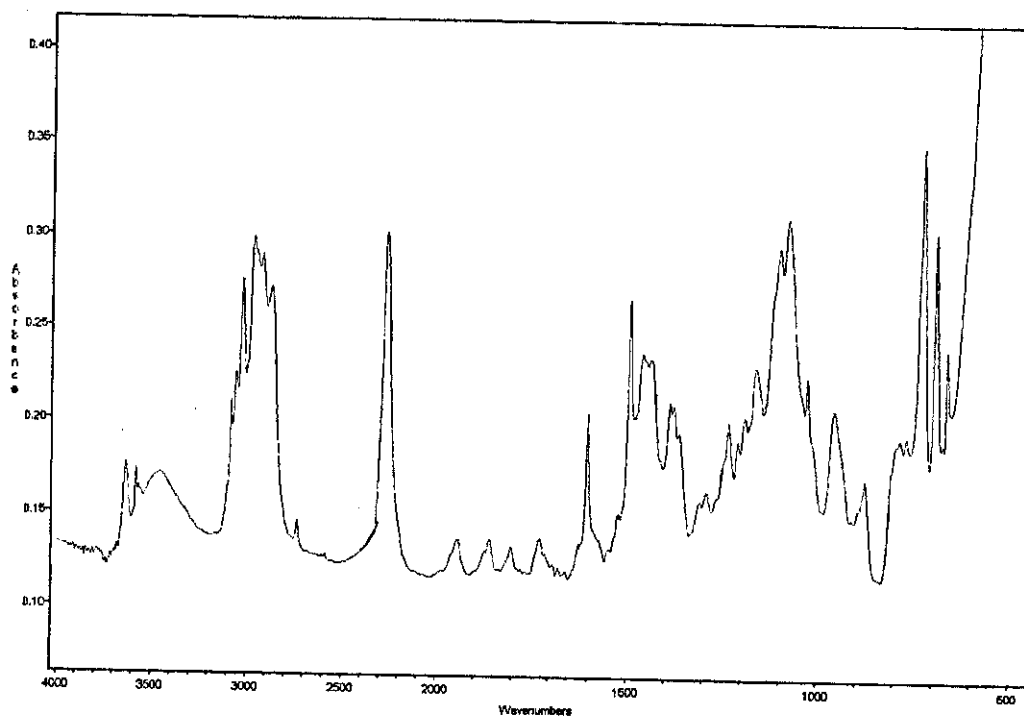
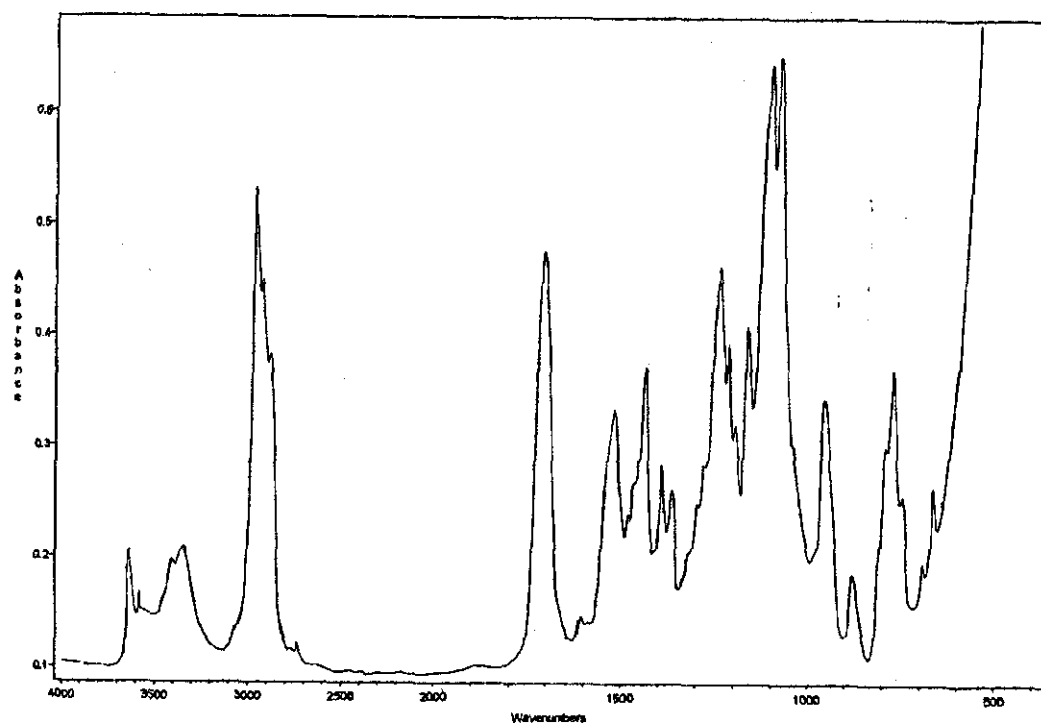
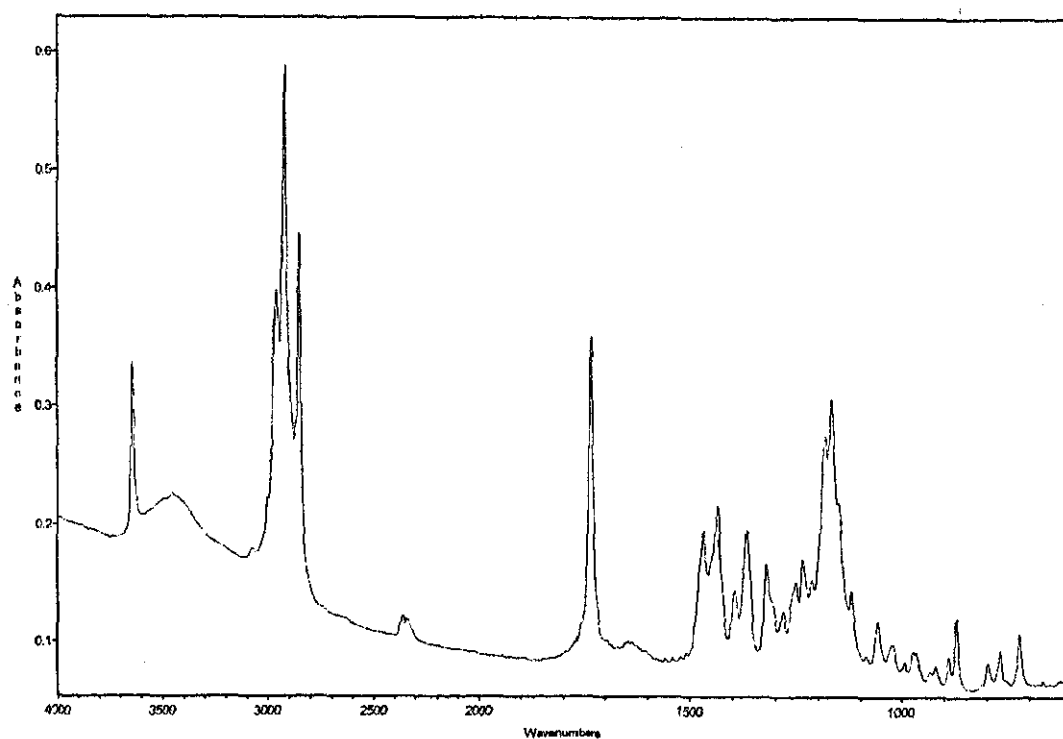


Figure 7-3 IR spectrum of DBHMP and TESP-NCO dissolved in Xylene: THF (8:1), immediately after mixing



**Figure 7-1 IR spectrum of the reacted TESP-U-DBHMP**



**Figure 7-5 IR spectrum of Irganox 1076**

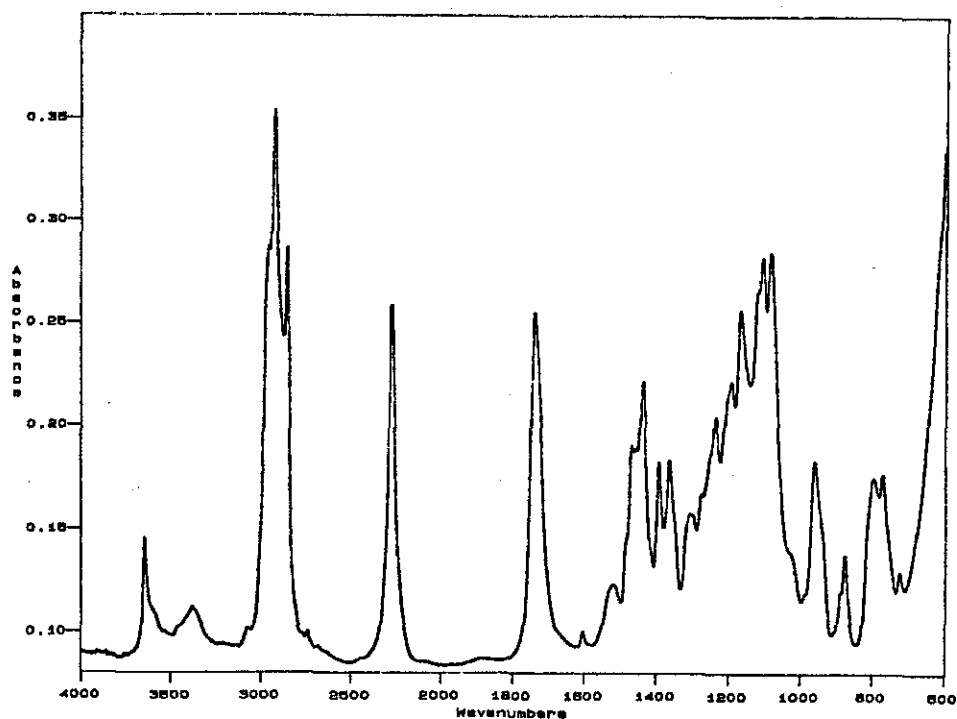


Figure 7-6 IR spectrum of TESP-NCO + Irganox 1076 after 53 hours of reaction at 80 °C

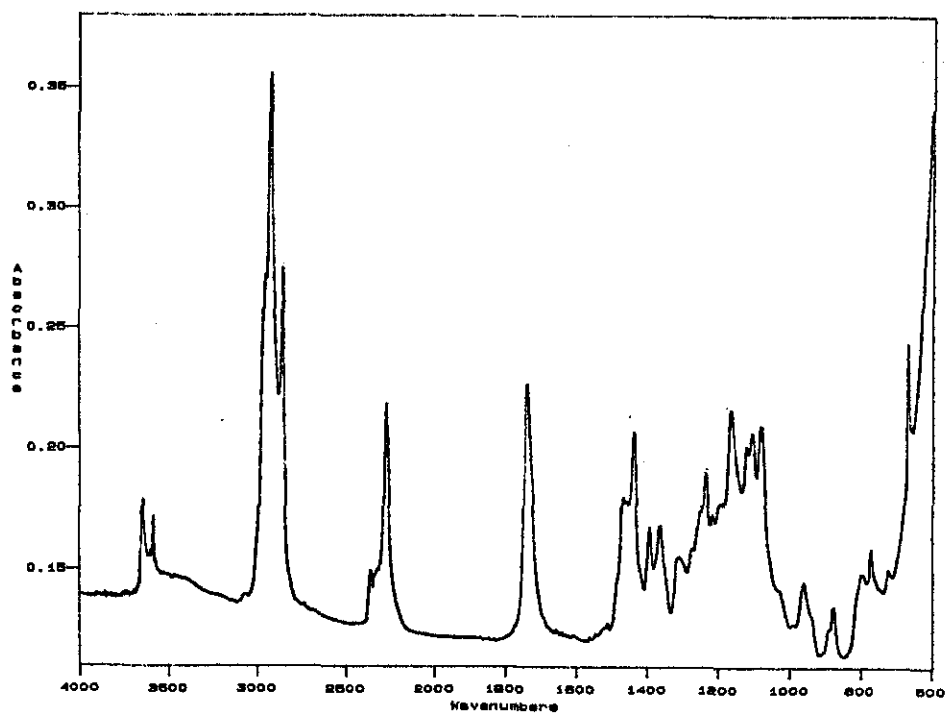
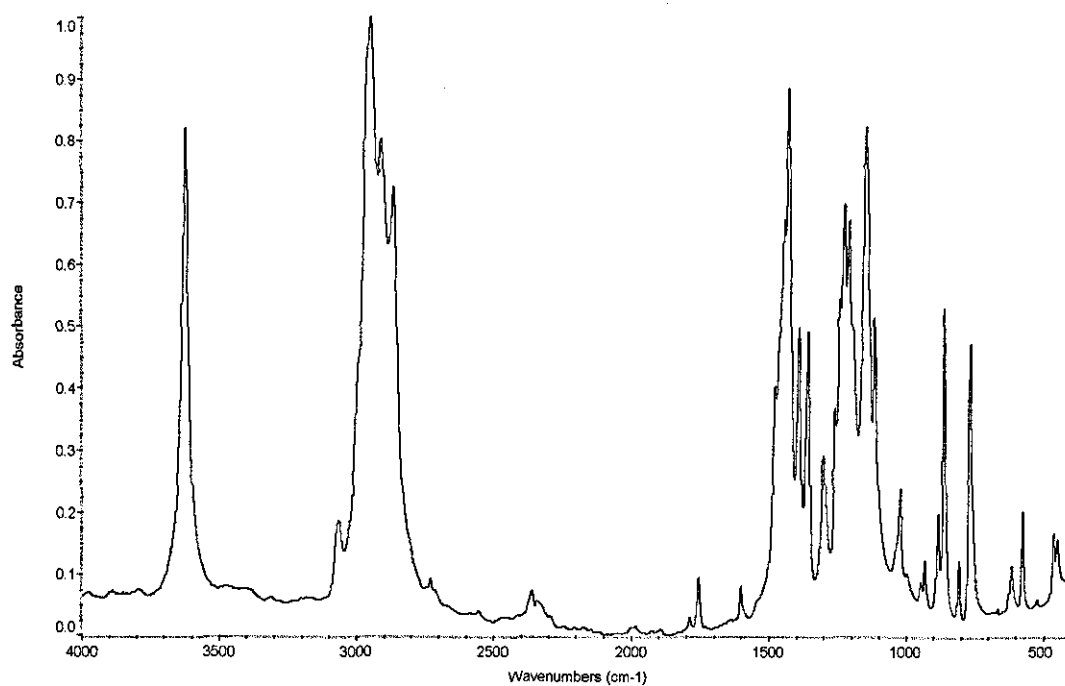
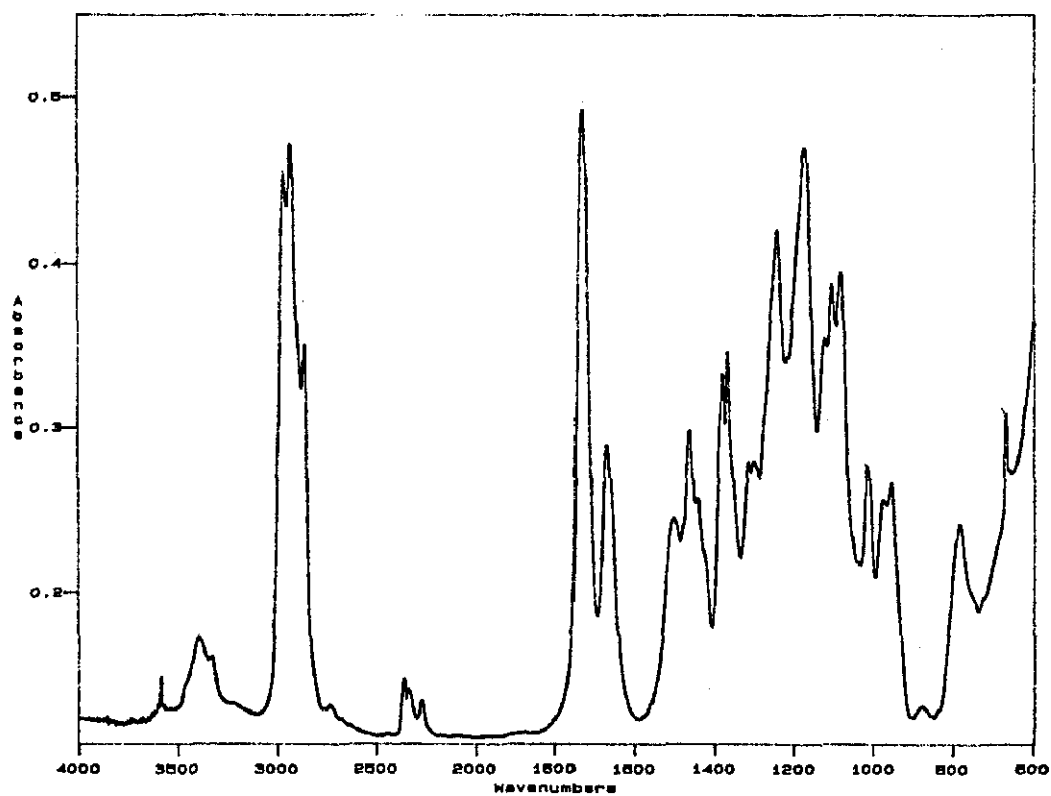


Figure 7-7 IR spectrum of Irganox 1076 and TMS-NCO (molar proportion 4:1) mixture after 2 weeks at 60 °C



**Figure 7-8 IR spectrum of BHT**



**Figure 7-9 IR spectrum of reaction mixture of TESP-NCO and Tinuvin 770 after 3 hours at 85 °C**

## 7.2 DSC of Sol-gel Silica

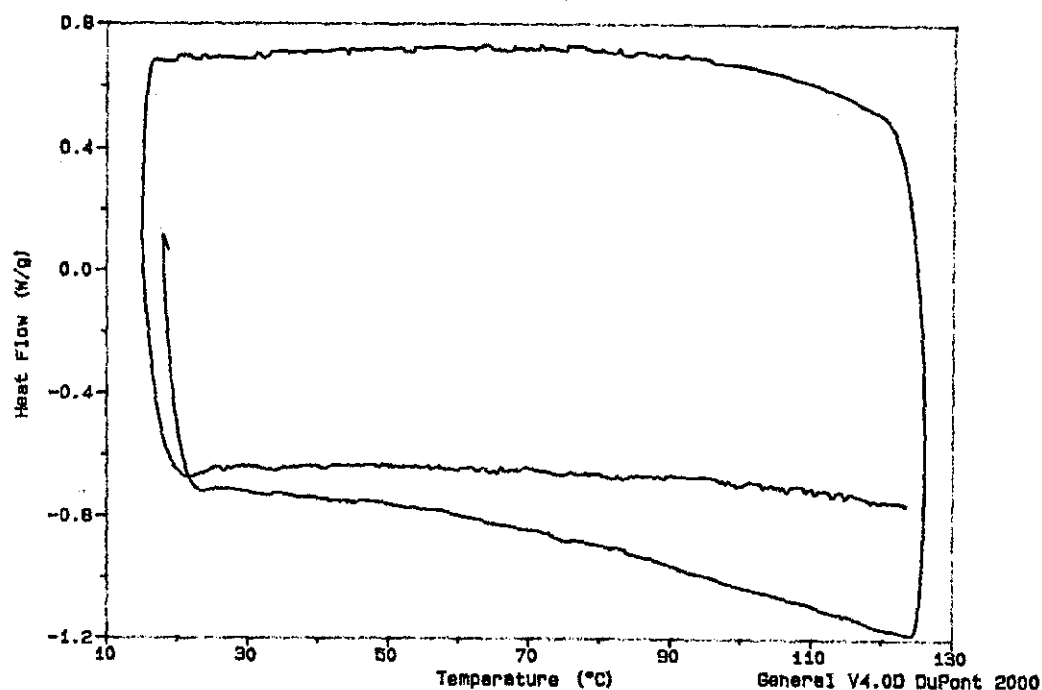


Figure 7-10 DSC thermogram of sol-gel silica

## 7.3 DSC of Silica – IPPD

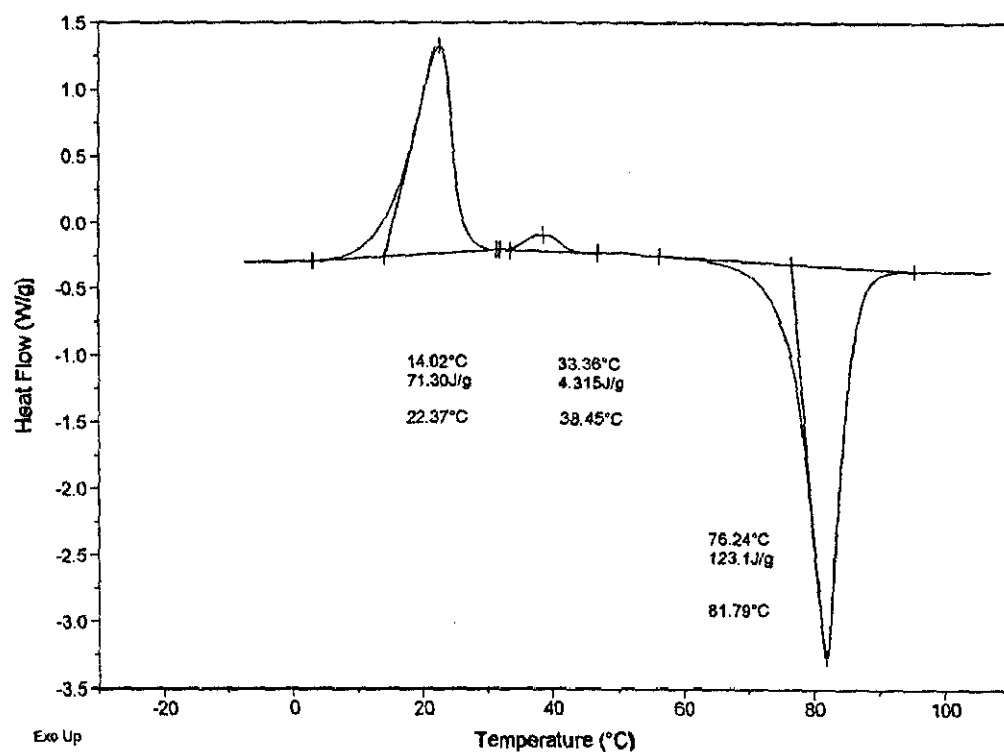


Figure 7-11 DSC thermogram of antioxidant IPPD

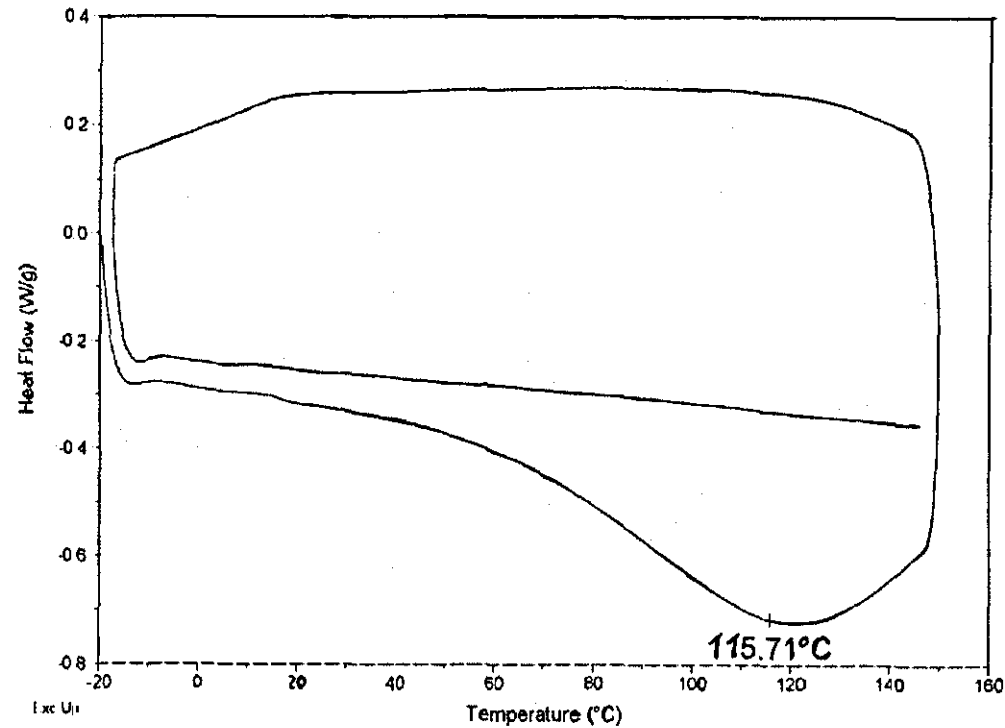


Figure 7-12 DSC thermogram of Sol-gel SiO<sub>2</sub> (80) / IPPD (20)

