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POLYPROPYLENE-CLAY NANOCOMPOSITES: EFFECTS OF INCORPORATING SHORT CHAIN AMIDE MOLECULES ON RHEOLOGICAL AND MECHANICAL PROPERTIES

By

Upul Nishantha Ratnayake

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Supervisor: Mr. B Haworth

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ABSTRACT

The influence of low molecular weight additives containing polar groups and polyolefin-based compatibilisers modified on polypropylene (PP)-clay nanocomposites (PPCN) has been studied, in terms of intercalation and degree of exfoliation achievable by melt state mixing processes. PPCN were prepared by melt mixing of two commercial PP homopolymers with organically modified clay (OMMT) in the presence of maleic anhydride grafted PP (PP-MA). X-ray diffraction (XRD) analysis shows that the interlayer spacing of clay increases dramatically, whilst transmission electron microscopy (TEM) results show a significant improvement of clay dispersion in the PP matrix, when nanocomposites are prepared with commercial PP containing short chain organic additives with polar groups (amide-type slip and antistatic additives). Subsequent studies based upon customised PP formulations, with short chain amide molecules (AM), confirm the intercalation of this additive into clay galleries. The maximum interlayer spacing is achieved with low concentrations of this additive (0.5 wt. %). Contact angle measurements and low shear melt flow properties (MFI) further confirm the diffusion of this additive (AM) into the clay galleries rather than migrating away from the bulk of the PPCN. The interaction between the polar group (CONH₂) of this additive and polar sites of the clay surface appears to be the driving force for the intercalation. Although this additive intercalates and allows the formation of an intercalated nanocomposite structure with non homogeneous dispersion of clay, an exfoliated PPCN structure is yet to be formed with this additive alone.

A new preparation method for PPCN has therefore been developed by co-intercalation of AM and PP-MA. PPCN were prepared by this method with a significant reduction of overall PP-MA concentration in the nanocomposite structure, relative to conventional PPCN prepared with compatibiliser (PP-MA) only. XRD and TEM analysis showed that nanocomposite structures are formed with significantly improved clay dispersion, compared to PPCN prepared using the conventional method. Quantification of clay exfoliation, using image analysis software, showed that higher degrees of exfoliation can be achieved in PPCN from this new cointercalation method. Normalised melt flow index (n-MFI) data showed the relationship between low shear flow properties and clay structure and is an

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appropriate parameter to examine clay exfoliation and its interaction with PP in PPCN. Enhanced thermal stability of PPCN, in comparison to pure PP, further demonstrates the improved clay dispersion in nanocomposite structures prepared by the co-intercalation method. A possible mechanism for the co-intercalation of AM and PP-MA into clay galleries has been proposed, based upon hydrogen bonding between these additives and the silicate layers.

Rheological characterisation of PPCN, using capillary rheometry experiments at high shear rates, shows a shear thinning, pseudoplastic behaviour similar to pure PP. However, a comparatively higher concentration of AM appears to reduce the shear viscosity of PPCN. Die swelling behaviour revealed a reduction in melt elasticity in PPCN melts in comparison to unmodified PP. Reduced die swell occurs as a result, together with a delay in the onset of melt fracture.

Sheet extrusion was used to produce PPCN products with increasing clay loading levels that were evaluated for a range of mechanical properties. Significant enhancement of modulus in PPCN is achieved in comparison to pure PP whilst maintaining similar strength characteristics. However, impact resistance of extruded PPCN sheets is not improved in comparison to unmodified PP. Results have been interpreted with reference to the degree of exfoliation, additive content and differences in PP crystallinity.

KEY WORDS: Polypropylene/ Clay/ Nanocomposites/ Co-intercalation/ Exfoliation/ Amide molecules/ Rheology/ Modulus.

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1 CHAPTER: INTRODUCTION AND OBJECTIVES

1.1 Introduction

Polyolefins, which are normally defined as polymers based on alkene monomers, are the most widely used group of thermoplastics today. The most common polyolefins are Polyethylene (PE) and Polypropylene (PP), both of which are semicrystalline polymers. PP, which is a versatile polymer, is extensively used in a wide range of applications mainly because of the overall balance of physical, mechanical, chemical and thermal properties that can be achieved, together with the ability to modify the polymer to suit specific applications. PP is used for a wide range of applications including automotive, packaging, textiles and in the construction industry. PP is synthesised by polymerisation of propylene monomer in the presence of a catalyst system. The range of available grades of PP has broadened considerably, as a result of recent developments in polymerisation catalysis allowing synthesis of more exact molecular structures in so-called 'metallocene' type polyolefins [1]. However the use of PP alone, without modification by additives, is not sufficient to achieve the desired properties for many industrial applications.

In order to enhance the properties and to reduce the cost of polymeric materials, there is a trend of using composite materials, which includes a continuous phase (polymer matrix) and a discrete phase (inorganic particles or fibres) dispersed in the matrix. One viable method of making composites by which properties can be modified is by the incorporation of inorganic, particulate fillers into polymers [2]. This is relatively common nowadays and PP is probably the most widely used, mineral-filled thermoplastic polymer for various applications. Fillers are added into PP mainly either to improve the mechanical properties (such as stiffness, heat deflection temperature or flammability resistance) or to optimise the overall performance-cost relationships for the material [3]. Generally, calcium carbonate, talc, mica and glass fibres are the typical fillers that are added to PP resins to attain cost-effective composite mechanical properties. The degree of property improvement of composite materials is affected not only by filler volume fraction but also depends on characteristics of these materials, including particle size/distribution, surface modifiers (and the subsequent dispersion

characteristics during the mixing process) and the filler-matrix interaction. It is well known that the addition of fillers and their characteristics significantly alter the rheological properties of PP composites [4]. In addition to these fillers, other additives are included in PP composites for special purposes. For example, slip additives are incorporated into PP composites to decrease the coefficient of friction and to reduce surface 'blocking' effects, especially in packaging applications. However, these additives have recently been found to modify the rheological properties of PP composites [5, 6]. Haworth and Khan [6] showed that increasing talc concentration in PP composites restricts the migration rate of fatty amide molecules to die wall boundary during processing, resulting in a reduced slip velocity compared to that of unfilled PP. Generally about 20-40 % of inorganic particulate filler is needed to achieve the desired property improvement in polymer composites and as a result the density of products is increased due to high density of the filler compared to that of polymer. The main disadvantages of highly filled thermoplastics are the reduction of strength and toughness of the composites [1].

However the addition of nano-scale particles, instead of conventional micro-scale fillers, enhances a wide range of performance such as mechanical, thermal and barrier properties, at relatively small loadings (< 6 % by weight) of nano-particles in polymer composites known as nanocomposites [7, 8]. Polymeric nanocomposites are a new class of particle filled polymers, for which at least one dimension of the dispersed particles is in the nanometre range. The most promising composite system is based on organic polymers and inorganic clay minerals consisting of layered silicates. Polymer nanocomposites based on clay are two-phase materials in which clay particles are dispersed towards the nanometre (nm) range in the polymer matrix. The most commonly used clays are smectite group minerals such as the montmorillonite (MMT) type, which belongs to the general family of 2:1 layered silicates. Generally hydrophilic MMT is not compatible with most of polymers and hence MMT is modified with organic surfactant (e.g. alkyl ammonium salt), by ion exchange with cation in clay galleries, to make it compatible with polymers [9].

Basically polymer-clay composites are divided into three general types: phaseseparated conventional micro-composites, intercalated nanocomposites, in which polymer molecules intercalate into clay galleries, and exfoliated nanocomposites, in which clay particles are separated into individual layers and dispersed uniformly in the polymer matrix. Polymer-clay nanocomposites have received increased attention in recent years because of two major findings. Firstly, Toyota research group investigated polyamide 6-clay nanocomposites and it was found that mechanical (tensile modulus and strength) and thermal properties (heat distortion temperature) are improved, in comparison with both conventional micro-scale composites and the unmodified polymer, at very low loading levels of clay [10, 11]. Secondly, the possibility of melt mixing of polymers with layered silicates without the use of organic solvents was demonstrated [12]. Since then a number of clay containing polymeric nanocomposites such as those based upon polystyrene [12], acrylic polymer [13], epoxy resins [14, 15], and polyolefins [16-19] have been reported in the scientific literature.

PP is one of the most widely used thermoplastic materials for applications such as automotive and packaging because of its versatility, overall balanced properties and its attractive property-cost ratios. Therefore PP-clay nanocomposites (PPCN) have attracted great interest to stimulate new research studies in the recent past, because of the property enhancement at low loading levels of clay [19, 20]. However, unlike polar polymers, non polar PP is not compatible with even organically modified clay (OMMT) and hence it proves difficult to exfoliate and disperse clay particles in a PP matrix. However, successful preparation of PP-clay nanocomposites (PPCN) has become a more realistic possibility by using functional oligomers as compatibilisers [19, 21]. Such a compatibiliser should contain sufficient polarity to interact with silicate layers and it should also be easily mixed with the bulk PP [22]. The most commonly used compatibiliser for the preparation of PPCN is maleic anhydride grafted PP [17, 18]. By grafting polar maleic anhydride onto non polar PP, it becomes compatible with clay and it also mixes easily with the bulk PP, during the compounding process. Exfoliation of clay particles into their individual clay platelets (i.e. nano scale particle) is the key factor, as with other clay based polymeric nanocomposites, to achieve the property improvements of PPCN. However conventional methods of preparing PPCN using PP-MA compatibiliser do not achieve a fully exfoliated nanocomposite structure [18, 19]. It has been further revealed that high PP-MA concentration in PPCN structures leads to phase separation and therefore affects the achievable mechanical properties of the PPCN [23, 24]. Therefore

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modified methods, which include using additional additives or improved compounding processes have also been investigated to improve intercalation and degree of exfoliation of clay and subsequently enhance the material properties of PPCN [25-27]. Zhang et el. [28] reported a new way of synthesising the PP-clay nanocomposite structures with the help of a swelling agent (maleic anhydride), reducing the PP-MA content in nanocomposite structures.

Low molecular weight additives containing polar groups are often used in PP formulations, for example slip additives (e.g. erucamide, olemide) for extruded film or moulded applications, to obtain specific surface properties in PP products. Generally these additives are able to migrate onto the surfaces when PP artefacts cool and consolidate, due to the incompatibility with the bulk PP and they subsequently change the chemical and physical nature of the surface.

Although extensive studies have been reported on the preparation and properties of PPCN, no literature has been found on how low molecular weight polar additives (such as amide type slip additives) affect the PPCN structure. Therefore this research project will examine, in addition to the effect of functionalised PP compatibiliser, the influence of these low molecular weight polar additives (e.g. amide type slip additives), some of which are present in commercial PP, on intercalation and exfoliation behaviour of clay in PP-clay nanocomposites.

Relatively little attention has been given to the rheological properties of PPCN, in spite of its importance in attempting to gain a fundamental understanding of the processability and structure property relationships for these materials. Therefore a complete rheological characterisation including (extrudate swell, melt fracture and wall slip behaviour) is yet to be reported on PPCN. Very recently it is reported that the addition of polar additives into particle-filled compounds alters the flow properties in comparison to filled polymers [6, 29]. However it is not known how low molecular weight polar additives (e.g. short chain amide molecules) affect the flow properties of PPCN.

Therefore potential outcomes from this research project are to produce PPCN, with improved clay dispersion based on short chain amide molecules and to reduce PP-MA concentration and as a result, to enhance the material properties of PPCN.

1.2 Objectives

Clay based PP nanocomposites will be prepared by melt blending different PP grades, some of which contain low molecular weight polar additives (slip and antistaic additives), compatibiliser and organically modified clay. Therefore the main objective of this study is to investigate the influence of short chain organic molecules containing polar groups on PP-clay nanocomposite structure and to develop a new method to synthesise PPCN with improved clay dispersion, based on short chain amide molecules. In addition, PPCN prepared with this new method are examined for processability in terms of rheological characterisation and for mechanical properties in the solid state.

The main objectives of this research are therefore summarised as follows.

- To prepare clay filled PP nanocomposites by melt blending of PP, organically modified montmorillonite and compatibiliser (i.e. maleic anhydride grafted PP) using a batch-mixer (Haake rheometer).
- To study the effect of compatibiliser (PP-MA) and its characteristics, and matrix molecular weight of PP on PPCN structure.
- To investigate the influence of low molecular weight polar additives (i.e. slip and antistatic agents), which are contained in some of commercial PP grades, on intercalation and exfoliation behaviour of PPCN structure.
- To develop a new method to synthesise PPCN based on short chain amide molecules and functionalised PP (PP-MA), so that the concentration of PP-MA can be reduced relative to conventional PPCN prepared with only PP-MA.
- To suggest a possible mechanism for the PPCN prepared with this new cointercalation of short chain amide molecules and compatibiliser.

- To characterise the PPCN structure prepared by this new co-intercalation method using different characterisation techniques (e.g. X-ray diffraction, TEM, contact angle and thermogravimetric analysis).
- To scale-up clay filled PP nanocomposite production, based on the cointercalation method, by melt blending of the same materials using a twin screw extruder.
- To perform a rheological characterisation of PPCN and especially the effect of short chain amide molecules and clay concentration on a range of viscoelastic deformation properties of PPCN melts.
- To investigate the mechanical properties of PPCN products that can be achieved with this new co-intercalation method (based on short chain amide molecules and functionalised PP) and to compare with conventional types of PP-clay micro composites.

2 CHAPTER: LITERATURE REVIEW: MATERIALS

2.1 Polypropylene

Polypropylene (PP) is a versatile thermoplastic material that is produced by polymerising propylene molecules (the monomer units) into very long polymer molecules or chains. PP is a commodity thermoplastic and it is grouped in with the polyolefin family. Although propylene was polymerised as early as 1869, it did not exhibit interesting properties for industrial applications. Crystalline isotactic PP was invented in the early 1950 by two independent groups in United States and Europe [30]. The commercial production of PP began in US and Europe in 1958.

Polypropylene is compatible with many processing techniques and used in many different industrial applications. Strong and versatile ranges of mechanical properties, ease of processing and moderate cost were the main cause to rapid development of this material for industrial applications. PP was developed for numerous versatile applications. Many available grades of PP with different properties is used in different applications such as fibres, films, injection moulded parts for automobiles, rigid packaging, flexible food packaging, domestic appliances and consumer products.

2.1.1 Production of PP

PP is prepared by polymerisation of propylene, a bi-product of petroleum refining, in the presence of a catalyst under carefully controlled heat and pressure. [31,1]. Propylene monomers are polymerised into long chain PP with the presence of catalyst mainly by Ziegler-Natta catalysis polymerisation and by metallocene catalysis polymerisation.

The Ziegler-Natta polymerisation was the first developed method and it was named after Karl Ziegler and Giulio Natta, who were the pioneers of this polymerisation process [31]. In this method the catalyst, which provides active sites for the polymerization process, is transition metal catalysis, like TiCl₃ and a co-catalyst which is usually based on group III metals such as aluminium.



Figure 2-1 Polymerisation of propylene into PP

These catalysts are multi-sited catalysts, containing several reactive sites. Therefore, as a result, the polypropylene made from this technique can contain PP molecules with a broad range of molecular weights and some branching off the main polymer chain [1]. However narrow molecular weight distribution in PP is preferred for some applications such as film, fibre and injection moulding products with thin walls. For a long time, this was the most useful and widely used polymerisation technique for the producing PP.

Recently, metallocene catalysis polymerisation methods have been developed to produce polyolefin thermoplastics. In contrast to Zeiger-Natta catalysts, metallocenes are single sited catalysts and properties such as molecular weight and stereo-structure of PP can be tailored to meet the needs of applications [1]. Metallocenes are organometallic compounds which consist of a transition metal ion (iron, titanium, zirconium) situated in between two cyclic organic compounds. Geoffery Wilkinson and Ernst O Fischer has discovered the structure of ferrocene which is the first metallocene catalyst [1]. From this method, it is possible to produce PP with varying microstructure, molecular weights and other properties by varying the transition metal and organic compounds used [32]. PP made using this polymerisation system can exhibit increased rigidity and transparency, higher heat distortion temperatures, improved impact strength and toughness even at sub-ambient temperatures. The metallocene catalysed PP has a very narrow molecular weight distribution, due to the uniformity of the PP chain, compared to that of conventional PP.

2.1.2 Chemical structure

Polymerisation of the non-symmetrical propylene molecule CH_2 =CHCH₃ leads to three different ways of linking of propylene monomer: head-to-tail, head-to-head and tail-to-tail ("head" refers to olefin carbon with a methyl group and the other olefin carbon refers to as "tail"). Therefore it is possible to form structural isomers in the PP chain. However, with the Ziegler-Natta or metallocene polymerisation, the propylene monomers link together in the head-to-tail fashion, although occasionally monomers do form head-to-head or tail-to-tail linkage but this tends to be very rare and this causes disruption the crystalline structure and lower the melting point of the polymer.



head-to-tail

tail-to-tail

head-to-head

Figure 2-2 Isomerism options in PP

2.1.3 Stereo-chemical isomerism (Tacticity)

Stereo isomers can be formed because of the asymmetric nature of the propylene molecule. Propylene monomers can link together such that the methyl groups can be situated in one spatial arrangement or another in the polymer chain and therefore it is possible to form three typical stereo configurations (Figure 2-3).

Isotactic PP (i-PP), the most common commercial form, in which all the methyl groups, as shown in figure 3 (a), are on the same side of the molecular chain. Due to this regular, repeating arrangement, i-PP has a higher degree of crystallinity. Syndiotactic PP (s-PP) is defined by methyl groups arranged alternatively on the either side of the polymer chain.



Figure 2-3 Stereo chemical configurations of PP

Atactic PP (a-PP) is formed with a sterically random sequence of methyl groups. Isotactic PP and syndiotactic PP are capable of crystallising because of their regular arrangement of the structure. Amounts of i-PP, s-PP and a-PP in a formulation are depending on the catalyst system used and the polymerisation condition. Most PP is predominantly i-PP with a small amount of a-PP.

2.1.4 Crystalline structure

PP is a semi-crystalline polymer; varying degrees of crystallinity and different types of crystal structures are possible depending on the stereo-chemical structure, the processing and the presence of additives. Crystallinity of PP arises because of the stereo-regularity of the molecular structure. However occasional irregularities such as branching and tail-tail or head-head additions limit the degree of crystallisation. Molecules are arranged themselves into crystals at the crystallisation temperature. Crystal growth can be spontaneous or can be induced by the presence of foreign particles such as nucleating agents or metal surfaces. There are three different crystal structures can exist in i-PP: the monoclinic (α) form, the hexagonal (β) form, the triclinic (γ) form. The α form of i-PP is the primary form of PP obtained under normal processing conditions [30]. β Form of the PP can be formed at relatively low isothermal crystallisation temperatures or in the presence of specific nucleating agents.

2.1.5 Types and new grades of PP

Different forms of PP are produced in commercially depending on the properties required for different applications. They can be mainly categorised as homopolymers, copolymers, thermoplastic olefins and thermoplastic vulcanisates.

(A) PP Homopolymers

PP containing only propylene monomer in the semi-crystalline solid form is referred to as homopolymer PP (HPP), which is the most widely used PP material. Homopolymer provides stiffness and toughness but exhibits low impact strength at low temperatures and optical clarity is too low for some applications. HPP is mainly used to make extrusion and injection moulded products.

(B) PP Copolymers

PP containing one or more different types of monomers such as ethylene and 1-butene in the PP chain at different levels is referred to as a copolymer. Copolymers (CP), which consist of ethylene monomer or less commonly 1-butene and 1-hexene monomers in PP, are usually copolymerised in a single reactor. CP based on ethylene generally contains 1-7 % of ethylene by weight in PP. The ethylene in the CP will lead to changes in some properties. Due to the presence of ethylene co-monomer, crystallinity of CP is reduced and, as a result, melting point is lowered. Generally CP has lower glass transition temperatures than homopolymer depending on the type, amount and distribution of co-monomer and hence it has comparatively higher impact strength. CP is basically used in film, blow moulding and injection moulding applications that require high clarity and good impact strength at low temperatures. The other co-polymer based on ethylene propylene rubber (EPR) or polyethylene is known as impact copolymer (ICP). Copolymer levels are in ICP range from 5-25 %. The impact resistance of ICP depends on type, amount and morphology of elastomeric phase [1]. Due to the presence of higher level of copolymer in ICP, it has higher impact resistance or toughness especially at very low temperatures (e.g. -20

°C). The ICP is used where enhanced impact resistance is needed at low temperatures especially freezer temperature and below.

(C) Blends

Thermoplastic olefins are blends of PP and ethylene propylene rubber (EPR) or ethylene propylene diene monomer as the elastomeric phase and usually elastomeric phase is above 20 % in thermoplastic olefins. Thermoplastic olefins are increasingly used in automobile industry, replacing traditional engineering thermoplastics due to their low cost and enhanced properties.

(D)Thermoplastic vulcanisate

Thermoplastic vulcanisate (TPV) is a blend of PP and a elastomeric phase which is similar to thermoplastic olefins but the rubber phase is cross-linked or vulcanised. Ethylene propylene diene rubber (EPDM) is most commonly used as the rubber phase in (TPV). Properties of TPV are similar to that of synthetic rubber and it can be processed using extrusion and injection moulding like thermoplastics. TPV are generally used in automotive, construction and medical applications.

(E) Metallocene PP

After developing the metallocene single-sited catalysis polymerisation, new PP grades which are characterised by extremely narrow compositional and molecular weight distribution have been developed. These characteristics differentiate the metallocene based PP from Ziegler-Natta based PP which are composed of broad molecular weight distribution. Metallocene catalysts are enabling to produce PP with very uniform polymer chain, with a narrow molecular weight distribution and with high crystallisation rates and small crystallite sizes. Because of these features, PP based on metallocene has better properties compared to that of conventional PP. For example, new PP grades for injection moulding have been developed from metallocene catalysis with high flow and with high stiffness and good transparency, similar to random copolymers. For low temperature applications, PP grades have been produced with improved impact strength at low temperatures [33]. Thermoplastic elastomers can also be produced from PP with isotactic and atactic PP blocks in same PP chain using metallocene catalysis polymerisation. [34].
2.1.6 Properties and applications of PP

PP has excellent and desirable physical, mechanical and thermal properties especially when it is used in room temperature applications. It is relatively stiff and has a high melting point (e.g. 160-170 °C), low density (e.g. 0.91 gcm⁻³) and relatively good resistance to impact. These properties can be varied in a relatively simple manner by altering the chain tacticity content and distribution, by varying the average chain length, by incorporating a co-monomer such as ethylene into the polymer chain.

Because of the balance of properties and the low cost, PP becomes a very versatile polymer and provides for a wide range of applications. PP is used in automobiles, in exteriors and interiors and it is used in automotive industry more than any other single polymer. One of the other main applications of PP is for packaging applications and PP has replaced more expensive packaging materials, especially for food packaging applications due to low cost and desired properties. In addition to automotive and packaging applications, PP is used mainly in construction industry, medical applications and as fibres and fabrics, etc.

2.2 Particulate fillers

Fillers are inorganic solid particles and a wide variety of particulate fillers is used in polymer composites ranging from apparently simple clays, chalks and limestone to rare earth magnetic powders. Particulate fillers have played a vital role in the development of commercial uses of polymers. Originally, they were mainly seen as cheap diluents, hence the term "fillers". However, their ability to beneficially modify or enhance many properties was soon realised and they are now used for many purposes. In some instances, specific fillers are used to provide special functions to the polymer and then the fillers are called functional fillers. Some examples for functional fillers are aluminium hydroxide and magnesium hydroxide used as flame retardants for many polymer types.

Some of the main reasons for using particulate filler are: cost reduction, density control, thermal conductivity, electrical and, magnetic properties, flame retardancy, improved mechanical properties such as hardness, stiffness, creep and abrasion.

However, no single filler provides all of these benefits. Each type improves some properties while having no influence or even a detrimental effect on others [35]. Based on the particle size, particulate fillers could be divided into two main groups. They are conventional micro-scale particulate fillers and nano- fillers.

2.2.1 Conventional micro-scale fillers

Micro-scale fillers are the particulates in the micron (μ m) range when they are dispersed to a primary size, in the polymer matrix. These fillers are added into polymers either as simple diluents or to improve some physical or functional properties of the filled composites.

Filler characteristics such as cost, hardness, density, thermal properties and etc. are important in selecting filler when it is used either as a diluent or for the improvement of any physical property. However it is known that the filler morphology (size, shape, size distribution and surface treatment) is a strong influence on the mechanical as well as flow properties of the filled polymer composites [2].

Particle size is the most widely used parameter for filler morphology. Most of the filler particles are irregular in shape and therefore most sizing methods use the concepts of the equivalent spherical diameter (ESD) which is the diameter of a sphere having the same volume as that of the particle. Particle shape is another important factor, affecting processing and composite properties. Typical "extreme" particulate filler shapes are illustrated in Figure 2-4.

Anisotropy or aspect ratio, which is mainly influenced by particle shape, is more important in improving factors such as stiffness and heat distortion temperature. The ability of particles to fill space by packing together is obviously related to their morphology and plays a very important role in determining the properties of filled polymers especially at high filler loadings. The maximum packing fraction (MPF) that is the maximum amount of filler particles incorporated in to a system is an important parameter in filled polymer composites.



Figure 2-4 Shapes of typical particulate fillers

Based on their production, there are two main types of fillers available. The first one is mineral fillers produced directly from natural sources. A mineral is a pure, usually crystalline, naturally occurring material with a definite composition. Minerals are generally found in nature as rocks or ores. Calcium carbonate, clay, talc and silica are some general mineral fillers.

The other filler type is synthetic fillers which are produced by chemical synthesis. These are generally used when desired mineral fillers are not readily available in nature or when high purity, special shapes, finer sizes than natural fillers are required. Examples for main synthetic fillers used in the polymer industry are carbon black, precipitated calcium carbonate, calcium sulphate and magnesium hydroxide. However calcium carbonate, talc, mica and magnesium hydroxide are the common micro-scale fillers used in PP filled composites.

2.2.1.1 Surface modification of fillers

Most particulate fillers are inorganic and polar in nature. As a result, their surfaces have poor compatibility with hydrocarbons and hence this affects the dispersion of fillers in matrix and processing behaviour. As a result, the properties of the final product will be affected. Surface modification of filler has been used to overcome these problems in many polymer applications.

There are two main classes of filler surface modifiers can be recognized: non coupling and coupling [36]. These are illustrated in Figure 2-5.





(A) Non coupling modifiers

The non-coupling types have a strong physical interaction with the filler surface but, although compatible with the polymer matrix, have no strong bond to it (e.g. fatty acid treatment). These types of modifiers are the widely used as they are generally low cost, easily applied and can provide many desirable benefits to the polymer composites. Fatty acids are the predominantly used as modifiers for this purpose and their carboxylic group is capable of forming a strong attachment to the surface of the many types of fillers (e.g. CaCO₃) through the formation of salts, while the hydrocarbon tail provides compatibility and interaction with many organic polymers. Stearic acid is the most widely used fatty acid type for the coating of many types of stearic acid coatings of fillers especially for CaCO₃ [37]. Generally, literature [38] reveals that in thermoplastics, stearic acid treated fillers improve the incorporation of fillers, create better dispersion and improved physical properties. Although the fatty acid treatments reduce the melt viscosity, Bohlin and co-workers have found that

when dolomite was coated with stearic acid, the melt viscosity was not affected at range of shear rates measured by a capillary rheometer [39]. In another study, Hancock and co-workers, observed no decrease on melt viscosity by the incorporation of stearic acid treated CaCO₃ into PP matrix [40]. However Miyata et al. [41] found a marked reduction in melt viscosity when stearic acid was used on magnesium hydroxide in PP. Previous studies carried out in IPTME, Loughborough university also showed that fatty acid coated fillers alter the flow properties of the composite [6, 42].

(B) Coupling modifiers

In contrast to the non coupling type, coupling agent has a strong interaction with both the filler and the polymer matrix. The interaction with polymer is usually due to chemical reaction, chain entanglement and co-crystallisation with polymer matrix. (e.g. organosilanes and functionalised polymers). Organosilanes are widely used with silica, silicates, oxides and hydroxides. Functionalised polymers, (for example maleic anhydride grafted polyolefins), are widely used in filled polyolefins where coupling to polymer is through chain entanglement and co-crystallisation.

2.2.2 Nano-fillers

While there is no precise definition, nano-fillers can be considered as particles which, when dispersed in polymers, are very small "nano-scale" in at least one dimension. However, as this concept is not appropriate (since with particles of up to at least hundred nanometres being described as nano-particles), Rothon et al. [2] has suggested a reasonable working definition. In this definition, at least one dimension of the effective particle, when dispersed in polymer matrix, should be no more than 20 nanometres. The term 'effective particle' describes these particles which are dispersed in the polymer matrix. This prevents some fillers, such as carbon black, where the primary particles could be in the specified range but aggregated in polymers, being considered as nano-fillers. Because of the nano dimensions, the specific surface area of the nano fillers is one to two orders of magnitude higher than that of conventional micro-scale fillers. For example, while most mineral fillers would have specific surface areas in the range of $1-10 \text{ m}^2\text{g}^{-1}$, a spherical silica nano-filler, with a diameter

of 10 nm, would have a specific area of 250 m²g⁻¹, nano-clay can have a specific surface area of 1000 m²g⁻¹ or more [2]. Because of the high surface area of the nano-fillers, the amount of modified polymer is larger in nanocomposites in comparison to that of conventional composites. The presence of modified polymer (with nano particles, up to 20% of the polymer can be affected) contributes to the improvement of mechanical and thermal properties of the nanocomposites. There are three types of main nano-filler forms depending on how many dimensions are in the nanometre range [2]. These are regular, rod-like and platy and are illustrated in Figure 2-6.



3 Nano-dimensional particle

2 Nano-dimensional particle



1 Nano-dimensional particle

Figure 2-6 Three basic types of Nano-particles

(A) Regular shape nano fillers

When all three dimensions are in the nanometre range fillers are categorised into this group [8]. These are generally made by controlled precipitation in the presence of surfactants, to prevent agglomeration and fusion of particles. The common regular shape nano-fillers are silicas and titanias.

(B) Rod-like nano fillers

In this group, two dimensions are in the nano-metre range and the third dimension is larger. These are generally called 'nanofibres' or 'nanotubes' and are mainly carbon or metallic in nature. These are generally used for electrical applications, where they produce conductivity at significant lower volume fraction than more conventional conductive fillers [2]. Useful nanofibres are carbon nanotubes, vanadium oxide, inorganic nanotubes and cellulose whiskers. However carbon nano-tubes are the main interest in polymeric nanocomposites. These carbon nanotubes have hollow tubular structures with a wall thickness of 0.07nm and interlayer spacing of 0.34 nm. They are either single-wall or multi-wall nanotubes [9]. Carbon nanotubes are used in polymer matrixes to improve the mechanical performance and to enhance electrical conductivity [38, 43].

(C) Platy nano-fillers

In platy nano-fillers (e.g. layered silicates), only one dimension is in the nanometre range and thus these fillers are in the form of sheets of one to few nanometres thick and hundreds to thousands of nanometres long [8]. The platy nano-fillers are the currently of commercial interest. The composites based on these fillers show improved mechanical and thermal properties than conventional composites, for example nylon 6/clay and PP/clay nanocomposites [11, 17, 19, 21].

These platy fillers are the most important in polymeric nanocomposites due to a combination of several factors. For example, they can be obtained from relatively inexpensive raw materials, especially certain clays, and because of the combination of shape and high specific surface area, their incorporation gives rise to some useful effects at relatively low loadings.

The most widely used platy nano-fillers are layered silicates (clay). As clay is the most important nano-filler in polymer nanocomposites and montmorillonite (i.e. one type of clay) is used in this research study, the following section describes more details of the clay structure and their modification.

2.3 Layered silicates (clay)

Common clays are naturally occurring minerals and these minerals are a part of a general group within the layered silicates (Phyllosilicates). Clays are crystalline, usually plate-shaped crystals with high aspect ratio and have large specific surface areas. They are typically flat, platy and have a sheet like structure and contain water trapped in between silicate sheets and also display good basal cleavage. The sheets are then connected to each other by layers of cations. These cations are weakly bonded to clay layers and often have water molecules and other neutral atoms or molecules trapped between the sheets. Many types of clay are aluminosilicates which consist of tetrahedrally bonded silica sheets and octahedrally bonded alumina sheets in variety of ways. For example kaolin clay consists of one sheet of silica and one sheet of alumina (1:1 or two-layer structure). However the clay commonly used in polymeric nanocomposites belongs to the structural family known as the 2:1 layered silicates (smectite group), which have a triple layer structure, in that octahedral alumino layer is sandwiched in between two tetrahedral silicate layers. The two main characteristic features of smectite clays are exploited in nanocomposites preparation. The first is that the clay particles can be dispersed into individual layers with a thickness of 1nm and the second is the ability to fine tune their surface chemistry through the ion exchange reactions with organic and inorganic cations. The commonly used smectite clays in polymeric nanocomposites are montmorillonite (MMT), hectorite and saponite.