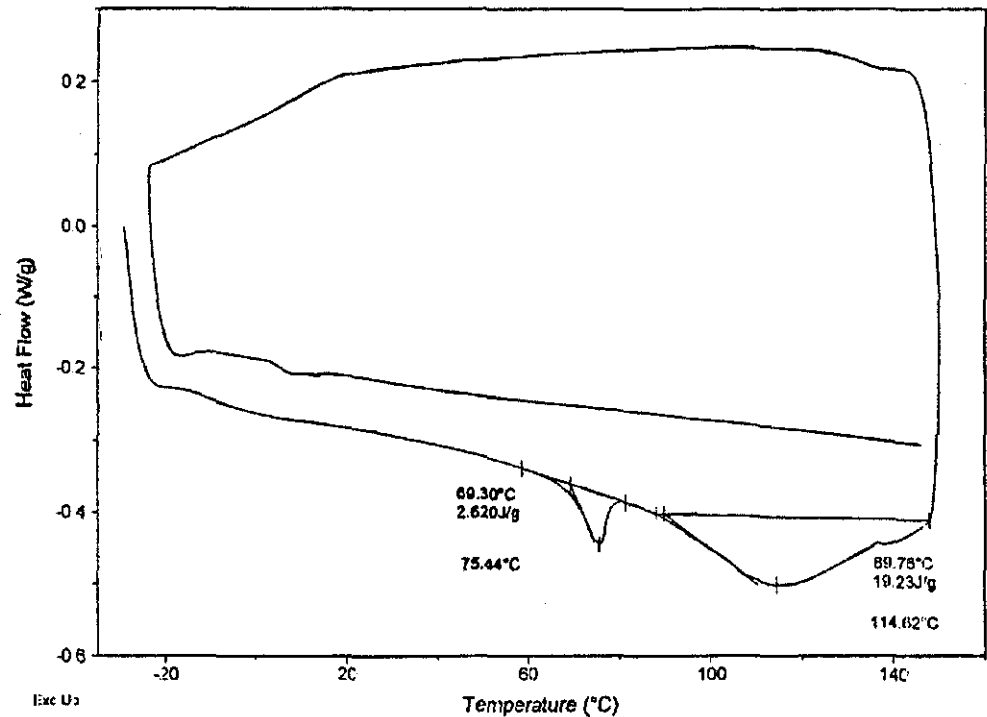


Figure 7-13 DSC thermogram of Sol-gel SiO<sub>2</sub> (70) / IPPD (30)

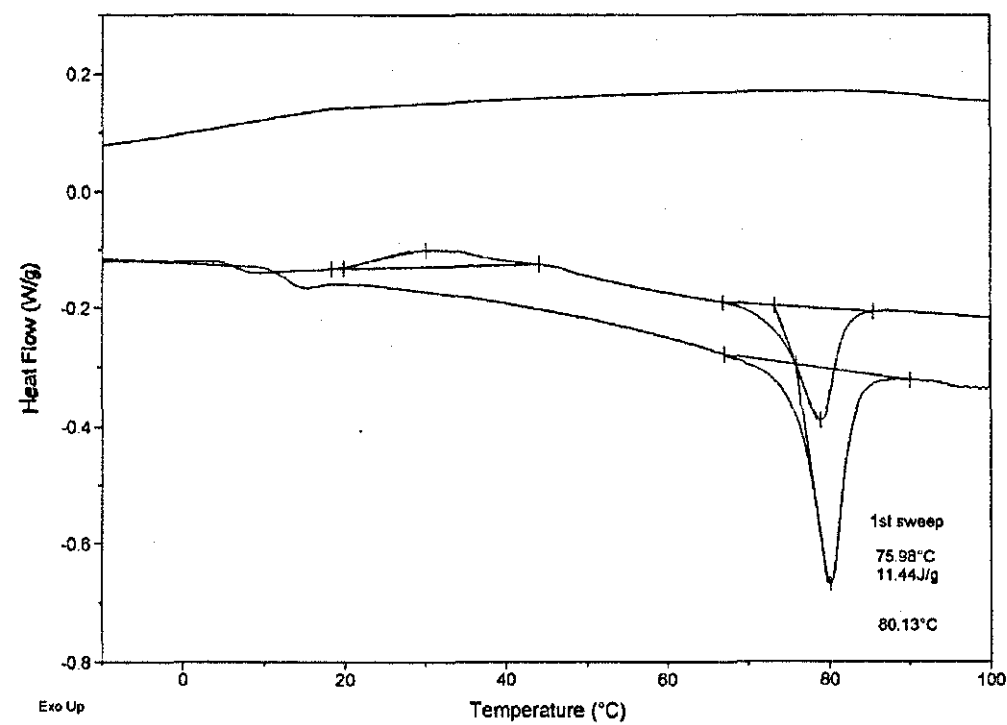


Figure 7-14 DSC thermogram of Sol-gel SiO<sub>2</sub> (60) / IPPD (40)

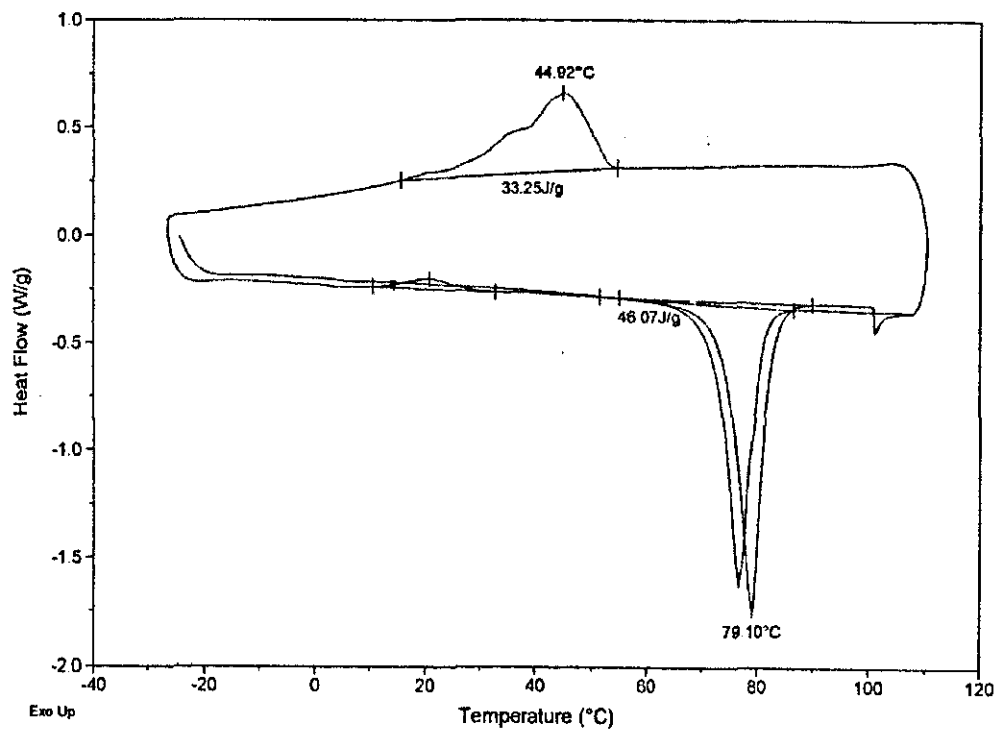


Figure 7-15 DSC thermogram of Sol-gel SiO<sub>2</sub> (40) / IPPD (60)

## 7.4 DSC of Silica – Tinuvin 770

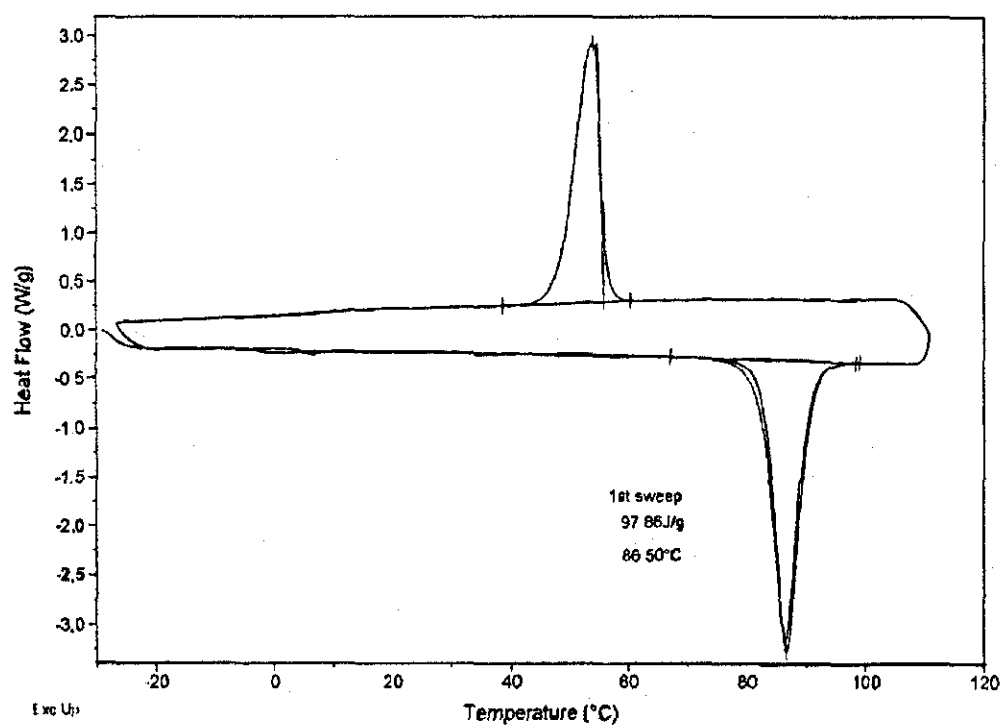


Figure 7-16 DSC thermogram of Tinuvin 770

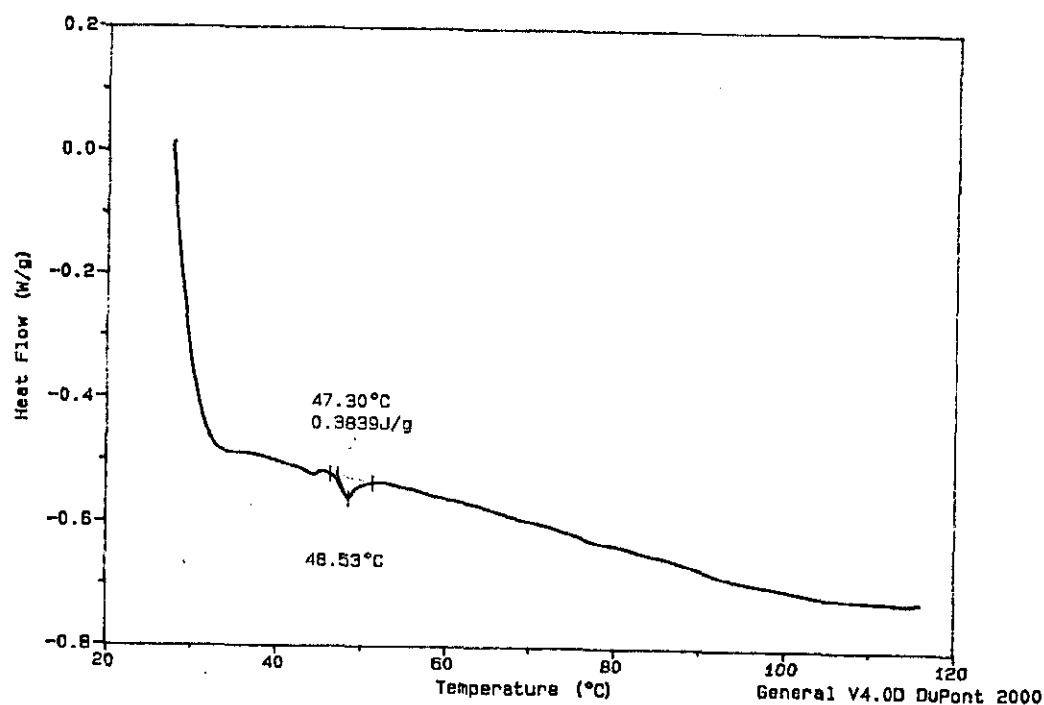


Figure 7-17 DSC thermogram of Sol-gel SiO<sub>2</sub> (92) / Tinuvin 770 (08)

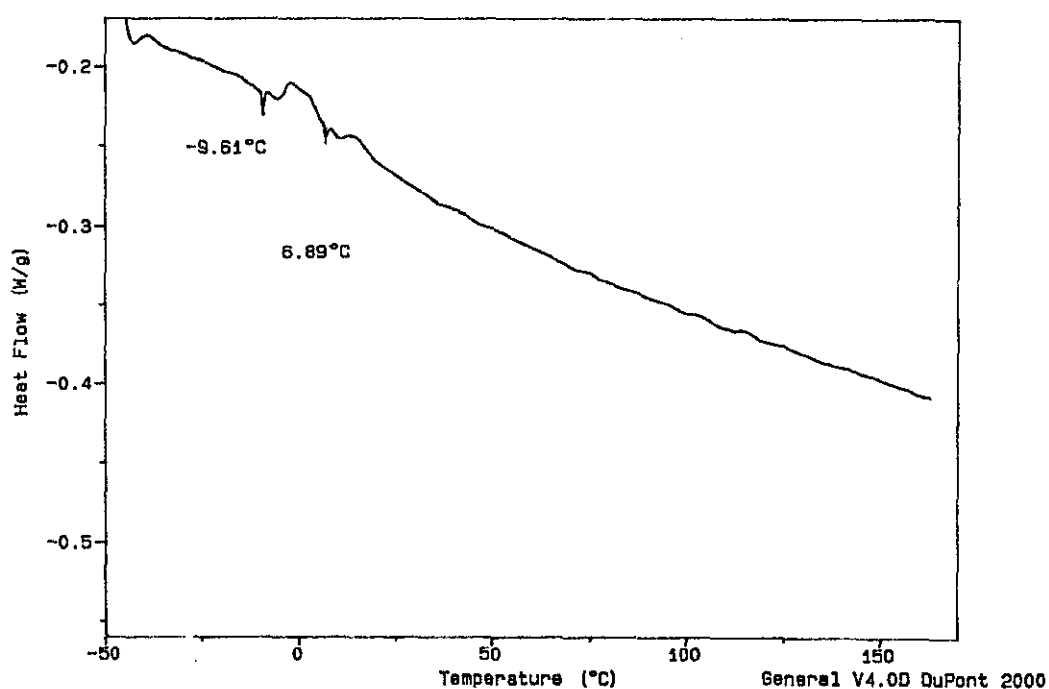


Figure 7-18 DSC thermogram of Sol-gel  $\text{SiO}_2$  (70) / Tinuvin 770 (30)

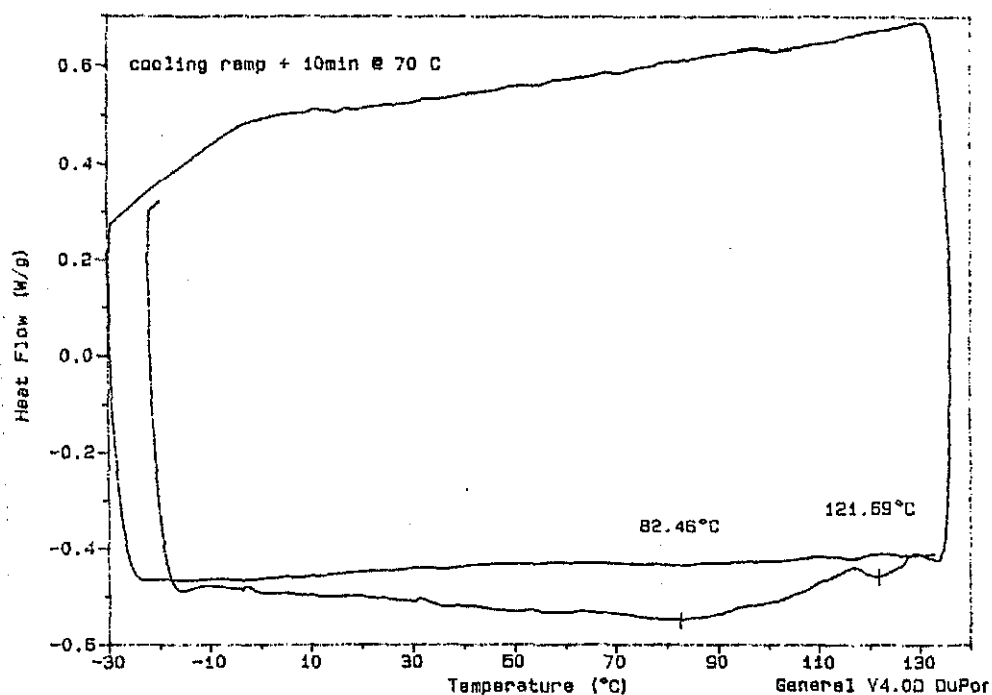


Figure 7-19 DSC thermogram of Sol-gel  $\text{SiO}_2$  (38) / Tinuvin 770 (62)

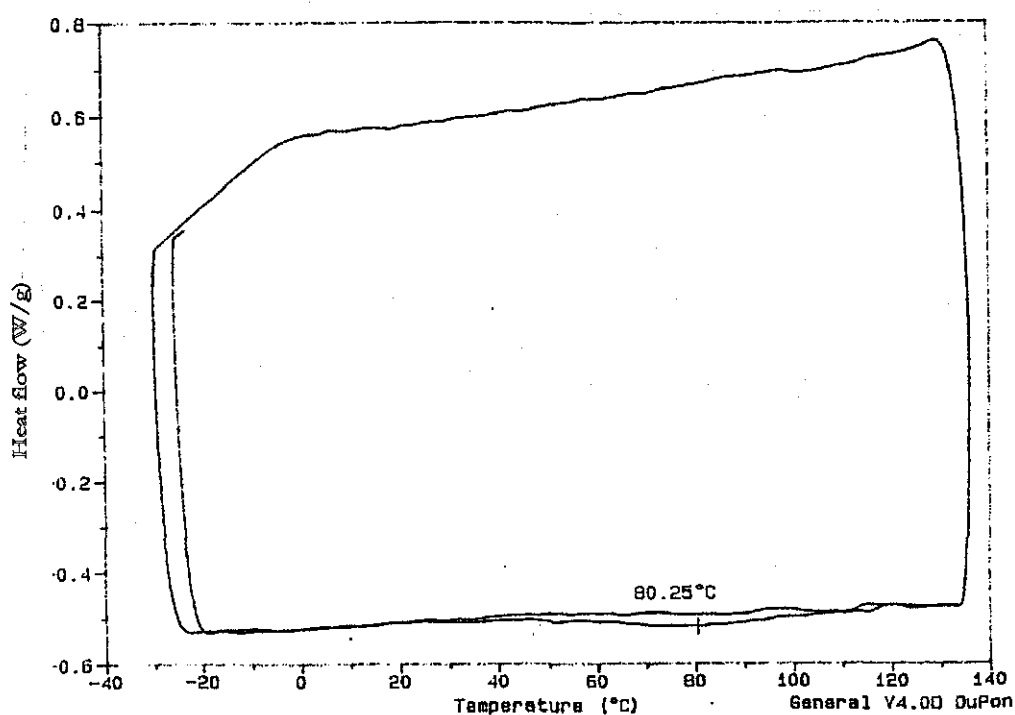


Figure 7-20 DSC thermogram of Sol-gel  $\text{SiO}_2$  (29) / Tinuvin 770 (71)

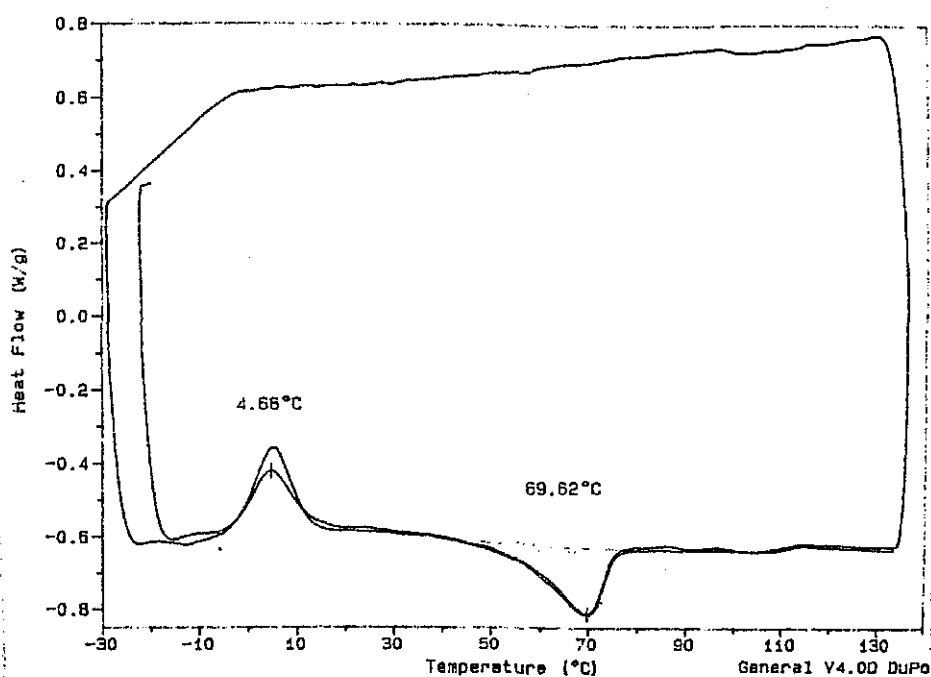


Figure 7-21 DSC thermogram of Sol-gel  $\text{SiO}_2$  (24) / Tinuvin 770 (76)

7.5 DSC of Silica – Irganox 1076

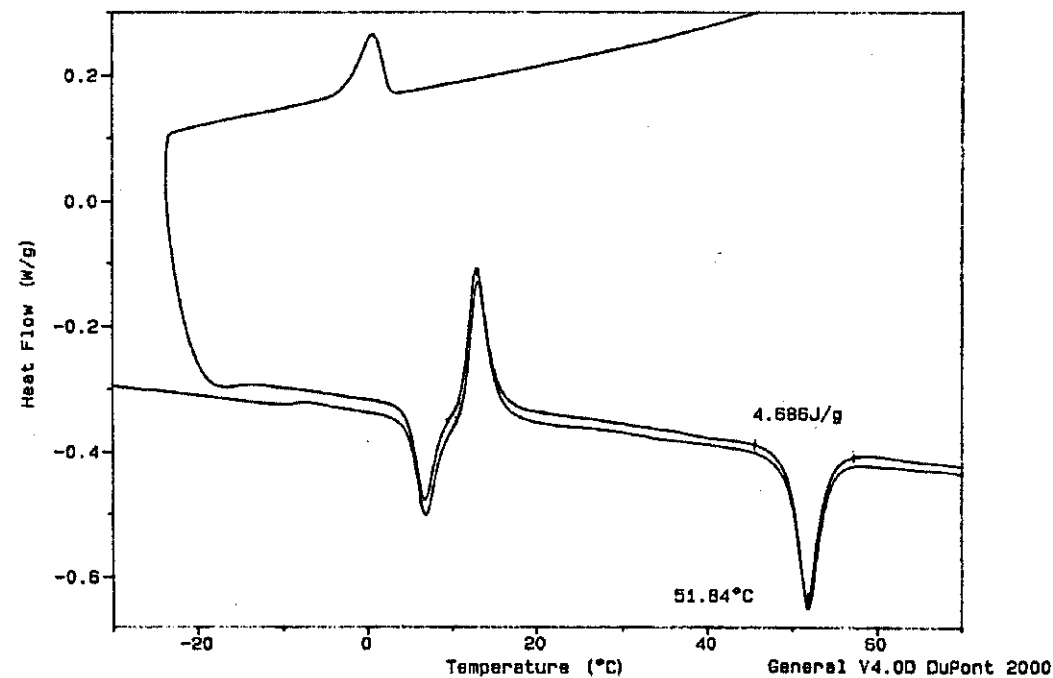


Figure 7-22 DSC thermogram of Sol-gel SiO<sub>2</sub> (95) / Irganox 1076 (05)

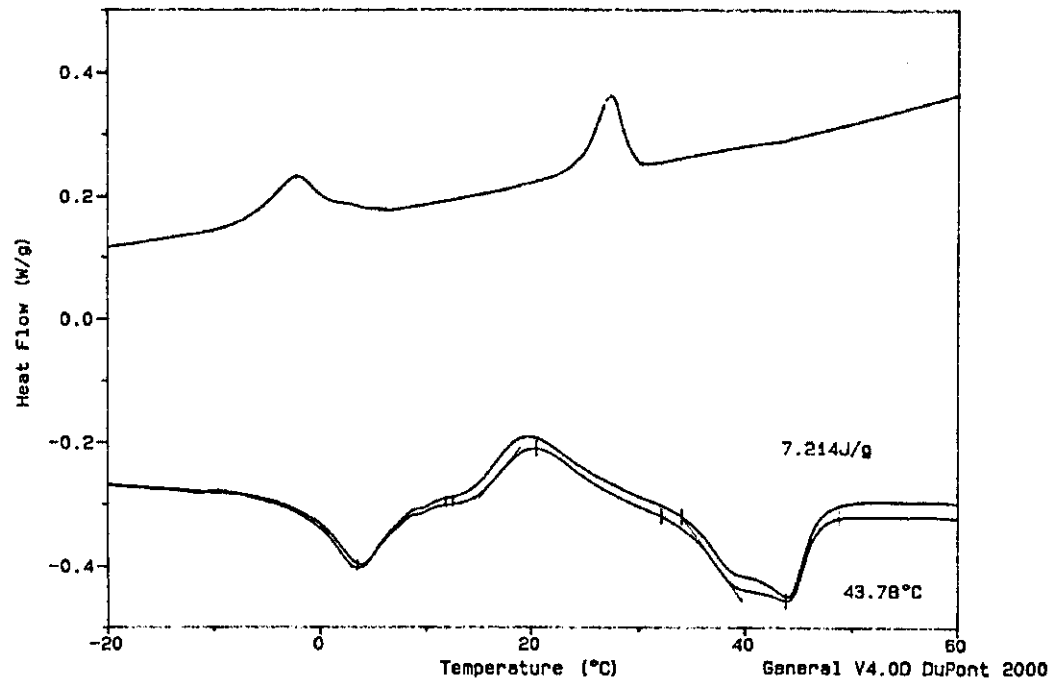


Figure 7-23 DSC thermogram of Sol-gel SiO<sub>2</sub> (86) / Irganox 1076 (14)

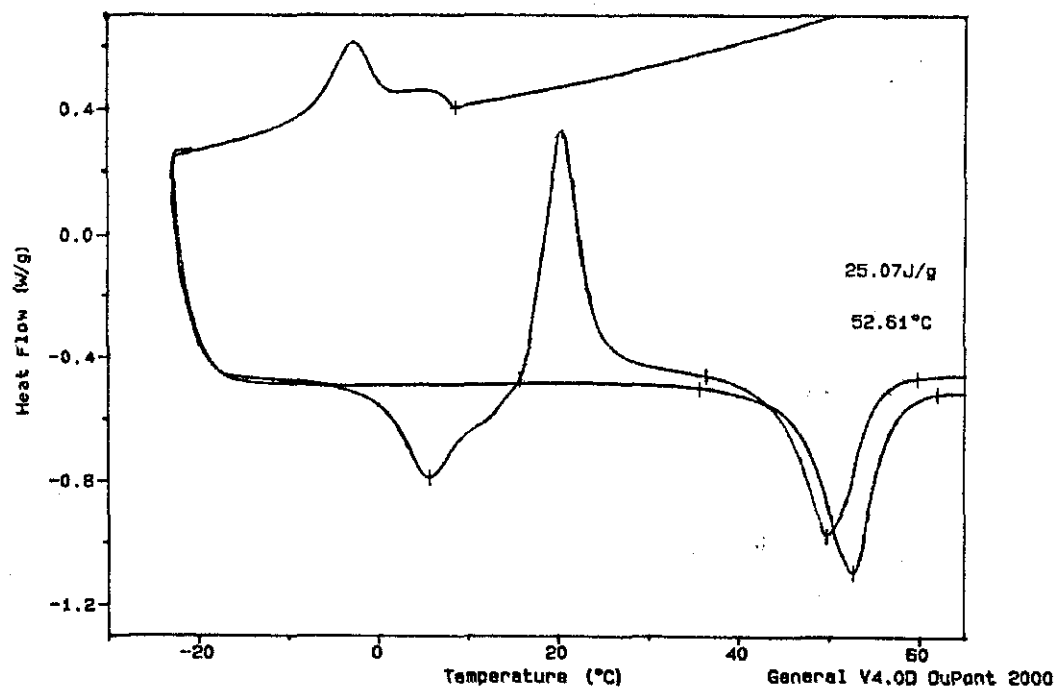


Figure 7-24 DSC thermogram of Sol-gel SiO<sub>2</sub> (72) / Irganox 1076 (28)

7.6 DSC of PEO – IPPD

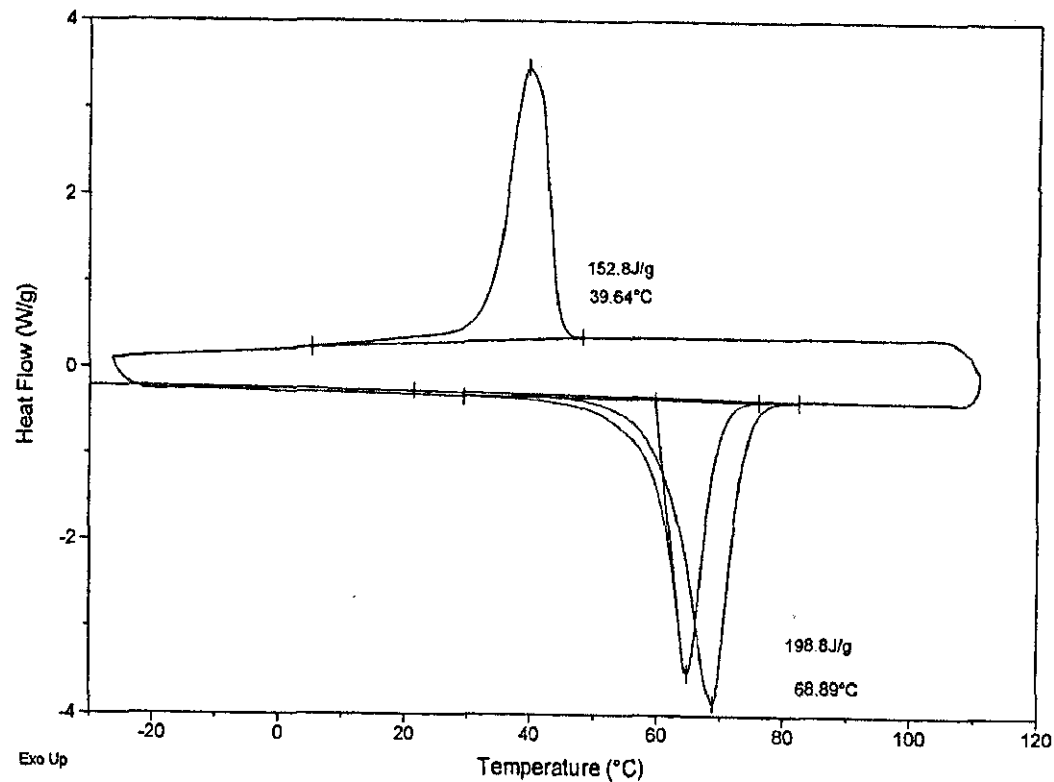


Figure 7-25 DSC thermogram of PEO

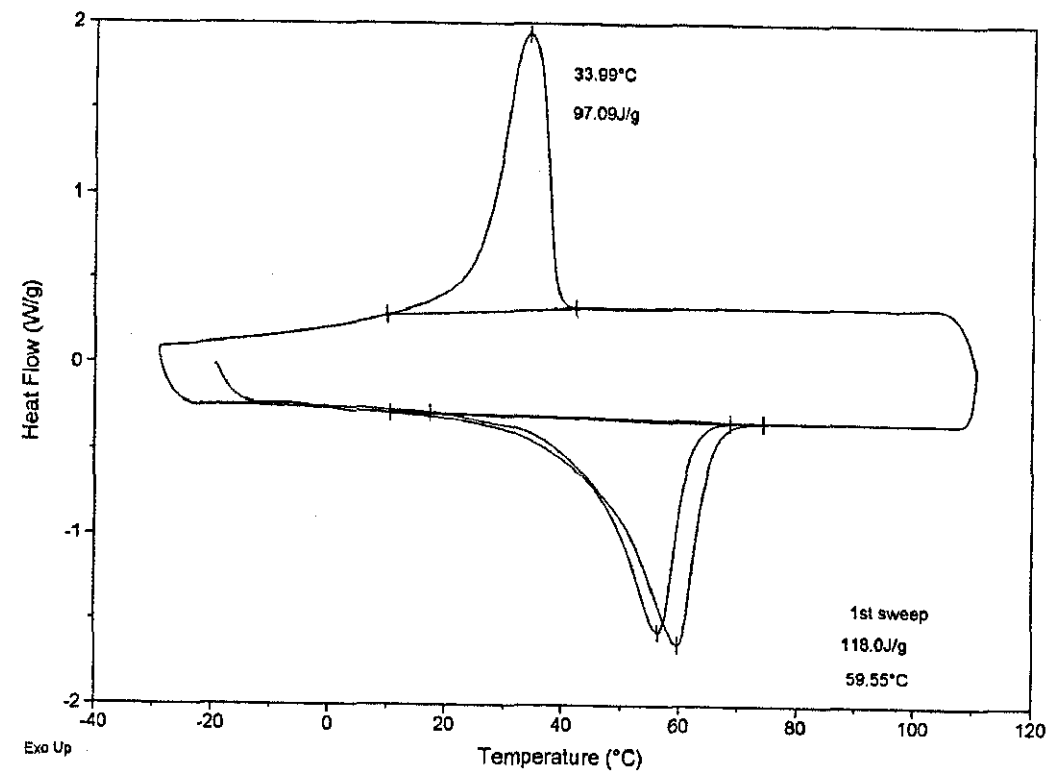


Figure 7-26 DSC thermogram of PEO (80) / IPPD (20)

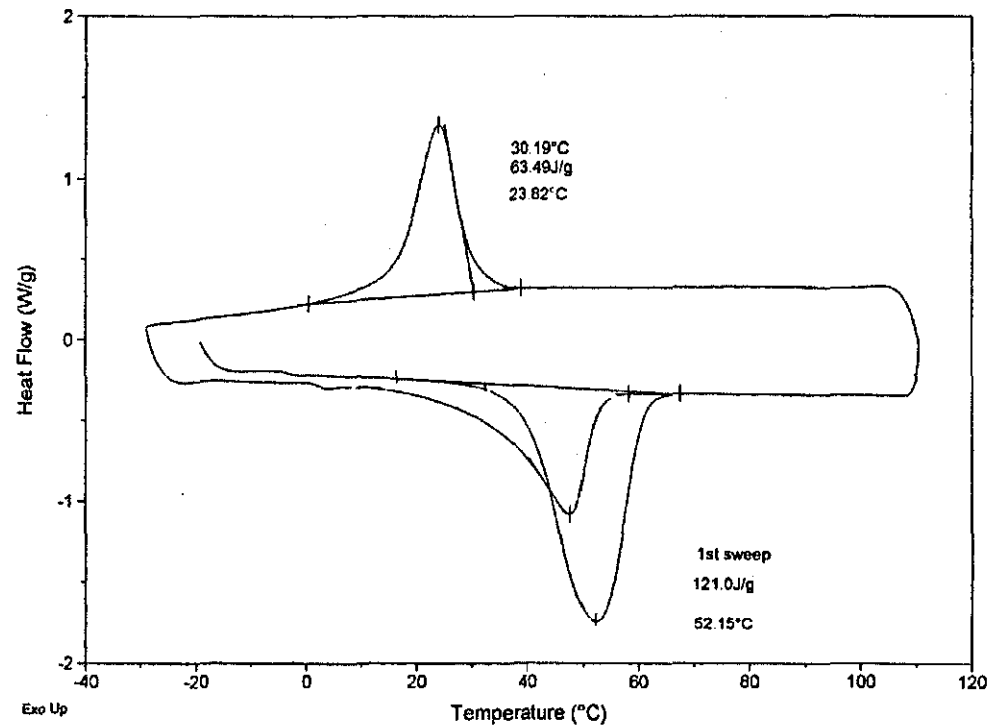


Figure 7-27 DSC thermogram of PEO (60) / IPPD (40)

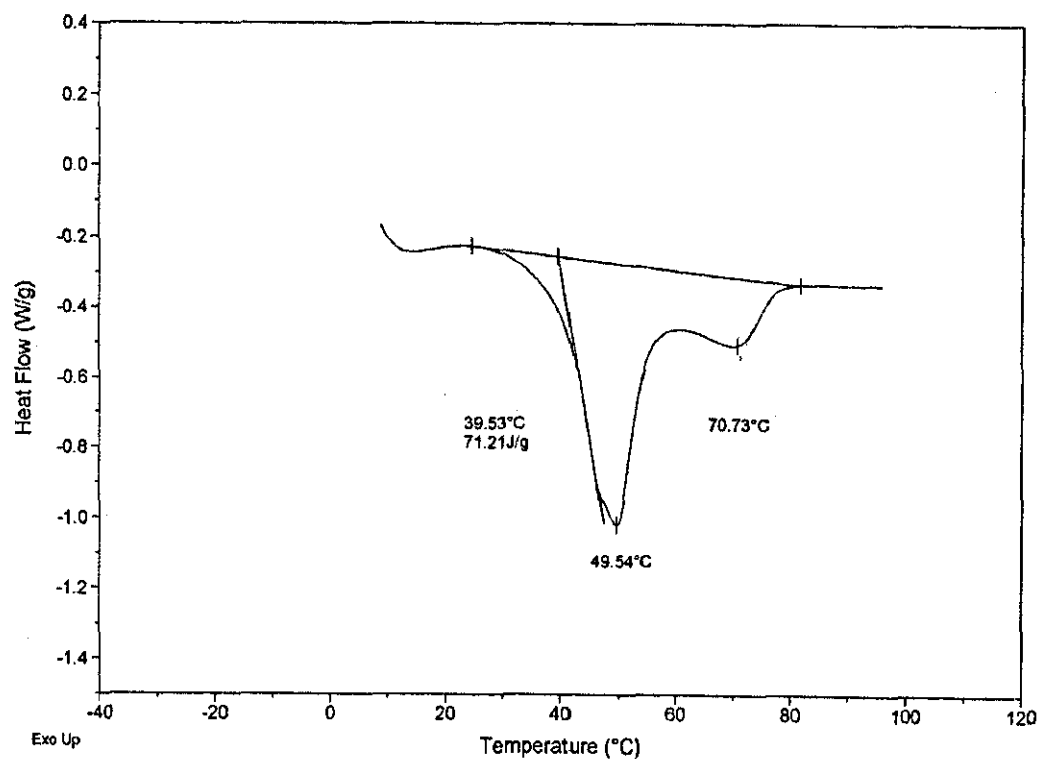


Figure 7-28 DSC thermogram of PEO (40) / IPPD (60)