However, the most common smectite clay type is MMT for the production of clay containing polymeric nanocomposites. The composition of MMT is vary, relatively wide range, depending not only geographic location but also with the deposit strata. The typical chemical formula of MMT is $[Al_{1.67} Mg_{0.33} (Na_{0.33})]$ Si₄ O₁₀ (OH)₂ (9). Usually MMT is pale yellow in colour but, depending on the composition the colour can be varied (e.g. red in colour due to Fe³⁺). Commercial montmorillonite clay is in powder form with about 6-8 μ m particle size, each containing about 300 platelets (individual layers). Clay platelets have a very high aspect ratio 50- 2000 with 750 – 800 m²/g specific surface area [9]. This high aspect ratio and high specific surface area, which affects the clay-polymer interaction, are the main features related to reinforcement of clay containing polymeric nanocomposites. In addition to the use of

clay for preparing polymeric nanocomposites, clay is being generally used as an absorbent, as a base for cosmetics, drugs and pesticides and organically treated clay is used as thixotropic additives to control the flow behaviour of oils, greases, suspensions, paints and printing inks.

In this study MMT will be used for the preparation of nanocomposites and therefore in the following sections, reference to clay or nano-clay generally refers to MMT type clay minerals.

2.3.1 Structure and properties of clay (MMT)

The crystal structure of clay is consists of two dimensional layers where a central octahedral sheet of alumina is fused onto two external silica tetrahedron by the tip so that the oxygen ions of the octahedral sheet do also belong to the tetrahedral sheets [7, 8]. The typical structure of the layered silicates is shown in Figure 2-7. Clay is a soft mineral with a hardness of 1.5-2.0 on Mohs hardness scale, density is about 2.3-3.0 gcm⁻³, and it can expand up to 30 times in volume with water.

The thickness of a clay layer (consists of two tetrahedron silicate sheets and a octahedral alumino sheet) is around 1nm and the lateral dimensions of these layers may be vary from 30 nm to several microns [7, 44]. These layers are organized in the form of stacks and this leads to a regular Van der Waal gap between the layers called the inter lamellar gallery, or gallery space. Clay layers are weakly bonded each other by Van der Waal interaction energy and this interaction energy is very much dependent on the distance between clay layers or the gallery space. The size of the gallery space is highly variable due to the absorption of water into clay. However the minimum thickness of the clay gallery space is 0.26 nm which corresponds to a monolayer of water molecules. Isomorphic substitution within the layers (for example Al^{+3} replaced by Mg^{+2} or Fe^{+2}) generates negative charges that counterbalance with alkali or alkaline earth cations situated inside the galleries. These cations can be ion-exchanged and the cation exchange capacity (CEC) is a characteristic feature of these types of clays. The CEC of MMT ranges from 0.8-1.2 meq g⁻¹.



Figure 2-7 Structure of clay (2:1 Layered silicates)[8]

The miscibility of polymers with pristine clay is difficult since the clay is hydrophilic in nature. Strong interaction between polymer and inorganic component (clay) leads to a good dispersion of clay in polymer matrix. Therefore to achieve a good dispersability of clay in polymers, it is necessary to convert the hydrophilic clay into organophilic by intercalation of organic molecules into clay galleries. There are several active sites on the MMT clay surface have been identified. The following three active sites are important in view of intercalation and exfoliation [9].

- Positive charges which are in platelet edges that attract negatively charged ions or molecules. These sites have been used to attach organic molecules but not effective for increasing interlayer spacing (d₀₀₁) as they are in platelet edges.
- The OH groups which participate in hydrogen bonding and chemical reaction. They are mainly bound to Si or Al ions.

• The anionic groups are on the MMT surface. Anionic groups on MMT surfaces are the most important active sites to drive organic cations into clay galleries which make them more organophilic.

2.3.2 Organic modification of clay

Pristine clay usually contains hydrated Na^+ or K^+ ions and therefore, these clays are miscible only with hydrophilic polymers such as poly(ethylene oxide) and poly(vinyl alcohol) [44-46]. In order to miscible with other polymers, hydrophilic clay needs to convert into organophilic. As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers is easy [47]. Intercalation of clay can be done by ion exchange reaction between cation which are within clay galleries and organic molecules. The cation exchange reaction of Namontmorillonite (Na-MMT) with organic cation (RH⁺) is occurred as below and it is a reversible reaction

$$RH^+ + Na^+ - MMT \iff RH^+ - MMT + Na^+$$

The main intercalants are organic-cation surfactants including primary, secondary, tertiary and quaternary alkyl ammonium or alkyl phosphonium cations. This organic modification of pristine clay mainly leads to lower the surface energy, increase the interlayer spacing of the clay and improve the interaction between the clay and the polymer matrix [7]. Additionally, the alkyl ammonium or alkyl phosphonium cation can provide functional groups that can react with the polymer matrix or in some cases initiate the polymerisation of monomers [48, 49]. The rate of cation exchange depends on the temperature, pH of the medium and concentration and geometry of clay particles. The most common cation-exchange method is using alkyl ammonium salt and it has been found that quaternary ammonium salt gives better bonding strength to MMT. Bonding strength to MMT increases with increasing a number of substituents in the ammonium cation as below [50].

$$NH_4 < RNH_3 < R_2NH_2 < R_3NH < R_4N$$

"R" refers to the alkyl chain attached to the N atom and different alkyl chains such as hydroxyl and carboxyl groups containing hydrocarbons and hydrogenated tallow oil (which typically consist of different length alkyl groups) are frequently attached to intercalants. However it has been found that interlayer spacing of layered silicates treated with alkyl ammonium salt depends on the length of the alkyl chain and as well as on the cation exchange capacity (CEC) of the clay [51]. Therefore organically modified clays, containing different intercalant have different interlayer spacing and their degree of compatibility with different polymer matrixes is also different. The following Table 2-1, list out some of the commercially available organo-clays with different intercalants and their interlayer spacing [9].

Although clay, with organic modification, becomes more compatible with a polymer matrix, there are several drawbacks in organically modified clay in preparation of clay containing polymeric nanocomposites. Organically modified clays are more expensive than pristine clay. Although clay becomes more organophilic with the organic treatment, they are not miscible directly with most polymers, for example polyolefins. The main disadvantage of alkyl ammonium intercalants, especially quaternary ammonium, is the thermal stability. These organic molecules start decomposing below 200 °C which may reduce the mechanical properties and causes discolouration. Lee et al. [52] showed that interlayer spacing of some organo-clay have been reduced to lower values than their original value after making PP-clay nanocomposites at 210 °C. However thermal stability of organo-clay can be improved by using phosphonium instead of ammonium intercalants, by using branched alkyl chain instead of linear and aromatic substituents instead of aliphatic in intercalants [53].

Organoclay	Organic Intercalant	Spacing
		d ₀₀₁ (nm)
Closite from southern clay		
6A	2M2HTA	3.59
10A	2MBHTA	1.93
15A	2M2HTA	2.96
20A	2M2HTA	2.47
25A	2MHTL8	2.02
30B	MT2EtOH	1.86
93A	M2HTA	2.36
Somasif from CO-OP chemicals		
MAE	2M2TA	3.0
MTE	М3О	2.5
MPE	M2EPPOH	5.0

 Table 2-1 Commercially available organo-clays with their intercalant and interlayer spacing [9]

- 2M2HTA :Dimethyl dihydrogenated tallow ammonium chloride
- 2MBHTA :Dimethyl benzyl hydrogenated tallow ammonium chloride
- 2MHTL8 :Dimethyl hydrogenated tallow 2-ethylhexyl ammonium methyl sulphate
- MT2EtOH :Methyl tallow di-2-hydroxy ethyl ammonium chloride
- 2M2TA :Dimethyl ditallow ammonium chloride
- M2HTA :Methyl di [hydrogenated tallow] ammonium
- M3O :Methyl trioctyl ammonium chloride

M2EPPOH :Methyl diethyl polypropylene glycol ammonium chloride

Lagaly [54] has suggested that according to wide angle X-ray diffraction (WARD) data that organic chains lie between the silicate layers, either parallel to the silicate layers forming mono or bi-layers or radiate away from the silicate layers forming mono or bimolecular arrangement depending on packing density, temperature and alkyl chain length.



Figure 2-8 Arrangements of organic chains between clay particles [54]

However these idealized structures have been shown to be unrealistic by Vaia et al using FTIR experiments [55]. They showed that alkyl chain can vary from liquid-like to solid like structure.

2.3.3 Exfoliation of clay

Exfoliation is the next step for the preparation of polymer clay nanocomposites and it is the key factor because most of the property improvements can be achieved when clay particles are exfoliated into individual platelets since it can increase the aspect ratio and specific surface area of clay particles. Principally clay can be exfoliated in three different methods such as reactive, in solution and mechanical. However, mechanical exfoliation method is the most promising as it is generated by conventional compounding methods [9]. In this method, intercalated clay is mixed with the polymer or in some cases, a compatibiliser is needed. However the degree of exfoliation depends on interaction between clay and polymer, viscosity of the polymer matrix and the residence time in the compounding machine [56]. Usuki has distinguished four different pathways to exfoliate clay particles depending on polymer matrices [57].

I. Hydrophilic matrix with strong polar groups, e.g. Polyethylene glycol

Clay water swollen clay Hydrophilic polymer polymer nanocomposites

2. Polymer with strong polar groups e.g. polyamide

Clay _______ intercalated clay ______ expanded clay ______ expanded clay _______ expanded clay _______ polymer nanocomposites

3. Polymer with strong polar groups e.g. polyamide

Clay <u>intercalant</u> intercalated clay + Polar polymer <u>compounding</u> polymer nanocomposites

4. Hydrophobic non -polar matrix e.g. polypropylene

Clay $_$ intercalated clay + compatibiliser $_$ polymer nanocomposites.

2.4 Additives

In addition to fillers, some other additives are used in PP formulations. Generally antioxidants, nucleating agents, slip additives and antistats are added either into virgin PP or to PP composites for special purposes.

For example, antioxidants are used to prevent oxidative degradation of PP. The oxidative degradation of PP occurs due to high temperature and in the presence of air. Oxidative degradation in PP decreases the molecular weight, resulting in lower viscosity. Antioxidants prevent the oxidative degradation by inhibiting the oxidative reaction. Nucleating agents are to increase the nucleation of crystallising PP. The addition of nucleating agents provides a large number of sites for the initiation of crystallisation, resulting in a smaller and a higher amount of spherulite than unnucleated PP. Slip additives and their role in PP will be discussed in detail in the next section since the effect of these additives on intercalation and exfoliation of behaviour of PPCN will be investigated in this research study.

2.4.1 Slip additives

Slip additives are added into PP composites to decrease the coefficient of friction and to reduce the surface blocking effects, especially in packaging applications. Slip additives are mainly amides, based on fatty acids derived from natural occurring feed stocks such as tallow rapeseed and palm oil, including primary and secondary amides. Primary amides are the most extensively used slip agents and some commonly used primary amides are erucamide, stearamide and oleamide. The commonly used secondary amides are stearyl stearamide and stearyl erucamide. Figure 2-9 illustrates the general structures of primary and secondary amide-slip additives:

CH₃(CH₂)₁₆C(O)-NH₂

CH₃(CH₂)₇CH=CH(CH₂)₁₁CONH₂

(a) stearamide

(b) erucamide

CH₃(CH₂)₁₆-C(O)-NH-(CH₂)₁₆CH₃

(c) stearyl stearamide

CH₃(CH₂)₁₆-C(O)-NH-(CH₂)₁₁CH=CH(CH₂)₇CH₃

(e) stearyl erucamide

Figure 2-9 General structures of slip additives

Slip agents are normally incorporated into polymer compounds, prior to processing. Slip additives migrate to the surface as the polymer cools down due to their limited compatibility and form an ultra thin layer that reduces the friction (slip effect) and adhesion forces (anti blocking effect). These slip additives are added into polymers to solve processing problems caused by the inherent friction and tackiness of polymers and therefore it improves the processing behaviour and subsequent performance of the polymers by reducing friction and adhesion with minimum effect on the mechanical and optical properties. For example these slip additives are added into PP during the extrusion process to decrease the friction both film-to-film and between film and production equipment [58]. Figure 2-10 shows the reduction of co-efficient of friction which measures the slip effect with time after extrusion due to the migration of slip additives on to the polymer surface when polymer melt cools down.

As shown in Figure 2-10 amide molecules are uniformly distributed in the polymer melt immediately after extrusion (A). When polymer cools down they migrate to the surface and forms a partial layer and hence friction drops rapidly (B). Finally complete layer of amide molecules is formed on the surface and therefore minimum friction is obtained (C).

However the migration speed of slip additives onto the surface is largely depend on the molecular weight of additives and the crystallinity of the polymer (58). Stearamide migrates faster than erucamide because of its low molecular weight but erucamide has higher heat stability.



Figure 2-10 Reduction of Coefficient of friction with time after extrusion [59]

Therefore two important properties should be considered in evaluating these slip additives: reduction in the coefficient of friction (COF) and thermal stability of the slip agent [32] Primary amides are the most extensively used slip agents and they migrate faster to the polymer surface as their molecular weights are relatively lower than secondary amides. Major applications of primary amides are in polyolefin films, in injection moulding process to improve mould release and in bottle caps to reduce releasing force. Secondary amides generally have higher molecular weights and lower volatility and hence are recommended for high temperature processing such as rotomolding application for engineering plastics.

Previous studies carried out by Khan and Guinebaud in IPTME, Loughborough University [60, 61], showed the changes in flow property in virgin PP, particularly extensive wall slip in flow, and this could be probably due to slip additives since it acts as external lubricants. Ahn and White [5] studied the influence of a range of structurally different additives of different polarities on the flow behaviour of thermoplastics and it was found that stearamide induced slippage in PP melt at the die wall of capillary rheometer due to their migration to the surface.

In this research study, we have chosen to investigate the influence of this additive (slip additive: primary and secondary amides) on intercalation and exfoliation of clay in PPCN structure and the flow properties of PPCN will be studied in detail.

3 CHAPTER: LITERATURE REVIEW: POLYMER MELT RHEOLOGY

Rheology is the study of deformation and flow; which means the all responses of the material under applied stress. Study of flow properties is very important for processing of either thermoplastics or rubber and particularly when filled composites are developed for particular applications. Therefore it is necessary to understand the melt flow of thermoplastics as well as filled thermoplastics in order to achieve a good quality product, as well as to optimise the processing conditions.

3.1 Flow behaviour

There are mainly three types of flow (deformation): shear flow, elongational flow and bulk deformation [62]. However only shear flow and elongational flow will be discussed here since these are more applicable to this study.



Figure 3-1 Geometry of simple shear flow [62]

In shear deformation a force (F) is applied in tangentially to an elemental volume as shown in Figure 3-1. The top layer is displaced by u and the deformation creates velocity v in the z direction.

Shear stress,
$$\tau = \frac{F}{A}$$
 [3.1]

Shear rate,
$$\gamma = \frac{v}{h}$$
 or $\frac{dv}{dx}$ [3.2]

A = surface area of the top layer

 $\mathbf{v} = \mathbf{v}$ elocity in the z direction



Figure 3-2 Geometry of elongational flow

An elongational flow is achieved by applying a tensile force (F) on to opposite faces as indicated in Figure 3-2.

Tensile stress,
$$\sigma = \frac{F}{A}$$
 [3.3]

Strain,
$$\varepsilon = \frac{l-lo}{lo}$$
 [3.4]

Strain rate,
$$\dot{\varepsilon} = \frac{dv}{dz}$$
 [3.5]

v = velocity in the z direction

3.2 Shear flow behaviour

Generally stress-deformation behaviour of a material can be classified into two main types: Newtonian and non-Newtonian behaviour.

3.2.1 Newtonian fluids

In Newtonian fluids, material flows with a viscosity which is independent of stress or strain rate. At very low stress levels polymer melts generally approach Newtonian behaviour [63].



Figure 3-3 Shear deformation of Newtonian fluid

Shear stress
$$(\tau) = \mu (\gamma)$$
 [3.6]

Shear viscosity = μ

Shear stress $(\tau) = \frac{F}{A}$

Shear rate $\dot{\gamma} = \frac{\mathrm{d}v}{\mathrm{d}r}$

Fluids which obey the above equation (3.6) are called Newtonian fluids, as long as the value of μ is constant (i.e. independent of shear rate).



In a shear stress-shear rate curve, the slope is equal to the coefficient of viscosity (μ). The viscosity is constant and does not depend on the shear rate [64]. In stress-time relationship, application of a fixed stress at t₁, causes deformation which increases steadily until t₂. When the stress is removed then the deformation becomes constant and remains permanent, i.e. viscous flow. Practically, many real materials such as polymer melts, suspension and filled polymers do not show simple Newtonian behaviour.

3.2.2 Non-Newtonian fluids

Generally three broad classes of non-Newtonian fluids can be identified

- (a) Time-independent fluids
- (b) The time-dependent fluids
- (c) Viscoelastic fluids

3.2.2.1 Time-independent fluids

The viscosity of time-independent fluids depends only on current shear rate. These fluids are defined mathematically by the following equation

$$\gamma = f(\tau)$$
 [3.7]

 $\gamma =$ Shear rate

 τ = Shear stress

Graphically it can be shown by a curve of shear stress plotted against shear rate as shown in Figure 3.5.





All sort of curves are possible and may occur. However, here only four basic types are shown.

A Bingham body (plastics) does not flow until the yield stress (τ_y) is reached and above the yield stress the shear stress increases linearly with increasing shear rate. Examples of these types of fluids are some suspensions, slurries and certain asphalts and bitumen [4].

For pseudoplastic fluids, the viscosity decreases with increasing shear rate (Figure 3-6), thus called shear thinning fluids. Most polymer melts, polymer solutions and filled polymer systems show pseudoplastic behaviour. The opposite behaviour to pseudoplastic is known as dilatancy. Dilatant materials show an increase in the viscosity with increasing shear rate. All these types of behaviour are shown graphically in Figure 3-6.





Figure 3-6 Apparent viscosity-shear rate relationship for time independent fluids (dilatant, Newtonian and pseudoplastic fluids)

Most polymer melts and filled polymers show pseudoplastic or shear thinning behaviour and many equations/models have been proposed to describe the pseudoplasticity. However, the Power law equation is the most widely used and simple model to describe the pseudoplastic behaviour. Power law equation (also known as the Ostwald-de Waele equation) is given below:

$$\tau = K(\gamma)^n$$
 [3.8]

 $\tau =$ Shear stress K = Consistency index

r = Shear rate n = Power law index

K and n are material parameters. K, the consistency index is a measure of fluidity of the material. A high value of K indicates a very viscous material. The power law index (n) (also known as the index of pseudoplasticity) is a measure of the non-Newtonian behaviour of the material. The condition where n=1 indicates Newtonian behaviour whereas n < 1 shows non-Newtonian behaviour. The more that n falls below 1.0, the fluid is more non-Newtonian. Power law can also be written by including apparent viscosity (η_a), as follows

Apparent viscosity by definition:

$$\eta_a = \frac{\tau}{\frac{\gamma}{\gamma}}$$
 [3.9]

By combining equation (3.9) and Power law (equation, 3.8):

$$\eta_a = K(\gamma)^{n-1}$$
 [3.10]

Convert into log scale:

$$Log\eta_a = Log K + (n-1) \log \gamma$$
[3.11]

This indicates that a log-log plot of apparent viscosity (η_a) vs. shear rate (γ) will give a straight line for Power law fluids, with a negative gradient (n-1) if the polymer melt is pseudoplastic. This is shown graphically in Figure 3-7.



Figure 3-7 Viscosity changes with shear rate in Newtonian fluid and pseudoplastic fluids

3.2.2.2 Time-dependent fluids

In time-dependent fluids, flow properties such as viscosity will change with the time of shearing even at constant shear rate. These effects are caused due to the structural changes within the material during the shearing time.





A reduction in viscosity with time is known as thixotropy and is exhibited by some filled polymer systems and pastes. Increase in viscosity with time is known as rheopexy or negative thixotropy [62].

3.2.2.3 Viscoelastic fluids

Viscoelastic fluids have the properties of both solids and liquids. Polymer melts are viscoelastic in their response to an applied stress. Thus under certain conditions they will behave like a liquid and will continually deform whilst the stress is applied. Under other conditions the material behaves like an elastic solid and on the removal of the applied stress there will be some partial recovery of the deformation [62]. The viscosity behaviour of polymer melts is illustrated in Figure 3-9.



Figure 3-9 Viscoelastic behaviour of polymer melts [62]

3.3 Rheological measurements (Rheometry)

Rheometry is experimentation for useful measurements of the deformation and flow properties of materials. These measurements are required to describe the fundamental properties of material and to produce data for process engineering design purposes for products. Basically rheometers (viscometers) are used to measure the flow properties of materials. Broadly there are two types of rheometers for the measurement of shear flow and elongational flow properties [65]. However only shear flow property measurements, which are important in this study, will be discussed here.

There are mainly two basic types rheometers used for shear flow measurements which are rotational and capillary rheometers. The most common rotational viscometers are cone and plate viscometer, concentric viscometer and rotating bob viscometer. Even though these rheometers can be used to measure the shear flow properties, it is only practical to make measurements at shear rates much lower than those employed in processes such as extrusion and injection moulding. In contrast to rotational viscometers, capillary rheometers can be used at high shear rates which are more comparable with processing methods (extrusion and injection moulding). Therefore, because of the more practical applicability and the method used in this study, flow in capillary and capillary (extrusion) rheometers will be discussed here in detail.

3.3.1 Flow through capillary dies

It is important to study the flow properties of polymer melts at high shear rates used in polymer processing. The usual capillary rheometer consists of a heated barrel, at the bottom of which is fitted a small capillary die. The polymer melt is forced through the capillary under an applied pressure or flow rate. In flow through a capillary die, the shear stress and shear rate can be found as the equations given below [64].

Shear stress at the die wall:

$$\tau_{\rm w} = \frac{\Delta PR}{2L}$$
 [3.12]

 $\tau_w (N/m^2)$ = Shear stress at the wall

 $\Delta P (N/m^2)$ = Pressure drop through the capillary

R(m) = Capillary radius

L(m) = Capillary length

Shear rate at the wall:

$$\dot{\gamma} = \frac{4Q}{\pi R^3}$$
[3.13]

 r_{γ} (s⁻¹) = Apparent shear rate at the wall

 $Q(m^3/s) =$ Volume flow rate

These two equations were derived based on the following assumptions of laminar shear flow [64].

- There is no slip at the wall
- The fluid is time-independent (i.e. the flow pattern is constant all along the tube)
- The flow is isothermal
- The melt is incompressible

In practice there are some possible errors that might occur. Therefore, it is important to make some corrections to the above equations when flow properties of polymer melts are measured through capillary dies.

3.3.1.1 End corrections

When viscous fluids progress from the reservoir to the capillary, the pressure changes along the length of the capillary (illustrated in Figure 3-10).

As shown in Figure 3-10, pressure is assumed independent of position in the reservoir. There is then a linear change in pressure with respect to the axial position along the whole length of the capillary and the pressure drops to zero at the point of exit.



Figure 3-10 Theoretical pressure changes along a capillary die

However the situation of polymer melts is different from the above because of the viscoelastic nature of polymer melts. When polymer melt passes through capillary, the pressure changes as in the following figure.



Figure 3-11 Practical pressure changes of polymer melt along a capillary [63]

As shown in Figure 3-11, a substantial pressure drop at the die entry region and some degree of non linearity just down stream of the capillary entrance can be observed. Further at the die exit, the pressure is not zero.

The pressure drop at the entrance (the entrance effect) has been ascribed to a combination of two contributory effects: a viscous dissipation of energy due to the converging flow prior to entry into the capillary; chain uncoiling leading to storage of elastic energy, some which may be recoverable. However, analysis of experimental studies has suggested that commonly at least 95 % of the entrance effect in polymer melts is due to the storage of elastic energy [64]. Therefore, it is necessary to make corrections to pressure drop at the entrance of the die, otherwise it will cause the flow curves to be in serious error.

Bagley has suggested a method to overcome the entrance effect, referred to as the Bagley correction ([6]. In this method, pressure drop is measured at different shear rates using dies having different lengths but constant radius. The pressure drop is plotted against to length to radius ratio (L/R) for each shear rate, as shown in Figure 3-12.



Figure 3-12 Bagley plot for the end correction [62]

According to the Bagley correction, the true shear stress at the wall can be rearranged as shown in equation 3.13.

$$\tau_{\rm true} = \frac{\Delta PR}{2(L+eR)}$$
 [3.13]

 τ_{true} = True shear stress at the die wall

 ΔP = Pressure drop through the capillary

R = Capillary radius

L = Capillary length

e = Bagley correction factor

The value of e can be read-off from the negative intercept on the base line of the Bagley plot. Commonly an increase in shear rate increases the value of e up to a limiting value. In practice this method has difficulties; using dies of different lengths requires the extensive experimentation.

: '

Cogswell and Lamb [67] suggested an alternative method using a long die and a zero length die with same radius. In this method, pressure is measured using both dies (i.e. Long die and zero length die) at same shear rate. The pressure obtained with the die L/R=0 is assumed to embrace both entrance and exit corrections. Therefore true shear stress at the wall is given as:

$$\tau_{\rm true} = \frac{(\Delta P - P_0)R}{2L}$$
 [3.14]

 ΔP = Pressure drop in the long die

 $\Delta P_o =$ Pressure drop in the zero length die

R = Radius of the die

L = Length of the long die

3.3.1.2 Rabinowitsch correction

Apparent shear rate at the wall needs to be corrected in order to achieve the true shear rate, since the velocity profile in the capillary is more 'plug like' rather than parabolic. Rabinowitsch has suggested a correction for the apparent shear rate and it shows in the following equation [64].

$$\dot{yt} = \frac{3n+1}{4n} \frac{4Q}{\pi R^3}$$
[3.15]

 γt = True shear rate

n = Power law index

Q = Volume flow rate

R = Radius of the capillary die

3.4 Rheology of filled polymers

Use of mineral fillers in polymers is common, not only as inactive diluents or cost reducing materials but also increasingly as functional additives in polymer applications. The incorporation of particulate fillers into polymers gives rise to composites with different mechanical and rheological properties. Addition of fillers into molten polymers yields a complex fluid and their rheological properties will deviate from the original unmodified polymer. Hence it is important and necessary to study the rheological properties of the filled polymers in order to understand the processing of these filled composites.

Researchers have concerned their attention on studying the mechanical properties of filled polymer composites. In contrast, comparatively less research has been done to understand the rheological properties, especially advanced flow properties such as die swell, melt fracture and wall slip of filled polymer composites. It is well understood that filler type and concentration affect the shear viscosity. However, not only filler

type and volume fraction but also other filler characteristics such as filler size, size distribution and filler surface treatment will affect the melt flow properties.((4). A literature review of the rheology of clay filled PP nanocomposites will be discussed separately, section 4.2.3

The volume fraction of filler (filler concentration) is an important factor to evaluate the flow properties. Generally with increasing filler concentration, the shear viscosity is increased due to the increase of inter-particle and polymer-particle interactions [4] Kitano et al. [68] studied the viscosity variation with the filler volume fraction using filled polyethylene and PP and it was found that relative viscosity (η_r) was increased with filler loading.

However viscosity of filled polymer melts are affected not only by filler volume fraction but also filler characteristics such as particle size, shape and surface treatment [9, 70]. These filler characteristics influence both particle dispersion and the degree of immobilised polymer at the filler polymer interface. Therefore an empirical model was developed for the effect of filler volume fraction on viscosity of filled polymer systems considering the filler characteristics. This relationship is refereed to as Maron-Pierce relationship. [3, 70, 71]

$$\eta_{\rm r} = \left[1 - \frac{\phi}{\phi_{\rm max}}\right]^{-2}$$
 [3.16]

 η_r = relative viscosity of the composite

 ϕ = volume fraction of filler

 $\phi_{max} = maximum packing fraction$

 ϕ_{max} is a characteristic of the particulate filler and this represents the maximum volumetric packing efficiency of the additive particles. This parameter is dependent upon particle size, morphology and surface treatment.

Filler surfaces are modified by pre-treatment processes with the view of improving filler-polymer compatibility or interactions in filled polymer systems. Surface treatment is meant to help the polymer wet the filler and disperse it. However the extent of wetting and degree of adhesion are different for each polymer, filler and surface modifier combination [4].

Although the principal function of surface treatment of fillers is to enhance particle dispersion in the polymer matrix, most of the surface treatments modify the rheological behaviour, particularly melt viscosity of filled polymer systems [42, 69, 72, 73]. Wah et el. [74] studied the melt viscosity of talc filled PP and showed that the viscosity was decreased and dispersion quality was improved in the presence of titanate coupling agents.

3.5 Melt elasticity

Polymer melts are viscoelastic, showing both viscous and elastic responses to an applied stress. Elastic effects of polymer melts are very important in processing especially in shaping operations such as extrusion. The elasticity of the polymer melts arise as a result of the entanglements of polymer chains [62]. In the absence of stress, there are entanglements between polymer molecules that are randomly oriented. When the polymer is deformed under the applied stress there will be some disentanglement and orientation in the direction of the applied stress. On the removal of stress, chains will tend to return to their equilibrium, random-coil state and thus there will be a component of elastic recovery. The most important elastic effects in polymer melt flow which will be described here are die swell, and melt fracture.

3.5.1 Die swell

In extrusion processes, the extrudate cross section is greater than the die cross section and the phenomenon is known as die swell, sometimes known as the Barus effect. Die swell behaviour is shown by polymer melts especially in the extrusion processes and it is associated with the elasticity of the polymer melt. A number of theories have been proposed to explain die swell but the perhaps the most useful working
hypothesis is to assume that the molecules are oriented in the die and on the emergence into the atmosphere, when stress reduces to zero, recoiling takes place with a contraction in the direction of flow being offset by lateral expansion [64].

The amount of the die swell depends of the shear rate applied and the length to diameter ratio of the die [62] as illustrated in Figure 3-13 and 3-14.



Figure 3-13 Effect of shear rate on die swell [62]



Figure 3-14 Effect of length to diameter (L/D) ratio of the die on die swell [62]

As shown in Figure 3-13, die swell increases with an increase of shear rate. However maximum die swell appears to occur at a point a little below the visual onset of melt fracture. It has also been found that at fixed shear rate, die swell decreases with an increase in temperature [75].

Die swell decreases with the increase of die length as shown in the Figure 3-14. At low L/D values, die swell is occurred mainly due to elastic recovery of elongational stress at the entry of the die [66]. These stresses relax during the flow in die and hence the die swell decreases with increasing L/D ratio of the die.

3.5.2 Melt fracture

Melt fracture is a flow instability phenomenon occurring when polymer melts are extruded through a die at high shear rates. It is associated with the elastic property of a polymer melt [62]. The shear stress at which the onset of melt fracture appears on the extrudate surface is referred to as the critical shear stress (corresponding shear rate is known as critical shear rate). When melt fracture occurs the form of distortion varies widely; screw-thread like, some times rod-like cross sections are twisted into the form of spirals, and sometimes the disturbance is periodic.

A number of researchers have investigated mechanisms of melt fracture or 'elastic turbulence' of polymer melts and hence there are many theories that have been proposed for melt fracture. The widely accepted theory is that fracture occurs due to the high tensile stress at the entry of the die. If this stress exceeds the tensile strength of the polymer melts then melt fracture occurs [64]. Generally, an increase in temperature causes a large increase in the critical shear rate but has less effect on critical shear stress.

3.5.3 Melt elasticity of filled polymers

In contrast to the direct effect on melt viscosity, the influence of particulate additives on melt elasticity (i.e. die swell, melt fracture) has received rather less attention. The presence of particulate fillers has been shown to decrease the elasticity of the polymer melts, with increasing filler volume fraction [76]. It was reported that extrudate swell decreased with increasing volume fraction of glass bead in polypropylene/glass bead composites [77]. Die swell of PP/glass bead composites decreases non linearly with an increase of the filler volume fraction of glass bead because, with an increase of filler concentration, the relative movement of polymer chains would become constrained and hence this leads to the reduction of the elastic properties and subsequent die swell.

However, less attention has been received on melt-state elastic properties of clay filled PP nanocomposites, so that the current research study will investigate the effect of nano clay on elastic properties of PP-clay nanocomposites.