7.7 DSC of PEO – Irganox 1076

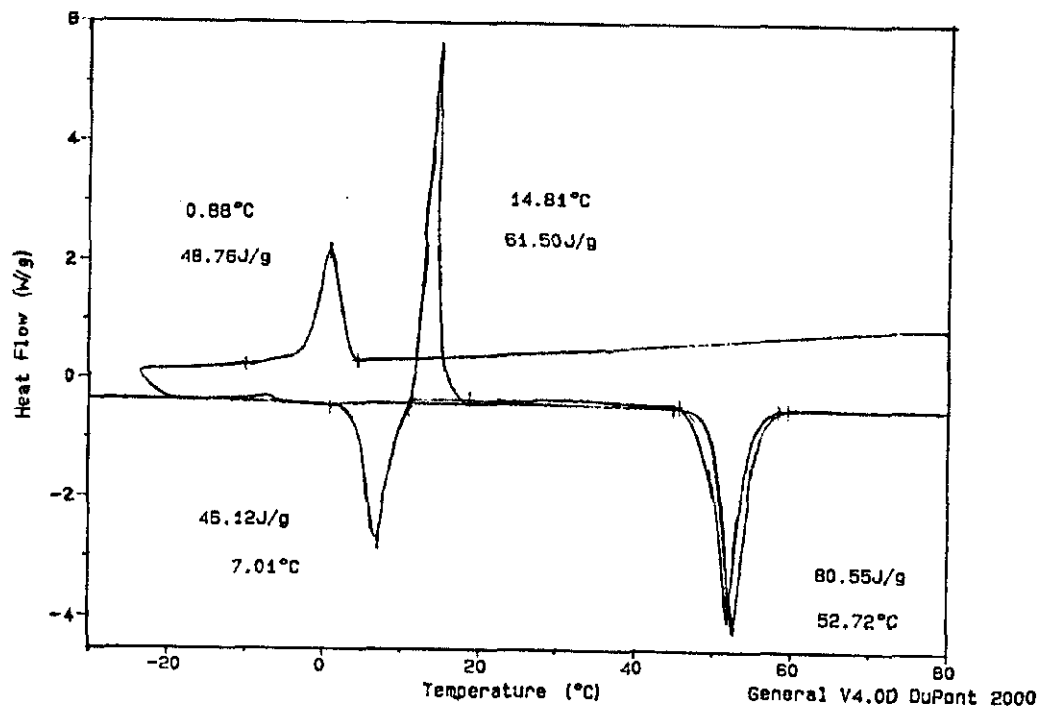


Figure 7-29 DSC thermogram of DSC of Irganox 1076

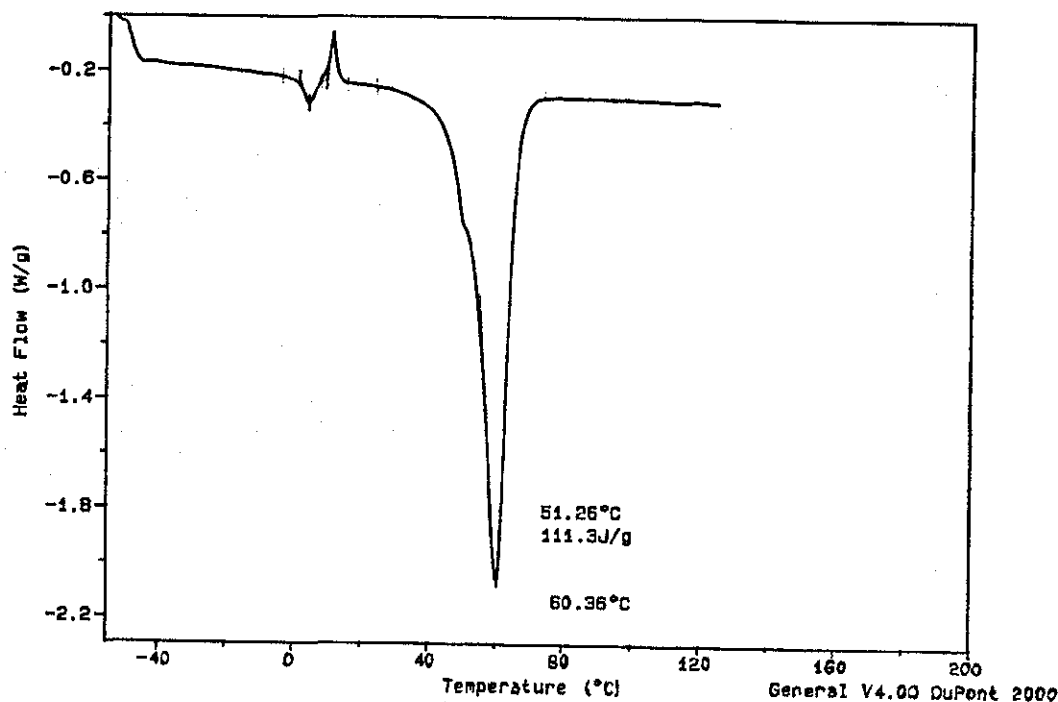


Figure 7-30 DSC thermogram of PEO (90) / Irganox 1076 (10)

### 7.8 DSC of PEO-SiO<sub>2</sub>-Irganox 1076 hybrids

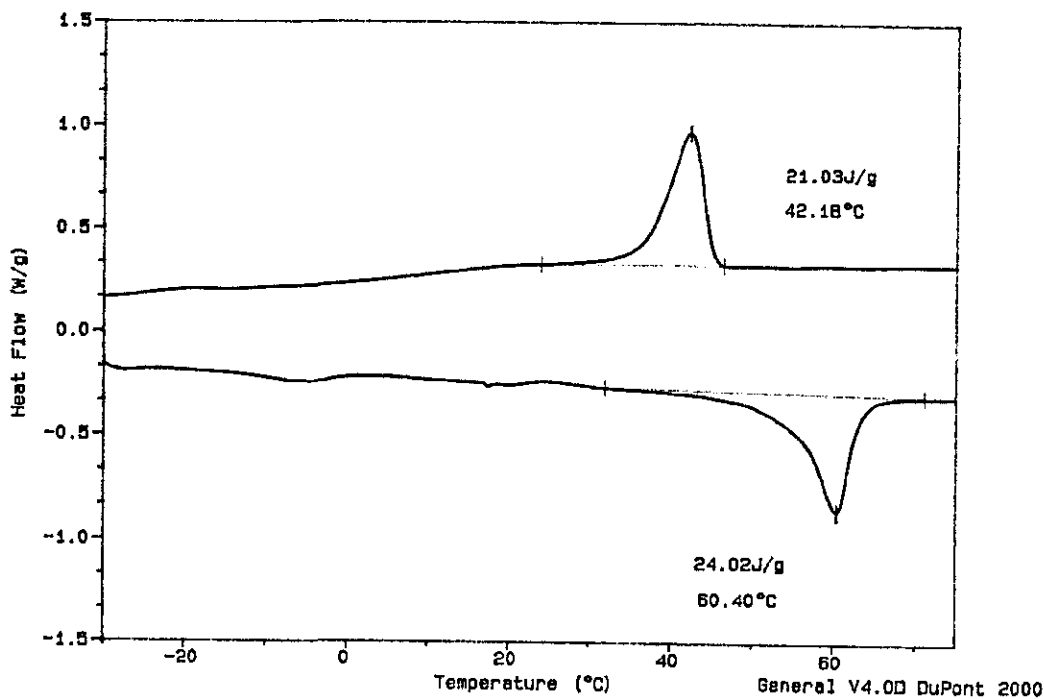


Figure 7-31 DSC thermogram of hybrid PEO (30) / SiO<sub>2</sub> (60) / Irganox 1076 (10)

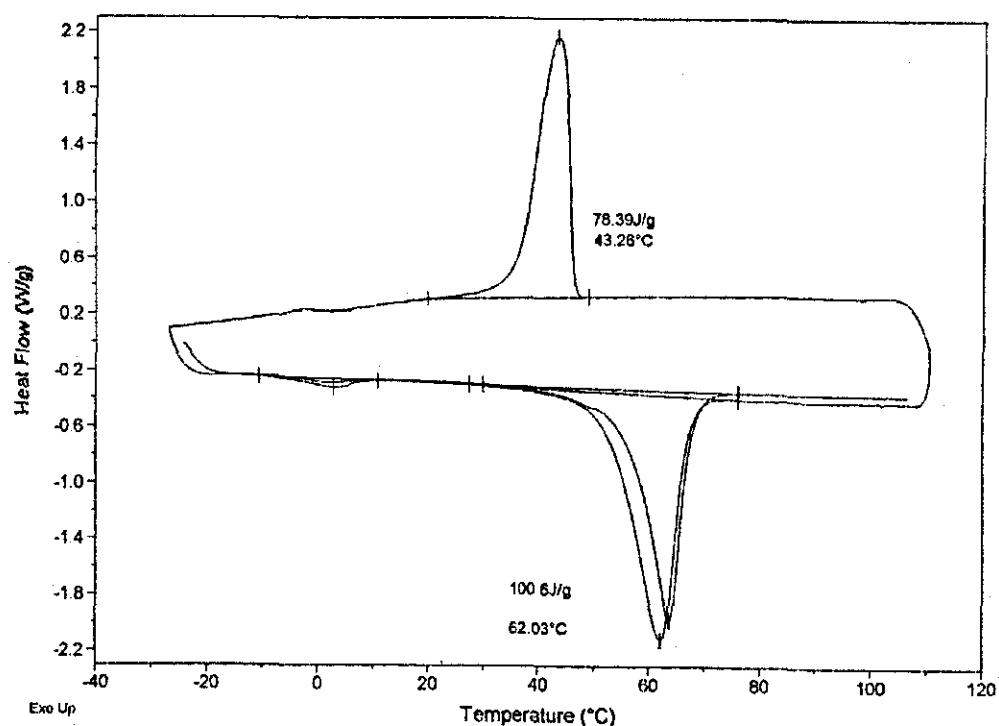


Figure 7-32 DSC thermogram of hybrid PEO (45) / SiO<sub>2</sub> (45) / Irganox 1076 (10)

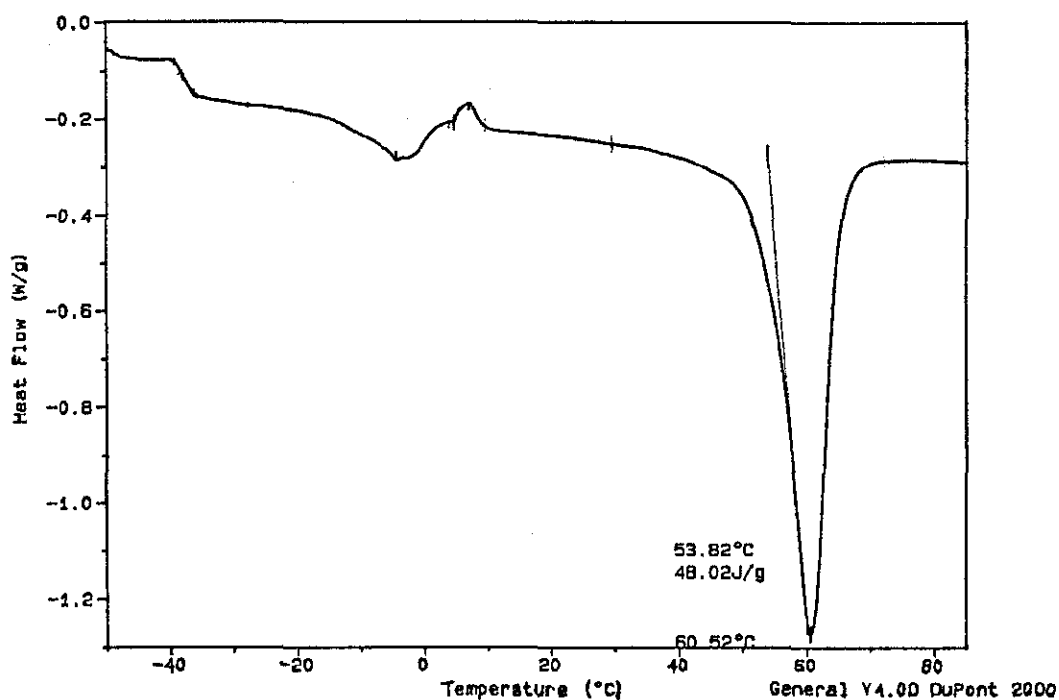


Figure 7-33 DSC thermogram of hybrid PEO (45) / SiO<sub>2</sub> (45) / Irganox 1076 (10)  
duplicate experiment, single ramp scan of a lower temperature range

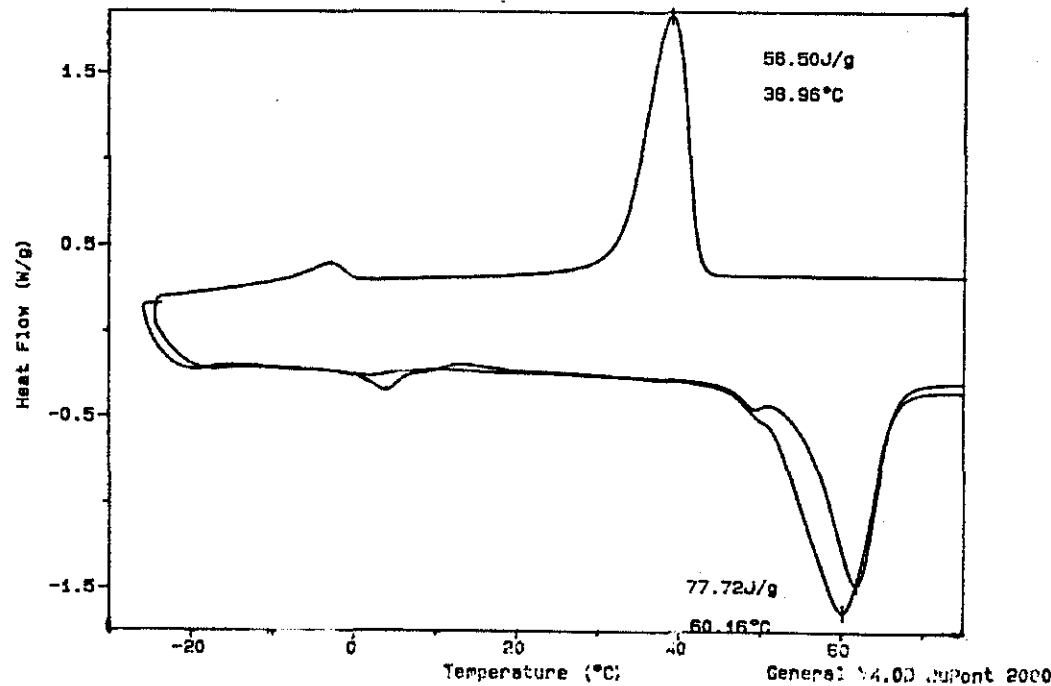


Figure 7-34 DSC thermogram of hybrid PEO (60) / SiO<sub>2</sub> (30) / Irganox 1076 (10)

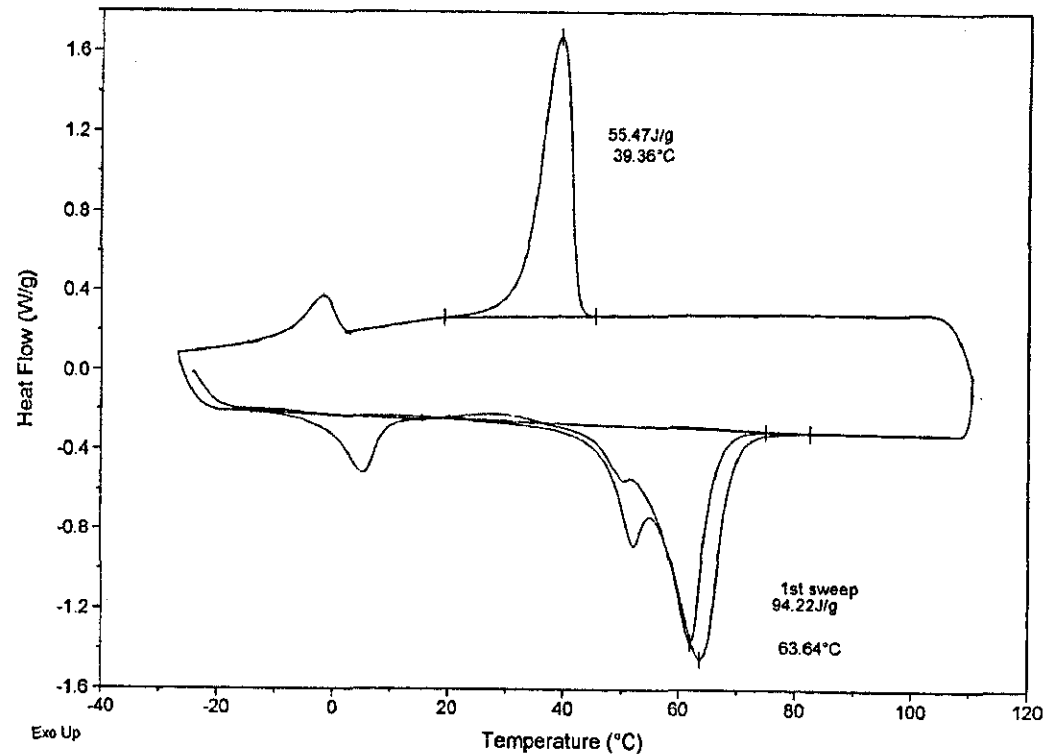


Figure 7-35 DSC thermogram of hybrid PEO (40) / SiO<sub>2</sub> (40) / Irganox 1076 (20)

### 7.9 DSC of PEO-SiO<sub>2</sub>-IPPD hybrids

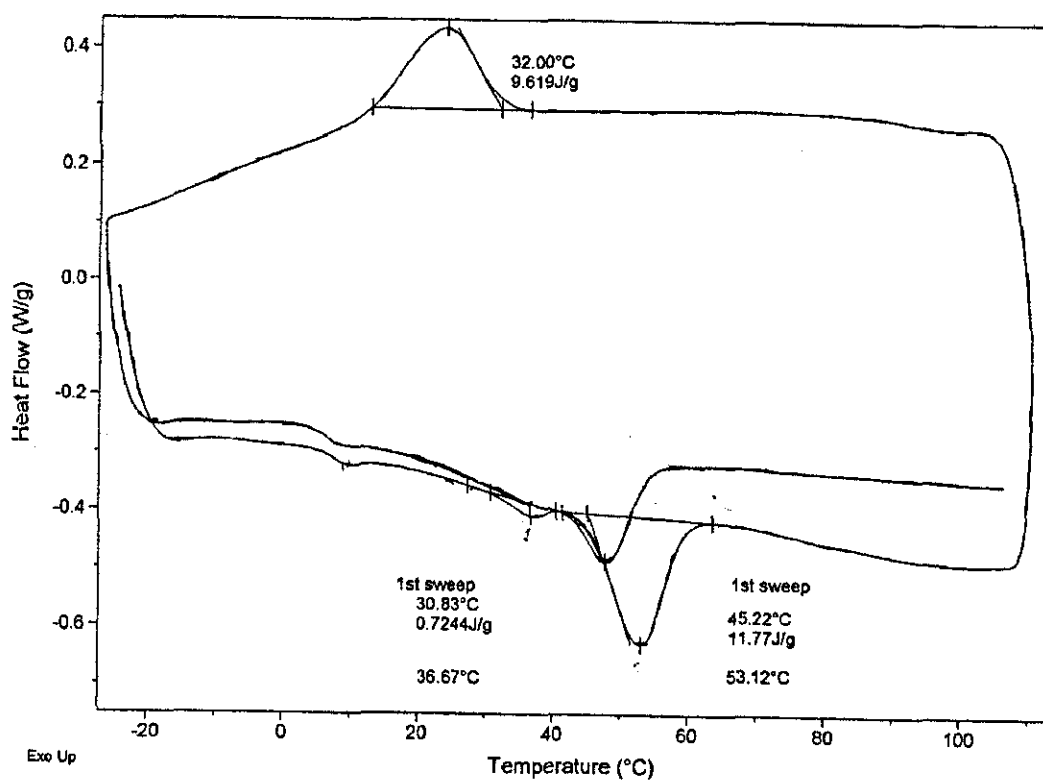


Figure 7-36 DSC thermogram of hybrid PEO (50) / Silica (30) / IPPD (20)

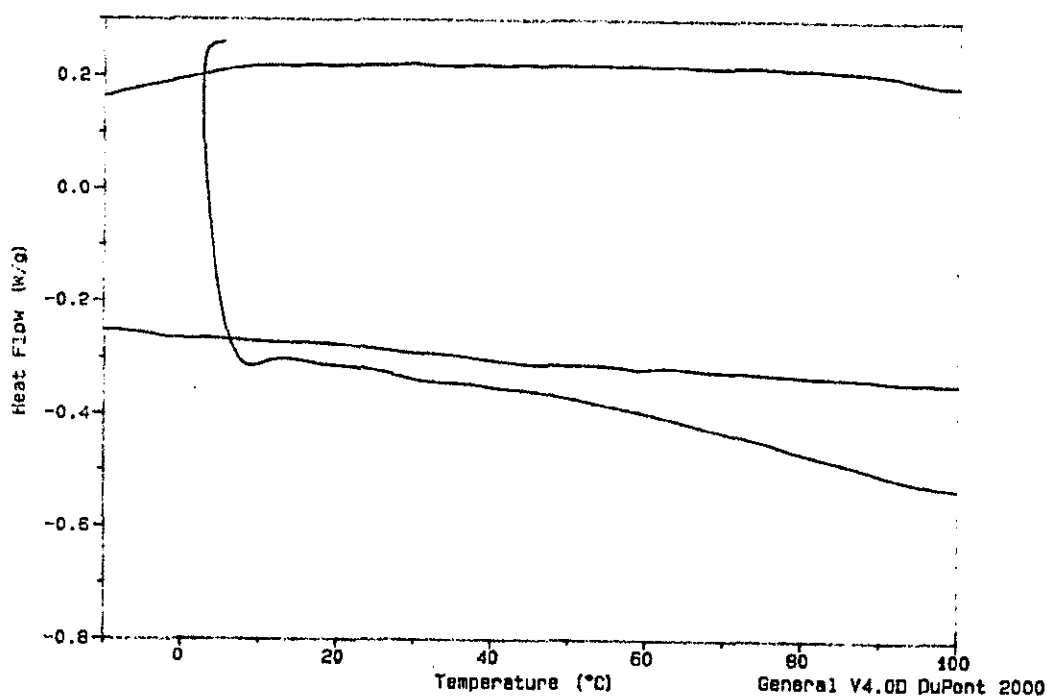


Figure 7-37 DSC thermogram of hybrid PEO (40) / Silica (40) / IPPD (20)

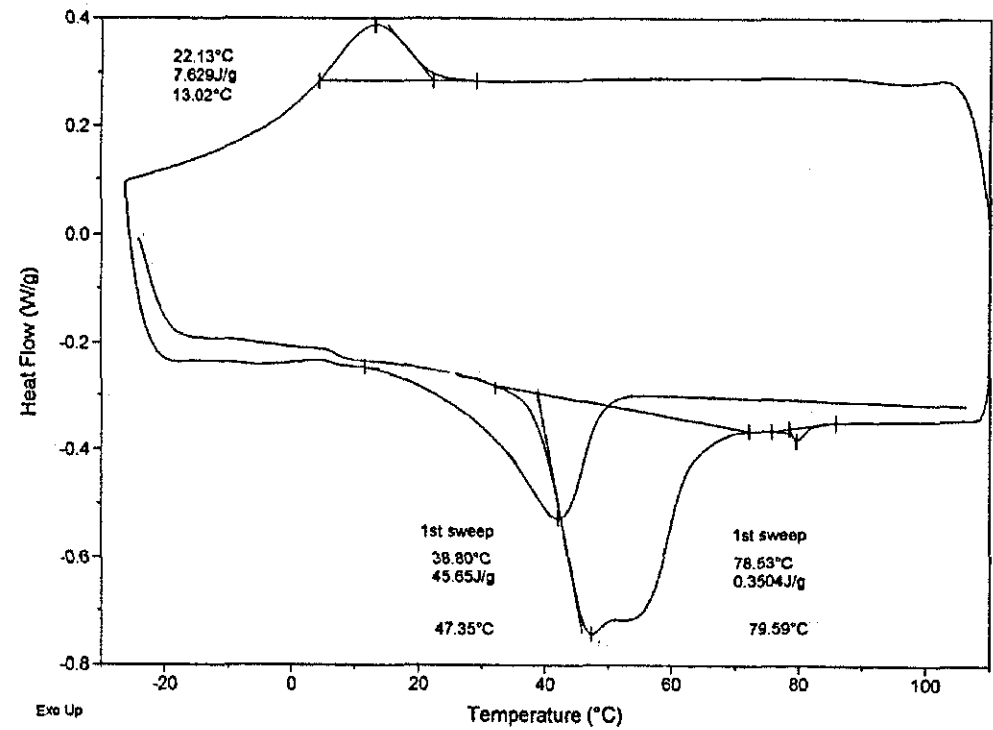


Figure 7-38 DSC thermogram of hybrid PEO (40) / Silica (20) / IPPD (40)

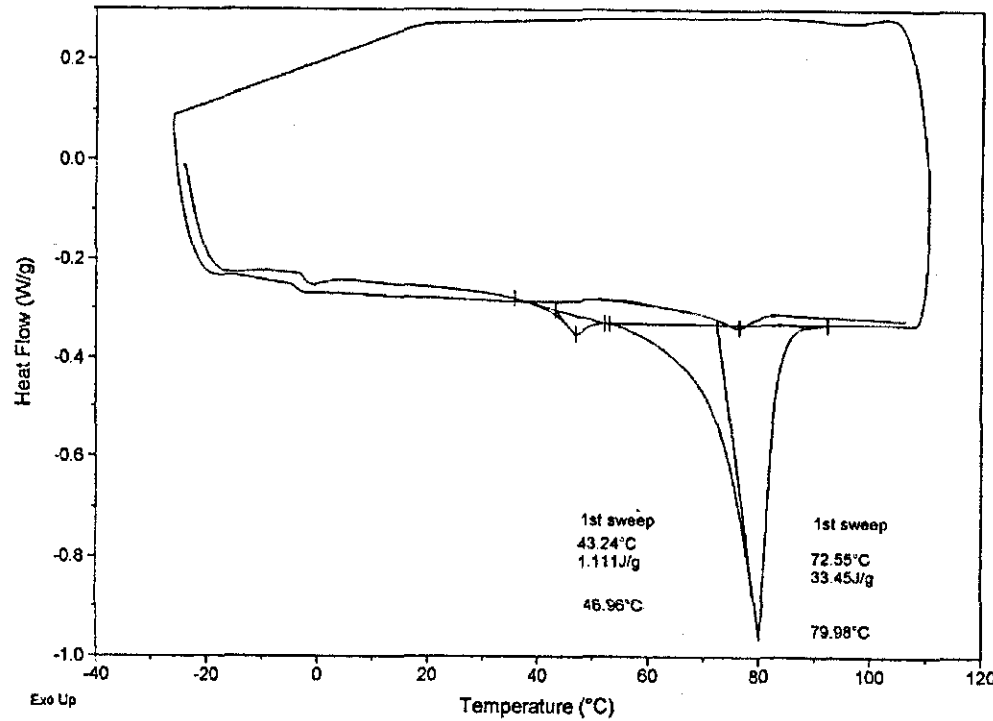


Figure 7-39 DSC thermogram of hybrid PEO (30) / Silica (30) / IPPD (40)

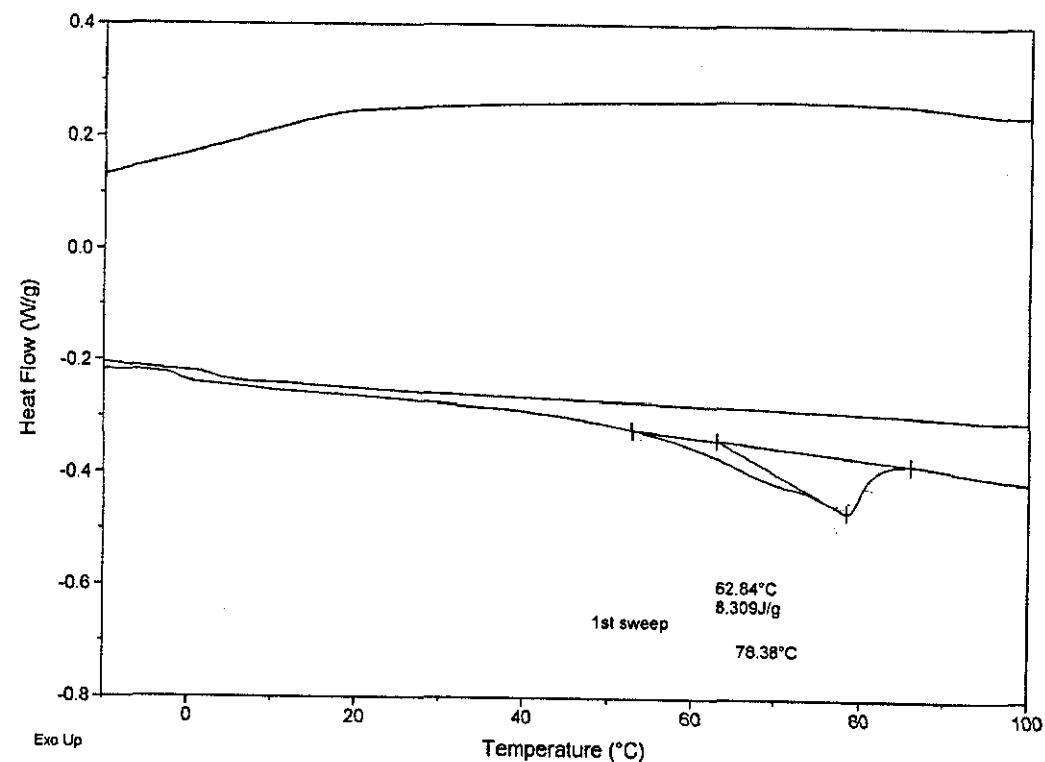


Figure 7-40 DSC thermogram of hybrid PEO (20) / Silica (40) / IPPD (40)

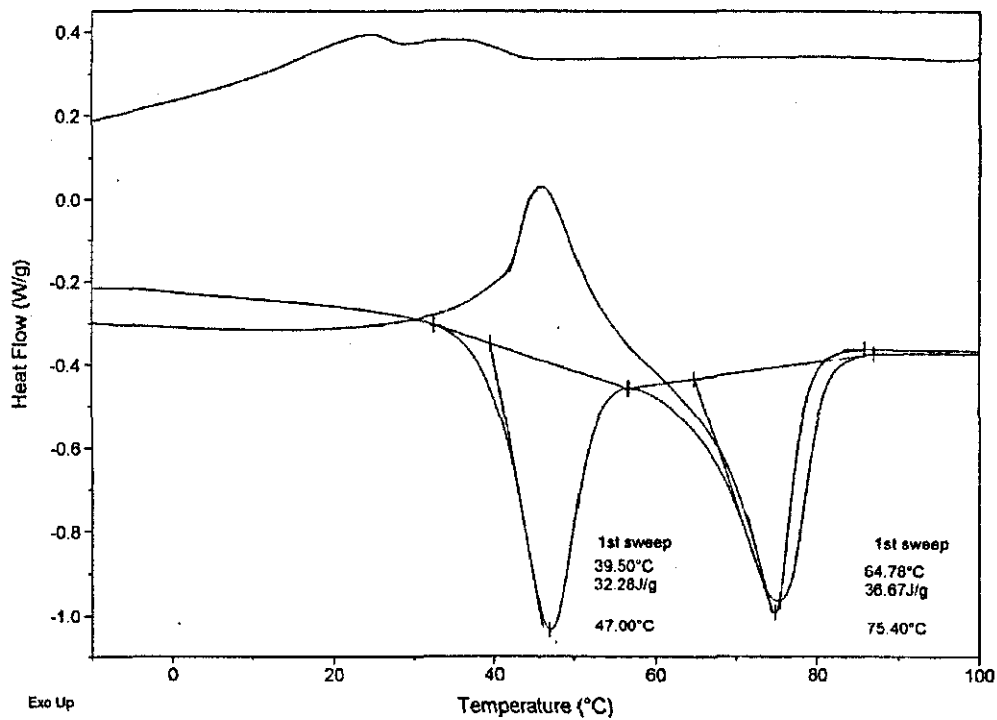


Figure 7-41 DSC thermogram of hybrid PEO (30) / Silica (10) / IPPD (60)

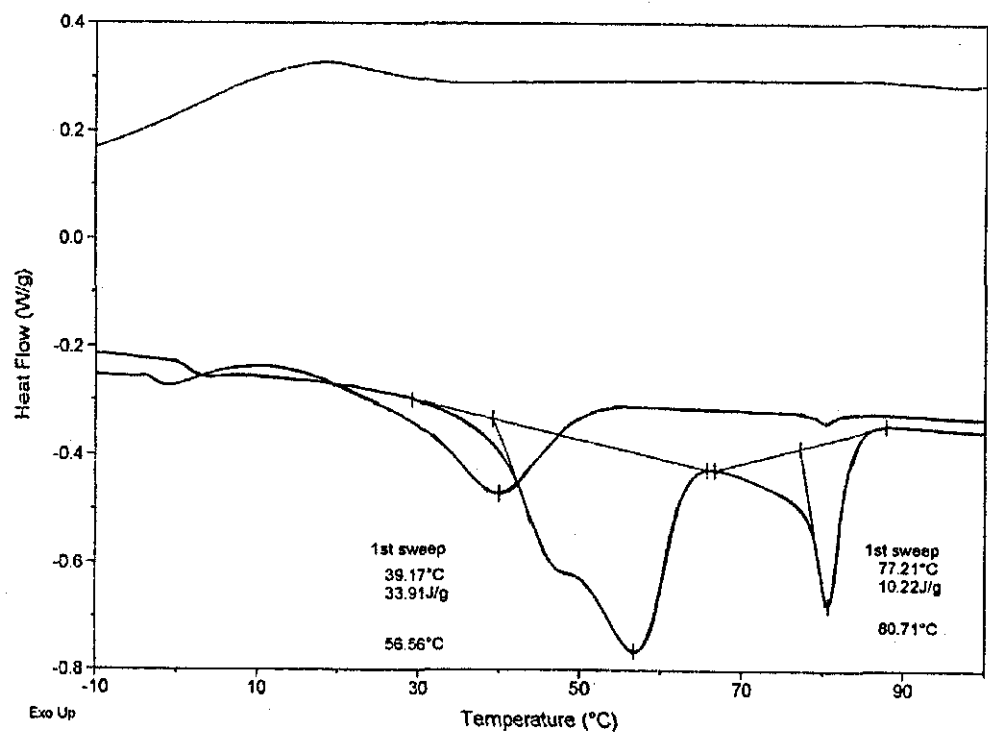


Figure 7-42 DSC thermogram of hybrid PEO (20) / Silica (20) / IPPD (60)

7.10 DSC of PEO-SiO<sub>2</sub>-BHT hybrids

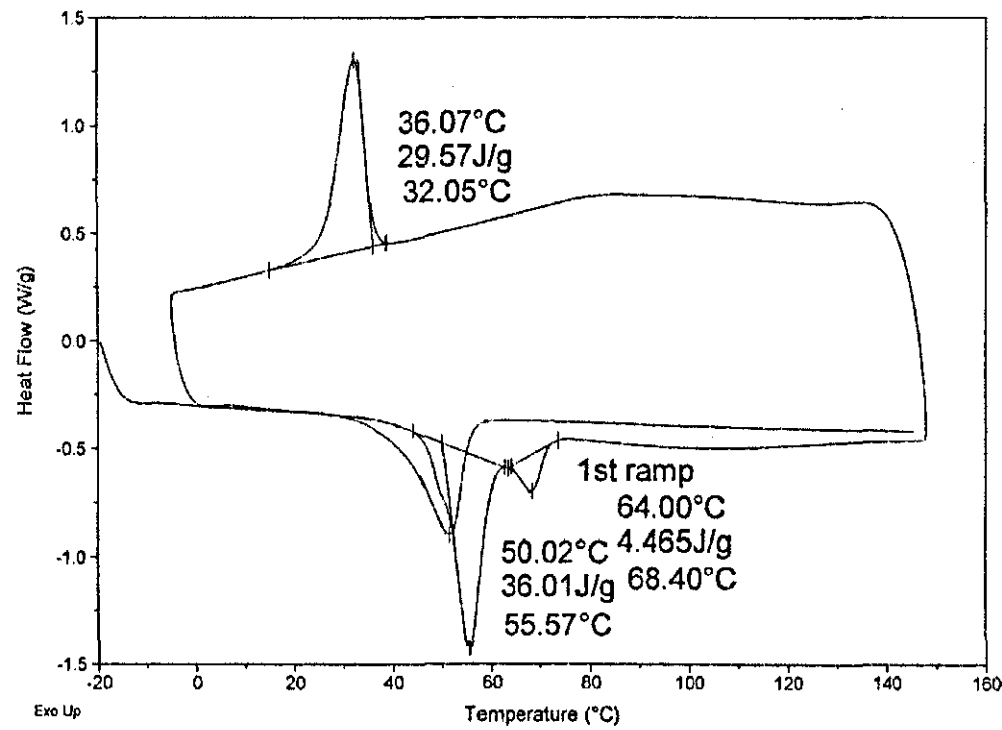


Figure 7-43 DSC thermogram of hybrid PEO (33.3) / Silica (33.3) / BHT (33.3)

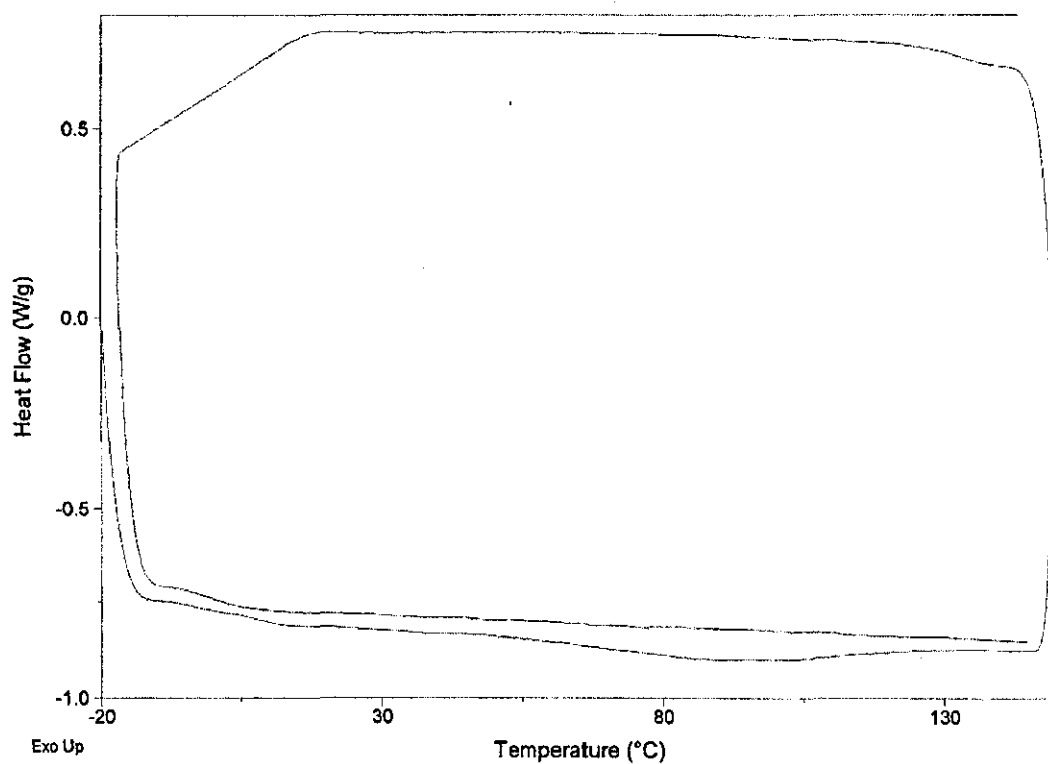


Figure 7-44 DSC thermogram of hybrid PEO (30) / Silica (50) / BHT (20)

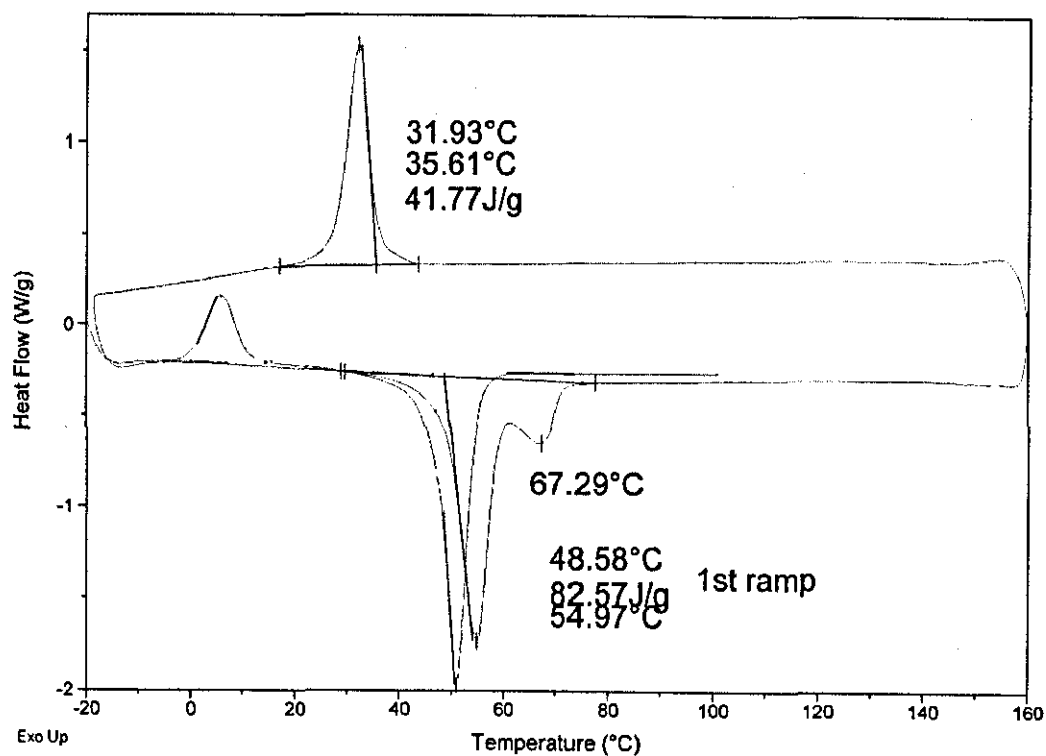


Figure 7-45 DSC thermogram of hybrid PEO (40) / Silica (10) / BHT (50)

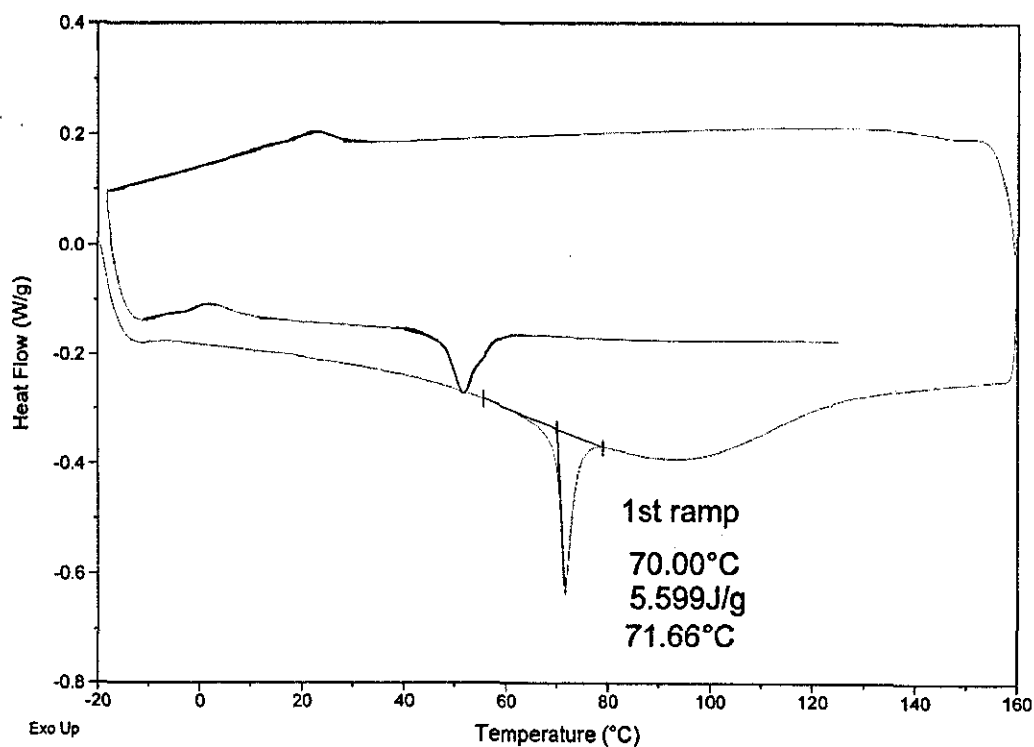


Figure 7-46 DSC thermogram of hybrid PEO (20) / Silica (60) / BHT (20)