3.6 Wall slip behaviour

It is assumed that there is no slip at the wall when steady-state shear flow occurs in a die and most of the rheological equations obtained for capillary flow are based on a 'no slip' condition [64]. However it has been observed that above a critical value of shear stress, the polymer melt slips at the contact wall of the die [78]. Hatzikirakors and Dealy [79] also studied the wall slip behaviour of high density polyethylene (HDPE) using a sliding plate rheometer and found that HDPE slipped when the wall shear stress exceeds a critical value of 0.09 MPa.

When slip occurs, the flow of polymer melt through capillary become more plug like and Figure 3-15 shows the difference of the flow profile of slip and no-slip condition in the capillary. As shown in Figure 3-18, because of the slip at the wall, the velocity is not zero at the flow boundary and hence the shear stress at the wall is reduced, for a given volumetric flow. Wall slip effects are particularly important in polymer processing since the no-slip condition is a fundamental assumption for shear flow theory and hence it affects the calculation of viscous properties of polymer melts. It is specific relevance to predictive models used to processes such as extrusion and injection moulding [69].

Basically there are two main mechanisms that have been proposed for slippage of polymer melts at the die surface; adhesive failure at the polymer-wall interface and cohesive failure within the polymer but close to the wall [69, 80].



Figure 3-15 Flow profile under 'no slip' and 'slip' condition [60]

According to the first mechanism, wall slip occurs due to the adhesive failure at the polymer-wall interface when the shear stress is greater than the critical shear stress, which is a function of the work of adhesion [81-83]. Hatzikiriakos et al. [80] studied the wall slip behaviour of linear low density polyethylene (LLDPE) by applying a fluoropolymer coating to the die wall and found that the slip velocity was increased by coating the surface. Based on these results, more evidence was obtained that slip is the result of adhesive failure at the polymer-die wall interface.

3.6.1 Slip velocity

There are several methods to determine slip velocity at the die wall. However, the measurement of wall slip by the classical Mooney technique is well established [63, 84].

In this technique, capillary measurements are taken with a series of dies of constant length to radius ratio (L/R) but varying the radius of the die. A plot of the apparent shear rate against the reciprocal of die radius reveals any evidence of wall slip.

As shown in Figure 3-16, when slip occurs, this plot will give a straight line with a slope equal to four times the slip velocity. A horizontal plot indicates a no-slip condition.



Figure 3-16 Plot of apparent wall shear rate against 1/R at fixed shear stress and temperature

3.6.2 Wall slip of filled polymers

Very few studies have been carried out to study the effect of fillers and their characteristics on wall slip behaviour in filled thermoplastics. Most of the studies were concentrated on wall slip behaviour of unfilled Polyethylene (PE) and the effect of PE and die interface interaction on wall slip.

However, studies carried out previously at IPTME revealed the effect of fillers on wall slip behaviour. Khan studied the wall slip behaviour of talc filled PP using a capillary rheometer [60]. It was shown that slip velocity was reduced with an increase of talc concentration into PP. It was further found that the unfilled PP consistently showed wall slip and this was attributed to additives present in the virgin PP grade.

In another study, it was reported that unfilled PP used in the investigations of flame retardant $Mg(OH)_2$ additives also exhibited significant wall slip in the capillary rheometer experiments [61].

Very recently Haworth et al. [6] reported the wall slip behaviour of talc filled PP compounds. In their study, wall slip was observed in an unfilled grade of PP and the slip velocity was increased with shear stress, beyond the critical stress value. However a reduced slip velocity was observed in talc filled PP compounds. It was suggested that short chain amide molecules induce slip in unfilled PP at die the wall and the incorporation of talc restricts the migration of these additives onto the die wall boundary.

In another study, it was demonstrated that small amount of low molecular weight additives including stearic acid, stearamide and zinc stearate are effective in inducing slippage of polyethylene and polypropylene [5]. Same authors have shown that slippage was induced when carboxylic acid (stearic acid) is mixed with polyethylene. However, a reduced slippage was observed when particulate fillers, particularly polar fillers, are introduced into PE [29].

However, no literature has been found on wall slip behaviour of clay filled PP nanocomposites and the effect of low molecular weight additives containing polar groups on wall slip behaviour of PP-clay nanocomposites. Therefore in this research study, wall slip behaviour of PP-clay nanocomposites and the effect of additives will be studied.

4 CHAPTER: LITRATURE REVIEW: POLYMER CLAY NANOCOMPOSITES

4.1 Introduction

In general, particles are incorporated into polymers to improve the stiffness and toughness, to enhance their barrier properties, to improve their resistance to fire or simply to reduce the cost of the composite material. Nanocomposites are materials that comprise a dispersion of nano-meter size particles. Depending on the matrix nature, nanocomposites can be polymeric, ceramic or metallic. This section reviews only polymeric nanocomposites and they are a new class of composites that are particle filled polymers in which at least one dimension of the dispersed particles is in the nanometre range. Nanoparticles used in polymeric nanocomposites can be divided into three categories, defining according to the number of dimensions in nano-meter size; one dimension (platelets), two dimensions (nanotubes), three dimensions (spherical particles).

However, amongst all polymer nanocomposites, the nanocomposites based on layered silicates (clay) have attracted greatest interest in academic studies and industry because they often exhibit remarkable improvements in material properties, at very low loading levels (2-5 wt %), when compared to that of virgin polymers or conventional micro-scale composites. These property improvements include high modulus, increased strength, heat resistance, dimensional stability, barrier properties (to gases and liquids), flame retardance and increased biodegradability of biodegradable polymers. In addition to these property improvements, the polymer layered-silicate nanocomposites have an advantage over other nanocomposites because the clay minerals are readily available and their intercalation chemistry has been extensively researched [47, 85].

Although the intercalation of polymers into modified clay has long been known, the nanocomposites based on layered silicates gained momentum recently because of two major findings in the recent past. First, Kojima and co workers (Toyota Research Group) produced nylon-6/Montmorillonite (MMT) nanocomposites [11]. They found that the improvement of thermal and mechanical properties can be achieved with very

low amounts of clay. Secondly, Vaia et al. [12] observed the possibility of melt mixing of polymers with layered silicates without using organic solvents.

Commercial applications of Polymeric nanocomposites have been started recently and its market grows in 18.4% in annually [53]. Current consumption of polymer nanocomposite is about few kilo tons per annum but it is projected to increase to 500 kilotons per annum by 2009 [9]. The main applications of clay containing polymeric nanocomposites are automotive industry and growing demand for packaging, building and construction industry.

4.1.1 Nanocomposite structures

Depending on the nature of the components used (layered silicates, organic cation and polymer matrix) and the method of preparation, three main types of composites may be obtained when clay is mixed with a polymer [7, 8, 86]. Figure 4-1 illustrates the three main types of polymer clay composites.

(A) Micro-composites

When the polymer is unable to intercalate into the clay galleries, a phase separated composite is obtained (Figure 4-1-(a)). Properties of these composites lie in the same range as traditional micro-scale composites.

(B) Intercalated nanocomposites

When polymer intercalates into the clay galleries, but the clay stacks remain unchanged, the resulting structure with alternating polymer and clay, is known as an intercalated nanocomposite (Figure.4-1- (b))

(C) Exfoliated nanocomposites

In exfoliated or delaminated clay nanocomposites, polymer initially intercalates into the layered silicates. The clay particles are separated into their primary platelets (individual clay layers) and dispersed uniformly in a continuous polymer matrix.



Figure 4-1 Different types of polymer clay composite structures [8]

4.1.2 Preparative methods

Basically, preparative methods of polymer clay nanocomposites can be divided into three main groups, according to the starting materials and processing techniques.

(A) Intercalation of polymer or pre-polymer from solution

This is based on a solvent system in which the polymer or pre-polymer is soluble and the silicate layers are able to swell. The layered silicates are first swollen in a solvent and then polymer and layered silicate solutions are mixed. The polymer chains intercalate into the clay galleries and, when the solvent is evaporated, the intercalated structure remains, resulting in polymer-clay nanocomposites. This technique has been widely used with water-soluble polymers to produce nanocomposites based on poly(vinyl alcohol), poly(ethylene oxide) and poly(vinylpyrolidone). [45, 46].

(B) In-situ intercalative polymerisation method

In this method, the layered silicates are swollen within the liquid monomer or monomer solution. The polymer formation is occurs between the silicate layers. Polymerisation can be initiated by either heat or radiation, by the diffusion of a suitable initiator or by an organic initiator or catalyst fixed through cation exchange inside the interlayer, before the swelling step [7, 8]. Nanocomposites based on nylon-6/montmorillonite (MMT) have been obtained from this technique [7].

(C) Melt intercalation method

Organically modified layered silicates are mixed with the polymer matrix in the molten state. When polymer mixes with layered silicates, if layered silicates are sufficiently compatible with the chosen polymer, the polymer can diffuse into the interlayer space and form either an intercalated or an exfoliated nanocomposite structure. This method has great advantages, such as environmental desirability due to the non involvement of organic solvents. Also, it is compatible with current industrial processes like extrusion and injection moulding, over the other two methods. A range of nanocomposites, for example polystyrene/clay, PP/clay, nylon 6/clay, EPDM/clay and most of other polymer-clay nanocomposites, with a structure of intercalated to exfoliate can be obtained from this method [7, 8].

A large number of polymers can be used in nanocomposites preparation with layered silicates. They include polyolefins, such as PE, PP and ethylene-propylene co-polymer, vinyl polymers such as styrene, poly (methyl methacrylate), polyamides and elastomers. However in this section, PP-clay nanocomposites are reviewed in detail as this research is mainly based on this type of nanocomposite.

4.2 Polypropylene clay nanocomposites

Today, polypropylene is one of the most widely used polymers due to its overall low cost and versatile range of properties. PP-clay nanocomposites (PPCN) have been studied extensively since they showed improved properties such as mechanical, thermal and barrier properties at very low loading levels when compared to conventional composites. However the direct intercalation of PP into organically modified silicate galleries is not possible because PP does not have any polar groups in its backbone. Hence a great deal of research has been carried out to suitable methods to intercalate PP molecules into clay galleries and disperse them homogeneously in the PP matrix.

4.2.1 Preparation of PP-clay nanocomposites

Since PP does not contain any polar groups it was not thought that the preparation of PP-clay nanocomposites would be realised. However, overcoming this difficulty, Usuki et al. [21] first reported a novel approach to prepare PPCN using a functional oligomer (PP-OH) as a compatibiliser. In this study, PP-OH was intercalated between the layers of organically modified montmorillonite (OMMT) and this OMMT was melt mixed with PP to obtain the nanocomposites with an intercalated structure. Further studies by the same group reported the preparation of PP/OMMT nanocomposites by melt blending of PP, maleic anhydride grafted PP oligomer (PP-MA) and clays modified with stearylammonium using twin screw extruder [19]. In this study, two types of malice anhydride grafted PP oligomers containing different amounts of maleic anhydride were used to understand the miscibility effect of oligomers on clay dispersion in PP matrix. It was found that there are two important factors to achieve exfoliated and homogeneous dispersion of clay layers in PP matrix: the intercalation capability of the oligomers and their miscibility with PP.

Hasegawa et al. [17] also reported the intercalation capability of maleic anhydride grafted PP oligomers (PP-MA) into clay galleries and successfully synthesised PP-clay nanocomposites. PP-MA was melt mixed with organically modified clay and it was shown that interlayer spacing was increased, as the ratio of PP-MA increased. Clay which was intercalated with PP-MA was then melt blended with PP to form PP-clay nanocomposites. However clay particles became smaller and were dispersed uniformly in PP matrix when the ratio of PP-MA was increased. The same author prepared PP-clay hybrids by melt blending of maleic anhydride grafted PP and organophilic clay, similar to the functional oligomers [18]. Modified PP (PP-MA) and organically modified clay was melt blended using a twin screw extruder at 200 °C. In contrast to the previous method (using PP-MA oligomers), clay particles were completely exfoliated and dispersed into nano-meter size (clay platelets), as there was no diffraction peak shown in X-ray diffraction results for the nanocomposite

structure, and this was achieved with modified PP with small amount of maleic anhydride groups (0.2 wt. %).

Generally for the preparation of PP-clay nanocomposites (PPCN), the clay needs to convert into organophilic state by ion exchange (as described in section 2.3.3) with an alkyl ammonium ion and the use of compatibiliser is also important as PP is not directly compatible with even organophilic clay. There are two major preparative methods that have been identified for PPCN. In the first method, polyolefin oligomers with polar OH groups or maleic anhydride groups and maleic anhydride grafted PP are used as compatibilisers in melt mixing of PP and organically modified clay [17, 19, 21, 23]. In this method, driving force of the intercalation originates from the strong hydrogen bonding between the OH groups of the polyolefin oligomers or maleic anhydride group (or COOH group generated from the hydrolysis of the maleic group) and the oxygen atom of the silicates. The interlayer spacing of the clay increases and the interactions between layers of silicates become weakened. When the intercalated clay is mixed with PP under applied shear stress the oligomers contact with PP resulting in the intercalated or exfoliated nanocomposite structure, depending on the mixing technique and the degree of miscibility of compatibilisers with PP. In the second method, organophilic clay is dispersed in a solvent at first, unsaturated monomers are polymerised in between the silicate layers in a solvent environment to expand the interlayer spacing and to form a intercalated clay compatible to PP. When intercalated clay is blended with PP, the silicate layers can be dispersed well, in the PP matrix [87, 88]. However melt intercalation method has received increased attention since it is more environmentally friendly and it is compatible with industrial processing techniques (e.g. extrusion)

(A) Effect of secondary intercalant

Since complete exfoliation of clay particles has not yet been successfully achieved using modified PP compatibiliser (PP-MA), there are some other methods which involved secondary intercalant, that have been investigated to prepare PPCN structures. Liu and Wu [25] prepared PPCN via grafting-melt compounding by using a new kind of co-intercalated organophilic clay which had a higher interlayer spacing than the ordinary organically modified clay which is only modified by alkyl ammonium. The co-intercalation was achieved by mixing modified clay with epoxypropyl methacrylate monomer, an unsaturated molecule, using a Haake Reocorder mixer for 1hr. The nanocomposites prepared using the co-intercalated clay and PP in a twin screw extruder at 190 °C showed that a larger interlayer spacing and strong interaction caused by grafting can improve the dispersion effect of silicate layers in the PP matrix.

Wang and Wilkie [89] prepared PPCN by an in-situ reactive blending process in which PP, organically modified clay and maleic anhydride were melt mixed in Barbender mixer. However, although it showed an increase of interlayer spacing of clay, the clay is non-homogeneously dispersed throughout the polymer matrix, but the polymer is inserted into the clay gallery.

Generally PPCN is prepared with organically modified clay. However Tang et al. [90] studied a novel method of preparing PP-clay nanocomposites starting with pristine clay. In this method pristine clay (MMT) is ground with hexadecyl trimethyl ammonium bromide and then the mixed powder is melt blended with PP and maleic acid modified PP. The X-ray diffraction and high resolution electron microscopy technique showed the formation of a nanocomposite structure.

(B) Effect of compatibiliser (PP-MA) and modified clay

Basically to prepare PPCN by the direct melt intercalation method, PP, organically modified clay and compatibiliser are essential components as described earlier. However, the nature of the clay, type of compatibiliser and its characteristics (i.e. molecular weight and maleic anhydride content) also significantly affect the intercalation and exfoliation of clay in the PP matrix. Therefore more research studies have been carried-out in order to investigate their effect on PPCN preparation.

Garcia-Lepez et al. [22] have studied the effect of compatibiliser agent on clay dispersion in PPCN. In their work, two different compatibilisers, diethyl-malate grafted PP (PPgDEM) and maleic anhydride grafted PP (PP-MA) have been used. They showed that PPgDEM is less effective compared to that of reference PP-MA which is the most widely used compatibiliser for PPCN, since the DEM has a comparatively lower polarity and hence less effective interaction with the clay. On the other hand maleic anhydride, with a permanent dipole moment, is a better compatibilising agent because polar interactions are stronger with polar clay surfaces compared to that of DEM. As a result, mechanical properties of PPCN prepared with PP-MA are improved, relative to PPCN prepared with PPgDEM.

In another study PPCN were prepared using five different grades of maleic anhydride grafted PP, with a wide range of molecular weights and maleic anhydride contents ranging from 0.5 to 4.0 wt % [91]. Nanocomposite structures were evaluated by X-ray diffraction and transmission electronic microscopy techniques and it was found that high maleic anhydride content and low molecular weight PP-MA led to a better intercalation and dispersion of clay. All compatibilisers showed improved dispersion of clay when 3:1 weight ratio of PP-MA to clay was used, except one consisting of very high MA content and very low molecular weight. From their study, it was found that there are two important factors that are responsible for better exfoliation and homogeneous dispersion of clay layers in PP matrix: intercalation capability and miscibility with PP. However, the addition of lower molecular weight PP-MA or high loading of PP-MA had a negative effect on mechanical properties of PPCN.

A similar type of result has been obtained from another study that low molecular weight and high MA containing PP-MA is more effective for the preparation of PPCN structure. In the same study, PP-MA was partially replaced with nylon 6 and the resultant PPCN structures showed an increasing interlayer spacing of clay. However these structural changes did not significantly improve the mechanical properties of the PPCN [92].

Kawasumi and co workers prepared PPCN by adding PP-MA at a concentration three times higher than that of clay and obtained the exfoliated nanocomposite structure [19]. Kato et al. [23] also showed from their results that a 3:1 ratio of PP-MA to clay is the most effective combination and further showed that PP-MA should have an acid number more than 7 (acid number of PP-MA is defined as the amount of potassium hydroxide that will react with the anhydride groups in PP-MA). However in the same study, they pointed out that if the acid number is more than 52, phase separation occurs in the resulting composites, and as a result mechanical properties deteriorate significantly. Other studies also revealed that a 3:1 weight ratio of PP-MA and clay provides better intercalation and exfoliation of clay in PPCN structures. [17, 93, 94].

Perrin-Sarazin et al. has also performed a similar kind of study to examine the effect of clays modified with two different intercalant and coupling agents based on maleic anhydride grafted PP. In this study, it was shown that the thermal stability clay intercalant is an important factor on clay dispersion in PPCN structure since it can lead to platelets collapse and clay particles aggregation due to thermal degradation of intercalant. In addition to the thermal stability of clay intercalant, they showed, as previous studies, the use of PP-MA with low molecular weight and high grafting content can lead to a relatively good, uniform intercalation but with no signs of exfoliation. However, in contrast to other studies [91, 95] the MA grafting content is very much higher (3.8 wt %) in this compatibiliser. The lack of miscibility of this PP-MA, due to high maleic anhydride ratio, with PP was the reason for the lack of exfoliation of clay in the PP matrix. However, a certain degree of exfoliation of clay was observed in PPCN structures using PP-MA with high molecular weight and low grafting content (0.5 wt %).

Merchant and Jayaraman investigated the importance of maleic anhydride distribution in PP-MA for the dispersion of modified clay in PP matrix [96]. Maleic anhydride can exist in three distinct forms in PP-MA such as un-reacted small molecules, as an oligomer and attached or bound to polymer chains. They found that the degree of exfoliation of clay in PP melt is sensitive to the distribution of maleic anhydride in PP-MA and it was also shown that the compatibiliser is more effective when a greater amount of bound maleic anhydride is present in PP-MA.

As shown in a number of studies, PP-MA and its characteristics are vital to achieve the intercalation and subsequent exfoliation of clay in PPCN structures. However a higher concentration of PP-MA has a negative effect on mechanical properties of PPCN. Therefore investigations were continued by researchers to prepare PPCN with a reduced concentration of PP-MA.

Zhang et el. [28] reported a new way of synthesising PP-clay nanocomposite structures with the help of swelling agents, reducing the PP-MA content in nanocomposite structures. In this study, organo-clay was first treated with a swelling agent (maleic anhydride) and then with a co-swelling agent. The resulting modified organophilic clay has an interlayer spacing between pristine clay (unmodified clay) and organophilic clay. The swollen clay was then melt blended with PP-MA to produce pre-intercalated composite and finally it was melt blended with PP to obtain PPCN. From X-ray diffraction and TEM results it was suggested that PPCN can be synthesised with the aid of a swelling agent using a small amount of PP-MA with a lower acid value. The final PP-MA has not become very low since PP-MA to clay ratio was 1:3. However, the overall effects of the swelling agent and the co-swelling agent on mechanical properties of PPCN were not reported in this publication.

The same author prepared polypropylene-clay nanocomposites by in-situ graftingintercalating in the melt state [27]. The organophilic clay was mixed with MA, an initiator (diphenyl-amine-2-carboxylic acid) and acetic ester in acetone to obtain modified organophilic clay. The X-ray diffraction results showed that it has a higher interlayer spacing compared to that of organophilic clay. Modified organophilic clay was melt blended with PP in an internal mixer to obtain a masterbatch of in-situ grafting-intercalating composite and then it was diluted with PP to obtain the final PPCN with different clay loading levels. It was suggested that grafting took place inside the gallery space of clay and the resulting maleic anhydride grafted PP further increased the interlayer spacing of clay. The PPCN prepared from this method showed the fully exfoliated nanocomposite structure as shown from X-ray diffraction and TEM techniques. However, in contrast to the previous method (using swelling agent), this method was able to reduce the PP-MA to clay ratio to 2 :1 The PPCN prepared with this new technique showed a good thermal stability and increased storage modulus, indicating the clay has a reinforcing effect in the PP matrix.

Merinska et al. [97] investigated a new method of preparing PPCN by co-intercalation of octadecylamine (ODA) and stearic acid (STA) into sodium montmorillonite (unmodified clay). In this method, a blend of unmodified clay (MMT), ODA and STA was prepared with different ratio of ODA to STA in a Thermomix laboratory mixer. X-ray diffraction results revealed that the co-intercalation process has increased the interlayer spacing significantly in comparison to MMT. PPCN was then prepared by melt blending of PP with the co-intercalated clay (blend of MMT, ODA and STA) in the presence of maleic anhydride grafted PP (PP-MA). The clay to PP-MA ratio was 1:1 for all nanocomposite structures. PPCN prepared by this method showed that lowest ratio of ODA and STA in co-intercalated clay improves the degree of exfoliation. However, the resultant nanocomposite properties are greatly influenced by the ODA and STA concentration in nanocomposite structures.

Wang et al. [98] also demonstrated a new approach for preparing PP-clay nanocomposites using ammonium terminated PP (PP-t-NH₄⁺CI⁻) instead of conventional maleic anhydride grafted PP. In this preparative method, PP-t-NH₄Cl⁻ powder and pristine Na-montmorillonite were mixed together and then the mixed powder was heated at 190 °C under vacuum to make the hybrid of PP-t-NH₃/MMT by ion exchanging the Na⁺ ion in clay with PP-t-NH₃⁺. The binary hybrid was then melt blended with PP to make the PPCN. The PPCN prepared by this method has an exfoliated structure. From these results it was shown that an alkyl ammonium intercalant was not needed to promote compatibility between ammonium terminated PP (PP-t-NH₃⁺) and pristine clay which offers significant material advantages such as eliminate thermal instability of alkyl ammonium intercalant during high temperature melt processing.

From all these studies, it has been shown that the intercalant used to modify the pristine clay and the compatibiliser based on maleic anhydride grafted PP and its properties play an important role for the intercalation and subsequent exfoliation of clay in PPCN structure.

(C) Effect of polymer matrix

However, fewer studies have reported the effect of PP matrix on intercalation and exfoliation behaviour of clay in PPCN and properties of PPCN. Very recently Gianelli et al. [99] studied the effect of PP matrix, particularly molecular weight of PP, on PPCN structure and its properties. Commercially available PP (homopolymer) and copolymer based on ethylene propylene rubber possessing different melt flow index (MFI) were used to prepare PPCN in this study. They reported that delamination of organophilic clay was enhanced during the melt blending process when low molecular weight homo-polymer and co-polymer were used.

However this result is in contrast with the study carried out on polyamide 6-clay nanocomposites where the delamination of clay was improved with a high molecular weight of polyamide matrix, indicating that larger shear stress (due to high molecular weight of the polyamide matrix) during the extrusion process improved delamination [100]. However in PPCN, Gianelli et al. [99] pointed out that organophilic environment created by combination of organic cation and PP-MA within clay layers drives exfoliation through a thermal diffusion process, implying a negligible effect from matrix molecular weight.

(D) Effect of process conditions

Most of the studies on preparation of PP-clay nanocomposites have focused on the chemical modification of clay and improvements in compatibility between organically modified clay and PP. However few studies have reported how processing conditions affect the PPCN structure.

Dolgovskij et al. [26] studied the effect of mixer type on clay dispersion in nanocomposite structure. PPCN was prepared by melt blending in five different mixers: two lab-scale internal mixers, a co-rotating vertical twin screw mixer, a 30 mm co-rotating twin screw extruder and a multi layer extrusion system. In their study, the effectiveness of each mixer on clay dispersion and mechanical properties was evaluated. They found that the effectiveness of clay dispersion was affected by both the shear stress and the residence time in the extruder.

Very recently Modesty et al. [101] reported the effect of processing conditions on morphology and mechanical properties of PPCN. PP-clay nanocomposites were prepared by a melt blending technique using an intermeshing co-rotating twin screw extruder. The extrusion was carried out at two different barrel temperatures and two different screw speeds (250 and 350 rpm). Results obtained from this study showed that, in contrast to the study reported by Dolgoviski et al. [26], shear stress exerted on the polymer is a much more positive influence on the extent of intercalation and delamination than the residence time. Therefore improved intercalation and exfoliated PPCN structures were obtained when a higher screw speed and lower barrel temperature were used during the extrusion process. However it was also shown that, even with optimum processing conditions, a high degree of intercalation and exfoliation was achieved only in the presence of strong compatibility between clay and PP.

4.2.2 Characterization techniques

In clay containing polymeric nanocomposites, the extent of intercalalation and the degree of exfoliation of clay are the key to achieving good performances of nanocomposites. Generally nanocomposite structures have typically been characterised by using X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. In addition to these common techniques, nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infrared spectroscopy (FTIR) techniques have also been used to characterise nanocomposite structures.

4.2.2.1 X-ray diffraction (XRD)

X-rays are electromagnetic radiation with wavelengths of between 0.1-10 Å. The X-ray diffraction method, in which the intensity of the diffracted X-rays is measured as a function of the diffracted angle, can be used to study the clay structures in polymer matrixes. XRD is the most commonly used technique to study the formation of polymer clay nanocomposite structure [86, 102-105].

From this technique, the interlayer spacing (d_{001}) is commonly determined from the X-ray diffraction spectrum as arbitrary intensity versus diffraction angle (θ). The interlayer spacing is calculated from Bragg's law: $d_{001} = n \mathcal{N}(2\sin\theta)$. Where n is an integer and λ is the X-ray wavelength; most X-ray machines use Cu-K α_1 radiation with 0.154 nm wavelength. The diffraction peak position (2θ) relates to the inter layer spacing whereas the intensity of the diffraction peak relates to the concentration of intercalated clay particles [106]. By monitoring the position, shape and intensity of diffraction peak, the polymer clay nanocomposite structure (i.e. intercalated or exfoliated) can be identified, for example shifting of X-ray diffraction peak to a lower Bragg angle (2θ) shows the intercalated nanocomposite structure. Usually in PP-clay nanocomposites, intercalation of PP-MA into clay galleries increases the interlayer spacing (d spacing) in comparison with the spacing of the organophilic clay used. Therefore the diffraction peak is shifted to a lower Bragg angle value. On the other hand, in an exfoliated structure, no diffraction peaks are visible in the X-ray diffractograms since at such large spacing (i.e. exceeding 8 nm) reduces the scattering intensity.

Although the XRD technique is used to measure the interlayer spacing of clay and to identify the nanocomposite structure (i.e. either intercalated or exfoliated), a little information can be obtained about the spatial distribution of the clay layers and any structural non-homogeneities in PPCN. Therefore any conclusion concerning the mechanism of nanocomposite formation and their structure based on solely on XRD patterns are only tentative.

4.2.2.2 Transmission electron microscopy (TEM)

TEM allows a qualitative understanding of internal structure and spatial distribution of clay in PP [7]. In this technique, a beam of electron transmits through a thin section of a sample, which is obtained using a microtome, and the transmitted beam is projected on to a screen where the image of the sample can be observed. However, TEM also offers a direct method for confirming the X-ray diffraction data and at low magnification, it can be used to evaluate the uniformity of clay particle dispersion. On the other hand from higher magnification of TEM images, presence of intercalated and exfoliated clay particles in the nanocomposite structures can be identified.

Dennis and co-workers suggested a method for quantification of TEM images [107]. In this method micrographs obtained with a magnification of 130,000 were covered with a mask in which twelve squares of 2.5 cm x 2.5 cm were cut out. The degree of clay dispersion was expressed as number of clay particles, either clay platelets or small clay stacks, per cm². Dispersion of clay obtained from this method was found to correlate well with tensile modulus.

Figure 4-2 illustrates the both typical X-ray diffractograms and TEM images of different types of nanocomposite structures. Morgan and Gilman [108] analysed several polymer-clay nanocomposites by TEM and XRD techniques and showed that the overall nano-scale dispersion in polymer matrix is best described by TEM, especially when mixed clay structure (i.e. intercalated and exfoliated) is present. XRD is useful to measure interlayer spacing of clay. However they pointed out that XRD is not a stand-alone technique and it should be used with TEM together. Therefore both the XRD and TEM techniques are essential to characterise the PPCN structure overall.



Figure 4-2 Typical WAXD patterns and TEM images for different nanocomposites [7]

4.2.2.3 Other characterization techniques

Although X-ray diffraction and TEM techniques are the main methods to identify the clay containing polymeric nanocomposite in terms of intercalation and exfoliation, some other techniques such as NMR, atomic force microscopy and FTIR can also be used to characterise the nanocomposite structure.

Very recently FTIR technique is used for characterisation of polymer-clay nanocomposites [109, 110]. This technique can be used to examine the interactions between clay layers, the intercalating agent and polymer since Si-O stretching vibration is sensitive to interactions [110]

4.2.3 Rheology and processing of PPCN

In order to understand the processability of the nanocomposites, it is necessary to understand the detailed rheological behaviour of these materials in the molten state. Understanding the rheological properties of the nanocomposite melts is not only important in gaining a fundamental knowledge of processability but is also helpful to understand the structure-property relationships of these materials. However, in contrast to the preparation and properties of clay filed PP nanocomposites, little attention has been given to the rheological behaviour of PPCN melt.

The rheological properties of in-situ polymerised nanocomposites with end-tethered polymer chains were first described by Krisnamoorti and Giannels [111]. From their study, it was shown that the flow behaviour of nylon-6 based nanocomposites differed significantly from that of the corresponding matrix.

Cho et al. [112] investigated the flow behaviour of modified clay filled PP nanocomposites. In this study, nanocomposites were prepared in a two step compounding process. First, organoclay masterbatch concentrate was prepared, then it was let down by PP/compatibiliser mixer into a nanocomposite with 6 wt % of clay loading. They found that nanocomposite melt showed a shear thinning non-Newtonian behaviour at high shear rates and further reported that shear viscosity of PPCN melt is same as the pure PP.

In another study, the linear and non linear rheological behaviour of PP-clay nanocomposite was investigated [113]. PP-clay nanocomposites prepared by melt blending of PP and organically modified clay in the presence of compatibiliser were analysed using a parallel plate rheometer in both linear and non linear shear rate ranges. The increase of storage moduli, loss moduli and dynamic viscosities of PPCN were reported in this study. The steady shear viscosity (which is useful information on the material processibility) is much higher than the pure PP at low shear rates. However, at high shear rates, the shear viscosities of the nanocomposites are comparable with, or even lower than that of pure PP, since clay particles are oriented to the flow direction.

Fornes et al. [100] have conducted steady shear capillary experiments over a large range of shear rates for pure nylon-6 with different molecular weights and their nanocomposites reinforced with clay. The steady shear capillary data showed that nylon-6-clay nanocomposites, based on high and medium molecular weights, exhibited lower viscosities compared to their pure polymer, whereas the viscosity of low molecular weight nylon-6 based nanocomposites was higher than its pure matrix. It was suggested that the lower shear viscosity for nanocomposites based on high and medium molecular weight than their matrices is due to higher degree of exfoliation and smaller clay particles. As a result smaller clay particles in nanometre scale are easily aligned during the shear flow. The nanocomposite based on low molecular weight showed higher viscosity due to the presence of large percent of non-exfoliated clay particles.

The rheological properties of PP based nanoclay compounds were studied at low and high shear rates using rotational and capillary rheometers respectively [114]. It was showed that, at low shear rates, the viscosity of PP nanocomposites was significantly higher than that of pure PP and displayed more significant shear thinning behaviour. However in capillary rheometry experiments (high shear rates), the shear viscosity of PP-clay nanocomposites was comparable with pure PP or slightly lower than that of PP alone.

(A) Relationship between rheology and clay dispersion

Rheological properties (at low shear rates) of particulate filled polymer melts are sensitive to the particle size, particle shape and therefore melt rheology can be used to evaluate the dispersion of nano-particles in melt state. In several research papers, melt rheology has been discussed to characterise the dispersion of clay particles in nanocomposite structure. Zhu and Xanthos studied the effect of processing conditions and mixing protocols on the structure of PPCN by melt rheology [115]. In this study, two screw configurations (high shear screw and low shear screw) and two different mixing methods (two step and single step mixing) were used to compound the materials. Melt flow index (MFI) measurements were used to study the melt rheology and morphology of the melt compounded PPCN. It was found that MFI (which is a low shear rate experiment) is an appropriate method to comparatively study the exfoliation of clay particles in nanocomposite structures.

Wagner and Reisinger have developed a novel method based on melt rheology to compare the degree of exfoliation in nanocomposites [116]. In this study, poly (butylene terephthalate)-clay nanocomposites prepared with different organically modified clay showed a shear thinning behaviour at shear rate range between 0.1 and 100 s⁻¹. It was revealed that the shear thinning exponent (n) is a semi-quantitative measure of the degree of exfoliation and it is consistent with mechanical properties measured since mechanical properties depend on exfoliation of clay particles in the nanocomposite structure. They also pointed out that this method can be used for a direct comparison of the degree of exfoliation in nanocomposite structures prepared by different conditions such as different intercalants, different compounding processes and different compatibilisers.

4.2.4 Properties of PP-clay nanocomposites

Nanocomposites consisting of a polymer and layered silicates (clay) frequently exhibit remarkably improved mechanical and material properties when compared to conventional composites or to pristine polymer. These property improvements in nanocomposites are achieved at very low loading levels of clay (less than 5 wt. %) whereas in the case of conventional composites higher filler content (typically more than 20 % by volume) is generally required to achieve the same property improvement. Improvement of nanocomposites based on clay includes higher modulus, increased strength and heat resistance, decreased gas permeability and flammability [7, 8, 86]. Reason for these property improvements are exfoliation of clay particles into smaller clay stacks, resulting in higher aspect ratio and high surface area for a given clay percentage and strong interfacial interaction between polymer matrix and clay.

However in this section, mechanical properties and barrier properties of PP-clay nanocomposites are reviewed, as these are generally important in PP-clay nanocomposite applications.

4.2.4.1 Mechanical properties

It has been found by many researchers that mechanical properties of PP are increased when nanocomposites are prepared with organically modified clay. The main reason for the mechanical property improvement is high aspect ratio of dispersed clay particles in PP matrix and high surface area resulting in improved interaction between clay and polymer matrix. Improvement of mechanical properties in PP-clay nanocomposites was looked at in detail by many researchers after successful preparation of PA6-clay nanocomposites and demonstrated their excellent mechanical and thermal properties, compared to that of pure PA6, at very low loading levels of clay. [10, 117-119].

Kawasumi et al. [19] compared the storage modulus of PPCN with PP-clay microcomposites. In their study, PPCN prepared by simple melt mixing of PP, PP-MA and modified clay were compared with PP-clay micro-composites prepared with only PP and clay. The dynamic storage moduli of PPCN are higher than that of PP-clay microcomposites over the temperature range tested.

Hasegawa et al. [18] also reported a similar type of study by preparing PP-clay hybrids using maleic anhydride modified PP oligomer as a compatibiliser. The dynamic storage moduli of all PP-clay hybrids prepared using different ratios of clay to compatibiliser were higher than that of pure PP up to 130 °C, indicating the reinforcement effect of clay. It was also shown that the tensile modulus of PP-clay hybrid was increased when the compatibiliser ratio was increased in the composite and tensile strength was almost equivalent to that of pure PP. However elongation of hybrids was decreased than pure PP, showing brittle fracture in comparison with PP. The same author and his group prepared PP-clay hybrids based on modified PP (maleic anhydride grafted PP), with a small amount of maleic anhydride groups, and organophilic clay and they were successful in dispersing clay particles into nanometre range in the matrix of modified PP. The tensile modulus and strength were increased with the increase of clay content in PP-clay hybrid, compared to that of unmodified PP [17].

Nam et al. [20] also studied the dynamic mechanical properties of PPCN having different percentages of modified clay. They reported that storage modulus of all

PPCN were increased with clay content over the investigated temperature range. This indicates the elastic response of PP towards deformation is strongly influenced by the presence of organically modified clay.

The tensile modulus of polymeric materials has been shown to be remarkably improved when nanocomposites are formed with layered silicates. There are number of studies that reported the tensile properties as a function of clay in PPCN. Nam at el. [120] compared the tensile properties of PPCN containing compatibiliser with PP/clay micro-composites. They showed that there is a sharp increase in tensile modulus in nanocomposites for very small clay loadings (< 3 wt. %) followed by a much slower increase beyond a clay loading of 4 wt. %. On the other hand in conventional PP/clay composites, the tensile modulus does not exhibit much improvement as much as in PPCN. In PPCN, the MA functional groups effectively transfer the stress from polymer matrix to the inorganic clay which results in a higher rate of increase in tensile properties, with clay content.

Richert et al. [121] investigated the effect of compatibiliser and organic modification of clay on mechanical properties of PPCN and revealed that considerable tensile property enhancement could be achieved only when appropriate PP-MA compatibiliser and organically modified clay is used. In another study, PPCN were prepared by using PP and organo clay co-intercalated with epoxy propyl methacrylate and showed that with an increase of co-intercalated organo clay, the tensile strength and modulus of the PPCN rapidly increased. However, the trend is less pronounced when the clay content increases beyond 5 wt % [25]. In the same study they noticed that the notched Izod impact strength of the PPCN was almost constant with an increase of clay content.

In another study, Vaxman prepared PPCN using different compatibilisers such as PP-MA, maleic anhydride modified ethylene vinyl acetate (EVA-MA), EPDM-MA, EPR-MA and ethylene octane grafted MA, and studied the effect of each compatibiliser on mechanical properties [122]. It was found that the PPCN prepared with PP-MA has a higher tensile strength and flexural modulus compared to that of all other PPCN. This is attributed to better clay dispersion in PP because of the compatibility of PP-MA with PP is high compared to other compatibilisers.

The effect of molecular weight and maleic anhydride content in PP-MA on mechanical properties has also been studied by Hua Wang and co-workers [92]. PPCN were prepared using three different PP-MA having different molecular weights and MA contents. They reported that low molecular weight and high MA content leads to a better interaction with clay. However, addition of low molecular weight PP-MA has a negative impact on mechanical properties whereas addition of high molecular weight PP-MA can improve both stiffness and toughness of PPCN.

However, from another study it was reported that beyond a certain concentration of PP-MA, the mechanical properties of PPCN were deteriorated [24]. In their study PPclay nanocomposites prepared with different concentration of PP-MA were investigated for mechanical properties, particularly tensile modulus as a function of compatibiliser concentration. It was found that tensile modulus of PP-clay nanocomposites showed a decreasing trend when compatibiliser content was increased beyond a certain concentration (about 10 wt. %). From this study, they pointed out that moderate concentration of compatibiliser is important to achieve the improved mechanical properties and when increased PP-MA content, incompatible blends are resulted, causing negative impact on mechanical properties.

From these studies, it can generally be seen that mechanical properties are improved in PP-clay nanocomposites compared to either pure PP or conventional type PP-clay micro-composites when maleic anhydride grafted PP is incorporated as a functionalised compatibiliser, since exfoliation of clay particles to a nanometre range is key to achieve improved mechanical properties. However, the concentration of PP-MA and its characteristics (molecular weight and maleic anhydride content) have a significant impact on mechanical properties and thus selecting an appropriate PP-MA is an important factor to improve the mechanical properties of PPCN.

Since the processing parameters also affect the dispersion of clay particles, as with the compatibiliser, Modesti et al. [101] studied the effect of processing conditions on mechanical properties of PPCN. PP-clay nanocomposites were prepared with a melt blending technique using a twin screw extruder at low and high shear intensity configurations, with two different barrel temperatures (high and low). All nanocomposites prepared showed a significant improvement with respect to unfilled PP and this enhancement was strictly related to the processing conditions and the

presence of compatibiliser. The tensile modulus results showed that the highest increase was obtained when PP was melt blended with clay at high shear rate, since clay particles are separated apart each other more effectively at high shear rates whilst higher tensile modulus was obtained at the lower barrel temperature profile. However the effect of processing conditions on yield stress and strain was not significant whilst a significant improvement on impact strength was reported on all PP nanocomposites prepared, in comparison with unfilled PP

Peltola et al. [114] studied the effect of rotational speed of a twin screw extruder on nanocomposite structure, rheological and mechanical properties of PPCN. Nanocomposite structures were prepared by melt blending of PP granules, coupling agent (PP-MA) and clay using co-rotating twin screw extruder at three different screw speeds: 200, 500 and 1000rpm. They showed the effect of screw speed on clay dispersion in nanocomposite structure from the TEM results and it was indicated that a higher rate of extrusion (higher screw speed) led to a more exfoliated structure. By adding 5 wt % nanoclay in PP, the stiffness of the material was improved by 10-20 % but yield strain decreased and tensile strength remained unchanged. However in contrast to the previous study by Modesti et al. [101], although better exfoliation was achieved with high screw speed, this has no significant effect on mechanical properties of PP-clay nanocomposites [114].

4.2.4.2 Gas barrier properties

Clays are believed to increase the barrier properties in polymers by creating a much more tortuous path that retards the progress of the gas molecule through the matrix resin.



Figure 4-3 Proposed model for the 'torturous zigzag diffusion path' in an exfoliated polymer-clay nanocomposite [7]

Figure 4-3 shows the proposed schematic diagram of forming tortuous path in polymer layered silicates nanocomposites. The direct benefit of the formation of such a path is clearly observed in polyimide/clay nanocomposites by dramatically improved barrier properties [11]. The polyimide /clay nanocomposite with a small fraction of organically modified clay exhibited reduction in the permeability of small gasses such as O_2 , H_2O , CO_2 and ethyl acetate vapours [123].

5 CHAPTER: MATERIALS AND EXPERIMENTAL PROCEDURES

5.1 Materials

In this research study, three grades of PP, two grades of PP functionalised (maleic anhydride) compatibilisers, two types of montmorillonite clays (unmodified and modified) and two different types of short chain amide molecules (primary and secondary amides) were used to prepare either PP-clay nanocomposites (PPCN) or PP-clay micro-composites (PPCC).

5.1.1 Polymers

Two commercial grades of PP; HB671 and HB306 supplied by Borealis were used in most of this study. Khan and Guinebaud showed from their studies that virgin PP homopolymer consistently showed wall slip behaviour and it was suggested that it could be due to polar additives present in PP homopolymer. [60, 61]. The above two PP grades have been selected in such a way that one grade contains slip additives (as in previous studies) but the other does not. The other properties are almost the same according to manufacturer. These two grades were used to study the effect of low molecular weight polar additives on nanocomposite structure and flow behaviour of PPCN.

HB671 is a nucleated PP homopolymer and does not contain any additives. The melt flow index (MFI) of this PP grade is 2g/10 min. when tested at 230 °C using 2.16 kg. It is primarily used for extrusion and thermoforming. Some general applications of this grade are high transparency trays and cups, blister packaging and thin wall packaging. The other PP grade, HB306 is also a nucleated PP homopolymer and MFI is same as the HB671, but in contrast to HB671, it does contain low molecular weight polar additives; erucamide and glycerol monostearate (GMS) as slip promoting additive and antistatic agent respectively according to manufacturer. Figure 5-1 illustrates the chemical structures of erucamide and GMS.

$CH_3(CH_2)_7CH=CH(CH_2)_{11}CONH_2 \qquad CH_3-(CH_2)_{16}C(O)-O-CH_2-CHOH-CH_2OH$

(a) Erucamide (b) GMS

Figure 5-1 Structural formulae of erucamide and glycerol monostearate (GMS)

Erucamide is a primary amide, derived from erucic fatty acid and contains a single unsaturation. GMS is a monoester and it is a common internal antistatic agent for PP.

Table 5-1 Manufacturer's technical data for each PP grade

Product name	HB671 TF	НВ306 МО	HP510 M	Test method
Product code	PP1	PP2	PP3	
Physical form	Pellets	Pellets	Pellets	
MFI (230 °C, 2.16 kg.), (g/10 min.)	2	2	9	ISO 113
Density (g/cm ³)	0.905	0.908	0.900	ISO 118
Tensile modulus (MPa)	1700	1450	1500	1SO 527-3
Tensile stress at yield (MPa)	38	34.5	34	1SO 527-3
Tensile strain at yield (%)	8	9	13	1SO 527-3

The technical data sheets obtained from the manufacturer are shown in Appendix A for more information.

In addition to the above two PP grades, another PP grade; HB510 which has a comparatively higher MFI value and does not contain any low molecular weight polar additives has been selected to study the matrix molecular weight effect on PPCN structure. HP510 supplied by Basell is also a homopolymer particularly suited for the extrusion of cast films. Table 5-1 summarises the technical data for each PP grade.

5.1.2 Functionalised compatibilisers

Two grades of maleic anhydride grafted PP (PP-MA); Polybond 3200 and Polybond 3002 supplied by Crompton Corporation have been used as functionalised PP based compatibilisers for the preparation of PP-clay nanocomposites.

Product name	Polybond 3002	Polybond 3200	Test method
Product code	PM	PB	
Physical form	Pellets	Pellets	
MFI (190 °C, 2.16 kg), (g/10 min.)	7	110	ASTMD1238
Density (g/cm ³)	0.91	0.91	ASTM D792
Maleic anhydride level (wt. %)	0.2	1.0	
Melting point (°C)	160-170	160-170	DSC

Table 5-2 Manufacturer's technical of	data for two PP-MA grades
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These two grades were selected mainly to study the effect of molecular weight of PP-MA and maleic anhydride grafted level hence functional group concentration in PP-MA on PPCN structure. Polybond 3200 (PB) shows higher MFI (lower molecular weight) value and has a higher grafting level of MA. On the other hand Polybond 3002 (PM) shows a lower MFI value (higher molecular weight) and lower grafting level of MA. Table 5-2 summarises the properties of the two PP-MA grades used in this study.

5.1.3 Clay

Natural montmorillonite type clay was used in this research study. Montmorillonite clay modified organically with dimethyl dihydrogenated tallow (Cloisite 15A) was supplied by Southern Clay Products. This Cloisite 15A grade was selected based on comparatively higher thermal stability of organic modifier and also it is a common clay grade to produce PPCN. Closite Na, unmodified montmorillonite supplied by the same supplier was also used as the reference. Table 5-3 shows the properties of the two grades of montmorillonite type clay.

Product name	Cloisite Na	Cloisite 15A
Product code	MMT	OMMT
Organic modifier	none	2M2HT
Cation exchange capacity (meq/100g)	92.6	-
Modification concentration (meq/100g)		125
Dry particle size (µm, by volume)	90% less than 13	90% less than 13
Density (g/cm ³)	2.86	1.66
Packed bulk density (g/cm ³)	0.32	0.30
Moisture (%)	<2	<2
Inter layer spacing, d ₀₀₁ , (Å)	11.7	31.5

Table 5-3 Properties of montmorillonite clay

The structure of the organic modifier is shown in Figure 5-2.

$$CH_3
|
CH_3 - N^+ - HT
|
HT$$

HT: Hydrogenated tallow

Figure 5-2 Structure of dimethyl dihydrogenated tallow (2M2H)

5.1.4 Short chain amide molecules

Two amide types of slip promoting agents; erucamide and stearyl erucamide supplied by Akzo Nobel Polymer Chemicals were used in this study. Erucamide (13-cis docosenamide), a primary amide and derived from erucic acid, has been selected to study the effect of this low molecular weight polar additive on nanocomposite structure.

Table 5-4 Properties of a	amide type slip	promoting additives
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Product name	Erucamide	Stearyl erucamide
Product code	AM	SE
Molecular weight	337	589
Appearance	White powder	Pastilles
Free acid (%)	0.1	1.9
Moisture (%)	0.02	0.1
Melting point (°C)	82	72

Erucamide has a single unsaturation and the chemical structure is shown in Figure 5-1. Steryl erucamide (secondary amide) was selected to study the effect of secondary amide molecules which has higher molecular weight compared to that of erucamide. Both these low molecular weight amide type additives are generally used to improve processing behaviour and end-performance by reducing the friction and adhesion forces between polymer and processing equipment and polymer to polymer surfaces, especially in polyolefin film and moulding applications, since they migrate onto the surface and form an amide rich layer when the artefact cools down. Table 5-4 shows the properties of the two types of short chain amide molecules.

5.2 Characterisation of materials

In order to characterise the materials used in this study, a number of techniques such as melt flow index (MFI), chromatography, spectroscopy, microscopy and thermal analysis methods have been employed.

5.2.1 Melt flow index (MFI)

The MFI of the all PP grades and compatibilisers (PP-MA) used in this study were determined by BS 2782-7: Method 720A: 1997 [124]. All the MFI measurements were carried out using a microprocessor-based MP600 extrusion plastometer. The operation is a dead weight type; the load used was 2.16 kg and the test temperature was 230 °C or 190 °C. About 4g of sample was charged into the cylinder and allowed 4 min. to preheat the material. An automatically timed test procedure was used in which the material was cut off at prior programmed piston heights. Three cut-offs were collected and the average weight of the three cut-offs was calculated. MFI, melt volume rate (MVR) and melt density were obtained after entering the average mass into the data analysis software.

5.2.2 Molecular weight determination

Three grades of PP samples (PP1, PP2 and PP3) were sent to RPRA Technology Ltd to determine the molecular weight distribution using high temperature Gel Permeation

Chromatography (GPC) technique. The principle of GPC analysis is that polymer molecules are separated according to their size by passing a polymer solution through a column containing a porous cross-linked polystyrene gel. The gel is completely immersed in a solvent and, when polymer solution runs through the gel, larger polymer molecules cannot move into pores easily and therefore they are eluted quicker than smaller polymer molecules which can move in and out of the pores easily. The eluted material is analysed using a differential refractometer.

Molecular weight analysis of three grades of PP was carried out using a Polymer Laboratories GPC 220 instrument. PP samples were prepared by adding 15 ml of solvent to 15 mg of sample and were heated for 20 minutes at 190 °C to dissolve. The solutions were then cooled to 160 °C and filtered through a 2 μ m metal sinter and the filtered solution was transferred to glass sample vials. The vials were placed in a heated auto-sampler and were allowed 30 minutes to equilibrate thermally before injecting into the chromatographic column. The chromatographic conditions are given in Table 5-5.

Columns	PLgel guard plus 2x mixed bed-B, 30 cm, 10µm
Solvent	1,2,4-trichlorobenzene (with antioxidant)
Flow rate	1.0 ml/min.
Temperature	160 °C
Detector	Refractive index

Table 5-5 Chromatographic conditions

5.2.3 Analysis of chemical composition by spectroscopic methods

Fourier transform infrared spectroscopy (FTIR) has been used to find out the chemical composition of materials qualitatively by means of functional group analysis. The
MATTSON 3000 FTIR was used for the analysis. IR radiation goes through the sample and the intensity of the transmitted radiation is detected using an infrared detector. The functional groups present in the sample were identified by plots of transmittance intensity versus wave number obtained from the instrument. Figure 5-3 illustrates the basic structure of a FTIR apparatus.

The tests were run in diffraction mode between wave numbers of 600-4000 cm⁻¹ with 200 scans per sample. Polymer samples were prepared by melt pressing into a thin film whilst clay samples and amide additives were prepared by mixing with potassium bromide (KBr) to make into pellets.



Figure 5-3 Schematic diagram of FTIR structure

Attenuted total reflectance (ATR) method, in which IR radiation reflects from the sample surface, was used to identify the surface composition of the PP grades. An ATR attachment was fixed into the same equipment and the measurements were carried out exactly as with the FTIR measurements. Compression moulded thin films were used for ATR analysis. Table 5-6 shows the typical peak positions (cm⁻¹) for bonds related to materials used in this study [125].

Bond	Absorption region (cm ⁻¹)	Vibration modes				
С-Н	3000-2800	Stretching vibration				
С-Н	1375, 1450	Symmetrical and asymmetrical bending of CH ₃				
С-Н	3100-3000	Aromatic C-H stretching band				
О-Н	3300	Stretching vibration				
C=0	1720-1706	Stretching vibration of acids				
N-H	3350, 3180	Stretching vibration of primary amides (symmetrical and asymmetrical)				
C=0	1650	Stretching of primary amides (amide I band)				
N-H	1655-1620	Bending vibration of primary amides(amide II)				
C=0	1735-1750	Stretching vibration of aliphatic esters				
Si-O	830-1110	Stretching vibration SiO ₂				

Table 5-6 Some characteristic absorption peaks for different bonds and their vibrational modes

5.2.4 Determination of melting and crystallisation temperature

Differential scanning calorimetry (DSC) method was performed to study the melting and crystallisation behaviour of pure polymer as well as compounded samples. DSC measurements were carried out using TA instruments DSC 2010. Figure 5-4 shows a schematic diagram of typical DSC equipment.

The two pans (i.e. sample pan and reference pan) are heated at the same heating rate (e.g. 10 $^{\circ}$ C /min.) and the heat flow difference between the sample pan and the reference pan is measured as a function of time in this technique. When a polymer

sample undergoes a phase transition, more or less heat (depending on endothermic or exothermic change) is needed to keep the sample and reference at the same temperature. This difference in heat flow is recorded, as a function of changing temperature.



Figure 5-4 Schematic diagram of a DSC instrument

The samples were cyclically (heating-cooling-reheating) heated and cooled between 20 °C and 200 °C at a rate of 10 °C /min. with a stabilisation period of 1 min. at the end of both heating and cooling. The peak temperatures of melting and crystallisation were determined from second heating and cooling thermograms respectively. Crystallinity of all PP grades was determined using the enthalpy of crystallising (ΔH_f) in cooling thermogram. The percentage of crystallinity was calculated using ΔH_f (enthalpy of =209 J/g for 100% crystalline PP) [126]. Crystallinity of PP-clay nanocomposites (PPCN) was determined using the following equation.

Crystallinity (%) =
$$\frac{\Delta H_f}{\Delta H_f \circ W_p} x100$$
 [5.1]

 ΔH_f = enthalpy of PP in composite ΔH_f° = enthalpy for 100% crystalline PP W_P = weight fraction of PP in composite

5.2.5 Clay morphology

Scanning electron microscopy (SEM) was used to study the morphology of clay used in this study. Camridge Steroscan 360 SEM was used to obtain the scanning electron micrographs. A small portion of clay sample was dispersed in ethanol and the aliquots of the suspension were placed on a glass slide and allowed to dry. The dried samples were plated with gold before observing under SEM.

Fracture surfaces of impacted samples of PPCN were also observed by scanning electron microscope (SEM) to study the failure mode of PPCN. The impacted samples were cut and mounted on a stud, with the fracture surface exposed. This was gold coated for conductivity, prior to observing.

5.3 Preparation of PP-clay nanocomposites

PP-clay nanocomposites (PPCN) were prepared by melt blending of PP with organically modified clay (OMMT) in the presence of maleic anhydride grafted PP (PP-MA) and short chain amide molecules (AM) using a Haake Rheomix 600 torque rheometer. This is an internal mixer and torque rheometer containing a temperature controlled mixing chamber where two removable 'roller rotors' revolving in opposite direction are fixed. All these compounding were carried out at 185 °C set temperature with 80 % of filling (by volume) of mixing chamber in order to achieve the optimum mixing. The sample mass (m) required to charge into mixing chamber was calculated using the following equation (5.2). Figure 5.5 shows the Haake Rheomix 600 torque rheometer

Sample mass (m) =
$$\rho V_c f$$
 [5.2]

 ρ = melt density of PP; 0.75 gcm⁻³ at 190 °C

 V_c = net chamber volume; 69 cm³

f = fill factor; 80%



Figure 5-5 Haake Rheomix 600 torque rheometer

The PP, PP-MA and OMMT were pre mixed in a sample tray before charging into the mixing chamber. The rotor speed of 100 rpm was used for all compounds. The torque required to rotate the rollers in the composite melt was measured as a function of time. The temperature variation during the mixing was also recorded. Rheographs of torque against time for some compounds are shown in Appendix B. Initially different mixing times were used to determine the optimum mixing time to prepare PPCN. The optimum mixing time and rotor speed of 100 rpm were used for all other compounds. On completion of the mixing cycle, the compound was taken out from the mixing chamber. Table 5-7 and 5-8 summarise composite codes and their exact compositions for PPCN and PP-clay composites (PPCC) respectively. In all composites, last digit of the code refers to the clay concentration. For example PP1-PB6-2 refers to PPCN prepared with PP1 grade with 6 wt. % of PB compatibiliser and 2 wt % clay.

PP-clay	PP1/PP2/PP3	PB/PM	AM/ SE	OMMT
nanocomposite (PPCN) codes	(wt. %)	(wt. %)	(wt. %)	(wt. %)
PP1-PM6-2	92	6	-	2
PP2-PM6-2	92	6	-	2
PP1-PB2-2	96	2	-	2
PP1-PB6-2	92	6	-	2
PP2-PB2-2	96	2	-	2
PP2-PB6-2	92	6	-	2
PP3-PB6-2	92	6	-	2
PP1-PB2-AM0.5-2	95.5	2	0.5	2
PP1-PB4-AM0.5-2	93.5	4	0.5	2
PP1-PB6-AM0.5-2	91.5	6	0.5	2
PP1-PB2-SE0.5-2	95.5	2	0.5	2
PP1-PB4-AM1-4	91	4	1	4
PP1-PB6-AM1.5-6	96.5	6	1.5	6
PP1-PB8-AM2-8	92	8	2	8

.

Table 5-7 Compositions of PP-clay nanocomposites (PPCN) prepared using the Haake rheometer

PM = Polybond 3002 (maleic anhydride grafted PP)

- PB = Polybond 3200 (maleic anhydride grafted PP)
- AM =Erucamide (primary amide)
- SE = Steryl erucamide (secondary amide)

PP-clay composites	PP1/PP2/PP3	AM/ SE	ОММТ	
(PPCC) codes	(wt. %)	(wt. %)	(wt. %)	
PP1-2	98	-	2	
PP1-4	96	-	4	
PP1-6	94	-	6	
PP2-2	98	-	2	
PP1-AM0.3-2	97.7	0.3	2	
PP1-AM0.5-2	97.5	0.5	2	
PP1-AM0.7-2	97.3	0.7	2	
PP1-AM1-2	97	1	2	
PP1-AM1.5-2	96.5	1.5	2	
PP1-AM2-2	96	2	2	
PP1-SE0.5-2	97.5	0.5	2	

 Table 5-8 PP-clay composites (PPCC) prepared without compatibiliser using the

 Haake rheometer

5.4 Characterization of PPCN structures

Basically as described in Section 4.2.2, two main techniques; X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM), were used to characterise the nanocomposite structures in terms of intercalation and exfoliation behaviour of clay in PP matrix. XRD was basically used to examine the intercalation of polymer molecules into clay galleries while TEM technique was used to look at the exfoliation and degree of dispersion and distribution of clay in PP matrix. These two

characterisation techniques were mainly used together to determine the formation of nanocomposite structures.

Composite materials were compression moulded for about 80 seconds at 190 °C under $10-12 \times 10^4$ N to make into 1.5 mm thick sheets. These compression moulded sheets were used for X-ray diffraction and TEM techniques.

5.4.1 X-ray diffraction

X-rays are electromagnetic radiation with a wavelength range of 0.1 to 10 Å, between gamma and ultraviolet radiation. Generally X-rays are produced when charge particles (i.e. electrons) accelerated by electric potential, impinge on a metal target. The interaction between electrons and the metal target leads to emit X-rays. These Xrays are characteristic to the metal target. The copper (Cu) metal is the common metal for generating X-rays in X-ray diffraction technique. X-ray diffraction method allows study of the crystalline structure of a material when a beam of X-rays interacts with a crystal structure and forms a diffracted beam.



Figure 5-6 Diffraction of X-rays by a crystal structure

Diffraction of X-rays by crystals occurs only when Bragg conditions are satisfied (i.e. path difference (2x) of scattered rays by adjacent planes is equal to the wave length of

X-rays). The following equation (5.3) shows the Bragg relationship for diffraction in crystalline solids [127].

$$n\lambda = 2d \sin\theta$$
 [5.3]

n = order of reflection

 λ = wavelength of the X-rays

d = interlayer spacing (d spacing)

 θ = angle between incident radiation and the atomic plane (Bragg angle)

In this study, X-ray diffraction (XRD) analysis was performed by using a Bruker D8 diffractometer to investigate the intercalation behaviour of clay in nanocomposite structures. The X-ray beam is Cu K α , ($\lambda = 0.154$ nm) radiation operated at 40 kV and 40 mA. The compression moulded PPCN samples were used for the X-ray analysis. The X-ray diffraction patterns were scanned over a Bragg angle (2 θ), range from 1-10° at a rate of 1°/100 sec. The interlayer distance (d spacing) of clay (OMMT) in PPCN was calculated using the Bragg equation (5.3). The shifting of characteristic diffraction peak (corresponding to 001 plane) of OMMT towards lower Bragg angle indicates an intercalated structure with increased gallery spacing of clay whilst the disappearance of this peak indicates either the exfoliated structure or disorder in clay structure. Diffraction peak intensity represents the degree of exfoliation but comparison of diffraction peak intensities is accurate only when the amount of clay in nanocomposite structures is same. However, TEM is a better tool to evaluate the degree of exfoliation since the clay particles can be seen in PPCN.

5.4.2 Transmission electron microscopy (TEM)

TEM was used to investigate the dispersion of clay particles in PP matrix since X-ray diffraction results do not give detailed or accurate information on clay dispersability

and degree of exfoliation. Electron microscopes are instruments that use a beam of highly energetic electrons to examine objects on a very fine scale. With TEM, a beam of electrons passes through the sample; the transmitted portion of electrons projected onto to a screen as an image. Dark areas of the image represent the thicker or dense areas of the sample (i.e. fewer electrons are transmitted) while lighter areas represent the thinner or less dense areas of the sample (i.e. more electrons are transmitted).

Compression moulded samples were used to make thin sections of samples. The Cambridge Huxley microtome was used with a diamond knife at room temperature to make thin sections (approx.100-150 nm) of samples. These thin sections were observed under TEM. TEM observation was performed by using a JEOL JEM 2000FX TEM; the electron acceleration voltage was 200 kV.

The quantification of clay dispersability in PPCN was carried out by counting the clay particles (both clay platelets and intercalated particles) at five cut outs of 64 cm^2 of TEM micrographs at magnification 25,000 and averaging them to compare the dispersability of clay in each PPCN structure.

5.4.3 Quantification of clay exfoliation using image analysis

In addition to the above manual method, the degree of exfoliation was quantified for PPCN prepared with PP-MA and AM using Image-Pro Plus analysis software. TEM micrographs at 50,000 (50k) magnification were used for the image analysis. However, the discrimination between greyish polymeric region and dark lines corresponding to clay platelets/stacks is not possible by the image analysis tool. Therefore TEM images were converted into black and white images. TEM images were first printed on A4 sheets. A transparency paper was placed on each printed image and dispersed clay platelets and/or stacks were traced over using a black permanent pen. Figure 5-7 shows the conversion of a TEM image into a black and white image. The resultant black and white image was electronically scanned and was imported into the image analysis software.

Clay particle (stack) thicknesses and their distribution in PPCN were obtained from the image analysis programme. Clay stack thickness relates to the exfoliation and thus the number of clay platelets (single layers) per stack was calculated using the following equation [128, 129].

$$\Gamma = (N-1) d_{001} + d_s$$
 [5.4]

T = thickness of a clay stack

 d_{001} = interlayer spacing

N = number of clay platelets per stack

 $d_s =$ silicate layer thickness: 0.94 nm



Figure 5-7 Conversion of a TEM image into a black and white image

The number of clay platelets per stack is inversely proportional to the degree of exfoliation. A smaller number of platelets per stack indicate a higher degree of exfoliation. The degree of clay exfoliation in PPCN was quantified with respect to the clay particles in conventional type PP-clay micro-composites (PP1-2) in which no intercalation or exfoliation takes place. The degree of exfoliation was estimated quantitatively using the following equation (5.5).

$$E(\%) = \frac{N_{PPCC} - N_{PPCN}}{N_{PPCC}} \times 100$$
[5.5]

E = degree of exfoliation

 N_{PPCC} = number of clay platelets per stack in PP-clay micro composite (PPCC: PP1-2) N_{PPCN} = number of clay platelets per stack in PPCN

TEM images of extruded PPCN sheets were used to determine the clay aspect ratio. TEM images were converted into black and white images as described above and they were analysed using image analysis software to determine the distribution of both clay particle length and thickness. In contrast to sections of compression moulded sheets, thin sections of extruded PPCN sheets were taken along the extrusion direction in order to see both clay particle length and thickness under TEM. Figure 5-8 shows the schematic illustration of oriented clay particles in an extruded PPCN sheet specimen.