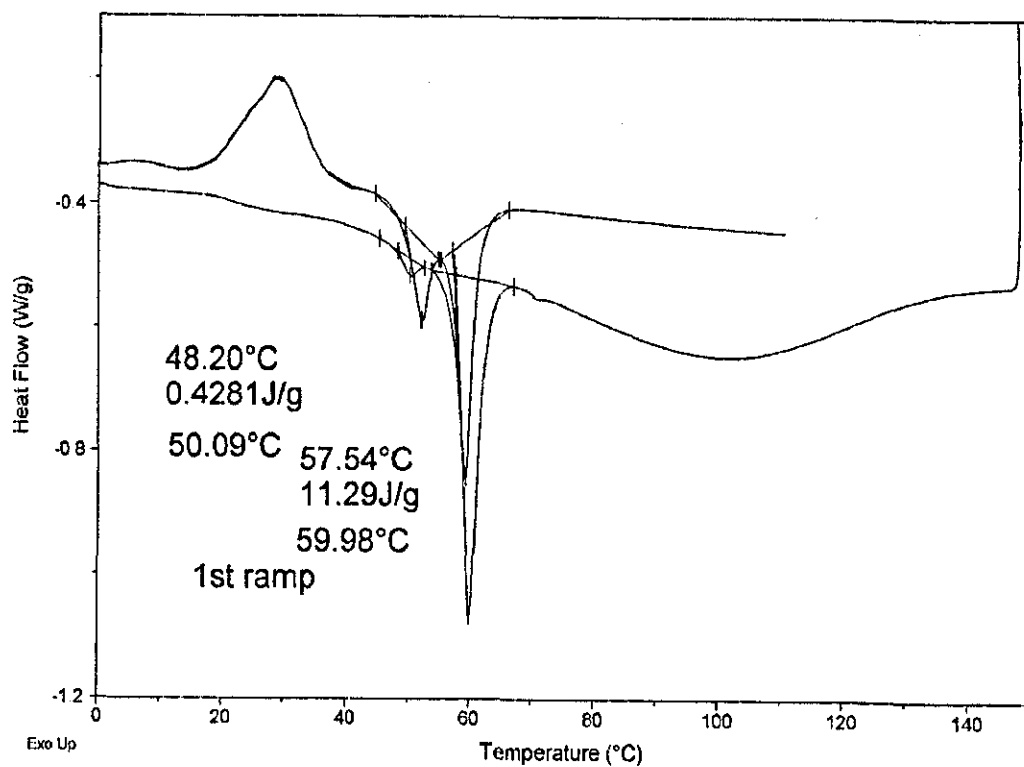
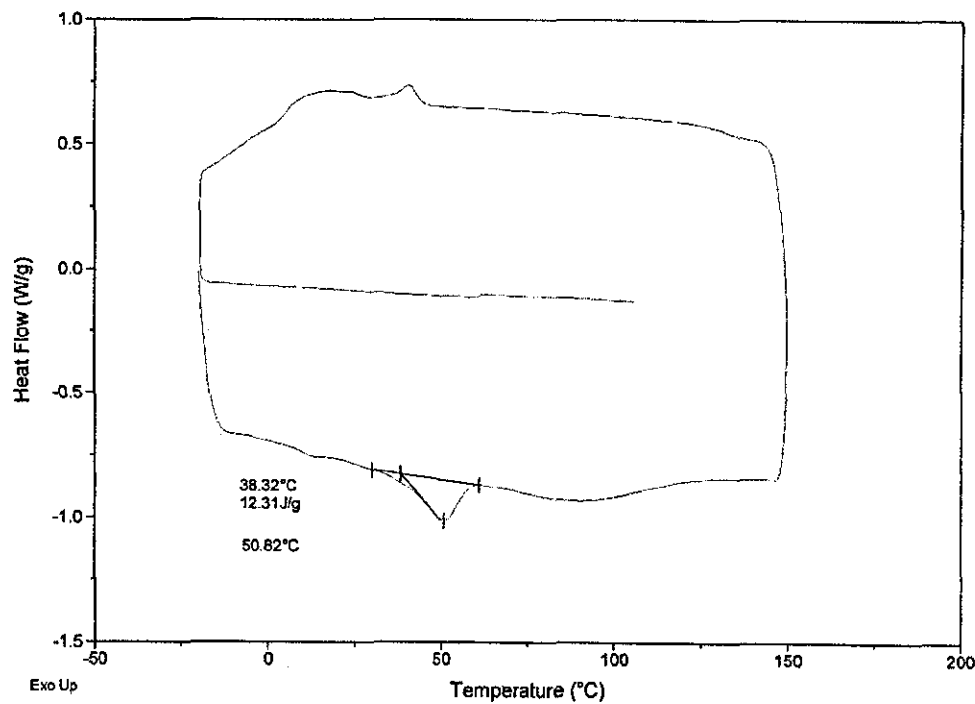
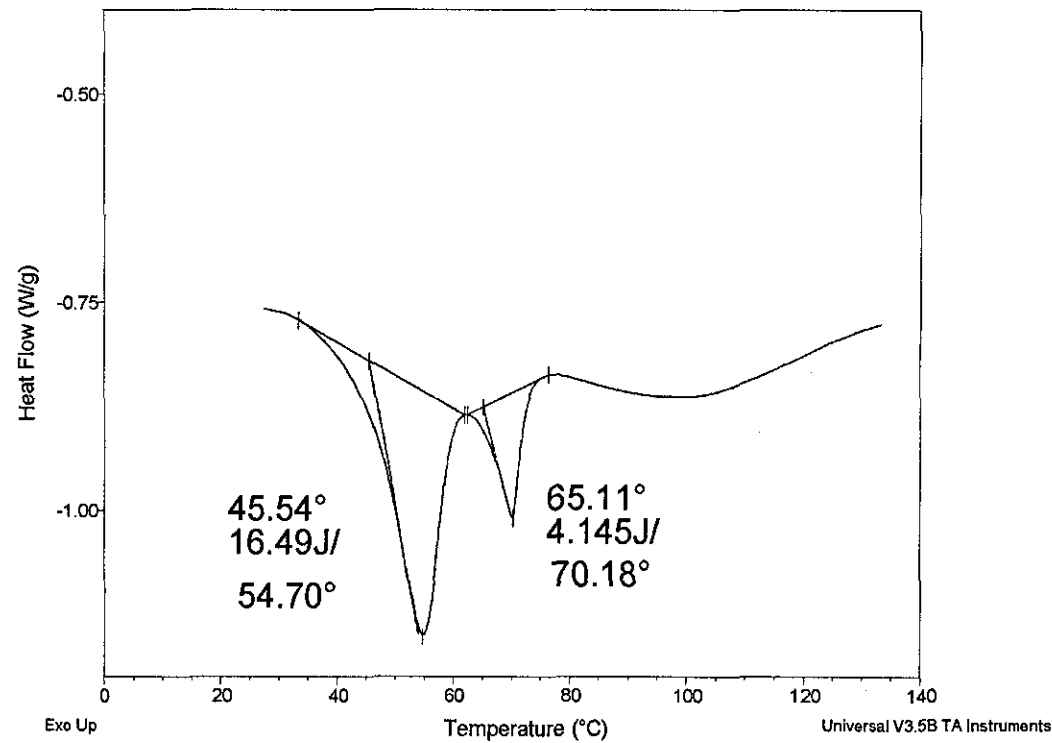


Figure 7-47 DSC thermogram of hybrid PEO (20) / Silica (50) / BHT (30)



**Figure 7-48 a) DSC thermogram of hybrid PEO (40) / Silica (40) / BHT (20), cured in oven at 60°C overnight**



**Figure 7-48 b) DSC thermogram of hybrid PEO (40) / Silica (40) / BHT (20) with different processing: solvent evaporated open at RT overnight**

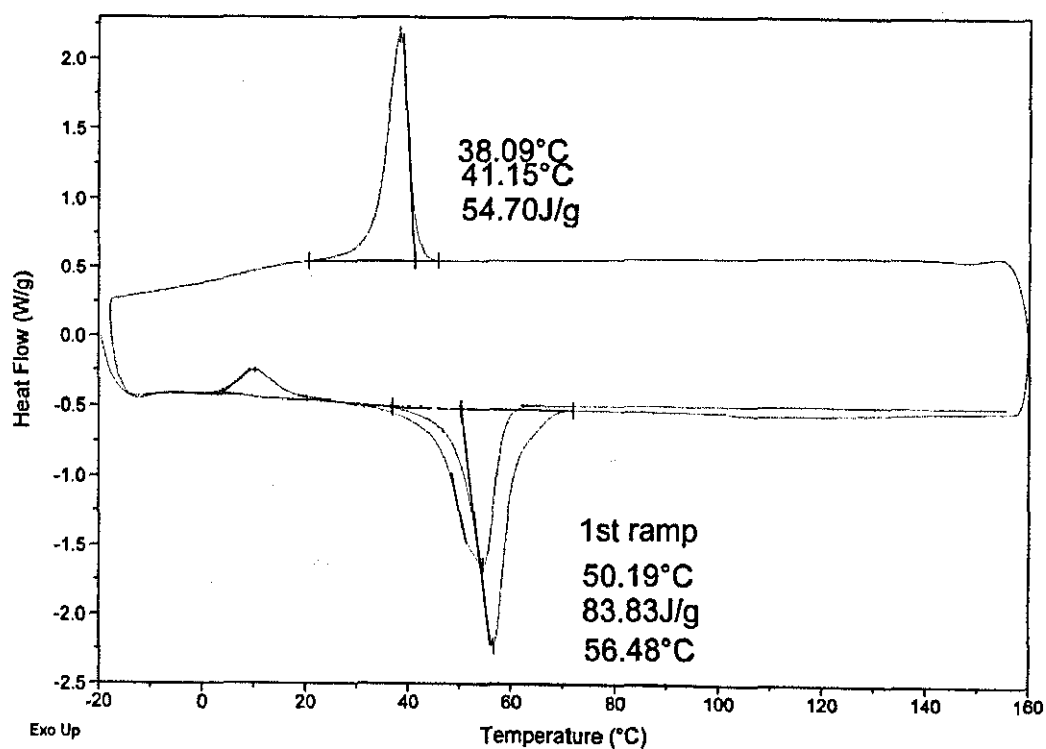


Figure 7-49 DSC thermogram of hybrid PEO (50) / Silica (10) / BHT (40)

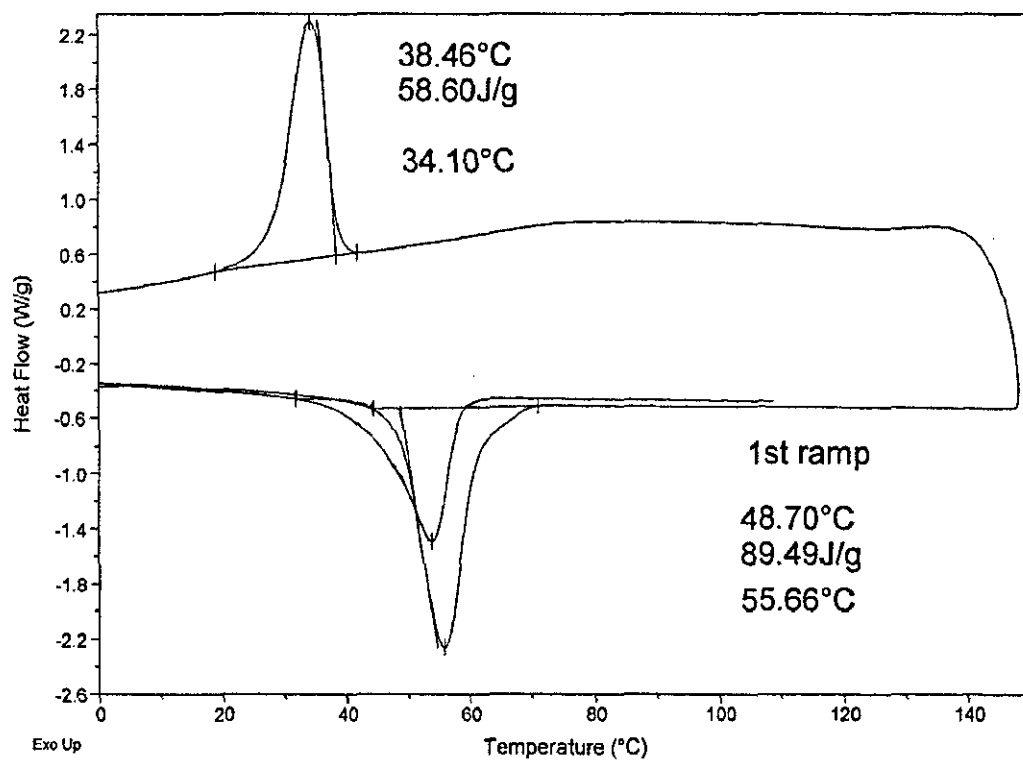


Figure 7-50 DSC thermogram of hybrid PEO (50) / Silica (20) / BHT (30)

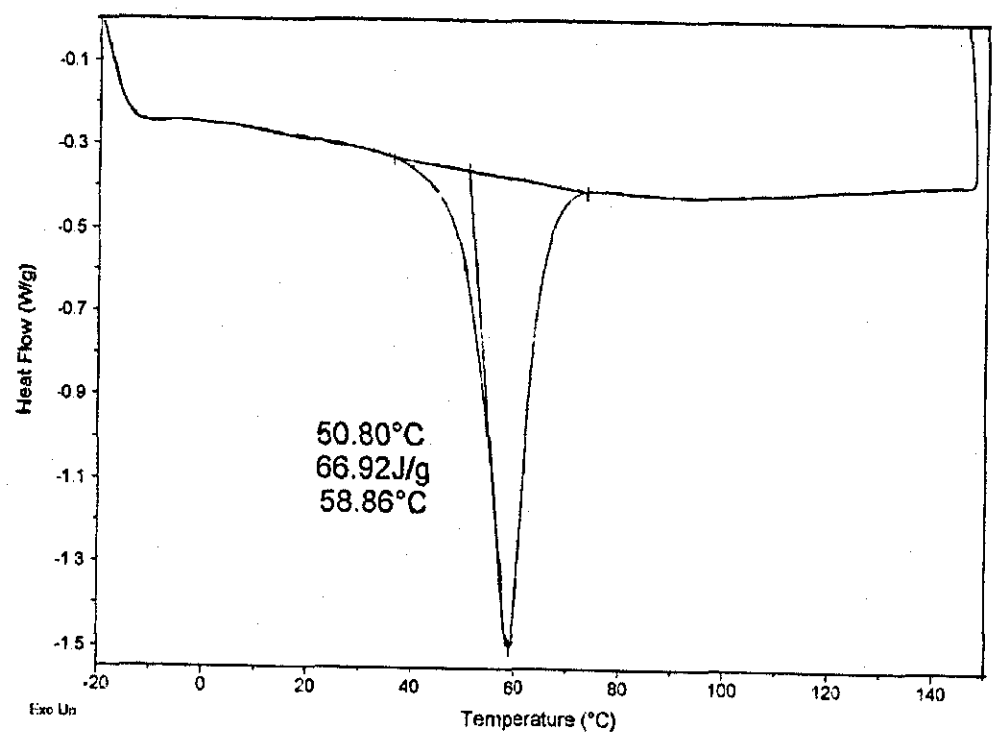


Figure 7-51 DSC thermogram of hybrid PEO (50) / Silica (30) / BHT (20)

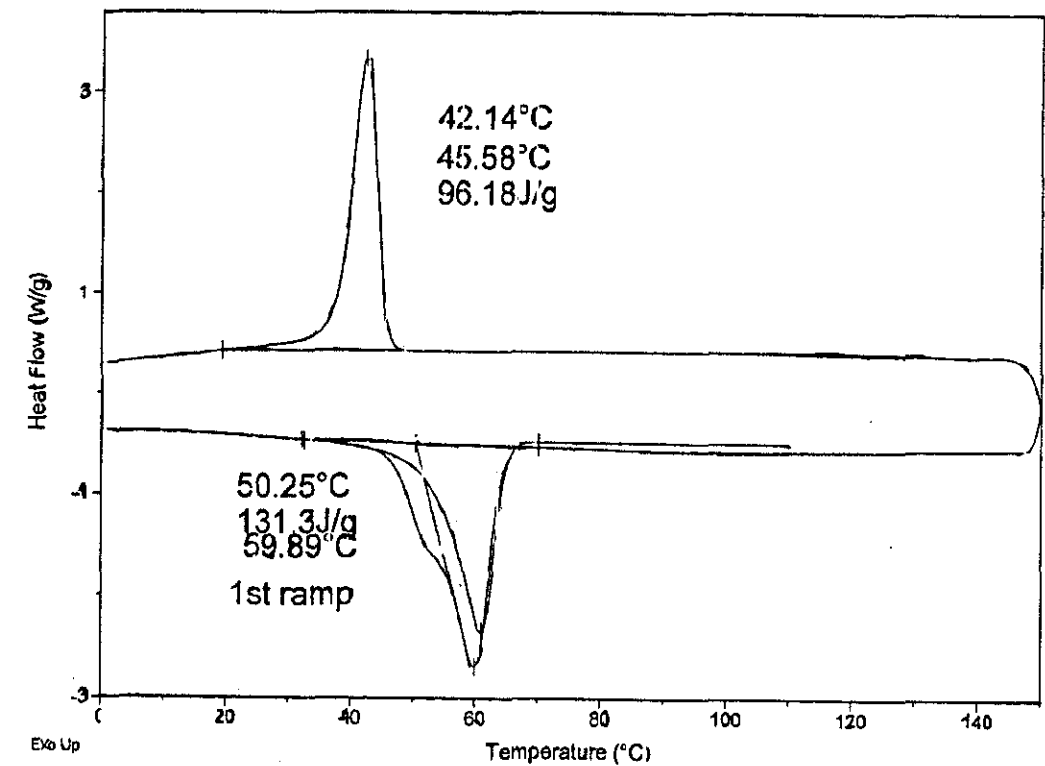


Figure 7-52 DSC thermogram of hybrid PEO (60) / Silica (10) / BHT (30)

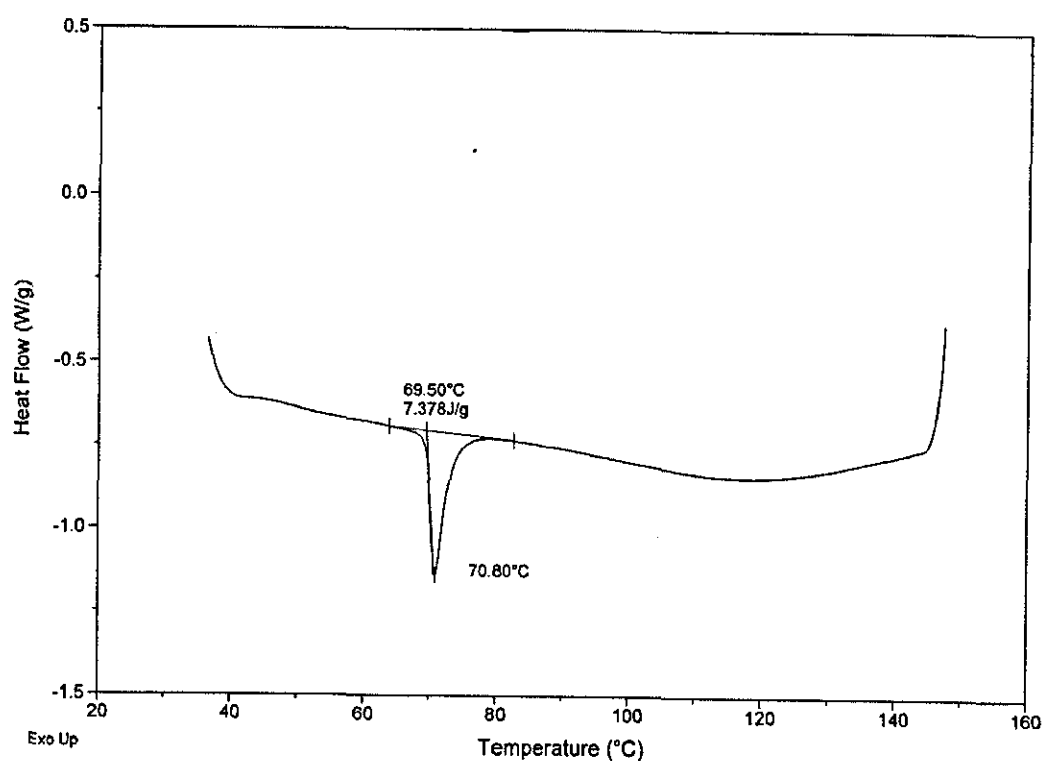


Figure 7-53 DSC thermogram of hybrid PEO (00) / Silica (80) / BHT (20)