Figure 5-8 Details PPCN specimen, (a) sheet with clay particles, (b) side view

5.5 Analysis of surface composition by contact angle measurements

Short chain amide molecules are generally able to migrate onto the surface when PP products cools down, due to the incompatibility with the bulk PP. Surface

composition of the PP-clay composites (PPCC) prepared with the addition of erucamide (AM) and PPCN prepared with both compatibiliser and AM were examined qualitatively using contact angle measurements to characterise the surface of moulded composite materials. Contact angle (Θ), the angle that a liquid (of known surface tension) makes while resting at thermodynamic equilibrium on a solid, measures the wettability or spreadability of a solid surface and this characteristic varies greatly with the chemical nature of the solid surface.

The contact angles of pure distilled water and diiodomethane (CH_2I_2) on compression moulded thin films were measured using a Dataphysics OCA20 (an optical contact angle instrument) at room temperature (20 °C). The moulded samples were analysed for contact angles after 10 days of preparing the samples as the surface is saturated with amide molecules during that period of time. Water or diiodomethane liquid was dispensed from a small syringe, which is attached to a motor driven plunger, at dosing volume and rate of 1 μ m and 2 μ m/sec. respectively to form a drop on the film surface.



Figure 5-9 Water contact angle for PP film

For each sample, 12-15 contact angle measurements were taken from optical images of water/diiodomethane drops on the surface. For each image, the contact angle values

were measured on both edges, as shown in the optical image below (Figure 5-9), using software supplied with the instrument.

The total surface energy (γ) of the sample and the polar and dispersion component of total surface energy was obtained from analysis software according to Owens and Wendet method (130). Overall surface tension of diiodomethane is 50.8 mN/m (polar component: 0.0 mN/m, dispersive component: dispersive component: 50.8 mN/m) and overall surface tension of pure distilled water is 72.8 mN/m (polar component; 46.4 mN/m, dispersive component 26.4 mN/m) (130).

$$\gamma_{\rm LV} \left(1 + \cos\Theta \right) = 2(\gamma^{\rm d}_{\rm S} \gamma^{\rm d}_{\rm LV})^{1/2} - 2(\gamma^{\rm p}_{\rm S} \gamma^{\rm p}_{\rm LV})^{1/2}$$
 [5.6]

 γ_{LV} = Surface tension of a liquid

 $\gamma_{\rm S}^{\rm d}$ and $\gamma_{\rm LV}^{\rm d}$ = Dispersion contributions to surface energy of the solid and liquid phases, respectively

 $\gamma_{\rm S}^{\rm p}$ and $\gamma_{\rm LV}^{\rm p}$ = Polar contributions to surface energy of the solid and liquid phases, respec respectively.

Surface Polarity of composite surface was calculated using the following equation

Surface polarity (%) =
$$\frac{\gamma^{p}s}{\gamma} \times 100$$
 [5.7]

 $\gamma = \text{Total surface energy} (\gamma^{p}_{S} + \gamma^{d}_{S})$

5.6 Investigation of clay particle dispersability and their interaction with PP

Melt flow index (MFI) is a pressure-imposed, capillary flow experiment and was used to study the relationship between low strain rate shear flow properties and clay structure in nanocomposites and the interaction between clay and PP matrix of PPCN prepared with the addition of PP-MA and amide molecules (AM). The blends of PP, PP-MA and AM were used as control samples. MFI measurements were performed for PPCN and their control samples as described in section 5.2.1.

It is known that the viscous behaviour of a PPCN composite (at any given particle concentration) is sensitive to the aspect ratio of filler and filler-matrix interactions, especially at low shear rates [9]. However, it is not only the clay structure but also the viscous properties of the polymer matrix that also influences the measured MFI or melt volume rate (MVR). Therefore in order to investigate clay structure in PP and its interaction with the continuous PP matrix, a "normalized" MFI (n-MFI/n-MVR) was calculated, as shown below (equation 5.8), in order to present comparative data. Zhu and Xanthos [115] have also used MFI measurements successfully to study the relationship between rheology and morphology of clay in PPCN. In this study, n-MFI/n-MVR of PPCN was compared with that of PPCC

Normalized MFI (n-MFI)
$$=\frac{MFI_{PPCN}}{MFI_{CC}}$$
 [5.8]

MFI_{CC} :MFI of corresponding control

The test temperature was set to 190 °C and a dead weight load of 2.16 and 5 kg were applied. For each composite sample, the final results were the averages of two sets of measurements.

5.7 Thermal stability of PP-clay nanocomposites

Thermogravimetric analysis (TGA) method was performed to study the thermal stability of PPCN in comparison to pure PP. TGA method involves the measurement of weight changes during heating of a sample in an inert or oxidising environment. The weight change over a specific temperature range provides the information of sample composition and thermal stability of the sample.

Thermal stability of PPCN and pure PP were investigated by thermogravimetric analysis (TGA) method using a TA instrument TGA 2950, at a heating rate of 15 $^{\circ}$ C/ min. in air environment. TGA and derivate thermogravimetry (DTG) curves were obtained from 20 to 800 $^{\circ}$ C.

5.8 Scale-up production of PPCN and PPCC using a twin screw extruder

PPCN were prepared by melt blending of PP1 with organically modified clay (OMMT) in the presence of compatibiliser (PB) and short chain amide molecules (AM) using an APV MP2030TC twin screw extruder with a three-stage mixing zone profile, the specification of which is shown in Table 5-9. PP-clay composites (PPCC) were also prepared by melt mixing of PP1 and clay in the same way as PPCN to carry out the comparative study. Figure 5-10 shows a schematic diagram of a typical compounder

Screw diameter	30 mm
Screw length/diameter ratio	30:1
Screw speed range	0-500 rpm
Direction of screw speed	Co-rotating
Screw action	Self-wiping, fully intermeshing

Table 5-9 Specifications of APV MP2030TC

Prior to compounding PP1 homopolymer, PB, AM and OMMT were mixed well in a sealed container. The output rate of feeders was determined by using the premixed sample. This was carried out by setting the screw speeds of the feeders manually and the sample output was collected at the exit of feeder by placing a plastic container. The sample was collected during the 3 minute intervals and it was repeated in three

times to obtain the average value. The weight of the material output was recorded at each time.



Figure 5-10 Schematic diagram of a compounder

For all PP-clay compounds, the out-put rate was set about 9 kg/hr. The screw rotational speed used was 300 rpm which was selected as the optimum screw speed by compounding PPCN at different screw speeds (i.e. 200, 300 4000, 500 rpm), for all compounds. The PPCC, which does not contain any compatibiliser (PB) or short chain amide molecules (AM), were also prepared as reference samples. The temperature profile for the compounder was set as shown in Table 5-10, starting from feeding end to die end. The torque, die pressure and actual temperature readings were recorded when the compounding was at steady state, for each compounding.

 Table 5-10 The set temperature profile of the extruder barrel

Barrel	Barrel	Barrel	Barrel	Barrel	Die
zone 1	zone 2	zone 3	zone 4	zone 5	
180	185	190	190	195	195

The extrudate composite strands were pulled-out through the water bath before entering through a hot-air drier into the cutter. The granulated samples were collected at the end of the cutter using a container. These were dried-out in an oven at 80 °C for 6 hours to remove the remaining moisture on the surface of the granules. Table 5-11 summarises the PPCN and PPCC compounds and their exact compositions.

Composite codes	P P 1	PB	AM	OMMT	
	(wt. %)	(wt. %)	(wt. %)	(wt. %)	
PP1	100				
PPCN2	95.5	2	0.5	2	
PPCN4	91	4	1	4	
PPCN6	96.5	6	1.5	6	
PPCN8	88	. 8	2	8	
PPCC2	98	-	-	2	
PPCC4	96	-	-	4	
PPCC6	94			6	

Table 5-11 Composition of PPCN and PPCC prepared using twin screw extruder

5.9 Ashing analysis

Ashing analysis was performed to determine the actual filler content incorporated into PPCN prepared using the twin screw extruder as above. The ashing test was carried out following the British standard: BS 2782-4: Method 470A: 1997 [131] in which PPCN samples were heated at 850 °C to burn-off the PP and organic intercalant included in clay, leaving only inorganic part of the clay.

About 5g of sample was accurately weighed (to ± 0.1 mg) using an analytical balance and was placed in a well cleaned, pre-weighed crucible which was prior heated in a muffle furnace at the test temperature until constant mass is reached. Crucibles with samples were put in the muffle furnace which was already stabilised at 850 °C. Samples were taken out after approximately 1 hour and placed them in a decicator before weighing using the same analytical balance. The same procedure was also used for OMMT to determine the organic intercalant percentage in OMMT. The following equations (5.9 and 5.10) were used to calculate the actual clay content in each PPCN sample.

Inorganic content of clay (%) =
$$\frac{W_2 - W_1}{W} \times 100$$
 [5.9]

Actual clay (%) = Inorganic clay (%) + Organic intercalant (%) in OMMT [5.10]

 W_2 = weight of crucible after ashing W_1 = weight of empty crucible

W = sample weight

5.10 Rheological characterisation of PPCN

The rheological properties of the virgin PP and PP-clay composites, prepared using the twin screw extruder, were studied using a twin-bore capillary rheometer (Rosand-RH-7). The Rosand RH-7 rheometer includes the following main parts (see also Figure 5-11).

- Two barrels
- Temperature control in three different zones at the barrel (top, middle and die).
- Motor driven piston (recommended speeds: 1-100 mm/s).

- Pressure transducer for each barrel (maximum pressure: left barrel: 60MPa, right barrel: 10MPa).
- Computerised control of temperature, motor, data acquisition and analysis managed by 'Flow Master' software package



Figure 5-11 Rosand RH-7 rheometer

Shear and elongational flow behaviour of composite melts were studied according to the following procedure. Before starting the experiment, the dies were fitted into the barrels and were allowed to heat for about 30 minutes at the set temperature to reach equilibrium. The materials were charged into the barrels and were compressed manually. After filling the barrels, the pistons were driven down inside the barrel for programmed compression and pre-heating. The first compression (0.5MPa) and pre-heating was for 3 minutes and was followed by 6 minutes at the second compression (0.5MPa) and pre-heating. As soon as nine minutes were over the pistons started to run at the first selected speed. The experimental results were analysed using Flow Master Software package.

5.10.1 Shear and elongational viscosity

Shear and elongational viscosity of unfilled PP and composite materials were analysed, using the above twin bore capillary rheometer, between the shear rate ranges of 50-1000 s⁻¹, at 200 °C (this temperature was selected to avoid degradation of OMMT). These shear rates were selected since higher shear rates (above 1000 s⁻¹) resulted in melt fracture of the composite extrudate. Bagley corrected shear stress and shear viscosity values were obtained from Flow master software package, using two dies (long and short die): 16:1 and 0:1 mm, technique. The following equations were used by the software to calculate the shear stress and shear rate:

Shear stress
$$(\tau) = \frac{(\Delta PL - \Delta Po)R}{2L}$$
 [5.11]

Shear rate
$$(\gamma) = \frac{4Q}{\pi R^3}$$
 [5.12]

 ΔP_L (Pa) = Pressure drop across the long die

- ΔP_0 (Pa) = Pressure drop across the zero length die
- R(mm) = Radius of the die
- L(mm) = Length of the long die
- $Q(m^3/s) =$ Volume flow rate

Elongational viscosity values were obtained from the pressure drop values of the zero length die, according to the Cogswell method [63]. When melt flows from the reservoir of capillary rheometer to zero length die, a strong extensional flow is produced into the die entrance. Following equations were used according to the Cogswell method to characterise elongational flow properties:

Elongational viscosity,
$$\lambda = \frac{9}{32} \frac{(n+1)^2}{\eta} \left(\frac{P_0}{\frac{\gamma}{\gamma}}\right)^2$$
 [5.13]

Elongational stress,
$$\sigma_{\rm E} = \frac{3}{8}(n+1)$$
Po [5.14]

Elongational rate,
$$\dot{\varepsilon} = \frac{\sigma_{\rm E}}{\lambda}$$
 [5.15]

P_O =Pressure drop at zero length die

 γ =Shear rate (in shear flow)

 η = Shear viscosity

n =Power low index

5.10.2 Die swell measurements

Die swell (a ratio between extrudate and die diameter) measurements of PPCN and conventional type PPCC was performed to characterise the elastic properties of the polymer melts. The test was carried-out with a single bore fixed with a long die (16:1 ratio) at 200 °C. The extrudate diameter was measured using a laser device, placed at 10 cm below the die to capture the extrudate diameter accurately, as shown in figure 5-11, when it comes out from the die.

The barrel was filled with composite material and pre-heating and compression was same as the method described in section 5.10. Shear rates used in this analysis were between 50–1000 s⁻¹ (50, 100, 200, 300, 400, 500, 600, 700, 800, 900 1000 s⁻¹) and the temperature was 200 °C. When the extrudate emerges from the die and passes across the laser beam, the dimensions of the extrudate are automatically measured and the data are subsequently transferred to the computer programme. Die swell values of PPCN and PPCC were plotted against the measured shear rates.

The elastic modulus in shear of composite melts was also calculated from the die swell measurements since post-extrusion swelling from a long die relates to recoverable shear strain [63]. The following equations were used to calculate the elastic modulus in shear for the composite melts according to the Cogeswell method [63].

Elastic modulus,
$$G = \frac{\sigma_i}{\gamma_k}$$
 [5.15]

Swelling ration from the long die, $B_L^2 = \frac{3}{2} \gamma_R \left[(1 + \frac{1}{\gamma_R^2})^{\frac{3}{2}} - \frac{1}{\gamma_R^3} \right]$ [5.16]

 γ_R = recoverable shear strain

5.10.3 Melt fracture measurements

The onset of melt fracture was observed to study the melt elasticity/rupture properties of PPCN prepared with increasing clay concentrations. The theory of melt fracture phenomena was presented in section 3.6.2

Onset of melt fracture was observed while die swell experiments were carried out using a single bore (long die) and fractured samples were collected at each shear rate. Critical shear stress and shear rate values, at which onset melt fracture appears on the extrudate, of PPCN were determined by visual observing the extrudate surface; these were then compared with unfilled PP.

5.10.4 Wall slip measurements

Wall slip analysis on PPCN prepared with the addition of both PP-MA and AM was performed to study the effect of short chain amide molecules (AM) on slip behaviour of PPCN. The so-called Mooney method to identify the wall slip behaviour and to determine slip velocity was described in section 3.7. Wall slip measurements of PPCN and their respective blends without clay (PP, PP-MA and AM only) were carried out and the critical stress for the onset of slip was also calculated for each of the composite sample. In this method, four dies with constant L/D ratio of 16 were used: Table 5-12 shows the die characteristics used in this experiment. This experiment was performed with single bore using above four different dies. Shear rate range used in this analysis was same as the die swell experiments and the temperature was 200 °C. The 'Flow master' software calculates and plots apparent shear rate against the reciprocal radius according to Mooney method as described in section 3.7.

Table 5-12 Dies, with constant L/D with variable length, used for wall slip measurements by the Mooney method

Die	Length (L)	Length (L) Diameter (D)	
	(mm)	(mm)	ratio
1	24	1.5	16
2	19.2	1.2	16
3	16	1	16
4	12	0.75	16

The plot of apparent shear rate against reciprocal of die radius shows the slip behaviour (as shown in section 3.7) and slip velocities of all samples were also obtained from the programme. The slip velocity values were plotted against shear stress values to find out the onset of wall slip for each composite material.

5.11 Mechanical properties

Mechanical properties including tensile and impact behaviour were analysed to study the effect of clay loading levels on mechanical property performance of PPCN in comparison to pure PP and PP-clay micro-composites. Twin screw compounded PPCN and PPCC samples, which are in granulated form, were extruded into about nominal 1 mm thick and 50 mm wide sheets. Sheets of unfilled PP were also made as control samples.

The sheet extrusion was carried out using Haake rheomix 600 with an attachment of extruder. This small scale extruder consists of a single screw with haul-off rollers to make smooth-finished sheets. Granulated composite materials were extruded at screw speed of 40 rpm and the temperature profile was set from feeding point to die end: 175, 180 185 195 °C, The extruded sheets, when emerging from the die, were run through haul-off rolls to make the final product. Figure 5-12 shows the Haake extruder



Figure 5-12 Haake rheomix 600 sheet extruder

5.11.1 Tensile properties

Tensile properties of PPCN prepared with increasing concentrations of clay were analysed according to British Standards: BS 2782-3: Method 321 1994 [132], using Hounsfield tensile machine with a 1000N load cell. Tensile property measurements were basically chosen to study the reinforcement effect of clay on PPCN, in comparison to pure PP. Dumbell shaped test specimens with 6mm width of narrow parallel portion and with 25 mm gauge length were fixed into two grips before machine was run at a crosshead speed of 100 mm/min speed. The width and thickness of the narrow parallel portion of each sample was accurately measured with a micrometer prior to testing. The extension of samples was measured using laser extensometer. Tensile modulus and stress at yield were obtained from stress strain curve from computer aided soft ware. The elongation at break was also measured.

5.11.2 Impact properties

The effect of clay loading levels on impact resistance of PPCN was studied using a free-falling dart method, using a Rosand Instrumented Falling Weight Impact (IFWI) Test machine at room temperature (16 °C). Impact resistance is determined by measuring the energy absorbed by a sample when it fails under specific conditions of impact of a free-falling dart from a specific height. The dart was a 10 mm diameter hemispherical head and is fitted on to a 2 kg mass.

Samples used for impact property measurements were extruded sheet samples. Thickness of the sheet samples were measured accurately $(\pm 0.01\text{ mm})$ using a micrometer and placed onto a sample holder. Impact measurements were performed by free-falling the dart with 2 kg mass onto a sample from 0.46 m height which produces of an impact velocity of 3 m s⁻¹. During the impact measurement, the resistive force exerted by the sample on the dart is measured as a function of time. The computer software attached to the IFWI outputs the data in the form of a graph of force (N) against deflection (mm). The values recorded by the software are peak force, deflection at peak, energy at peak force, deflection at failure, failure force and energy at failure. Typical curves of force versus sample deflection for a ductile and brittle failure are shown in Appendix C, showing how each parameter is measured. Impact energy (i.e. energy at peak and energy at failure) is determined by integrating the area under the curve.

For each sample, five specimens were tested and the average value and the standard deviation were calculated.

6 CHAPTER: RESULTS AND DISCUSSION 1: PREPARATION AND CHARACTERISATION OF PPCN

6.1 Raw material characterisation

A number of techniques was used to characterise the raw materials (i.e. PP, PP-MA, short chain amide molecules: AM and SE and OMMT) used in this study, including process-based properties, chromatographic, spectroscopy analysis and thermal characterisation. All raw materials were fully described in section 6.1.1 to 6.1.3

6.1.1 Polypropylene and PP based compatibiliser (PP-MA)

Three grades of PP and two grades of maleic anhydride grafted PP (PP-MA) were used in this research study as described in section 5.1.1 and 5.1.2.

Melt flow index (MFI) measurements were used for process based characterisation as an indirect method for molecular weight comparison of the above materials. MFI is a pressure imposed, low shear rate capillary flow experiment and this was performed for all PP and PP-MA grades used in this study as described in section 5.2.1. Table 6.1 presents the results for MFI, melt volume flow rate (MVR) and melt state densities. Generally, MFI values can be taken as an indication of molecular weight of polymers since MFI is inversely related to molecular weight and to shear viscosity. Low molecular weight polymers tend to flow through the die faster than high molecular weight polymers for a given load, hence resulting in higher MFI values.

As shown in Table 6-1, the experimental results of all grades of PP and PP-MA are almost comparable with the manufacturer's specifications which are shown in section 5.1.1 and 5.1.2. Both PP1 and PP2 are medium flow rate PP grades and the results showed that both have similar MFI and MVR values, indicating closer molecular weight values. However the MFI value of PP2 could mislead molecular weight interpretations since PP2 itself contains low molecular weight polar additives (slip additives and antistatic agents). P3 shows comparatively higher MFI and MVR values and therefore it can be considered as a low molecular weight PP grade compared to

that of the other two PP grades. In comparison to the two PP-MA grades (PB and PM), PB has higher MFI and MVR values than PM, indicating its lower molecular weight than PM.

Material	MFI (g/10 min)	MVR (cm ³ /10 min)	Melt density (gcm ⁻³)	
HB671 (PP1), 230°C	2.45	3.36	0.73	
HB306 (PP2), 230°C	2.55	3.44	0.74	
HP510 (PP3), 230°C	9.65	13.24	0.73	
PB3200 (PB), 190°C	104.56	141.30	0.74	
PB3002 (PM),190°C	5.28	7.00	0.75	

Table 6-1 MFI, MVR and melt density results of PP and PP-MA grades

Molecular weight distribution of three PP grades was analysed using GPC (Gel permeation chromatography) technique as described in section 5.2.2. The molecular weight distribution result obtained from GPC analysis is shown in Appendix D. Table 6-2 summarises the average values of two runs obtained from GPC analysis.

As shown in Table 6-2, there is no significant difference in molecular weight between PP1 and PP2 but PP2 appears to be of marginally higher polydispersity (broader distribution). These results are in agreement with the molecular weight interpretation from the MFI data. The grade of PP3 clearly shows a significant lower molecular weight compared to that of other two grades.

Sample	Weight Average Molecular weight (M _w)	Number Average molecular weight (M _n)	Molecular weight distribution (M _w /M _n)	
PP1	375,000	79,900	4.7	
PP2	386,000	72,350	5.4	
PP3	252,500	42800	6.0	

A spectroscopic method was used to confirm the presence of low molecular weight polar additives in PP2 grade and their migration on to the surface. FTIR analysis was carried out as described in section 5.2.3 in order to characterise each PP grade by identifying the additives contained in each homopolymer grade. Figure 6-1 shows the FTIR spectra of pure PP1, PP2 and PP3. All these spectra show typical peaks corresponding to PP hydro carbon chains. However in addition to these typical peaks, there are two additional peaks at 1716 cm⁻¹ and 3194 cm⁻¹ in all spectra and these peaks might represent carbonyl (C=O) and aromatic C-H stretching vibrations respectively. From these peaks it is suggested that these PP grades are nucleated homopolymer and the nucleating agent could be based on aromatic carboxylic acid.

The spectrum of PP2 which contains slip and antistaic agents shows more additional peaks compared to the other two spectra (PP1 and PP3). In comparison to PP1 spectrum which does not contain polar additives, there are a few additional peaks that appear in PP2 spectrum and these peaks are responsible for the polar additives present in PP2. There is a prominent medium peak at 1649 cm⁻¹ and this corresponds to carbonyl (C=O) stretching vibration (amide I band) of primary amide molecules whilst the peak relevant to N-H₂ stretching (symmetrical and asymmetrical) vibration is shown at 3350 cm⁻¹. There is a weak peak shown at 1745 cm⁻¹ which is overlapped with C=O stretching peak of nucleating agent. This weak peak (1745 cm⁻¹) might be due to C=O stretching of aliphatic esters which corresponds to antistatic agents (glycerol monostearate).



Figure 6-1 FTIR spectra of PP1 (HB671), PP2 (HB306) and PP3 (HP510)

From these spectroscopic analyse, the presence of amide molecules (erucamide) and glycerol monostearate (GMS) as slip and antistatic agents respectively in PP2 can be confirmed whereas no such low molecular weight polar additives exist in PP1 and PP3 grades. Low intensity of these peaks related to polar additives further suggests that PP2 contains very low concentrations of these polar additives.

Generally, the short chain amide molecules (erucamide) migrate onto the surface and form an amide rich layer when the polymer cools down following processing. Therefore an attenuated total reflectance (ATR) analysis was also carried out to identify the surface chemical composition of PP2 which contains low molecular weight polar additives. Figure 6-2 shows ATR spectra of PP1 and PP2 surfaces. It clearly shows that ATR spectrum of PP2 has additional peaks in the range of 1600-1650 cm⁻¹ in comparison with the ATR spectrum of PP1. The peak corresponding to

amide-1 band (1649 cm⁻¹) appeared in PP2 spectrum, indicating the presence of an amide molecule layer on the surface.



Figure 6-2 FTIR-ATR spectra of PP1 and PP2

From this result, it can be further verified that the presence of low molecular weight polar additives and their migration onto the surface of PP2 takes place; there are no such additives present in PP1 grade.

Conventional differential scanning calorimetry (DSC) method, as described in section 5.2.4, was performed to determine the melting and crystallisation temperatures and percentage crystallinity of virgin PP grades (PP1, PP2 and PP3) and PP-MA grades (PB and PM) used in this study. Figures 6-3 and 6-4 show the second heating and cooling DSC thermograms of PP1 and PP2. The other DSC traces of PP3, PB and PM are shown in Appendix E.



Figure 6-3 DSC heating and cooling thermogram of PP1 at heating and cooling rate of 10°C/min

When polymers crystallises they give off heat and therefore an exothermic peak (as shown in Figures 6-3 and 6-4) shows the crystallisation range for PP. The highest point of peak gives the crystallisation (T_c) temperature of PP. An endothermic peak, which implies absorption of energy, shows the melting of PP and the highest point is considered as the melting temperature (T_m). The area under the peak shows the heat absorbed or heat given off during melting or crystallisation process.

Table 6-2 summarises the melting and crystallisation data obtained from the DSC thermograms of the three grades of PP and two grades of PP-MA. There is no significant difference in melting temperature amongst the PP grades used in this study. The crystallisation temperature of PP3 is lower than that of both PP1 and PP2, indicating accelerated crystallisation of PP1 and PP2 in comparison to PP3. This is attributed that the presence of higher concentration of nucleating agents in both PP1 and PP2 grades. The percentage crystallinity of PP1 and PP2 is also higher than PP3 since accelerated crystallisation results in a higher percentage of crystallinity. PP based compatibilisers also showed similar melting and crystallisation behaviour in comparison to PP grades used in this study.



Figure 6-4 DSC heating and cooling thermogram of PP1 at heating and cooling rate of 10°C/min

Polypropylene and PP-MA		2 nd heating			Cooling			
grades	Tom	T _m	ΔH _f	Crys.	Toc	Te	ΔH_{f}	Crys.
	(°C)	(°C)	(J/g)	(%)	(°C)	(°C)	(J/g)	(%)
PP1	153	169	124	59	133	128	124	59
PP2	156	167	121	57	123	117	121	58
PP3	155	169	92	44	117	110	92	45
PB	153	168	113	54	116	111	113	54
РМ	159	169	125	59	125	119	125	60

Table 6-3 Thermal properties of PP grades and PP-MA grades

T_{om} = Onset melting temperature

 $T_m = Melting temperature$

Toc = Onset crystallisation temperature

 $T_c = Crystallisation temperature$

 $\Delta H_f =$ Enthalpy of total crystallisation

6.1.2 Montmorillonite clay

Organically modified montmorillonite (OMMT) and unmodified montmorillonite (MMT) were used in this study. Technical specifications of these two clays are shown in section 5.1.3.

FTIR analysis was performed on both unmodified montmorillonite (MMT) and organically modified montmorillonite (OMMT) in order to confirm the presence of alkyl ammonium ion as an organic modifier in OMMT. The chemical structure of organic modifier (dimethyl dihydrogenated tallow) was shown in section 5.1.3. Figure 6-5 shows both FTIR spectra of MMT and OMMT. There are peaks which correspond to Si-O bond stretching vibration (1048 cm⁻¹) of silicate layers and to the O-H vibration, appeared on both spectra for MMT and OMMT.





The peak related to H-O-H bending vibration of water molecules appeared at 1636 cm⁻¹ in both MMT and OMMT spectra and the intensity of this peak decreased in OMMT spectrum as the amount of absorbed water molecules reduced with the presence of organic modifier [133]. A broad peak (3150 – 3550 cm⁻¹) and a sharp peak (3632 cm⁻¹) appeared due to O-H stretching of absorbed water molecules and to structural O-H respectively on both spectra of MMT and OMMT. However, OMMT spectrum clearly shows additional peaks that appeared at 2920, 2850 and 1468 cm⁻¹. These additional peaks represent the C-H stretching and C-H bending vibration of alkyl chains of the organic modifier included in OMMT. The FTIR analysis confirmed the presence of organic modifier in OMMT.

A thermogravimetric analysis (TGA) method was used, as described in section 5.7, to study the thermal stability, which is important information when clay is melt blended with PP at high temperatures, during processing. Organic modifier percentage of the clay was also determined from the final remaining residue percentage (after burning off the organic part) at the end of the experiment.





Figure 6-6 shows the TGA curve of organically modified clay. As shown in Figure 6-6, there were two mass loss steps that appeare for the organically modified clay (OMMT) in the temperature range between 20–800 °C. Degradation of clay starts just above 200 °C and the degradation continued up to weight loss about 30 % at a temperature of 460 °C. This step is due to the degradation of alkyl ammonium (2 methyl dihydrogenated tallow ammonium) chain included as an organic intercalant in clay and due to the hydrated water molecules. The second step of degradation is due to the dehydroxylation of aluminosilicate [134]. The final inorganic content of the clay, which was obtained from final residue content of TGA analysis, was 57.70 % at 800 °C, indicating a presence of about 42.30 % of organic modifier in OMMT. The ashing analysis was also carried-out as in section 5.9 to determine the organic modifier percentage of clay. The organic modifier is 43.50 % according to the ashing analysis method and this is in agreement with the result determined from the TGA method.

Scanning electron microscopy (SEM) was used to study the morphology of OMMT, as explained in the experimental section 5.2.5. Figure 6-7 shows the SEM micrograph of OMMT at lower magnification. This shows both primary clay particles and agglomerated particles, as clusters, that exist in the size range about 5-20 μ m.



Figure 6-7 SEM micrograph of OMMT (magnification 1900)


Figure 6-8 SEM micrograph of OMMT (magnification 5600)

The technical data sheet of OMMT shows that 50 % by volume is less than 6 μ m and 90% by volume is less than 13 μ m. The particle size determined from SEM images is tally with the data given in technical specification Figure 6-8 shows the same image of OMMT at higher magnification and it shows platy like morphology of clay particles.

Organically modified clay (OMMT) used in this study has a higher interlayer spacing (basal spacing) than the unmodified clay (MMT), according to the technical specifications (section 5.1.3, Table 5-3), because of the organic modifier present in OMMT. X-ray diffraction analysis method was performed, as described in section 5.4.1, to determine the interlayer spacing of clay. The Bragg equation was used (as shown in experimental section, 5.4.1, equation 5.3) to calculate the interlayer spacing.

As shown in Figure 6-9, the X-ray diffraction peak (001) of unmodified clay (MMT) is at 7.22 degrees while the X-ray diffraction peak of modified clay (OMMT) shifted to a lower Bragg angle (2.92 degrees). The shifting of X-ray diffraction peak into lower Bragg angle indicates the higher interlayer spacing (d spacing) when clay is modified organically. The interlayer spacing of OMMT is increased from 12.2 Å (interlayer spacing of MMT) to 30.2 Å There is a low intense peak in OMMT

spectrum similar to the diffraction peak of MMT and this is due to the presence of small amount of unmodified clay particles in OMMT sample. These interlayer spacing values are comparable with the manufacturer's specifications shown in section 5.1.3.



Figure 6-9 X-ray diffraction patterns of modified and unmodified clay

6.1.3 Short chain amide molecules

There were two types of amide molecules (erucamide and steryl erucamide) used in this study, as explained in section 5.1.4. Erucamide (AM) is a primary amide while steryl erucamide (SE) is secondary amide. FTIR spectroscopic analysis method was used to distinguish these two amide molecules. Figure 6-10 shows the FTIR spectra of both erucamide and steryl erucamide.

FTIR spectrum of erucamide shows the typical peaks (N-H stretching, amide-1 and amide-11 bands) corresponding to primary amide [125].



Figure 6-10 FTIR spectra of erucamide and steryl erucamide

Two moderate intense peaks appear at 3394 and 3189 cm⁻¹ corresponding to N-H stretching (asymmetric and symmetric) vibration and C=O stretching band (amide 1 band) appear at 1646 cm⁻¹ with overlapping of amide II band (N-H bending vibration). The spectrum related to steryl erucamide also shows similar peaks to the FTIR spectrum of erucamide. However, unlike erucamide, steryl erucamide (which is a secondary amide) shows a separate peak at 1537 cm⁻¹ relates to N-H bending vibration (amide II band) and N-H stretching peak appears at 3324 cm⁻¹. The other peaks shown in both spectra are related to the alkyl chain of amide molecules: C-H stretching and C-H bending vibrations.