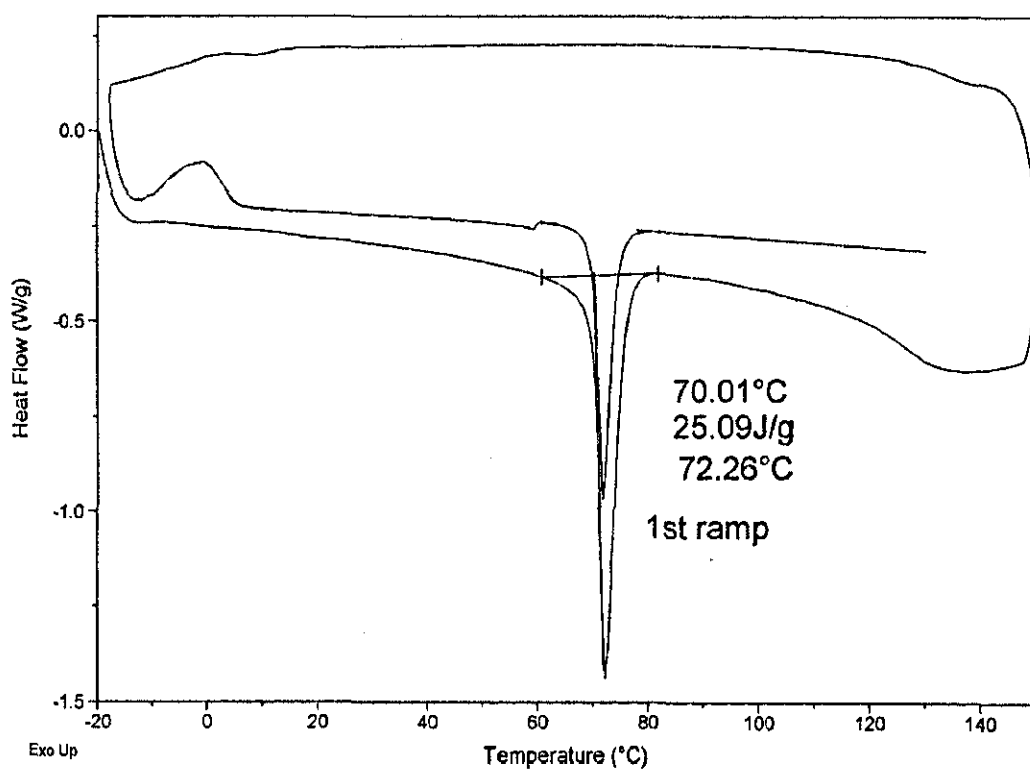


Figure 7-54 DSC thermogram of hybrid PEO (00) / Silica (50) / BHT (50)

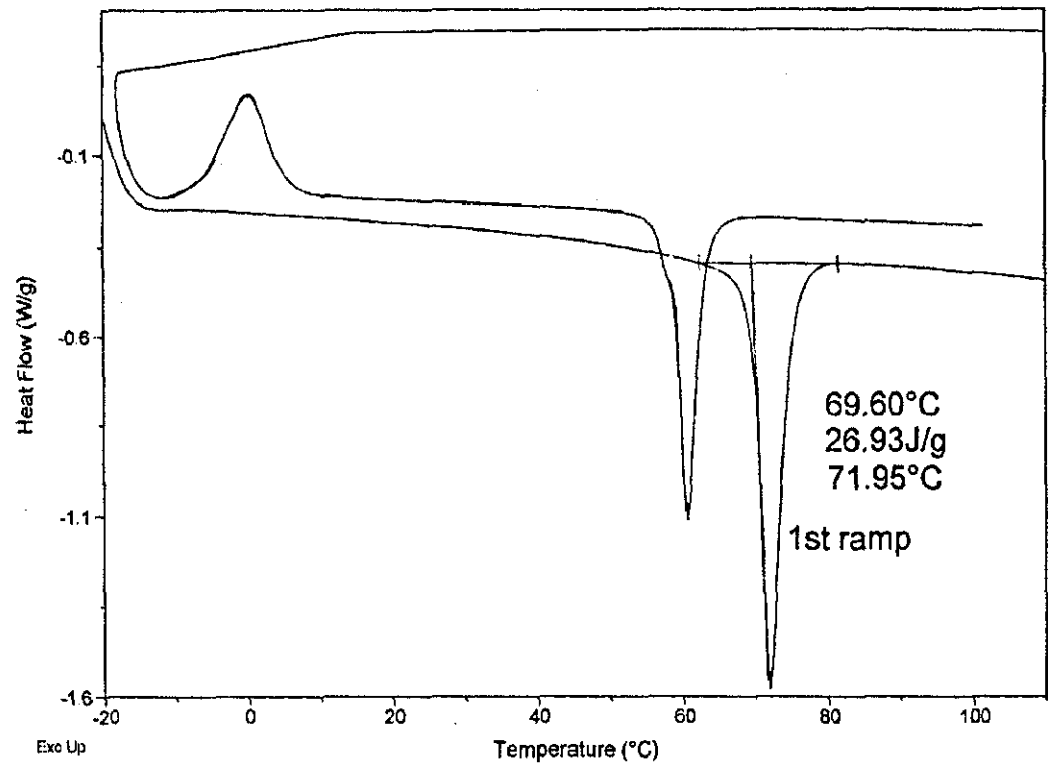


Figure 7-55 DSC thermogram of hybrid PEO (10) / Silica (50) / BHT (40)

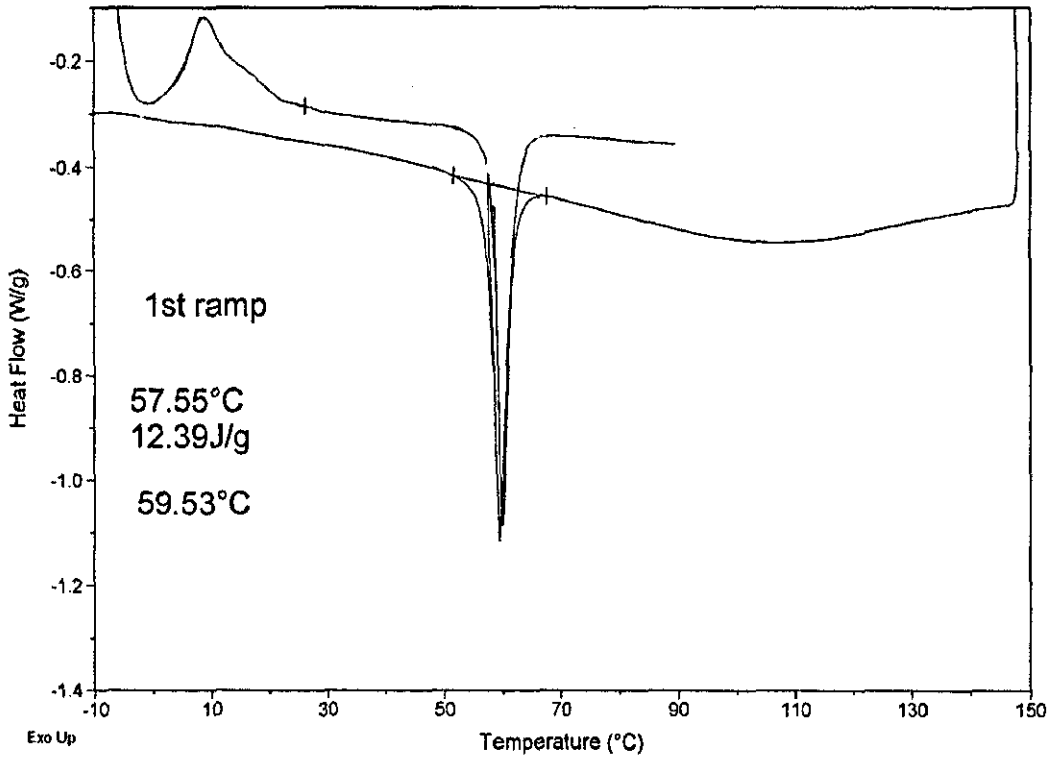


Figure 7-56 DSC thermogram of hybrid PEO (10) / Silica (60) / BHT (30)

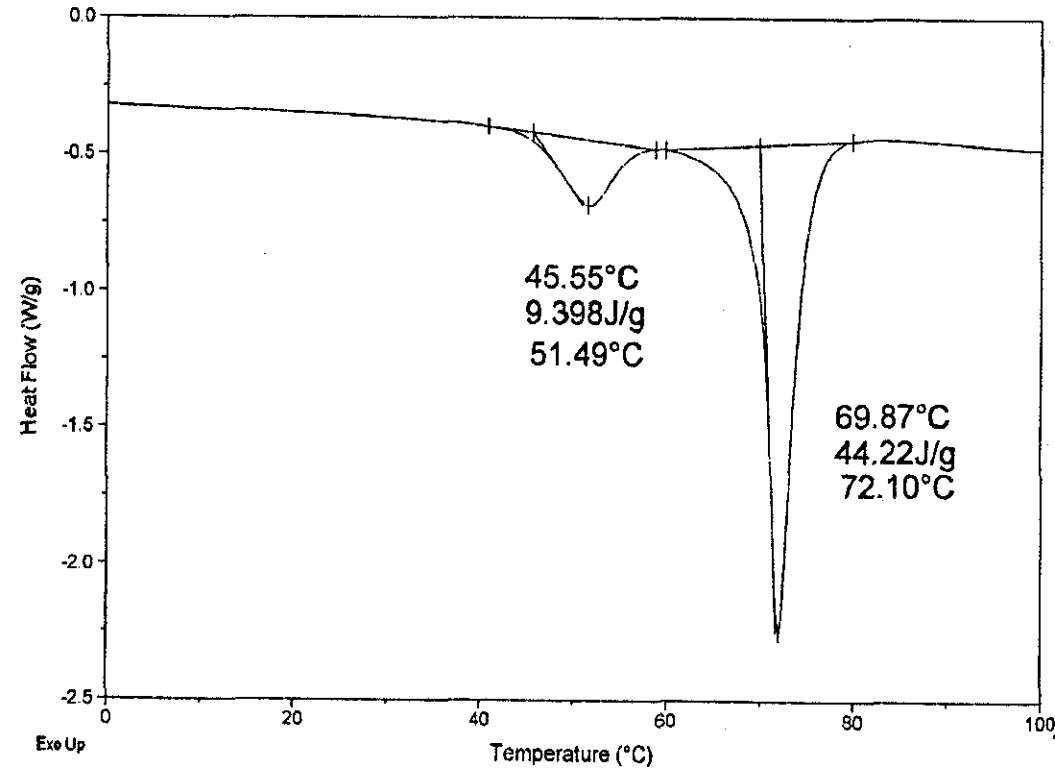


Figure 7-57 DSC thermogram of hybrid PEO (20) / Silica (20) / BHT (60)

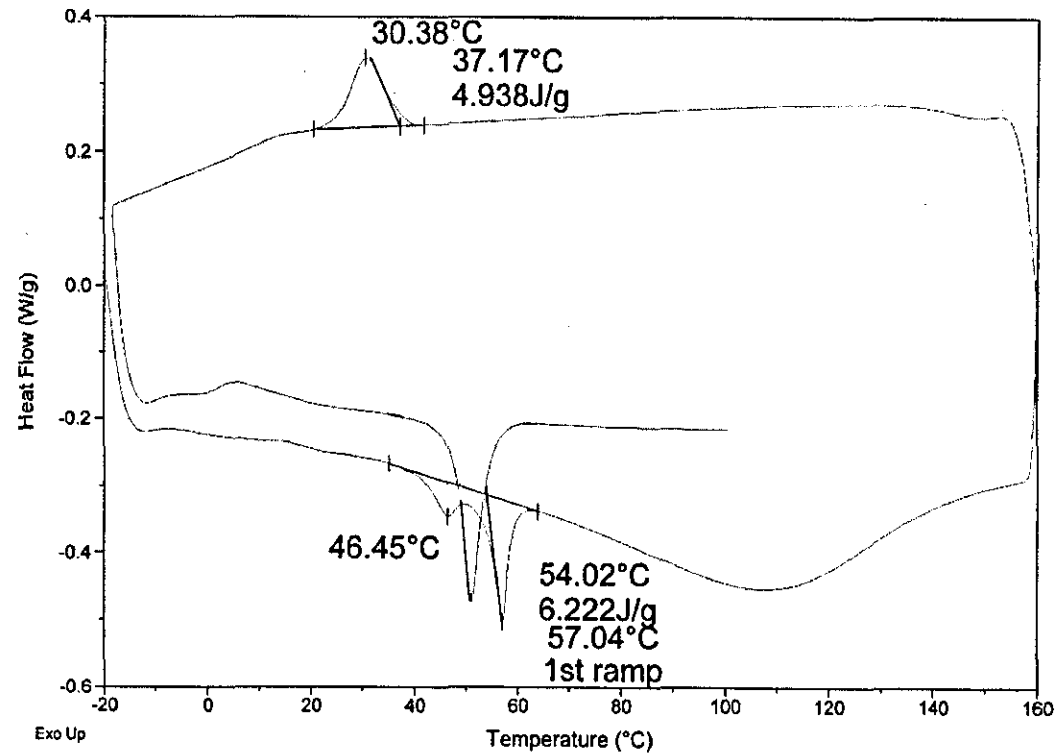


Figure 7-58 DSC thermogram of hybrid PEO (20) / Silica (50) / BHT (30)

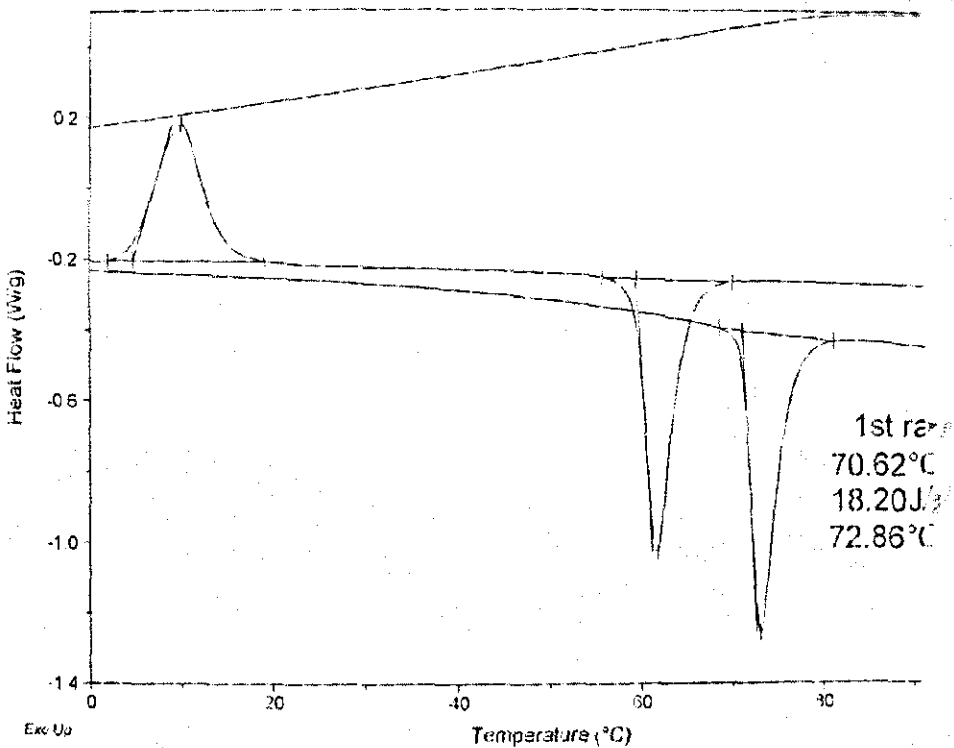


Figure 7-59 DSC thermogram of hybrid PEO (00) / Silica (70) / BHT (30)