In summary, out of three commercial grades of PP used in this study, only PP2 (HB306) grade contains low molecular weight polar additives and they migrate onto the surface of PP2, formed as a thin layer. Organically modified clay (OMMT) has a significantly higher interlayer spacing, in comparison to MMT, due to the presence of organic modifier. Erucamide is used as short chain amide molecules for the preparation of PP-clay nanocomposites (PPCN).

6.2 Preparation of PP-clay nanocomposites (PPCN)

Having characterised all raw materials, PPCN was prepared by melt blending of PP and organically modified clay (OMMT) in the presence of PP-MA in the Haake Rheomix 600, as described in section 5.3, to investigate the optimum conditions to form nanocomposite structures. Initially, the effect of mixing time and the effect of PP-MA and its characteristics (i.e. molecular weight of PP-MA and maleic anhydride concentration in PP-MA) on nanocomposite structures have been evaluated. After optimising the above conditions, the effect of low molecular weight polar additives and matrix molecular weight effects were also studied. However, the set temperature for the preparation of all PPCN in the Haake Rheometer was 185 °C. This set temperature was selected as the most suitable temperature for compounding PP with OMMT since TGA results (section 6.1.2) showed that OMMT started to degrade just above 200 °C and hence it was required keep the temperature below 200 °C during the compounding process.

6.2.1 Effect of mixing time

PP1 which does not contain polar additives, PP-MA (PM grade) and clay were melt mixed in the Haake compounder for different time periods (i.e. 6min. 10min. and 14 min.) to study the effect of mixing time on PPCN structure. The composition of each nanocomposite (PP1-PM6-2) is same (6 wt. % PM and 2 wt % clay) as shown in Table 5-7. The last digit of the composite code refers to the mixing time. For example, PP1-PM6-2-6 refers to 6 wt. % of PM, 2 wt. % of clay and 6 minutes melt mixing time, likewise PP1-PM6-2-10 indicates the 10 minutes mixing of the compound. Figure 6-11 shows the X-ray diffraction patterns of OMMT and PPCN prepared with different mixing times.



Figure 6-11 X-ray diffraction patterns of PP1-PM-clay nanocomposites prepared by different melt mixing times

When the mixing time was increased up to10 and 14 minutes, the diffraction peaks shifted slightly to higher Bragg angles whereas the same peak was shifted to a slightly lower angle when the mixing time was reduced to 6 minutes compared to the Bragg angle of OMMT. Interlayer spacing of clay in each composite was calculated from the Bragg equation (5.3), as shown in section 5.4.1. Figure 6-12 shows the effect of mixing times on interlayer spacing of clay.

Results clearly show that if the mixing time is 10 minutes or more, the resultant clay in the composite has a lower d-spacing (27.6 Å) than pure organically modified clay (30.2 Å). This could be due to the start of the degradation of alkyl ammonium ion occupied as an organic modifier within the clay and this could have occurred due to the longer mixing period at this temperature range (185-200 °C) and the shear stress used for compounding. Therefore this is a clear indication that 10 minutes or more of compounding time is not suitable for the preparation of PPCN with this particular organically modified clay.



Figure 6-12 Effects of mixing times on interlayer spacing of clay in PP-clay nanocomposite (PP1-PM6-2)

Dologoviski at el. [26] also showed the importance of mixing time on preparation of PPCN using an internal batch mixer because mixing time allows the intercalation of polymer molecules into clay galleries during the compounding process. However in this study, it was not reported how the decrease of gallery space occurred with longer mixing times. Dharaiya and Jana also [135] studied the thermal decomposition of alkyl ammonium ion included in organically modified clay. It was shown from X-ray diffraction results that heating of clay at high temperatures resulted in a slight decrease in interlayer spacing of clay. This X-ray diffraction result was further verified from contact angle and FTIR analysis method.

On the other hand, PP1-PM6-2-6, which was prepared with 6 minutes compounding time, shows slightly a higher interlayer spacing (30.6 Å) than pure OMMT, indicating that no degradation was involved. Therefore, the 6 minutes was selected as the most appropriate compounding time for all other PPCN prepared using the Haake Rheomix compounder. However the slight increase of interlayer spacing of clay in PP1-PM6-2-6 implies that PP molecules do not intercalate effectively into clay galleries to form

the nanocomposite structure. This could be due to characteristics of PP-MA grade (PM) used to prepare PPCN structures.

6.2.2 Effect of maleic anhydride grafted PP (PP-MA)

Since the study in section 6.2.1 revealed that this PP-MA grade (PM) does not intercalate into clay galleries effectively, the effect of PP-MA and its characteristics (i.e. molecular weight and maleic anhydride content) on intercalation and exfoliation behaviour were studied in detail using two PP-MA grades: PB and PM. As shown in technical data of each grade of PP-MA in section of 5.1.2, PB is low molecular weight and has a higher content of maleic anhydride (1 wt. % MA) whereas PM is high molecular weight and has a lower content of maleic anhydride (0.2 wt. %).

PPCN were prepared by melt blending of PP with OMMT using two different PP-MA grades (PM and PB) in the Haake compounder. The exact composition of each composite is shown in section 5.3 (Table 5-7). The mixing conditions were same as the previous experiment.

(A) Intercalation behaviour

Figure 6-13 presents the X-ray diffraction peaks of PPCN prepared with two different grades of PP-MA (PM and PB) in two grades of PP (PP1 and PP2) while Table 6-3 summarises the peaks (001 and 002) positions and calculated interlayer spacing (d_{001}) of each PPCN.

As shown in Figure 6-13 and Bragg angle position shown in Table 6-4, diffraction peaks (001) were shifted to lower Bragg angles and the resulted interlayer spacing was increased when PB was used to prepare PPCN using either PP grade (PP1 or PP2), compared to that of PPCN prepared with PM. The gallery spacing of clay was increased by 1.4 Å when PB was used with either grade of PP (PP1-PB6-2 and PP2-PB6-2), compared to that of PPCN prepared with PM (PP1-PM6-2 and PP2-PB6-2), compared to that of PPCN prepared with PM (PP1-PM6-2 and PP2-PB6-2). This can be explained by PB diffusing into clay galleries more effectively since it has low molecular weight and has a higher content of MA, resulting higher polarity. This higher polarity improves the affinity towards silicate layers and as a result, enhanced the interaction between silicate layers and PB through hydrogen bonding [17, 23].

From this result it is suggested that characteristics of PP-MA (i.e. molecular weight and MA content) significantly affects the intercalation of clay.



Figure 6-13 X-ray diffraction patterns of PPCN prepared with two different grades of PP-MA (PM and PB) in different grades of PP (PP1 and PP2)

The similar effect of PP-MA and its characteristics was explained in literature review, Section 4.2.1 [136, 137].

Wang at el. [95] pointed out the effect of molecular weight of PP-MA on preparation of nanocomposite structure using four different PP-MA grades which have different molecular weights and MA grafting ratios. From their study it was shown that low molecular weight and high maleic anhydride content in PP-MA led to a better intercalation into clay galleries. However, on the other hand Kawasumi at el. [19] reported that although high MA content enhances the melt intercalation of PP-MA into clay galleries, it may lead to immiscibility with the PP matrix and is therefore detrimental to mechanical properties of the PPCN.

PPCN material	Peak (001) Position (degrees)	Interlayer spacing (d ₀₀₁), (Å)	Peak (002) Position (degrees)
OMMT	2.92	30.2	-
PP1-PM6-2	2.88	30.6	-
PP1-PB6-2	2.76	32.0	-
PP2-PM6-2	2.28	38.7	4.40
PP2-PB6-2	2.20	40.1	4.36

Table 6-4 Interlayer spacing of clay in PPCN prepared with two different grades of PP-MA (PM and PB)

Narh et al [24] also investigated the effect of compatibiliser concentration on preparation and mechanical properties of PPCN and reported that a moderate amount of compatibiliser was important to achieve intercalation as well as to improve the mechanical properties of PPCN.

Interestingly in the current study, when PPCN were prepared with PP2 which contains low molecular weigh polar additives (slip and antistatic additives), irrespective of the PP-MA grades, the diffraction peak (001) of PP2-PM6-2 and PP2-PB6-2 has been further shifted (Figure 6-13) to a lower Bragg angle and becomes slightly narrower, in comparison to either PP1-PM6-2 or PP1-PB6-2. The resulting interlayer spacing (d₀₀₁), corresponding to 001 diffraction peak of PP2-PM6-2 and PP2-PB6-2, has been increased from 30.2Å (d spacing of OMMT) to 38.7 Å and 40.1 Å respectively (Table 6-4). It is proposed that this higher interlayer spacing could be due to the diffusion of low molecular weight polar additives (which are compatible with OMMT) present in PP2 itself, in addition to the PP-MA, into clay galleries. As a result of this more PP macro molecules can intercalate into clay galleries. The second peak (002) appeared at 4.40 and 4.36 degrees for PP2-PM6-2 and PP2-PB6-2 structures respectively can be considered due to the 2nd order reflection according to Bragg's law. However the first peak (001) is stronger and therefore it is considered to calculate the interlayer spacing of all PPCN structures.

(B) Exfoliation behaviour

Since X-ray diffraction results do not give any clear indication of clay dispersability and degree of exfoliation, TEM analysis was also performed to study the effect of PP-MA on clay exfoliation in a PP matrix. Figures 6-14 and 6-15 present the TEM images of PPCN prepared with two grades of PP (PP1 and PP2). The dark areas represent the cross sections of clay particles and grey areas represent the PP matrix of PPCN.



(a)

(b)

Figure 6-14 TEM micrographs of PPCN showing the effect of changing the compatibiliser (PM and PB) within polymer PP1 (magnification 25,000), (a) PP1-PM6-2, (b) PP1-PB6-2

In the comparison of TEM images of PPCN prepared using PP1 grade, Figure 6-14-(b) (PP1-PB6-2) shows comparatively smaller clay stacks and they are distributed more homogeneously in PP1 than in Figure 6-14-(a) (PP1-PM6-2) which contains comparatively larger clay stacks and are not shown homogeneous distribution through out the PP1 matrix. Although PP1-PB6-2 (Figure 6-14-(b)) shows improved exfoliation of clay, they are not completely exfoliated. However, very few thin dark lines can be seen that can be considered as completely exfoliated clay particles.



(a)

(b)

Figure 6-15 TEM micrographs of PPCN showing the effect of changing the compatibiliser (PM and PB) within polymer PP2 (magnification 25,000), (a) PP2-PM6-2, (b) PP2-PB6-2

When PB (low molecular weight and higher percentage of functional group containing PP-MA) was melt mixed with PP1 and clay, the PB intercalates more

effectively than PM, resulting higher gallery spacing, as shown in XRD results (Table 6-4). The higher gallery spacing lead to weaken the forces between clay layers and as a result, clay particles are more easily exfoliated into smaller stacks and distributed well in the PP1 matrix, during the compounding process.

When PPCN was prepared using PP2 grade, the PB enhances the clay dispersion slightly (in comparison to PM) as shown Figure 6-15 (a) and 6-15 (b), same as with the PPCN prepared with PP1 grade. However, in comparison between PPCN prepared with PP1 and PP2, it is clear that improved clay exfoliation has been occurred in nanocomposite structures prepared with PP2 grade. This would suggest that not only PP-MA compatibiliser but another factor has a significant effect on clay dispersion in PPCN prepared with PP2. This additional factor could be the low molecular weight polar additives present in PP2 grade. The influence of low molecular weight polar additives present in PP on intercalation and exfoliation of PPCN structure is discussed in detail in section 6.2.3

From these X-ray diffraction and TEM results, it can be concluded that low molecular weight and high MA containing PP-MA (i.e. PB) improves the intercalation and clay exfoliation in PP matrix and therefore a mainly intercalated nanocomposite structure was formed with few completely exfoliated clay layers. The PB grade was therefore used as the compatibiliser for all future experiments in this study since it was found to be the most suitable compatibiliser for the preparation of PPCN.

6.2.2.1 Effect of PP-MA to clay ratio

However it has been reported elsewhere that not only the polarity (relating to MA content) of compatibiliser but also the clay to PP-MA ratio is also important to achieve a good exfoliation and dispersion of clay in PP matrix since there should be sufficient amount of compatibiliser to promote compatibility of clay particles with bulk PP [93, 94, 121].

Therefore our research was further continued to investigate the effect of PP-MA to clay ratio on the PPCN structure.

(A) Intercalation behaviour

The following nanocomposites structures (PP1-PB6-2, PP1-PB2-2, PP2-PB6-2 and PP2-PB2-2, the exact composition of each composite was shown in Table 5-7) were prepared using two different ratio of PB to OMMT; 3:1 and 1:1. Figure 6-16 shows the X-ray diffraction spectra of these nanocomposite structures.



Figure 6-16 X-ray diffraction patterns of PPCN prepared with different compatibiliser to clay ratio (polymers: PP1 and PP2)

Comparing the X-ray diffraction patterns of PP1-PB2-2 and PP1-PB6-2, it is clear that increasing the PB content does not enhance the intercalation, hence the resulting X-ray diffraction peaks (001) are at the same Bragg angle (2.76 degrees) and therefore resulting the same gallery spacing (32Å) for both nanocomposite structures. This can be explained since PB contains a higher level of MA (1 wt. %) and therefore PB to clay ratio of 1:1 is sufficient to achieve the maximum intercalation. However, the diffraction peak of PP1-PB6-2 shows much lower intensity than PP1-PB2-2. This lower intensity of diffraction peak could be attributed to a higher degree of exfoliation, resulting in clay stacks with less number of platelets. Therefore PB to clay

ratio of 3:1 could improve the clay exfoliation in PP1-PB6-2 structure, in comparison to PP1-PB2-2 since a high concentration of PB enhances the compatibility of clay with bulk PP.

Similar X-ray diffraction patterns are shown (Figure 6-16) for PPCN prepared with PP2 grade using low and high concentration of PB. Both diffraction peaks (001) corresponding to PP2-PB6-2 and PP2-PB2-2 are at the same Bragg angle position (2.20 degrees), resulting in interlayer spacing of 40.1 Å (Table 6-4). This implies that an increase of PB concentration (i.e. PB to clay ratio of 3:1) does not improve the intercalation of clay. However, in contrast to the PPCN prepared with PP1 grade, no significant difference of diffraction peak intensity was shown between PP2-PB2-2 and PP2-PB6-2, indicating higher concentration of PB may not improve clay exfoliation in this system. However XRD results alone is not appropriate to explain the degree of exfoliation and therefore TEM results of these nanocomposite structures will be discussed in the next section.

(B) Exfoliation behaviour

TEM analysis of the above nanocomposites was also performed to study the effect of PP-MA concentration on degree of exfoliation. Figure 6-17 and 6-18 show the PP1-PB2-2 and PP2-PB2-2 nanocomposite structures respectively.

The large dark areas shown in Figure 6-17 are attributed to non-exfoliated clay particles. As shown in Figure 6-17 clay particles are not exfoliated into smaller stacks and do not disperse uniformly throughout the PP1 matrix. It is clearly shown that this PP1-PB2-2 nanocomposite structure contains comparatively larger particles and less dispersion throughout the PP1 matrix compared to that of PP1-PB6-2 (Figure 6-14-(b)) which contains a higher concentration of PB. When figure 6-17 is compared with Figure 6-14-(b), an enhanced degree of clay exfoliation is achieved in PP1-PB6-2 (Figure 6-14-(b)). The higher concentration of PP-MA improves the compatibility between clay and PP1 and as a result, improved clay exfoliation is achieved during the melt compounding process. These TEM results are in agreement with the X-ray diffraction results (i.e. diffraction peak intensities of PP1-PB2-2 and PP1-PB6-2) shown in figure 6-16.



(10k)

(25k)



However, as shown in Figure 6-18, when PPCN was prepared with PP2 clay particles were exfoliated into much more smaller stacks and they were dispersed homogeneously throughout PP2 matrix, in comparison to Figure 6-17 (PP1-PB2-2). This improved clay dispersion in PP2-PB2-2 nanocomposite structure (Figure 6-18) indicates the significant effect of low molecular weight polar additives (which are present in PP2) on clay exfoliation. This can be due the intercalation of both polar additives and compatibiliser (PB), resulting higher interlayer spacing (Figure 6-16) and hence highly exfoliated smaller clay stacks are formed during the compounding process. This nanocomposite structure (PP2-PB2-2) also showed the co-existence of intercalated and exfoliated clay particles as with other nanocomposite structures (i.e. PP1-PB6-2 and PP2-PB6-2).

However in contrast to PPCN prepared with PP1, the high concentration of PB did not significantly enhance the clay exfoliation and dispersion in PP2 (comparison of

Figures 6-18 and 6-15-(b)). This TEM result is comparable with X-ray diffraction results (Figure 6-16) as both PP2-PB6-2 and PP2-PB2-2 structures showed the same diffraction peak intensities. Presence of low molecular weight polar additives could be the possible reason for the improved clay dispersion in PPCN prepared with PP2 grade compared to PPCN prepared with PP1 grade.



(10k)

(25k)



From these X-ray diffraction analyse (Figures 6-13 and 6-16) and TEM images (Figures 6-15 and 6-18), strong evidence is obtained that low molecular weight additives containing polar groups present in PP2 grade has a significant impact on intercalation and exfoliation behaviour of clay in PPCN structures.

6.2.3 Effect of polar additives present in PP2 on PPCN structures

To confirm the effect of low molecular weight polar additives on intercalation and exfoliation behaviour of clay, studies were continued by melt mixing each PP grade (PP1 and PP2) with clay in the absence of PP-MA. Both PP1-2 and PP2-2 samples refer to 2 wt. % of clay containing PP-clay composites.



Figure 6-19 X-ray diffraction patterns of PP-clay composites (PPCC) prepared with two PP grades (PP1 and PP2)

Figure 6-19 presents the X-ray diffraction spectra of PP-clay composites (PPCC) prepared with each of these two PP grades, relative to the organically modified clay (OMMT).

The comparison between the respective diffraction peaks of PP1-2 and PP2-2 composites clearly shows that the X-ray diffraction peak (001) corresponding to PP2-2 composite shifts significantly to a lower Bragg angle, resulting in a higher interlayer spacing. This XRD result further confirms that low molecular weight polar additives (which are compatible with OMMT) intercalate into clay galleries and therefore

increase the interlayer spacing from 30.2Å (inter layer spacing of OMMT) to 38.7 Å. The diffusion of these low molecular weight polar additives into clay galleries and resulting higher interlayer spacing could also promote the intercalation of PP molecules into clay galleries. Interaction between these polar groups of these additives (slip and antistatic agents) and silicate layers is likely to be the driving force for the intercalation of these additives into clay galleries.

The XRD peak of PP1-2 remains at the same Bragg angle position as pure OMMT, since non polar PP molecules do not intercalate into clay galleries and, as a result, only the phase separated conventional type micro-composite is formed. This non intercalation of PP into clay galleries in the absence of PP-MA is agreeable with literature that showed the addition of functionalised compatibiliser is necessary to prepare PPCN structures by melt intercalation method [17, 19, 21, 23].

However, The XRD peak of PP2-2 is narrower and has higher peak intensity compared to that of either PP2-PB2-2 or PP2-PB6-2 (Figure-6-16). This could imply that although low molecular weight polar additives are able to diffuse into clay galleries, most of the organised clay structures remain unchanged. The stress applied during the melt mixing process is not sufficiently intense to separate the inorganic phase into smaller units, since there is no compatibiliser to transfer deformational energy from matrix to clay particles.

Since the X-ray diffraction results do not show the effect of these additives on clay dispersability, TEM analysis was also carried out on both PP1-2 and PP2-2 structures to examine the effect of these additives on clay dispersability in the PP matrix. TEM micrograph of PP1-2 (Figure 6-20-(a)) shows significantly larger clay particles which are not intercalated and as a result conventional 'micro-composite' structure is formed, presumably due to the absence of PP-MA. This TEM image is agreeable with the result obtained from the X-ray diffraction (Figure 6-19). On the other hand figure 6-20-(b) shows comparatively smaller clay particles than figure 6-20-(a), consistent with higher interlayer spacing of clay in PP2, and so that clay particles are separated into comparatively smaller units during the melt mixing process. However, in comparison with PPCN prepared by incorporation of PP-MA (Figure 6-18), clay stacks in PP2-2 composite are comparatively larger, showing that they are not dispersed homogeneously through out the PP2 matrix, in the absence of PP-MA

compatibiliser. Although these low molecular weight polar additives in PP2 are able to intercalate into clay galleries, they are not compatible with PP (in the same way as PP-MA), and therefore clay particles do not distribute homogeneously throughout the matrix.



(a)

(b)

Figure 6-20 TEM micrographs of PP-clay composites (magnification 25,000), PP1-2 and (b) PP2-2

6.2.4 Effect of matrix molecular weight

Two grades of PP (PP1 and PP3) have been used to understand the effect of matrix molecular weight on PPCN structure. As shown in GPC analysis of PP grades in section 6.1.1 (Table 6-2), PP1 is comparatively higher molecular weight than PP3. Both PP grades (PP1 and PP3) were melt mixed with 2 % by weight of clay and 6 % by weight of PB in the Haake rheometer operating the same mixing conditions as in previous experiments. PPCN prepared with two different grades of PP were

investigated under X-ray diffraction and TEM techniques to evaluate the intercalation and exfoliation behaviour of clay with respect to the PP matrix, investigating the influence of molecular weight hence melt viscosity.



Figure 6-21 X-ray diffraction pattern of PPCN prepared with PP grades PP1 and PP3.

Figure 6-21 shows that the X-ray diffraction peak of PPCN prepared with PP3, a low molecular weight PP, has been shifted to a lower Bragg angle and therefore resulting in a higher interlayer spacing in comparison with the PPCN prepared with high molecular weight PP (PP1). Interlayer spacing of clay has been increased to 36.2Å when PP3 was used to prepare PPCN whereas the interlayer spacing of clay was 32.0 Å when PP1 was used. From this X-ray diffraction result, it is clear that PP3 intercalates with compatibiliser into clay galleries more effectively than PP1. The low molecular weight PP3 is less viscous and as a result it diffuses with compatibiliser (PP-MA) into clay galleries more easily, during the compounding process and subsequently increases the interlayer spacing.

TEM analysis was also performed for PPCN prepared with low molecular weight PP3 (PP3-PB6-2) to study the effect of matrix molecular weight on clay dispersability in nanocomposite structure. TEM image of PP3-PB6-2 (Figure 6-22), at different magnifications (10k and 25k), shows that clay particles are exfoliated into smaller stacks and distribute homogeneously throughout the PP3 matrix.



(10k)



(25k)



However, in comparison of this nanocomposite structure with PPCN structure (PP1-PB6-2, Figure 6-14-(b)) prepared with high molecular weight PP1, no significant enhancement was observed in clay dispersability in PPCN prepared with low molecular weight PP3 grade, although it has a higher interlayer spacing as shown in X-ray diffraction (Figure 6-21). This could be due to the lower stress generated during the compounding process because of lower melt viscosity (i.e. low molecular weight) of PP3 and therefore exfoliation of clay particles is not enhanced as expected.

6.3 Effect of short chain amide molecules on PPCN structure

It has been shown from X-ray diffraction and TEM results that both types of polar additives (slip and antistatic agents), which are present in PP2 grade, are able to intercalate into clay galleries. Based on these results, short chain amide molecules (erucamide: 13-cis-docenamide) were then selected to study their influence on intercalation and exfoliation behaviour of clay in PP. The technical specifications of short chain amide molecules (AM) used in this study are shown in section 5.1.4.

PP-clay composites (PPCC; without compatibiliser) were prepared by incorporation of amide molecules (AM) to examine the intercalation behaviour of these molecules into clay galleries and they were analysed using the X-ray diffraction technique to examine the changes in interlayer spacing of clay. Figure 6-23 presents the comparison of X-ray diffraction patterns of PPCC prepared by addition of AM (PP1-AM0.5-2) with that of organically modified montmorillonite (OMMT) and a PP-clay composite (PP1-2) prepared without amide molecules.



Figure 6-23 X-ray diffraction patterns of PPCC prepared in the presence and absence of short chain amide molecules (AM)

The characteristic diffraction peak (001) of OMMT is at 2.96° Bragg angle (2 θ), corresponding to a basal spacing of 30.2 Å. The diffraction peak (001) of PP1-2 composite prepared without amide molecules (AM) remained at the same Bragg angle position as with the OMMT (Table 6-5), resulting in no changes in the interlayer spacing compared to OMMT. This result indicates that non polar PP molecules do not intercalate into clay galleries since they are not compatible with organophilic clay.

However, the X-ray diffraction peak of PP-AM0.5-2 prepared with 0.5 wt. % of short chain amide molecules (AM) shifted towards a lower Bragg angle from 2.96° to 2.36° (Table 6-5), resulting in higher interlayer spacing in comparison to OMMT. This can be explained since polar amide molecules intercalate into OMMT galleries and as a result, PP molecules are also likely to be diffused into clay galleries. Therefore the interlayer spacing of OMMT has been increased from 30.2 Å to 37.44 Å. The driving force for the diffusion of AM into clay galleries is likely to be the attraction of polar group (CONH₂) in AM to the polar silicate layers. Short chain amide molecules are likely to be bonded with silicate layers by hydrogen bonding.

Composite materials	Bragg angle (2θ), (degrees)	Interlayer spacing (d ₀₀₁), (Å)	
MMT	7.22	12.2	
OMMT	2.92	30.2 34.24	
AM-OMMT	2.58		
PP1-AM0.5-2	2.36	37.44	
PP1-2	2.96	29.6	

Table 6-5 Interlayer spacing of various modified clays and PP-clay composites

6.3.1 Melt mixing of AM with OMMT

In order to further verify the intercalation ability of AM into clay galleries, OMMT was ground with AM powder and heated-up in an oven at 100 °C for about 30 minutes to diffuse AM into clay galleries. The resultant clay treated with amide molecules (AM-OMMT) was analysed using X-ray diffraction and FTIR method to investigate the intercalation ability of this additive into OMMT. X-ray diffraction patterns of unmodified clay (MMT) and various modified clays (i.e. OMMT and AM-OMMT) are shown in Figure 6-24. Table 6-5 presents characteristic diffraction peak (001) position and interlayer spacing for various modified clays.



Figure 6-24 X-ray diffraction patterns of modified and unmodified clays

As shown in Figure 6-24, organically modified clay (OMMT) has a characteristic diffraction peak (001) at 2.92 degrees, corresponding to a basal spacing of 30.2Å (Table 6-5), since pristine clay (MMT) is modified with alkyl ammonium salt. As expected, when OMMT was treated with short chain amide molecules (AM), the diffraction peak (001) of AM-OMMT further shifted to a lower Bragg angle (2.58 degrees). As a result, the resultant basal spacing was increased from 30.2 to 34.24 Å

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(Table 6-5) when OMMT was treated with AM. However, although the diffraction peaks of both AM-OMMT and PP1-AM0.5-2 are expected to be at the same Bragg angle position since both compounds have the same clay to AM ratio (clay 4:1 AM), the diffraction peak of PP1-AM0.5-2 was at a slightly lower Bragg angle than AM-OMMT (Table 6-5). This is due to the effective mixing involved in the Haake compounder when PP1-AM0.5-2 was prepared, in comparison to manual grinding of OMMT with AM. However, it can be seen that diffraction peak of AM-OMMT becomes broaden towards lower Bragg angle, indicating the presence of clay stacks with higher interlayer spacing. From these results it is clear that AM intercalates into clay galleries and as a result, higher interlayer spacing is achieved.

FTIR analysis was also performed on organically modified clay (OMMT) treated with AM (AM-OMMT) to further confirm the X-ray diffraction results (Figure 6-24). Figure 6-25 shows the FTIR spectra of OMMT and AM-OMMT.





In comparison of these two spectra, it is clear that AM-OMMT spectrum shows additional peaks which corresponds to amide molecules in OMMT. The two moderately intense peaks correspond to N-H stretching vibration (asymmetric and symmetric) and these appear at 3386 and 3184 cm⁻¹. The asymmetric N-H stretching band (3386 cm⁻¹) overlaps with a broad peak related to O-H stretching vibration of OMMT. In addition, amide I (C=O, stretching) peak is also seen at 1646 cm⁻¹. From these X-ray diffraction and FTIR results, it is clear that short chain amide molecules (AM) intercalate into clay galleries and as a result, a higher interlayer spacing was achieved.

6.3.2 Effect of amide molecule (AM) concentration

Further investigations were continued to examine the effect of amide molecule (AM) concentration on intercalation of clay and to find-out the optimum AM concentration to achieve the maximum interlayer spacing. Figure 6-26 shows the X-ray diffraction peaks of PP-clay composites (PPCC) prepared with different concentrations of AM and 2 wt. % of clay (without compatibilizer), which clearly show that all diffraction peaks (001) shift to lower Bragg angles when AM is incorporated into PPCC, in comparison to pure OMMT. Interlayer spacing of clay increases with increasing AM concentration and Table 6-6 presents the Bragg angle position and basal spacing calculated according to Bragg equation. When 0.3 and 0.5 wt % of AM was added into PPCC, the interlayer spacing of clay was increased to 33.46 and 37.46 Å respectively. However, as shown in Table 6-6, on increase of AM up to 0.7 and 1 wt. % is not effective in terms of modifying the interlayer spacing further, probably due to the migration of additional amide molecules to the surface, as occurs in pure PP.

The highest interlayer spacing was achieved by the addition of 0.5 % (by weight) of AM. Diffraction peaks related to each composite structure show different peak intensities and peak areas. However these data could not indicate any information about the degree of exfoliation as the number of clay particles can be quite different in each composite structure. From this result it is suggested that low concentration of amide molecules (AM) is sufficient to achieve the maximum interlayer spacing of clay in PP1 matrix.



Figure 6-26 X-ray diffraction patterns of PP-clay composites prepared with different concentrations of short chain molecules (AM)

 Table 6-6 Interlayer distance of clay in PP-clay composites prepared with

 different concentrations of AM

Composite material	Bragg angle (2θ), (degrees)	Inter Layer Spacing (d ₀₀₁), (Å)
OMMT	2.92	30.2
PP1-AM0.3-2	2.64	33.46
PP1-AM0.5-2	2.36	37.44
PP1-AM0.7-2	2.42	36.48
PP1-AM1-2	2.36	37.44

However, in comparison with XRD results of PP2-2 composite structure (which prepared with PP grade containing polar additives, Figure 6-19), interlayer spacing of

PP1-AM0.5-2 composite (37.44 Å) is slightly smaller than that of PP2-2 (38.7 Å). This would suggest that not only short chain amide molecules (erucamide) but also antistatic agents, which are present in PP2 itself, intercalates into clay galleries, resulting in a higher gallery space in PP2-2 composite than PP1-AM0.5-2.

These short chain amide molecules (AM) are generally incorporated into some PP formulations to reduce the surface friction as they migrate onto the surface when PP products cool down, due to the incompatibility with bulk PP. In order to further confirm the interaction of AM with silicate layers and to study the their migration behaviour and subsequent accumulation on composite surface, PPCC prepared with different AM concentrations and their relevant blends (PP1 and AM only) were analysed using melt flow index (MFI) and contact angle (CA) techniques.

Figure 6-27 shows the melt flow index (MFI) values of PP1-AM-clay2 composites (PP1-AM-2) prepared with increasing concentration of AM (exact compositions are shown in Table 5-8) and their corresponding PP-AM blends.

As shown in Figure 6-27, MFI values of PP1-AM blends are increased significantly with increasing of AM concentration, in comparison with pure PP1, and then it starts to level off when AM concentration increases more than 1 % by weight. This can be attributed to the fact that short chain amide molecules (AM) are likely to act as an internal lubricant, at the melt stage, by penetrating through PP molecules and increasing the slippage of PP chains over each other under an applied constant stress (2.16 kg load) at a given temperature (190 °C). As a result of this, the melt viscosity of PP-AM blends is decreased remarkably, resulting higher MFI values in PP1-AM blends.

However by adding clay into PP-AM blends, the MFI values are reduced dramatically compared to that of their corresponding PP-AM blends. As shown in Figure 6-27, MFI values of PP1-AM-2 are not changed up to 0.7 wt. % of AM and they are almost equivalent to that of MFI of PP1-clay2 composite prepared with out AM. This implies that AM molecules are not available as free molecules, at the melt stage, to provide the lubrication effect on PP chains. This result further supports the suggestion that most AM molecules diffuse into clay galleries, especially at low concentrations of AM. However, when AM concentration is increased more than 0.7 wt. %, the MFI

values start to increase, due to some of AM molecules remaining in the bulk of PP and decreases the melt viscosity of PP1-AM-2 composite, resulting comparatively higher MFI values.



Figure 6-27 Effect of amide molecule concentration on MFI values of PP1-AMclay composites and PP1-AM blends

6.3.3 Effect of amide molecules on surface properties of PPCC

Generally, when short chain AM are incorporated into pure PP, they migrate onto the surface and a thin amide-rich layer is formed on cooling due to the incompatibility with the PP matrix; as a result, the surface composition is changed [58, 138]. Contact angle measurements are sensitive to the chemical nature of polymer surfaces. Water and diiodomethane (CH_2I_2) contact angles on PP1-clay (2 wt. % of clay) composite films prepared with the addition of different concentrations of AM and their corresponding blends (PP1 and AM only) were measured (as described in section 5.5) to study the migration and subsequent accumulation of these molecules on the composite surface, when it cools down.

Figure 6-28 shows water contact angle values of PP1-AM-clay2 composites prepared with different concentrations of AM and their corresponding blends (PP1-AM) whilst diiodomethane contact angle values for these two compounds (PP1-AM-clay2 and PP1-AM) are shown in Appendix F. Water contact angle of pure PP1 film shows at 106°. However, when amide molecules (AM) are incorporated into PP1, the water contact angles of PP1-AM blends are decreased significantly with an increase of AM, in comparison to pure PP1, and reached steady values (at about 93°) with a further increase of the additive concentration above 0.7 wt. %. This implies increased wettability of PP1-AM blend surfaces as contact angle decreases, due to the migration of AM, resulting in higher polarity on the surface, as expected. Steady values are obtained at high concentrations of AM since the surface is becoming saturated with AM molecules.



Figure 6-28 Water contact angle values for PP1-AM blends and PP1-AM-clay2 composites

As shown in Figure 6-28, there is no significant difference in contact angles between PP1 and PP1-clay2 (without AM). This implies that addition of clay into pure PP1 does not change the surface properties of PP1. However, by adding clay (2 wt. %) into PP1-AM blends, water contact angles are increased significantly, compared to those of the respective PP-AM blends. As shown in Figure 6-28, when clay was added into PP1-AM0.3 blend, the water contact angle of the composite (PP1-AM0.3-clay2) was increased from 97.4 to 105.5 degrees. Similarly, the water contact angle of PP1-AM0.5-clay2 composite was increased by 10.4 degrees compared to the corresponding blend (PP1-AM0.5). This implies that PP1-AM-clay2 composites have comparatively lower wettability than their corresponding blends, since most of the amide molecules interact with clay particles without migrating onto the surface. Especially at low concentrations (less than 0.7 wt. %) of AM, most of amide molecules intercalate and subsequently interact with clay particles without migrating to the surface and as a result, water contact angles of PP-AM-clay2 become similar to that of PP-clay2 composite. However, when AM is increased to more than 0.5 wt. %, water contact angles showed a slight decreasing trend. This can be explained since there is an excess of AM in the system and as a result, this excess AM migrates onto the composite surface as occurs in PP1-AM blends.

The migration of AM and its accumulation on the surface of PP1-AM-clay composites can also be explained from surface energy values obtained from water and diiodomethane contact angles (as shown in section 5.5) for PP1-AM-clay composites and the equivalent matrix formulation. Figure 6-29 presents the effect of AM concentration on total surface energy whilst Table 6-6 summarises the polar and dispersive components of surface energy for both PP1-AM-clay2 composites and PP1-AM blends.



Figure 6-29 Surface energy for PP1-AM-clay2 composites and their blends

As shown in Table 6-7, the polar component of surface energy of pure PP1 is close to zero since no polar additives are present in pure PP1. However, when AM was added into PP1, the polar component of surface energy was increased significantly compared to that of pure PP1 and reached a steady value (about 1.60 mNm⁻¹) at high concentrations of AM. As a result, surface energy values of PP1-AM blends are also increased with the increase of AM towards steady values of just below 32 mNm⁻¹ (Figure 6-29).

It can be seen from Table 6-7 that the addition of clay into PP1-AM blends reduced the polar component of total surface energy significantly, in comparison to their respective blends. As a result, surface energy of PP1-AM-clay composites (Figure 6-29) becomes lower (in comparison to the respective PP1-AM blends at similar additive concentration) since most AM interacts with clay particles rather than migrating onto the surface. However, at high concentrations of AM (at concentrations greater than 0.7 wt %), surface energy of PP1-AM-clay composites is increased since

all AM does not intercalate into clay galleries and as a result, part of the AM migrates on the surface.

Table 6-7 Surface energy and surface polarity values of PP1-AM-clay compositesand PP1-AM blends

Composite	Surface energy (S.E), mNm ⁻¹			
material	Polar	Dispersive	Total S.E	
PP1-AM				
PP1	0.11	26.51	26.62	
PP1-AM0.3	0.86	28.88	29.74	
PP1-AM0.5	1.59	29.17	30.76	
PP1-AM0.7	1.69	29.83	31.52	
PP1-AM1	1.60	29.78	31.38	
PP1-AM1.5	1.66	29.65	31.31	
PP1-AM2	2.13	28.65	30.79	
PP1-AM-clay2				
PP1-2	0.04	27.22	27.25	
PP1-AM0.3-2	0.12	26.85	26.97	
PP1-AM0.5-2	0.29	25.80	26.09	
PP1-AM0.7-2	0.54	25.95	26.49	
PP1-AM1-2	0.68	27.06	27.74	
PP1-AM1.5-2	1.32	27.33	28.65	
PP1-AM2-2	1.25	26.54	27.78	

From this surface property analysis, it can be further verified that most of the AM (especially at low concentrations) intercalates into the clay galleries and interacts with them without migrating on to the surface.

6.3.4 Effect of amide molecules on clay dispersability

Since XRD results and contact angle measurements confirm the interaction of AM into clay galleries, TEM micrographs of PP-AM-clay composites were analysed to evaluate the effect of AM on clay dispersability in PP1 matrix. Figure 6-30 shows the TEM micrograph of PP1-AM-0.5-2 and whilst Figure 6-31 shows the TEM micrograph of PP1-clay (PP1-2), which contains same clay percentage as PP1-AM0.5-2 but without amide molecules (AM).

As shown in both figures 6-30 and 6-31, clay particles in both structures are not delaminated into smaller clay stacks and they are not dispersed homogeneously throughout the PP matrix as well. However PP1-AM0.5-2 structure contains slightly bigger clay stacks compared to that of PP-2 structure. This can be explained since AM intercalates into the clay galleries and increases the interlayer spacing and this is in agreement with the XRD results shown in Figure 6-26. However clay particles are not exfoliated and, as a result, the organised clay structure remains unchanged, resulting in comparatively bigger clay particles in the PP1-AM0.5-2 structure.

By looking at the TEM micrograph of PP1-AM0.5-2 (Figure 6-30) at higher magnification, it can be seen clearly that clay particles consist of regions of alternating dark and light bands, indicating the intercalated clay structure due to the presence of AM within clay galleries. However, the TEM micrograph of PP1-2 (Figure 6-31) at the same magnification does not show such a clay structure since no intercalation takes place, due to the absence of AM. The presence of alternating light and dark bands in clay particles reveals the intercalated clay particles and as a result, the gallery spacing increases.



(X25k)

Figure 6-30 PP1-clay composite (PP1-AM-2) prepared with the addition of amide molecules (AM)

This would confirm that the intercalated clay structure is formed, as already suggested from the X-ray diffraction results, when AM is incorporated into PP-clay composites. Although clay particles are intercalated, they are not exfoliated and dispersed homogeneously throughout the PP matrix in the presence of AM only during the compounding process. Addition of AM into PP-clay composites forms an intercalated and non homogeneously dispersed clay structure due to the incompatibility of clay with the PP1 matrix.



(X25k)

Figure 6-31 TEM micrographs of PP-clay composites (PP1-2)

In summary, the addition of short chain amide molecules (AM) into PP-clay composites results the higher interlayer spacing compared to organically modified clay due to the intercalation of AM into clay galleries. The maximum interlayer spacing can be achieved with very low level of AM concentration (0.5 wt. %) and with this concentration of AM, the composite surface property is not affected by AM. However higher concentration of AM alters the PP-clay composite surface. Although an intercalated clay structure is formed with the addition of AM, exfoliation of clay particles could not be achieved.

6.4 Co-intercalation of AM and PP-MA into clay galleries

Since clay particles do not exfoliate towards the nano-meter scale in the presence of AM only, PP1 was melt blended with clay in the presence of both short chain amide molecules (AM) and PP-MA to prepare PP-clay nanocomposite (PPCN) structures,
using the Haake rheometer as described in section 5.3. The exact compositions of PPCN prepared using both AM and PP-MA are shown in Table 5-7.

6.4.1 Effect of PP-MA concentration on intercalation

X-ray diffraction analysis for PPCN, prepared with the addition of 0.5 wt. % of AM and different concentrations of compatibiliser (PP-MA), was performed to study the effect of PP-MA concentration on nanocomposite structure containing AM. Figure 6-32 presents the X-ray diffraction spectra of PPCN (contains both AM and PP-MA) and conventional type of PPCN prepared by melt blending of PP1 and OMMT in the presence of PP-MA only. Table 6-8 shows the diffraction peak (001) positions and interlayer spacing for each nanocomposite structure. In literature it was reported that PPCN can be successfully prepared with the incorporation of PP-MA since it improves the compatibility between non polar PP and OMMT [17, 19, 21, 23].



Figure 6-32 X-ray diffraction of patterns of PPCN prepared by AM and different concentrations of PP-MA (PB)

Diffraction peaks (001) of all PPCN prepared with addition of both AM and PP-MA shifted to lower Brag angles, in comparison to the conventional type PPCN (PP1-PB2-2). The diffraction peak (001) of PP1-AM0.5-PB2-2 was shifted from 2.76 degrees (i.e. diffraction peak position of PP1-PB2-2) to 2.36 degrees (Table 6-8) when 0.5 wt. % of AM was incorporated into the nanocomposite structure. This indicates that both AM and PP-MA co-intercalate into clay galleries since each of these are compatible with OMMT. As a result, the inter layer spacing was increased from 31.3 Å (the inter layer spacing of PP1-PB2-2) to 37. 44Å.

As shown in Table 6-8, the diffraction peak (001) does not shift further to a lower Bragg angle with an increase of PP-AM concentration in PPCN structures (PP1-AM0.5-PB4-2 and PP1-AM0.5-PB6-2) and therefore it remains at 2.36 degrees for all PPCN prepared by co-intercalation of PP-MA and AM. As a result of this, the increase of PP-MA concentration more than 2 wt % does not enhance the interlayer spacing of clay in PPCN since the highest possible interlayer spacing was achieved with 0.5 % by weight of AM and low concentration of PP-MA (2 % by weight); a further increase of compatibiliser content is not effective in terms of increasing interlayer spacing.

PP-clay nanocomposites (PPCN)	Bragg angle (2θ), (degrees)	Interlayer spacing (d ₀₀₁), (Å)	
OMMT	2.92	30.3	
PP1-PB2-2	2.76	31.3	
PP1-AM0.5-PB2-2	2.36	37.44	
PP1-AM0.5-PB4-2	2.36	37.44	
PP1-AM0.5-PB6-2	2.36	37.44	

 Table 6-8 Interlayer distance of PPCN prepared with different concentrations of

 PP-MA

However the intensity of diffraction peaks of PPCN prepared with higher concentrations of PP-MA (PP1-AM0.5-PB4-2 and PP1-AM0.5-PB6) is lower compared to that of PPCN prepared with a low concentration of PP-MA (PP1-AM0.5-PB2-2). This could be due to the comparatively higher degree of exfoliation achieved with higher concentration of PP-MA. However, interpretation of peak intensities for the degree of exfoliation is not accurate because the number of clay particles present in the sample can affect the peak intensity. Therefore TEM analysis is a more appropriate method to study the clay exfoliation in PPCN structures. It has been reported in the literature that a high concentration ratio of PP-MA has a negative impact on mechanical properties of PPCN [137, 139].

6.4.2 Effect of AM and PP-MA on clay exfoliation

TEM analysis was also performed on conventional type PPCN (prepared using only PP-MA) and PPCN prepared by co-intercalation of AM and PP-MA, in order to evaluate the effect of both these additives on clay dispersability in PP1 matrix. Figure 6-33-(a) and (b) show the TEM micrographs of PP1-AM0.5-PB2-2 and PP1-AM0.5-PB4-2 respectively, showing the effect of both AM and PP-MA on clay exfoliation.

As shown in Figure 6-33-(a) and (B), clay particles are exfoliated into thinner stacks containing less number of clay layers and dispersed homogenously through out PP1 matrix when PPCN (PP1-AM0.5-PB2-2 and PP1-AM0.5-PB4-2) is prepared by cointercalation of PP-MA and AM. It was found from section 6.2.2.1 that when PPCN prepared with only PP-MA (which is considered as a conventional type PPCN), higher PP-MA to clay ratio (PP-MA: clay 3:1) is important to achieve better exfoliation of clay in PP matrix. The improved clay dispersion with higher content of PP-MA was shown in TEM micrograph of PP1-PB6-2 (Figure 6-14-(b)) compared to that of PP1-PB2-2 (Figure 6-17).

However, in contrast to the TEM micrograph of PP1-PB2-2 (Figure 6-17), TEM micrographs of PP1-AM0.5-PB2-2 (figure 6-33-(a)) and PP1-AM0.5-PB4-2 (Figure 6-33-(b)), which consist of lower concentration of PP-MA (i.e. clay 1:1 PP-MA and clay1:2 PP-MA respectively) have shown comparatively much smaller clay stacks and they are dispersed homogeneously throughout the PP1 matrix. Therefore these TEM

pictures (Figure 6-33) reveal that the incorporation of AM along with PP-MA into PPCN structures significantly enhances the degree of clay exfoliation and hence it allows a lower ratio of PP-MA relative to clay (i.e. PP-MA 1: 1 clay) in PPCN to be used, than in conventional type PPCN (PP-MA 1:3 clay).





(a)

(b)



Improved clay dispersion in these nanocomposite structures (PP1-AM0.5-PB2-2 and PP1-AM0.5-PB4-2) is achieved since both AM and PP-MA with PP molecules intercalate into clay galleries, resulting in a higher interlayer spacing, as shown in XRD results (Table 6-8). Therefore the attractive forces between clay layers become weaker so that clay particles are dispersed homogenously throughout the PP matrix during the compounding process since compatibility between clay and PP is achieved through PP-MA, even with a lower concentration of PP-MA.

Since this co-intercalation method (i.e. using both AM and PP-MA) has promising effects on clay exfoliation in the PPCN structure, PPCN was also prepared with another PP grade (PP3), which has a comparatively lower molecular weight (as shown from the GPC analysis, Table 6-2) than PP1 grade, to further verify the positive effect of AM on clay exfoliation. Figure 6-34 shows the TEM micrograph of PP3-AM0.5-PB2-2.



Figure 6-34 TEM micrograph of PP3-AM0.5-PB2-2 (magnification 25, 000)

Similar to the PPCN prepared with PP1 (Figure 6-33), this PPCN prepared with PP3 grade (Figure 6-34) has also shown homogeneous dispersion of clay in the nanocomposite structure. In comparison with PP3-PB6-2 (Figure 6-22), clay particles are exfoliated to smaller stacks when AM is incorporated into nanocomposite structure (PP3-AM0.5-PB2-2), even with lower concentration ratio of PP-MA. This appears that co-intercalation method is effective for PP grades with different molecular weights

6.4.3 Comparison of clay dispersion by a manual method

The different levels of clay dispersion in (1) PPCN prepared by co-intercalation of AM and PP-MA and (2) PPCN prepared by conventional method were quantified by counting the number of clay platelets (nanometer size) and intercalated clay particles (sub-micron) in each TEM micrograph at 25,000 magnification, as described in section 5.4.2. Table 6-9 summarises the TEM results as the average number of clay particles per 64 cm² and standard deviations of PPCN structures prepared by both these methods. The higher number of clay particles indicates the better dispersion of clay in the nanocomposite structure.

Table	6-9	Quantification	of	clay	dispersion	of	PPCN	prepared	by	co-
interca	latio	n of PP-MA and	AM	and	conventional	PP	CN			

PPCN materials	Clay platelets and intercalates p 64 cm ² (X 25, 000)		
PP1-AM0.5-PB2-2	16.8 ± 2.17		
PP1-AM0.5-PB4-2	14.6 ± 0.5		
PP3-AM0.5-PB2-2	9.4 ± 1.52		
PP1-PB2-2	3.2 ± 2.3		
PP1-PB6-2	10.4 ± 2.41		
PP3-PB6-2	8.2 ± 1.79		

As shown in Table 6-9, PP1-PB2-2 nanocomposite structure which was prepared by the conventional method shows the lowest number of clay particles per unit area. However, when the compatibiliser (PB) concentration increases, PP1-PB6-2 structure shows a significant increase in number of clay particles, showing the positive effect of PB concentration on clay dispersion, in the conventional method.

PP1-AM0.5-PB2-2, which was prepared by co-intercalation method with a lower concentration of PB, shows a significantly higher number of clay particles than that of the conventional type of PPCN (PP1-PB6-2 and PP1-PB2-2). From this new method, even with a low concentration of compatibiliser (PB to clay ratio 1:1), improved clay dispersion can be achieved with the addition of AM into the nanocomposite structure. However, by increasing the compatibiliser (PP-MA) concentration (PB to clay ratio 1:2; PP1-AM0.5-PB4-2), the dispersion does not significantly change compared to that of PPCN prepared with lower concentration of PP-MA (PP1-AM0.5-PB2-2). Similar improvement of exfoliation is also shown for the low molecular weight grade of PP (PP3-AM0.5-PB2-2) with lower concentration of PP-MA in comparison to conventional PPCN prepared with higher concentration of PP-MA (PP3-PB6-2). These quantification results from TEM micrographs further demonstrate that this co-intercalation method has a strong effect on exfoliation and dispersion of clay in nanocomposite structure.

6.4.4 Quantification of clay exfoliation by image analysis

By examining these nanocomposite structures (PP1-AM0.5-PB2-2, PP1-AM0.5-PB4-2 and PP3-AM0.5-PB2-2) at higher magnification (Figure 6-35), evidence shows that these are mainly intercalated nanocomposite structures, containing very small clay stacks (less number of clay layers) with a range of sizes.





(b)

(c)

Figure 6-35 TEM micrographs, at higher magnification (50k), of PPCN prepared with co-intercalation of PP-MA and AM, (a) PP1-AM0.5-PB2-2, (b) PP1-AM0.5-PB4-2, (c) PP3-AM0.5-PB2-2

This would suggest that intercalated clay structures contain a different number of clay layers, as there is a size distribution of intercalated clay particles.

Since the TEM micrographs (Figure 6-35) of PPCN prepared by the co-intercalation method have shown intercalated clay particles with different sizes, the distribution of clay particle thickness in PPCC (PP1-2) and PPCN (PP1-AM0.5-PB2-2, PP1-AM0.5-PB4-2 and PP3-AM0.5-PB2-2) was determined using image analysis software to quantify the degree of exfoliation in PPCN, as described in section 5.4.3. Clay particle thickness gives a qualitative measurement of clay platelets (layers) per stack. The numbers of platelets (N) per clay stack was also calculated using equation 5.4, as shown in section 5.4.3.

The number of clay platelets (N) per stack is inversely proportional to the degree of exfoliation and hence less number of platelets (N) per stack indicates a higher degree of exfoliation. The PP1-2 (PP and clay only) was taken as a reference sample since no

intercalation and exfoliation (conventional PP-clay micro composite) occurs in this sample.

Figure 6-36 shows the black and white TEM image (25k), which is prepared from the original TEM image as explained in section 5.4.3 of PP-clay micro-composite (PP1-2) and its distribution of clay particle thickness while figures 6-37 to 6-39 show black and white TEM images (50k) of PPCN prepared by co-intercalation of PP-MA and AM and their distribution of clay particles thicknesses.



Figure 6-36 Image analysis of PP1-2, TEM image and distribution of clay stacks thickness



Figure 6-37 Image analysis of PP1-AM0.5-PB2-2, TEM image and distribution of clay stack thickness



Figure 6-38 Image analysis of PP1-AM0.5-PB4-2, TEM image and distribution of clay stack thickness



Figure 6-39 Image analysis of PP3-AM0.5-PB2-2, TEM image and distribution of clay stack thickness

Quantification of clay stack thicknesses clearly shows that all PPCN structures contain very thin clay stacks compared to the clay stacks in PP1-2, resulting in a lower number of clay platelets per particle in PPCN structures. As shown in Figure 6-36, there are no clay particles below 20 nm in PP1-2 composite (as expected), since it is a conventional PP-clay micro-composite. On the other hand, about 30-40 clay stacks are below 20 nm (Figures 6-37 and 6-38) in both PPCN structures prepared with PP1 grade whereas about 22 clay stacks are below 20 nm in PPCN prepared with PP3 grade (Figure 6-39). Clay particle thickness distribution further shows that about 90 % of intercalated clay particles are below 50 nm in all PPCN structures. Table 6-10 shows the statistics of clay stack thickness obtained from image analysis software and whilst Table 6-11 presents clay platelets per clay stack calculated, as explained in 5.4.3 for PP1-2 and PPCN structures.

As shown in Table 6-11, PP1-2 contains clay particles with a higher number of clay layers per stack in comparison to PPCN structures (PP1-AM0.5-PB2-2, PP1-AM0.5-PB4-2 and PP3-AM0.5-PB2-2). There are 76 average numbers of clay platelets per

clay particle in PP1-2 structure. However, in comparison to PP1-2 structure, clay stacks in PPCN structures have a lower number of clay platelets since a greater degree of exfoliation is occurred due to the co-intercalation of PP-MA and AM.

Table 6-10 Statistics of clay stack thickness and the total number of clay stacks in PPCC and PPCN

Composite	C	Total number of			
sample	minimum	maximum	mean	S.D	(per µm ²)
PP1-2	83	546	232	153	6/8.89
PP1-AM0.5-PB2-2	5	75	21	17	60/2.2
PP1-AM0.5-PB4-2	4	81	18	16	46/2.2
PP3-AM0.5-PB2-2	4	48	16	9	28/2.2

 Table 6-11 Statistics of platelets per clay stack and degree of exfoliation of clay in

 PPCN

Composite sample	Number	Mean degree of exfoliation		
	minimum	maximum	mean	(%)
PP1-2	28	182	79	
PP1-AM0.5-PB2-2	2	21	6	92
PP1-AM0.5-PB4-2	2	22	6	92
PP3-AM0.5-PB2	2	14	4	95

As shown in Table 6-11, all PPCN structures consist of clay stacks with average of 4-6 clay layers, resulting in a very high degree of exfoliation. There is no significant difference in the number of clay platelets per clay stack between PP1-AM0.5-PB2-2 and PP1-AM0.5-PB4-2, which has comparatively higher concentration of PP-MA, indicating that a higher concentration of PP-MA does not further enhance the exfoliation in this system.

The degree of exfoliation of PPCN structures was also determined by considering the mean numbers of clay platelets per stack as defined by the term "degree of exfoliation" in section 5.4.3 (Equation 5.5). Table 6-11 shows that all PPCN structures have a very high degree of exfoliation (92-95 %) relative to the clay particles in PP1-2 composites. From these image analysis results, it can be suggested that, although PPCN consist of mainly intercalated clay particles, this co-intercalation method significantly enhances the degree of exfoliation, resulting in much smaller clay stacks with 4-6 clay layers in the PPCN structures.

From these quantitative results, the data in Table 6-10 and 6-11 show that the addition of *both* AM and PP-MA is more effective on the intercalation and exfoliation behaviour of clay in PP matrix in comparison to that of PPCN prepared with PP-MA only. This new preparation method for PPCN also effectively reduces the PP-MA concentration (without any negative impact on clay dispersion) in PPCN structures, in comparison to the conventional method of preparation of PPCN which involves only PP-MA as a compatibilising agent.

6.4.5 Mechanism of co-intercalation

It was shown from X-ray diffraction and TEM analysis that both short chain amide molecules (AM) and compatibiliser (PP-MA) intercalate into clay galleries and as a result, this enhances clay dispersion in PP matrix. Studies were continued to determine the driving force for the intercalation of these molecules and to suggest a possible mechanism for intercalation.

Initially the intercalation behaviour of AM into clay galleries was studied. There is a greater affinity of amide molecules (AM) towards silicate layers since there is a

strong possibility of interaction between the amide group (CONH₂) and silicate layers through hydrogen bonding. If this hydrogen bonding occurs, the bond strength of both the amide group and Si-O in the silicate layers could be changed with a different environment created due to the interaction of AM with silicate layers.



Figure 6-40 FTIR spectra of Si-O bond of OMMT and AM intercalated OMMT

Figure 6-40 shows FTIR spectra of Si-O bonding in different composites and Figure 6-41 shows the FTIR spectra of carbonyl bonds (amide-1) for both pure AM and organically modified clay treated with AM (AM-OMMT).

As shown in Figure 6-40, the peak related to Si-O bond stretching vibration appears at 1048 cm⁻¹ in the OMMT spectrum. When OMMT was treated with AM (AM-OMMT), the Si-O bond was shifted slightly to lower frequency (1047 cm⁻¹), although

we would expect a greater shift towards a lower frequency, due to hydrogen bonding. However, when PP1 was melt mixed with 2 wt. % of clay (OMMT) and different concentrations of AM (0.5- 1.5 wt. %), the FTIR spectra (Figure 6-40) show that peaks corresponding to Si-O bonding were shifted to a lower frequency (1043/1044 cm⁻¹) in comparison to the OMMT spectrum. The complete FTIR spectrum for each PP1-AM-clay composite is shown in Appendix G.

However on the other hand, as shown in Figure 6-41, The FTIR spectrum of AM-OMMT shows a doublet (1646 and 1667 cm⁻¹) for the peak corresponding to C=O stretching vibration, in comparison to the peak (1646 cm⁻¹) related to C=O stretching vibration for pure AM (Appendix G shows both complete spectra of AM and AM-OMMT).



Figure 6-41 FTIR spectra of C=O of AM and AM-OMMT

Although it is expected to shift the C=O peak towards a lower wave number due to hydrogen bonding between C=O and O-H groups in the silicate layer surface, the C=O peak of OMMT-AM shifted to a higher wave number (1667 cm⁻¹). This can be explained since pure AM consists of intra and inter molecular hydrogen bonding within the amide molecules (i.e. densely packed) and as a result, the C=O peak appeared at lower wave number (1646 cm⁻¹). However, when AM intercalates into clay galleries (Figure 6-41: AM-OMMT) and interact with silicate layers, the amount of intra molecular H bonding reduces and, as a result the C=O peak appears as a doublet with a higher wave number peak.

These FTIR results along with the XRD results (i.e. increase in interlayer spacing due to intercalation of AM) are strong evidence for the formation of hydrogen bonding between the silicate layers and AM and this is suggested as the driving force for the intercalation of AM into clay galleries. The hydrogen bonding causes an interaction between AM with silicate layers and therefore prevents the diffusion of these short chain amide molecules (AM) towards the composite surface.

However, when PPCN was prepared by the co-intercalation method, not only AM but also PP-MA is also added into the system. The addition of PP-MA may result in more complex chemical reactions between these three components (i.e. silicate layer, AM and the maleic anhydride functional groups in PP-MA), at the melt stage during the compounding process.

In literature, the most frequent explanation for intercalation of PP-MA into clay is polar interaction between maleic anhydride group of functionalised PP and the silicate layers [7, 23]. Okada et al. [23, 140] pointed out the possibility of reacting PP-MA with octadecylamine (used for organic modification of clay) and possible formation of imide groups. However Szazdi et al. has carried out a comprehensive study on interactions between components in PPCN [141]. He showed that PP-MA can react with organic modifier used in clay, if it contains active hydrogen atoms (hexadecylamine used in their study), and this leads to the formation of amides. He further mentioned the possibility of formation of cyclic imides but could not prove their existence since characteristic vibration peak of imide group appears in the same range with other peaks.

In our system, when PP-MA was melt mixed with AM, there is also a possibility of forming imide groups by reaction of active H atoms of AM and highly reactive maleic anhydride group of PP-MA. This imide groups could also react with silicate layers through hydrogen bonding. However, the existence of imide groups in the system could not be detected from FTIR spectroscopy since there is a very low percentage of MA in PPCN structure and also due to the overlapping of peaks related to imide bond with other peaks (as mentioned above).

Therefore in this new co-intercalation method, it can be suggested that intercalation can occur by either AM and PP-MA separately or as a reacted product (imide), or both together. Figure 6-42 shows a schematic illustration for the co-intercalation of AM and PP-MA in to clay galleries.



Figure 6-42 Schematic illustration of PPCN preparation by co-intercalation of AM and PP-MA

6.5 Effect of secondary amide molecules on PPCN structures

Steryl erucamide (SE), a secondary amide molecule, has also been used to study the effect of secondary amide molecules on PPCN structure in terms of intercalation and exfoliation since it has now been shown that primary amide molecules (AM) can be used to enhance clay intercalation and exfoliation in PP matrix. Steryl erucamide (SE) is a secondary amide molecule and its chemical structure is shown in section 2.4.1. One of the H atoms in amide group is replaced by erucamide chain and hence SE has a higher molecular weight than AM (erucamide).

PP1 was melt blended with clay with the addition of SE in a Haake rhrometer, similar to the preparation of PP-clay composites (PPCC) with primary amide molecules (AM). The PPCC prepared with SE was analysed using X-ray diffraction and TEM techniques to examine whether these molecules (SE) have a similar effect on clay structure as with AM.

Figure 6-43 shows the X-ray diffraction pattern of PP-clay composite (PPCC) prepared by the addition of SE.



Figure 6-43 X-ray diffraction pattern of PPCC and PPCN prepared with secondary amide molecules (AM)

X-ray diffraction peak of PP1-SE0.5-2 (the composition is shown in Table 5-8) has been slightly shifted to a lower Bragg angle in comparison to organically modified clay (OMMT) and hence basal spacing of clay was increased to 32.10 Å. This implies that SE also intercalates into clay galleries, similar to AM shown in Figure 6-27 and therefore increasing the interlayer spacing of clay. Table 6-12 shows the interlayer spacing of PP-clay compounds prepared with primary amide molecules (AM) and secondary amide molecules (SE).

Table 6-12 Comparison of Interlayer spacing of PP-clay compounds prepared with AM and SE

PP-clay compounds	Interlayer spacing, (d ₀₀₁), (Å)
OMMT	30.2
PP1-AM0.5-2	37.44
PP1-SE0.5-2	32.10
PP1-AM0.5-PB2-2	37.44
PP1-SE0.5-PB2-2	32.10

However as shown in Table 6-12, the gallery spacing of clay in PP1-SE0.5-2 has been increased by only 1.9 Å than OMMT whereas the gallery spacing of clay PP1-AM0.5-2 has been increased by 7.24 Å (Table 6-12). This suggests that intercalation ability of secondary amide molecules (SE) is less effective compared to that of primary amide molecules (AM). The same figure shows the X-ray diffraction peak of PPCN (PP1-SE0.5-PB2-2) prepared by co-intercalation of SE and PP-MA. The addition of PP-MA into the composition is not effective in terms of interlayer spacing since diffraction peak (001) of PP1-SE0.5-PB2-2 does not shift to a lower Bragg angle compared to that of PP1-SE0.5-2, resulting in same interlayer spacing (Table 6-12). A similar effect of PP-MA on PPCN prepared with AM (PP1-AM0.5-PB2-2) was also observed (Table 6-12). However these X-ray diffraction results do not show the effect of SE on clay dispersability in PP matrix, so that TEM analysis was also carried out on these nanocomposite structures.

Figure 6-44 shows the TEM image of PPCC prepared by adding SE molecules into the composite formulation. It clearly shows that clay particles are not separated into smaller stacks and they are not dispersed uniformly as well throughout the PP1 matrix. However, at higher magnification, TEM image shows the presence of dark and light bands alternatively in clay structure, similar to the TEM micrograph of PPCC prepared with AM (Figure 6-30), and this implies the intercalation of SE into clay galleries.





Figure 6-44 TEM micrograph of PPCC prepared using secondary amide molecule (SE), PP1-SE0.5-2

This result is in agreement with the X-ray diffraction results shown in Figure 6-43. Although SE molecules intercalate into clay galleries, they do not improve clay dispersion in PP1 matrix since SE does not promote the compatibility between clay and PP matrix, as was the case with AM.