7.11 DSC of Oxygen Induction Time

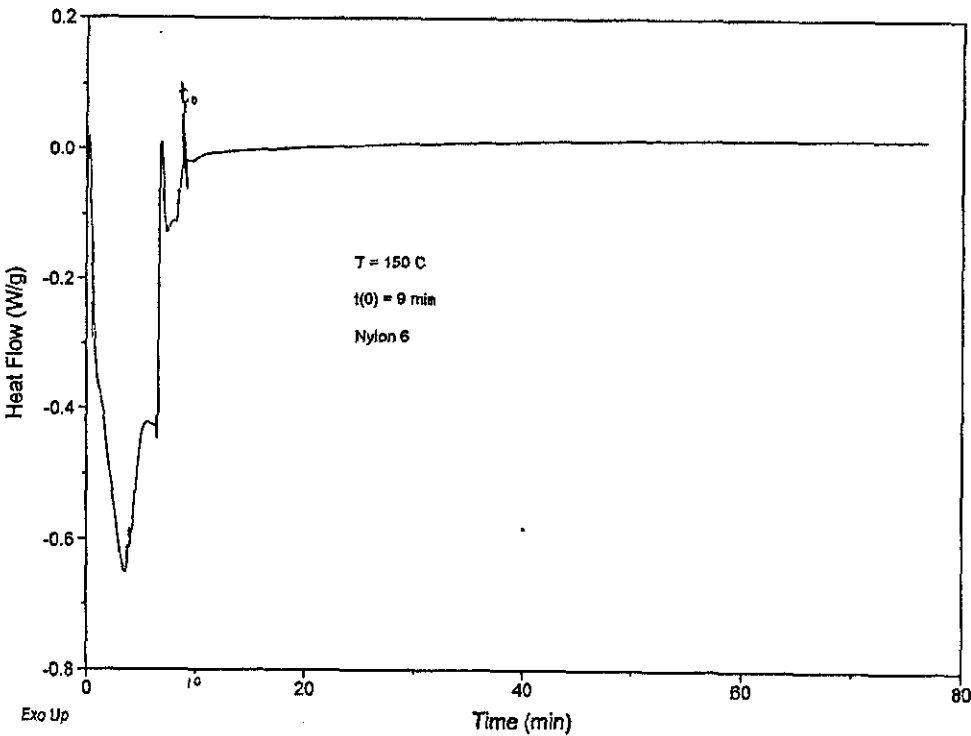


Figure 7-60 DSC thermogram of oxygen induction time at 150°C

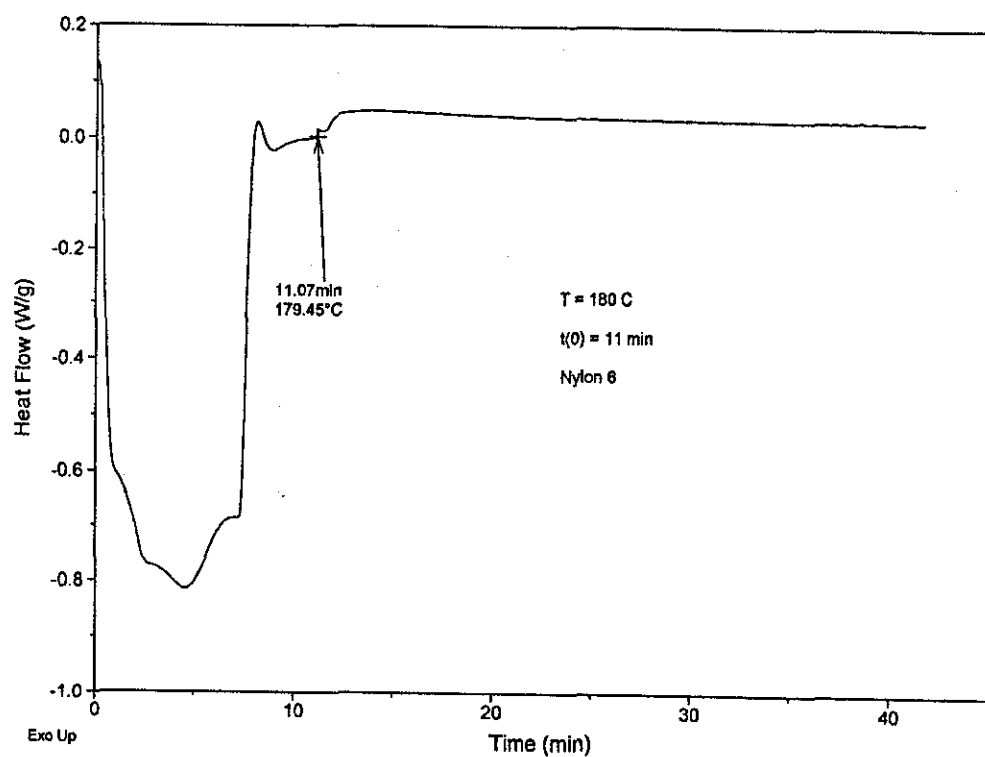


Figure 7-61 DSC thermogram of oxygen induction time at 180°C

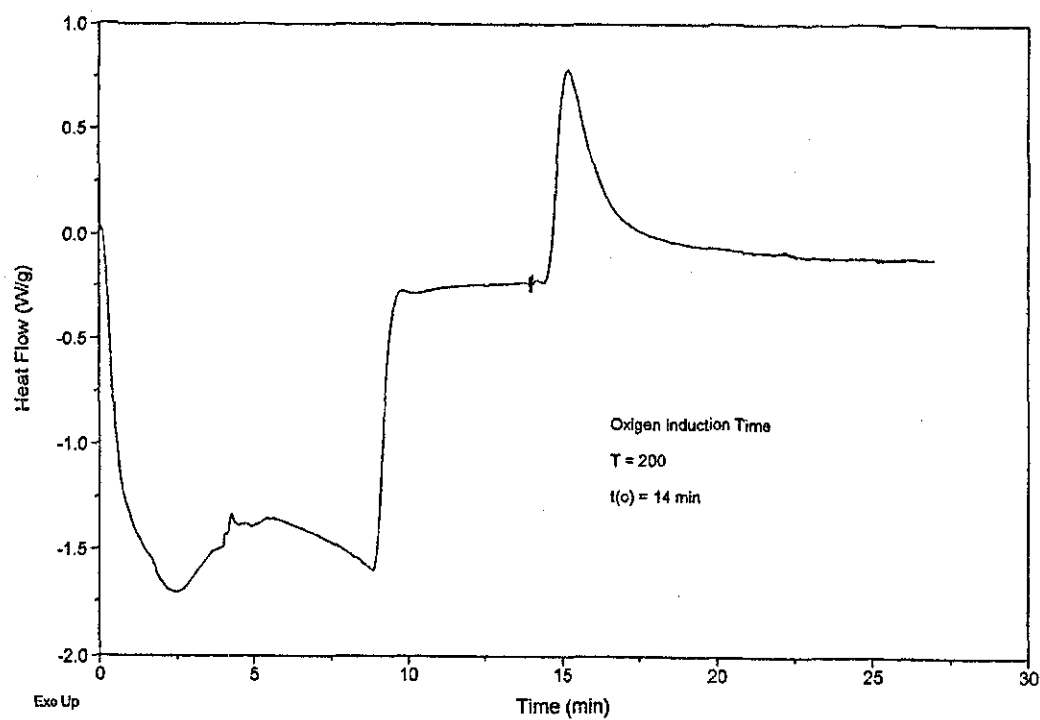


Figure 7-62 DSC thermogram of oxygen induction time at 200°C

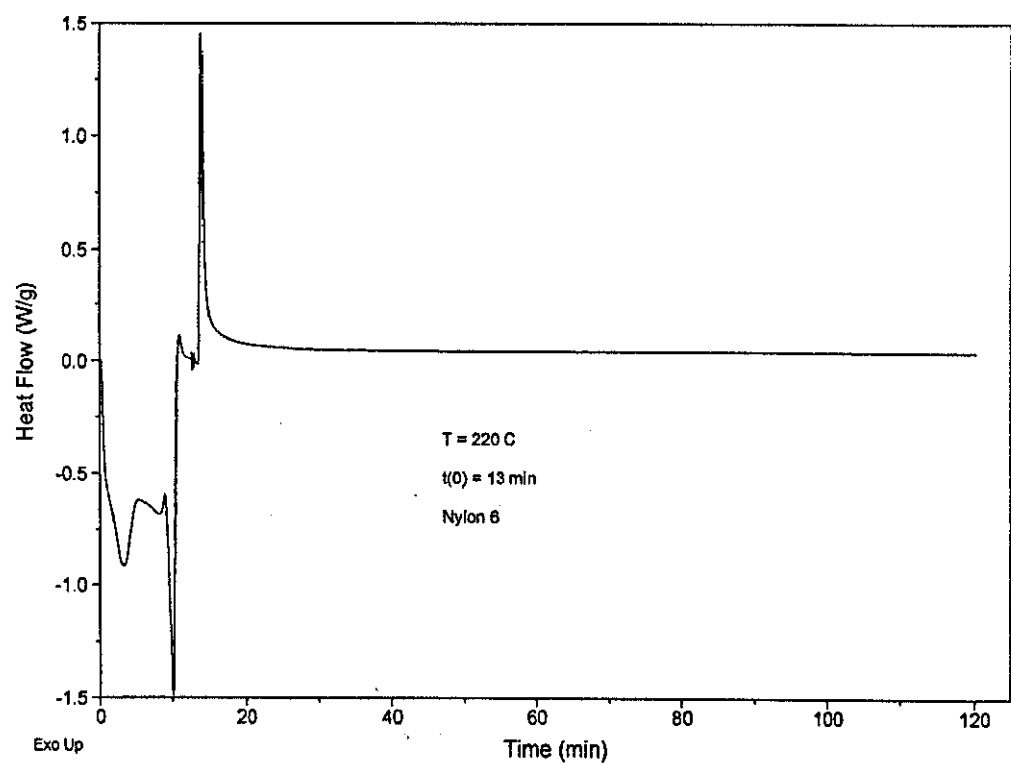


Figure 7-63 DSC thermogram of oxygen induction time at 220°C

### 7.12 SEM of PEO-SiO<sub>2</sub>-Irganox 1076 hybrids

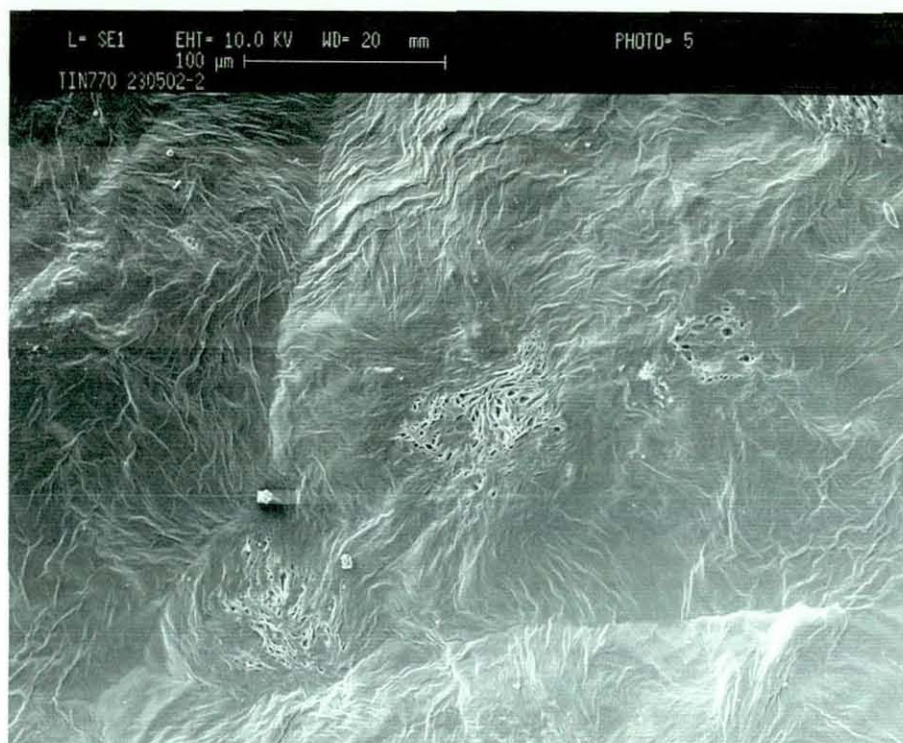


Figure 7-64 SEM micrograph of hybrid PEO (45) / Silica (45) / Irganox 1076 (10)



Figure 7-65 SEM micrograph of hybrid PEO (45) / Silica (45) / Irganox 1076 (10)



Figure 7-66 SEM micrograph of hybrid PEO (45) / Silica (45) / Irganox 1076 (10)

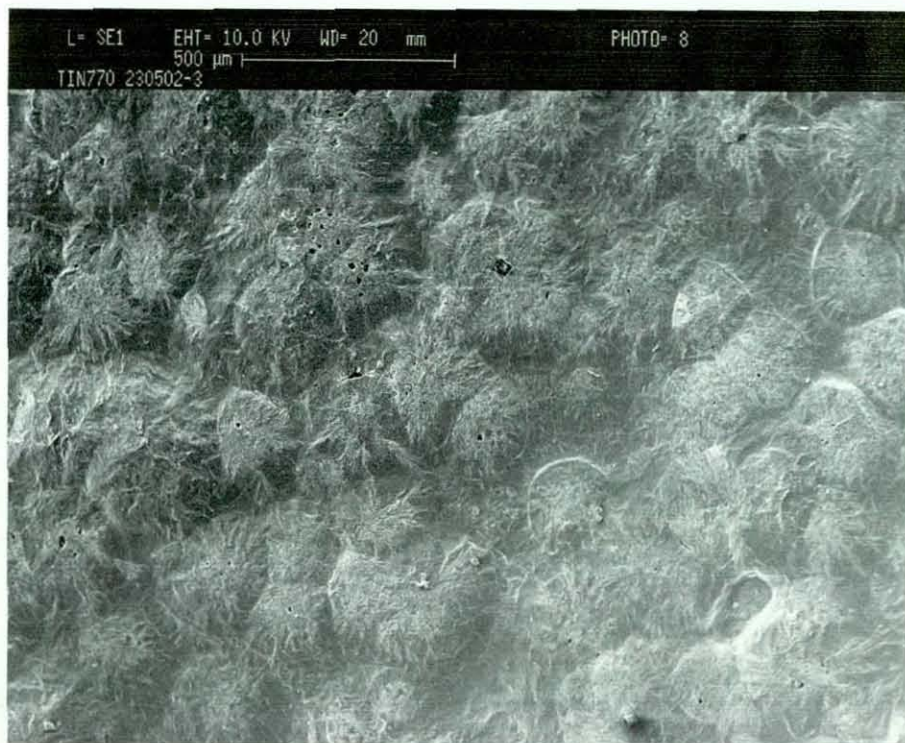


Figure 7-67 SEM micrograph of hybrid PEO (40) / Silica (40) / Irganox 1076 (20)

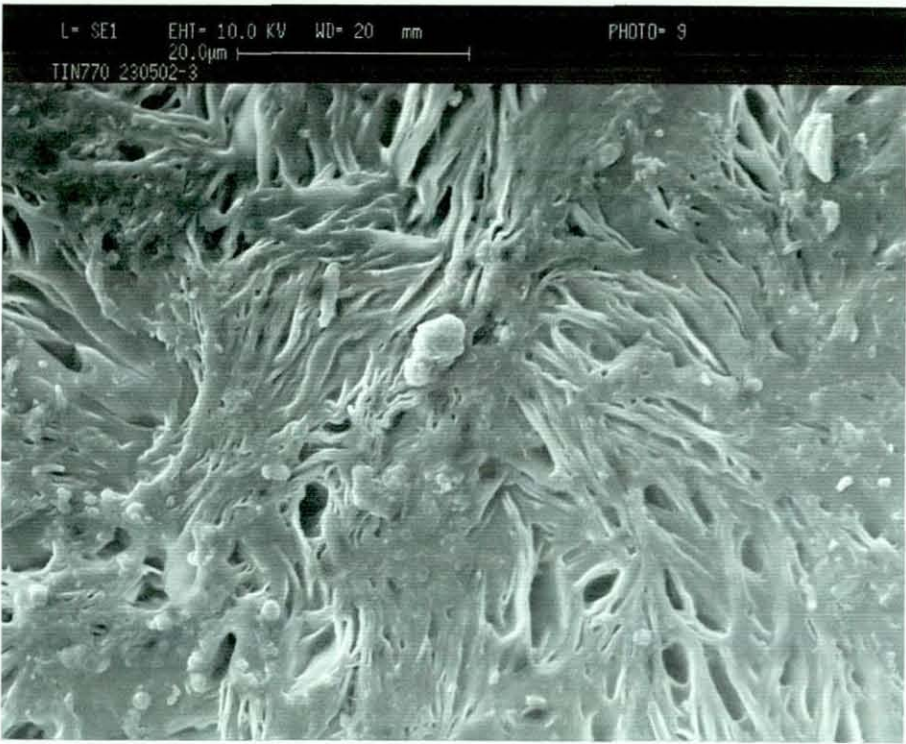


Figure 7-68 SEM micrograph of hybrid PEO (40) / Silica (40) / Irganox 1076 (20)

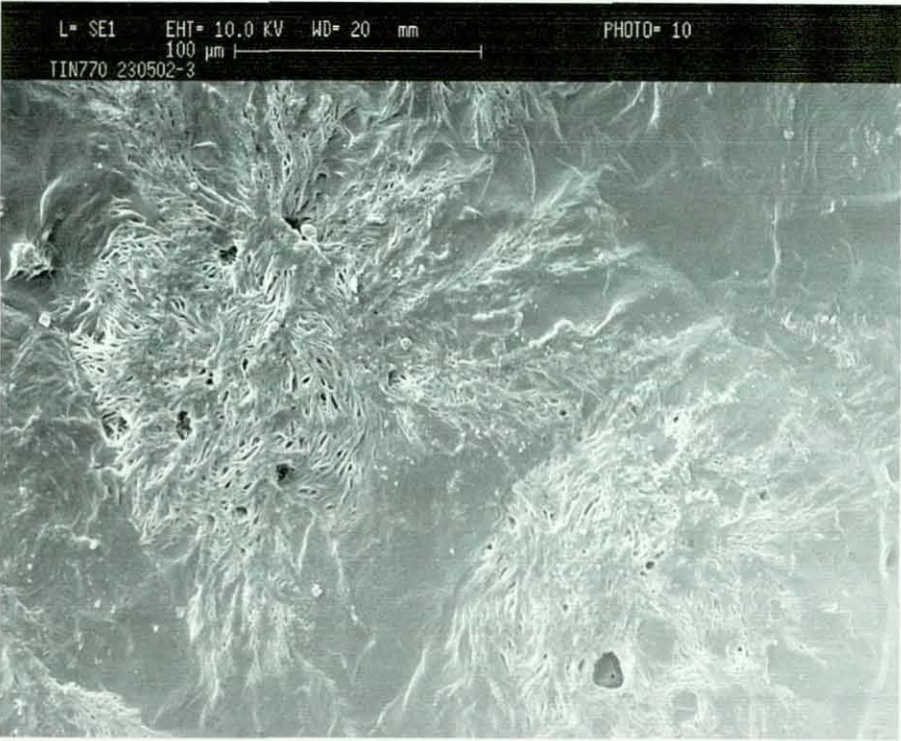


Figure 7-69 SEM micrograph of hybrid PEO (40) / Silica (40) / Irganox 1076 (20)

7.13 SEM of PEO-SiO<sub>2</sub>-IPPD hybrids

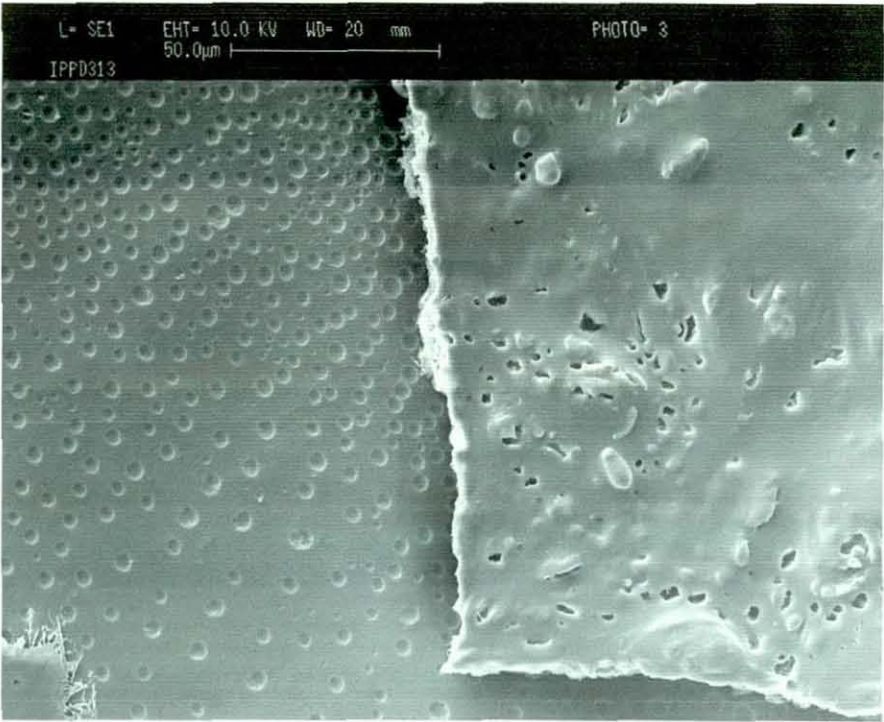
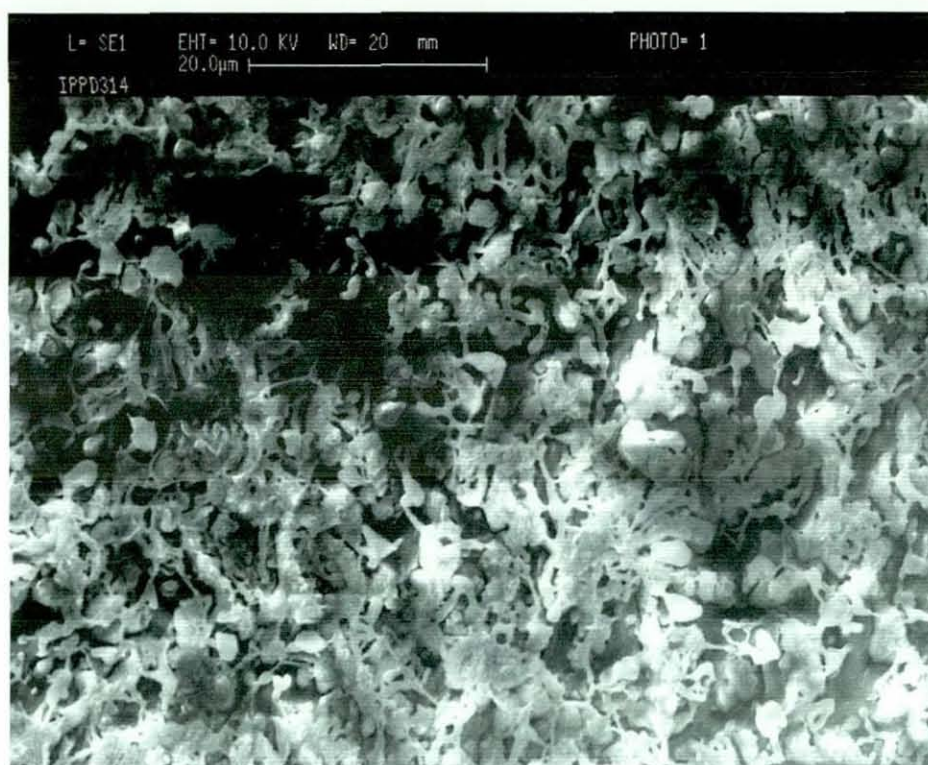


Figure 7-70 SEM micrograph of hybrid PEO (40) / Silica (20) / IPPD (40)



Figure 7-71 SEM micrograph of hybrid PEO (40) / Silica (20) / IPPD (40)



**Figure 7-72 SEM micrograph of hybrid PEO (30) / Silica (30) / IPPD (40)**



**Figure 7-73 SEM micrograph of hybrid PEO (30) / Silica (30) / IPPD (40)**

### 7.14 SEM of PEO-SiO<sub>2</sub>-BHT hybrids

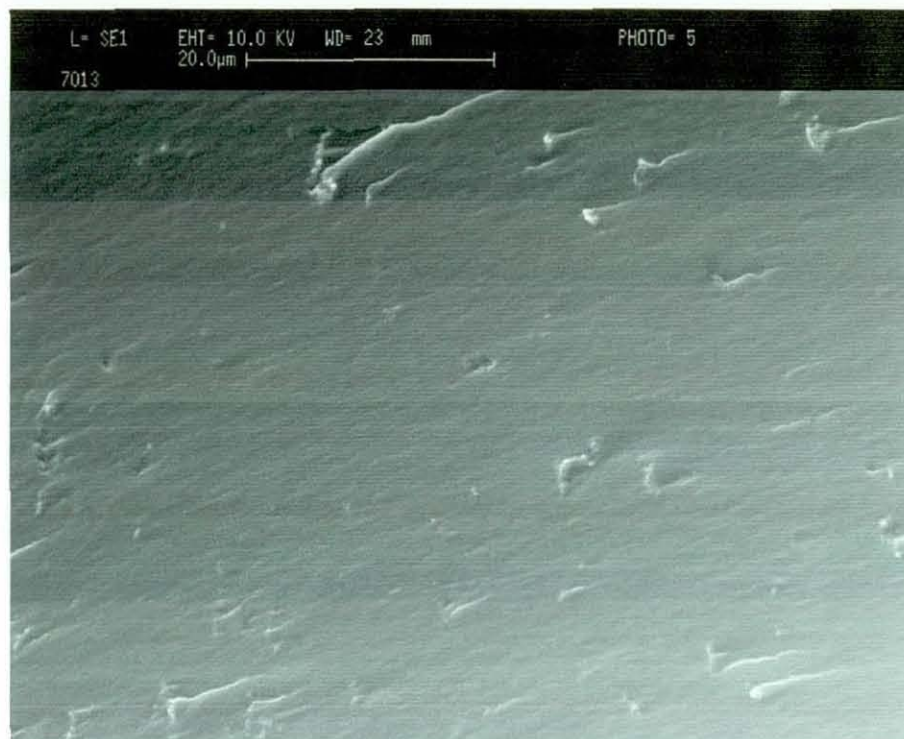


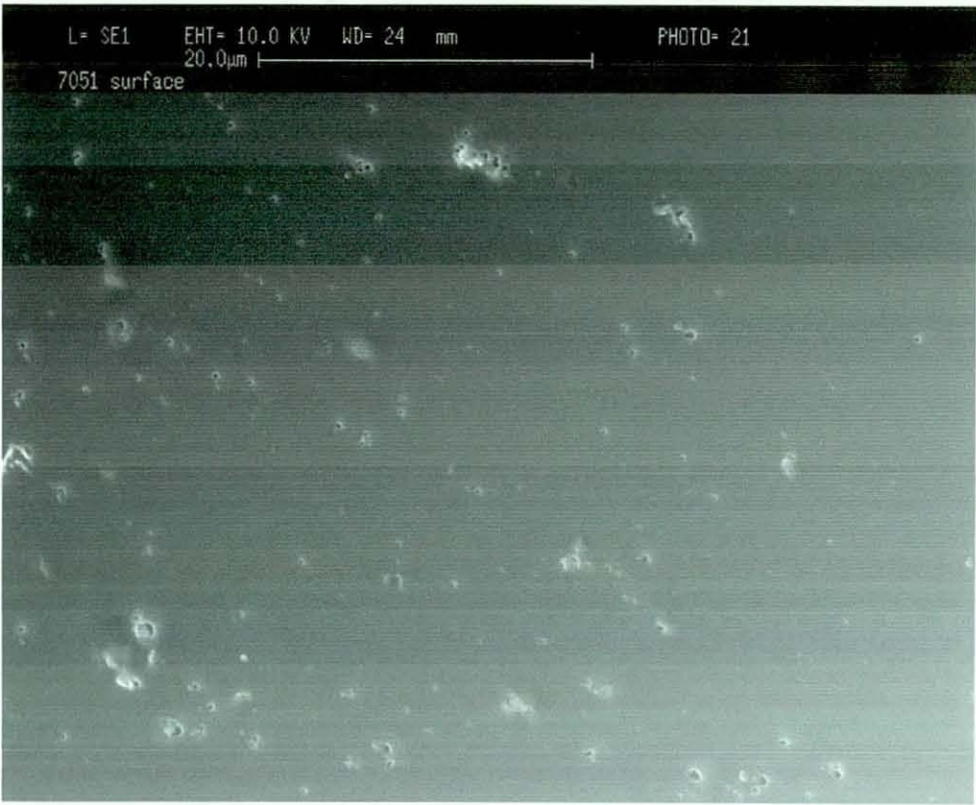
Figure 7-74a) SEM micrograph of hybrid

PEO (40) / Silica (40) / BHT (20) dried at 60°C



Figure 7-74b) SEM micrograph of hybrid of hybrid

PEO (40) / Silica (40) / BHT (20) dried at RT



**Figure 7- 75 SEM micrograph of hybrid PEO (30) / Silica (50) / BHT (20)**