Figure 6-45 presents TEM micrographs of PPCN prepared by melt blending of both SE and PP-MA. In contrast to the TEM image of PP1-SE0.5-2 (Figure 6-44), clay particles in PP1-SE0.5-PB2-2 (Figure 6-44) are exfoliated into much smaller stacks and they are dispersed uniformly throughout the PP1 matrix. When PPCN was prepared by co-intercalation of SE and PP-MA, clay dispersion was improved significantly, similar to PPCN prepared by co-intercalation of AM and PP-MA, as already explained in section 6.4.



(X25 k)

(X50 k)



However in comparison with the PP1-AM0.5-PB2-2 structure (Figure 6-33-(a) and 6-35-(a)), the improvement of clay dispersion caused by secondary amide molecules (SE) is less than primary amide molecules (AM). This could be explained since AM has two H atoms attached to N and as a result, more interaction towards silicate layers through H bonding than SE which has only one H atom attached to N for H bonding formation.

From these results it is clear that both primary and secondary amide molecules have intercalation ability when they are melt blended with PP and clay. However primary amide molecules (AM) are more effective in intercalation and subsequent exfoliation compared to that of secondary amide molecules (SE). As a result of this PPCN structures prepared with AM has improved clay dispersion.

6.6 Characterisation of PPCN prepared by co-intercalation

It has been shown from previous results that a new way of synthesising PPCN by cointercalation of PP-MA and AM is more effective on exfoliation and dispersion of clay throughout PP matrix. PPCN were then prepared by this new method with increasing clay concentration. The nanocomposite structures were prepared by melt blending of PP1 with clay in the presence of compatibiliser (PB) and short primary amide molecules (AM) using the Haake rheometer as described in section 5.3. The concentration ratio between clay, PB and AM (clay 1: PB1: AM 0.25) is kept constant for all PPCN structures, whose compositions were shown in Table 5-7, since it was found that above ratio is the most suitable for dispersion of clay in PP matrix. The last digit of the composite code refers to the weight percentage of clay (i.e. PP1-AM0.5-PB2-2)

Figure 6-46 shows the X-ray diffraction spectra for PPCN prepared with increasing clay concentrations and Table 6-13 shows diffraction peak (001) position (Bragg angle) and interlayer spacing (d_{001} spacing) for each nanocomposite structure. As shown in Table 6-13, all PPCN structures prepared with increasing clay loading have higher clay gallery spacing than clay. However, for PPCN prepared with higher loading levels of clay (i.e. 4 and 6 wt.%), diffraction peaks are shifted to slightly a higher Bragg angle compared to that of PPCN prepared with lower loading level of

clay (i.e. 2 wt. %). This implies the slight reduction of gallery spacing (d_{001}) in clay when the clay loading level is increased and this could affect the degree of exfoliation. Diffraction peak intensity shows a gradual increase with the increase of clay content since the number of clay particles is increased gradually.



Figure 6-46 X-ray diffraction patterns of PPCN prepared with increasing concentrations of clay

Table	6-13	Interlayer	spacing	(d_{001})	of	PPCN	prepared	with	increasing
concen	tratio	n of clay							

PPCN structures	Bragg angle (2θ) (degrees)	Inter layer spacing (d ₀₀₁) (Å)
OMMT	2.96	30.2
PP1-AM0.5-PB2-2	2.36	37.44
PP1-AM1-PB4-4	2.44	36.17
PP1-AM1.5-PB6-6	2.42	36.52

However more prominently, PP1-AM1.5-PB6-6 shows a very high intensity and higher diffraction peak area in comparison to other PPCN structures (PP1-AM0.5-PB2-2 and PP1-AM1-PB4-2) prepared with a lower concentration of clay. This can be explained since there is a high concentration of intercalated clay particles in PP1-AM1.5-PB6-6 structure, indicating less degree of exfoliation due to the high content of clay in this structure.

These X-ray diffraction results suggest that, although the intercalated nanocomposite structure is formed, the degree of exfoliation of clay could be reduced in PP1 matrix when clay loading level is increased more than 4 % by weight.

6.6.1 Analysis of PPCN by melt flow index (MFI)

PPCN prepared with increasing concentration of clay were analysed by melt flow index (MFI) and melt volume rate (MVR) to study the relationship between melt rheology and clay dispersability in the PPCN. It is known that the viscous behaviour of a PPCN composite (at any given particle concentration) is sensitive to the aspect ratio of filler and filler-matrix interactions, especially at low shear rates. However, it is not only the clay structure but also the viscous properties of the polymer matrix that also influences the measured MFI and MVR. Therefore in order to investigate clay structure in PP and its interaction with the continuous PP matrix, a "normalised" MFI/MVR (defined as shown in the experimental section, 5.6) was calculated in order to present comparative data. Zhu and Xanthos [115] have also used MFI measurements successfully to study the relationship between rheology and morphology of clay in PPCN; their results showed that MFI data are able to provide an indication of exfoliation and dispersion of clay in the PP matrix. Figures 6-47 and 6-48 show how the normalised MFI (n-MFI) and normalised MVR (n-MVR) change with increasing clay concentration for both PPCN and PP-clay composites (PPCC) respectively.



Figure 6-47 Normalised MFI for PPCN and PPCC prepared with increasing clay concentrations

As shown in figure 6-47, when PP is melt blended with clay but without either PP-MA or AM (PPCC), the n-MFI does not change with increasing clay loadings, because clay particles remain in their original state and there is also no significant interaction between clay particles and the polymer matrix. As a result, the clay simply acts as conventional diluent filler in the PP matrix, having little influence on shear flow properties at such a relatively low volume concentration of clay.

However on the other hand, when PP-MA and AM were also added into composites (PPCN), the n-MFI shows a significant reduction compared to that of PPCC. The steady reduction of n-MFI in PPCN is shown with increasing clay loading (from 2-8 % by weight), when it was measured with constant loads of 2.16 kg and 5kg. This demonstrates a viscosity increase, as a result reducing n-MFI, due to the exfoliation of clay into smaller stacks with the addition of PP-MA and AM, hence increasing the aspect ratio and specific surface area of clay particles in the nanocomposite structures. A steady reduction of n-MFI with an increased clay concentration further implies that the interaction between clay and the PP matrix is achievable. PP based functionalised

compatibiliser (PP-MA) interacts with clay through functional group (MA) and interacts/entangles with PP matrix and as a result, PP-clay interaction is achieved, hence higher viscosity.



Figure 6-48 Normalised MVR of PPCN and PPCC prepared with increasing clay concentrations

A similar trend for n-MVR, similar to n-MFI, was also observed (Figure 6-48) for both PPCN and PPCC. The n-MVR of PPCN showed a steady reduction with increasing clay loading, whereas no such reduction of n-MVR was observed in PPCC structures.

The positive effect of amide molecules (AM) and PP-based compatibiliser (PP-MA) on clay dispersability is further verified from these results, which are agreeable with the TEM images of PP1-clay composites (Figure 6-31) and PP1-AM-PB-clay nanocomposites (Figure 6-33). These results suggest that MFI and MVR data can effectively be used to evaluate the degree of clay exfoliation in composite structures, since low shear flow properties are affected by characteristics of clay particles. The steady reduction of n-MFI in PPCN would suggest that PP molecules diffuse into clay

galleries with PP-MA and AM, creating increased interactions and consequently, a higher shear viscosity (lower n-MFI/n-MVR).

6.6.2 Surface properties of PPCN

Surface properties of compression moulded films of PPCN prepared using PP-MA and AM were analysed using contact angle measurements to evaluate the percentage of AM migrating onto the surface with increasing concentrations of clay in nanocomposites structures. Figure 6-49 presents the water contact angles and resulting polar component to surface energy of PPCN prepared with increasing clay concentrations. Diiodomethane contact angles and surface energy values of PPCN are shown in Appendix H

As shown in Figure 6-49, water contact angles show a gradual reduction when PPCN was prepared with increasing concentrations of clay and AM (clay to AM ratio; 1 to 0.25, is constant for all nanocomposites). Water contact angle of PP1 is 106 ° and it gradually reduced when clay concentration was increased from 2 to 8 wt. %. Water contact angle was reduced to 102 ° in PPCN prepared with 8 wt. % clay. The gradual reduction of water contact angles of PPCN structures indicates that small amount of AM migrates onto the composite surface and, as a result, the polar component to the surface energy is increased gradually, as shown in figure 6-49, when PPCN was prepared with increasing concentration of clay.

Water contact angle of PPCN with 2 wt. % clay (105°) is similar to that of water contact angle of pure PP1 (106°) and therefore there is no significant difference of polar component between pure PP1 (0.11 mN/m) and PP1-AM0.5-PB2-2 (0.15 mN/m). This would suggest that almost all AM is involved in intercalation of clay, leaving no free AM to migrate onto the surface. However when PPCN was prepared with more than 2 wt. % of clay, the polar component of the surface energy is marginally increased compared to pure PP1, indicating that a small part of free AM is available in bulk PP to migrate on to the surface. Although most AM molecules diffuse into clay galleries during the compounding process of PPCN, small fraction of AM migrates onto the surface, especially PPCN with high concentration of clay.



Figure 6-49 Water contact angles and polar component to the surface energy of PPCN prepared with increasing clay concentrations

Surface polarity values for each PPCN were also calculated as described in section 5.5 (Equation 5.7) and the surface polarity reduction for PPCN was determined with respect to the surface polarity values of PP1-AM mixtures. Appendix H shows the surface polarity values for both PPCN and PP1-AM blends. As shown in figure 6-50, about 90 % of surface polarity is reduced in PP1-AM0.5-PB2-2 compared to that of PP1-AM0.5. However when PPCN was prepared with increasing concentration of AM and clay, the percentage reduction of surface polarity is decreased significantly and only about 55 % surface polarity is reduced when 8 wt. % (P1-AM2-PB8-8) of clay was used.

These results show that, although the addition of AM provides slip effect and reduces surface friction of pure PP, no slip effect could be achieved in PPCN, especially at low concentration of clay and AM (PP1-AM0.5-PB2-2) since almost all AM diffuses into the clay galleries, leaving no free AM to migrate to the PPCN surface. However a

comparatively reduced slip effect could be predicted in PPCN prepared with higher concentrations of clay (PP1-AM1.5-PB6-6 and PP1-AM2-PB8-8) since a fraction of amide molecules (AM) migrates onto the composite surface.



Figure 6-50 Percentage surface polarity reduction of PPCN in comparison to PP1-AM mixture.

6.6.3 Melting and crystallisation development in PPCN

Melting and crystallisation behaviour of PPCN prepared by co-intercalation of PP-MA and AM and their corresponding blends without clay were analysed using differential scanning calorimetry (DSC) to study the effect of clay on melting and crystallisation of PPCN. Table 6-14 shows the peak melting and peak crystallisation temperatures determined from second heating and cooling DSC thermograms of PPCN and their corresponding blends respectively. Some examples of DSC traces of PPCN are shown in Appendix I.

As shown in Table 6-14, the melting temperatures (T_{mp}) of PPCC (PP1-2) and PPCN with increasing clay concentrations were not significantly changed in comparison to

that of pure PP1. This implies that the clay particles do not affect the crystallite perfection, hence the similar melting temperature of PP in PPCN structures.

 Table
 6-14
 DSC
 melting
 and
 crystallisation
 temperatures
 of
 PP-clay

 nanocomposites (PPCN) and their blends (with out clay)

 </

Composite	T _{mp} (°C)	T _{co} (oC)	Т _{ср} (°С)	ΔT _{cp} (°C)
PP1	169	133	128	-
PP1-2	170	131	126	-2
PP1-AM0.5-PB2	168	119	115	-
PP1-AM0.5-PB2-2	167	122	119	4
PP1-AM1-PB4	167	115	109	-
PP1-AM1-PB4-4	169	118	113	4
PP1-AM1.5-PB6	169	115	109	-
PP1-AM1.5-PB6-6	167	118	114	5

T_{mp}= Peak melting temperature

 T_{cp} = Peak crystallization temperature

T_{co}= Onset crystallisation temperature

 ΔT_{cp} = difference of peak crystallisation temperature of PPCN and corresponding blends

However, in comparison with pure PP1, the crystallisation temperatures (T_{cp}) of PP1-AM-PB blends (Table 6-14) showed a decreasing trend with increasing compatibiliser and AM content. Crystallisation temperature of pure PP1 is 127 °C and when PP-MA (PB) and AM are added into PP1, the crystallisation was initiated at a lower temperature, resulting in lower crystallisation temperatures in PP1-AM-PB blends. This result suggests that either functional group (maleic anhydride) in PP-MA or AM significantly affects the nucleation process for PP and therefore resulting lower crystallisation temperatures.

However as shown in Table 6-14, by introducing clay, the crystallisation temperatures of PPCN (e.g. PP1-AM0.5-PB2-2) increase slightly compared to their corresponding blends (e.g. PP1-AM0.5-PB2). However there is no increase in crystallisation temperature of PP-clay2 composite (PP1-2), in comparison to pure PP1. As shown in Table 6-14, the crystallisation temperature of PPCN prepared by increasing clay content is about 4-5 °C higher than that of their corresponding blends. This can be attributed to the fact that clay (possibly due to the exfoliated clay particles) acts as a heterogeneous nucleating agent, resulting in higher crystallisation temperatures in PPCN, whereas no increase in crystallisation temperature was observed in PP-clay composite (PP1-2), in comparison to pure PP1 since there is no exfoliation of clay occurring in this structure. Nucleation effect of clay on the crystallisation of PP-clay nanocomposites has been reported elsewhere in the literature [142, 24, 137, 143]. These results clearly show that exfoliated smaller clay stacks lead to crystallisation at a slightly higher temperature and this is in agreement with the nanocomposite structure of PP-AM0.5-PB2-2 shown in the TEM image (Figure 6-33).

The crystallinity of PP in PPCN was obtained using heat of fusion data from crystallisation peaks, in DSC thermograms (Appendix I) to examine the effect of clay on percentage crystallinity of PP in PPCN structure. The percentage crystallinity of PP in PPCN prepared with increasing clay contents was calculated as explained in section 5.2.4 (Equation 5.1). Figure 6-51 shows percentage crystallinity of PP1 for PPCN prepared by increasing clay concentration.

Pure PP1 shows 59 % crystallinity. When PPCN was prepared with the addition of clay, the percentage crystallinity of PP1 decreased for all PPCN structures. The crystallinity of PP in PPCN containing 2 wt. % clay decreased from 59 % (crystallinity of pure PP1) to 52 and to 43 % for 8 wt. % clay in PPCN. This would suggest that, although clay particles initiate crystallisation at slightly a higher temperature, maleic anhydride in PP-MA (or AM) may have a negative impact on crystallite growth process, resulting in reduced crystallinity in PP. However, more

required to understand the effect of clay and these additives (PP-MA and AM) on microstructure of PPCN, especially when PPCN prepared with nucleated PP



Figure 6-51 Crystallinity for PPCN prepared with increasing clay content

6.6.4 Thermal stability of PPCN

The thermal stability, for which nanocomposite morphology and structure play an important role, of pure PP and PPCN was analysed using thermogravimetric analysis (TGA) method under air environment. Figure 6-52 shows the TGA curves of pure PP1 and PPCN with different clay concentrations whilst Table 6-15 presents temperatures corresponding to 10 % weight loss (which is considered as the onset of degradation, T_{10}), 50 % weight loss (T_{50}) and the temperature of maximum rate of weight loss (T_{mr}), obtained from TGA and derivate thermogravimetric (DTG) experimental curves. DTG curves for PPCN are shown in Appendix J.

As shown in Figure 6-52, incorporation of clay into PP1 significantly enhances thermo-oxidative stability of PPCN compared to that of pure PP1. Thermal stability increases marginally when clay concentration is increased more than 4 wt % clay in PPCN structures. The onset of thermal degradation of PP1 (temperature

corresponding to 10 % wt. loss) is about 273 °C; however, the onset thermal degradation of PPCN containing 2 wt. % and 4 wt. of clay (PP1-AM0.5-PB2-2 and PP1-AM1-PB4-4) was increased by 45 °C and by 57 °C respectively (Table 6-15) compared to PP1.

The temperature for 50 % weight loss is parallel with the 'onset of degradation' temperatures and shifted markedly towards higher temperatures when clay is introduced into PP1. As shown in Table 6-15, temperature corresponds to 50 % weight loss of PP1-AM-PB2-2, and PP1-AM1-PB4-4 was increased from 336 °C (T_{50} of pure PP1) to 402 °C and 416 °C respectively but the temperature corresponding to 50 % weight loss of PP1-AM1.5-PB6-6 was increased further by only 5 °C, compared to PP1-AM1-PB4-4.

This enhanced onset of thermal degradation of PPCN indicates that PPCN are able to be processed at higher temperatures but thermal degradation of organic modifier used in OMMT (Figure 6-6) starts at comparatively lower temperature is a critical factor for high temperature processing of PPCN.



Figure 6-52 TGA curves of PP 1 and PPCN as a function of clay content

Temperatures of the maximum rate of weight loss (T_{mr} , from derivative data) of all PPCN were higher than that for pure PP1 (Table 6-15), which indicates the slowing down of weight loss and degradation in all the PPCN, in comparison to pure PP1.

A similar enhancement in thermal stability, by introducing organically modified clay, has been reported for PPCN [144-147]. Zanetti et al. [148] also studied the thermooxidative degradation of PP-clay nanocomposites using TGA method. It was found that nanocomposites were more stable in comparison to neat PP and they proposed a mechanism that oxygen will attack at the carbon radical within the PP chain by 'H' abstraction. Therefore, the enhanced thermal stability, in an oxidative environment, of PPCN can be explained since the exfoliated and well dispersed clay layers act as barriers to reduce the oxygen permeability into the nanocomposite structure and at the same time reduce the diffusion of volatile degradation products from the composite matrix to gaseous phase.

Composite	T ₁₀ (°C)	T ₅₀ (°C)	T _{mr} (°C)	
PP1	273	336	368	
PPCN2	318	402	424	
PPCN4	330	416	448	
PPCN6	324	421	450	

Table 6-15 TGA data for PP1 and PPCN with 2% to 6% clay content

The thermal stability of PPCN with higher concentration of clay (PP1-AM1.5-PB6-6) does not significantly improve compared to that of PPCN with lower concentration of clay (PP1-AM1-PB4-4). This could be due to the reduce degree of exfoliation at high concentrations of clay in PPCN structures. This improved thermal stability of PPCN further confirms the nanocomposite structure, with exfoliated clay particles, obtained by co-intercalation of PP-MA and short chain amide molecules (AM).

7 CHAPTER: RESULTS AND DISCUSSION 2: PROCESSING AND RHEOLOGICAL PROPERTIES OF PPCN

From the previous section (Chapter 6: Preparation and Characterization of PPCN), it has been shown that a new way of synthesising PPCN is by co-intercalation of PP based compatibiliser (PP-MA) and short chain amide molecules (AM), resulting in a nanocomposite structure with improved clay dispersion compared to that of conventional type of PPCN prepared with only PP-MA. This chapter describes the rheological properties of PPCN, particularly the effect of this AM additive and clay loading level on flow properties, since rheological characterization is important to understand the processability of PPCN in commercial practice

7.1 Preparation and analysis of PPCN using twin screw extruder

PPCN were prepared by melt blending of PP1 with OMMT, PP-MA and AM, as described in section 5-8, using a twin screw extruder to scale-up the PPCN production since more materials are required for the rheological characterisation.

7.1.1 Effects of changing screw speed

Section 5.8 explains the mixing conditions (i.e. temperature profile, feeding rate) used for the preparation of PPCN in a twin screw compounder. However, the effect of screw speed of the twin screw extruder on intercalation and degree of exfoliation was examined since it is important to break down clay agglomerates and subsequently delaminate clay particles towards nano-meter range, in the presence of PP-MA and AM. PPCN were prepared by incorporating 2 % by weight of clay in the twin screw extruder operated at different screw speeds; 200rpm, 300rpm, 400rpm and 500 rpm.

Figure 7-1 shows the X-ray diffraction results of PPCN prepared at different screw speeds while Table 7-1 presents the Bragg angle position of diffraction peak (001) and corresponding interlayer spacing of each nanocomposite structure. As shown in Figure 7-1, diffraction peaks appeared at very similar Bragg angle positions for all PPCN except of PPCN prepared at 500 rpm. Diffraction peak positions (Table 7-1)

were generally not changed with respect to screw speed of the twin screw extruder and, as a result, same interlayer spacing (35.34Å) resulted for all PPCN prepared at different screw speeds. However at very high screw speed (500 rpm), interlayer spacing decreases slightly. This could be due to less intercalation due to less residence time at a higher screw speed. These results suggest that higher screw speeds do not further enhance the intercalation of clay. At low screw speeds, PP-MA and AM diffuse effectively into clay galleries and allow the maximum achievable interlayer spacing during the compounding process.

However, there is significant difference of peak intensities among PPCN and this could be due to the effect of screw speed on degree of exfoliation. The diffraction peak of PPCN2-300 rpm has a lower intensity than PPCN2-200 rpm, indicating more exfoliation of clay particles at comparatively higher screw speed (300 rpm). Comparatively higher screw speed (300 rpm) exerts higher shear stress on clay particles and it causes to enhance the clay exfoliation in PP matrix.



Figure 7-1 X-ray diffraction patterns of PPCN prepared using different screw speeds in a twin screw compounder
However further increase of screw speed does not show further reduction of diffraction peak intensity (PPCN2-400rpm), in fact showed comparatively higher peak intensity.

Table 7-1	Interlayer	spacing of	of PPCN	prepared	with	different	screw	speeds	of
APV com	pounder								

PPCN structure with screw speeds	Peak (001) position (2 θ)	Interlayer spacing (d ₀₀₁) (Å)		
OMMT	2.92	30.2		
PPCN2-200rpm	2.50	35.34		
PPCN2-300rpm	2.50	35.34		
PPCN2-400rpm	2.52	35.02		
PPCN2-500rpm	2.7	32.71		

This could be due to the less degree of exfoliation due to less residence time or that clay particles are broken down (reducing the aspect ratio) into particles with comparatively smaller particle length at higher screw speed (400 rpm), resulting higher number of clay particles in PPCN2-400rpm sample. However it is not clear why diffraction peak of PPCN2-500rpm has lower diffraction peak intensity.

From this X-ray diffraction results it is clear that higher screw speed is not effective in terms of intercalation and exfoliation of clay particles but moderate screw speed is more effective on exfoliation of clay particles. Therefore, a screw speed of 300 rpm was selected as the optimum speed for the compounding of all PPCN prepared using the twin screw extruder.

7.1.2 Ashing analysis

PPCN were prepared by melt compounding of PP1 grade (which does not contain any low molecular weight polar additives) with OMMT in the presence of PP-MA and AM using the twin screw extruder at 300 rpm, as described in section 5-8. PPCN were prepared with increasing clay concentrations and the exact amount of each component (i.e. PP-MA, AM and clay) in the nanocomposites structure is shown in Table 5-11. The twin screw compounded nanocomposites are coded as PPCN and the last digit of the code refers to the clay weight percentage of each composite. For example PPCN2 refers to PPCN with 2 wt. % of clay and likewise PPCN4 refers to 4 wt. % clay-filled nanocomposite structures.

Ashing analysis was carried out on PPCN prepared with different clay loading levels, as explained in section 5.9 to find out the actual clay weight percentage in each nanocomposite structure. The actual clay content was calculated from ashing analysis data, using the equation 5.9. Table 7-2 presents the actual clay content and percentage loss of clay during compounding process. The final actual clay percentage is the average value of three sets of measurements for all PPCN.

Composite material	Targeted clay percentage (wt. %)	Actual clay percentage (wt. %)	Error percentage (%)
PPCN2	2	1.86	7
PPCN4	4	3.60	10
PPCN6	6	5.22	13
PPCN8	8	7.19	10

Table 7-2 Actual clay percentage and error percentage of PPCN

As shown in Table 7-2, the ashing analysis revealed that the actual clay percentage is always below the targeted clay percentage, for all PPCN structures. For 2 wt. % clay-filled sample, ashing results showed that the actual clay percentage is 1.86 % and the error percentage is about 7%. When PPCN was prepared with higher clay percentages (4-8%), the error percentage became about 10 %, resulting in a lower clay percentage than the targeted value. Actual clay percentage is always lower than the targeted value since small percentage of clay can be lost during the feeding of pre-mixed compound from the hopper to the extruder and during the compounding process. The clay percentage obtained form ashing analysis is considered as the actual clay weight percent for all PPCN prepared using the twin screw extruder.

7.2 Shear flow behaviour of PPCN

Shear flow behaviour of unfilled PP1 and PPCN prepared by co-intercalation of PP-MA and AM over a range of constant shear rates, was studied using a twin bore Rosand RH-7 Capillary Rheometer at a temperature of 200 °C, as described in section 5.10.

(A) Shear flow curves

Figure 7-2 shows the plot of corrected shear stress versus shear rate, on double logarithmic scale known as flow curves, for unfilled PP1 and PPCN prepared with increasing clay loading levels. As shown in Figure 7-2, flow curves are linear and hence unfilled PP1 and PPCN filled with increasing clay loading levels used in this study follow the power law behaviour (shear stress (τ) = consistency index (K). shear

rate $(\gamma)^n$ or log $\tau = \log K + n \log \gamma$ for the range of shear rates used. In these flow

curves (the plot of log τ versus log γ), if the graph is linear the slope is the power law index (n) which describes the behaviour of composite melt. For a Newtonian fluid n is equal to 1 (n = 1) and for pseudoplastic power law fluids, n is less than 1 (n < 1). The intercept on to the Y axis is log K (Consistency Index) which indicates the flow resistance of the composite melt. Table 7-3 presents the power law index (n) and consistency index (K) values for PP1 and PPCN prepared with increasing clay concentrations. As shown in Table 7-3, power law index of all PPCN is less than 1 and there are no significant variations with the increase of clay concentrations in PPCN. Therefore all PPCN showed very similar flow behaviour (pseudoplastic behaviour), same as with pure PP1 over the measured range of shear rates.



Figure 7-2 Shear flow curves of PP1 and PPCN prepared with different clay loading levels (2-8 wt. %) at 200 °C

There is no significant difference of flow curves between unfilled PP1 and PPCN filled with 2 and 4 wt. % of clay. However, although we expect same or enhanced shear stress, it clearly shows gradual decrease of shear stress when clay concentration is increased more than 4 wt. % (6 and 8 wt. %) in nanocomposite structures, in comparison to unfilled PP1 across the shear rate range used in this study. This could be due to the increase of AM concentration with clay concentration (clay 1: AM 0.25). This higher concentration of AM could act as a lubricating agent between PP molecules and as a result reduces the melt viscosity of nanocomposite, resulting reduced stress at high concentration of clay.

Composite material	Power law index (n)	Consistency index (K), Pa s ⁿ
PP1	0.31	17300
PPCN2	0.33	14400
PPCN4	0.31	16000
PPCN6	0.32	12600
PPCN8	0.32	11600

Table 7-5 Fower law muex (n) and consistency muex (K) values for FF	able	2	7-3	3	Power	law	ind	lex	(n)) and	consistency	index	(K)	values	for	PP	С	Ν
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In addition to a possible lubricating effect, at high concentration of AM in nanocomposite structures, free AM could migrate on to interface between die wall and composite melt and hence induce wall slip at the die wall during the capillary rheometry experiment. Haworth and Khan (6) showed that low molar mass polar additives migrate on to the die wall surface and induce wall slip during capillary flow of unmodified PP.

Figure 7-3 shows the shear viscosity with respect to shear rate using the equation of $\log \eta = \log K + (n-1) \log \gamma$ for PP1 and PPCN. This is an alternate form of the flow curve, more relevant to viscosity data that will give the same power law constants (K and n) as given in Table 7-3. These shear viscosity data reveal that all PPCN showed shear thinning non-Newtonian behaviour and therefore they can be processed as similarly to pure PP.

Shear viscosity data are parallel with shear stress data (Figure 7-2) and the shear viscosity of PPCN2 and PPCN4 were not significantly changed, over the measured shear rate range, compared to that of pure PP1 and hence they followed the similar shear flow behaviour as unfilled-pure PP1.



Figure 7-3 Shear viscosity of PP1 and PPCN filled with increasing concentrations of clay at 200 °C

The exfoliated clay particles are likely to be aligned into flow direction in nanocomposite melt over the measured shear rates range and hence it is less significant on shear viscosity at such high shear rates. As a result, shear viscosity of PPCN is governed by molecular weight and their distribution of PP1 matrix as same as with pure PP1. However, addition of higher loading levels of clay (6 and 8 wt.%) shows a decreasing trend in shear viscosity in comparison to pure PP1. This would suggest that short chain amide molecules (AM), used for the preparation of PPCN structure, play a significant role in reducing shear viscosity, especially the PPCN with comparatively higher loading level of clay (6 and 8 wt. %). This can be explained since the amount of AM is increased in PPCN6 and PPCN8 structures and as a result it can act as a plasticiser and/or cause slipped at the die wall, especially at high shear rates (wall slip behaviour of PPCN is described in section 7.5).

Cho et al. [112] also pointed out that PPCN melt with 6 wt. % of organically modified clay shows shear thinning non-Newtonian behaviour and its shear viscosity is practically the same as with pure PP.

(B) Comparisons: PPCN and PPCC

Studies were continued on shear flow behaviour on PP-clay micro–scale composites (PPCC) and they were compared with the shear flow behaviour of PPCN prepared by co-intercalation of PP-MA and AM. Figure 7-4 presents the shear flow behaviour of 4 and 6 wt. % of clay-filled micro-scale composites (PPCC) and nanocomposites (PPCN).



Figure 7-4 Comparison of shear viscosity between PPCC and PPCN at 200 °C

There is no significant difference of shear viscosity between PP1, PPCC (PPCC4 and PPCC6) and PPCN prepared with 4 wt. % of clay. Irrespective of composite structure (i.e. whether nanocomposites or microcomposite), clay concentration has no significant impact on shear viscosity, particularly with this low loading level of clay, over measured shear rates range since clay particles are aligned to a flow direction. However, as shown in Figure 7.4, PPCN prepared with 6 wt. % of clay showed the reduction of shear viscosity compared to that of PPCC6 prepared with same clay

loading level. This would further confirme that AM has a significant effect, as explained earlier, on shear viscosity of PPCN, especially with comparatively higher concentration of clay.

7.3 Extensional flow behaviour

Extensional characteristics of PPCN was also determined using capillary rheometry by the pressure drop values in zero length die (Cogswell method) [63], as described in section 5.10.1, at the same constant shear rate experiment used to study the shear flow behaviour of PPCN but with extensional data.

Figure 7-5 shows the extensional viscosity changes with the extension strain rate, on double logarithmic scale, for pure PP1 and PPCN prepared with increasing clay loading levels (2–8 wt. %) at 200 °C.



Figure 7-5 Extensional viscosity of PPCN prepared with increasing clay concentrations at 200 °C

Extensional viscosity of PPCN showed a decrease versus extension rate, measured in a zero length die. There is no significant difference between PPCN prepared with increasing clay loading levels and they are almost similar to pure PP1. Similar to the shear viscosity, clay particles do not significantly affect to the extensional viscosity at the high extension rates used in this experiment.

7.4 Melt elasticity of PPCN

Since elastic properties of polymer melts are very important in polymer processing, especially with shaping operations like extrusion, elastic properties of PPCN melts were also investigated. Die swell measurements and melt fracture studies were carried out on PPCN prepared with increasing clay loading levels in order to study the melt elasticity of PPCN and the influence of clay concentration.

7.4.1 Die swell

In polymer melt rheology, die swell is the recovery of the elastic component of strain when the stress is removed at the die exit in capillary rheometry experiments. The swelling behaviour of PPCN was characterised using a long die (16:1 mm) at 200 °C. The extrudate diameter of the composite melt was measured as explained in section 5.10.2 using a laser device placed underneath the die, as shown in Figure 5-11. Die swell ratio of PPCN was also compared with pure PP1 and PPCC prepared with an equal weight percentage of clay, as with PPCN to study the elastic recovery of shear strain between PP-clay nanocomposites (PPCN) and PP-clay (PPCC) micro-scale composites.

Figures 7-6 and 7-7 show the effect of shear rate on die swell ratio for both PPCN and PPCC filled with 2 wt % and 4 wt. % of clay respectively. As expected, swelling behaviour is shear rate dependent and all composites (PP1, PPCN and PPCC) show increasing swelling with an increase of shear rate. The increased die swell across the shear rate range implies a higher elastic recovery of strain at the die exit when the stress is released.

As shown in Figure 7-6, PPCN has a significantly lower swelling ratio compared to that of pure PP1 and PPCC at all shear rates range. The swelling ratio of PPCC is lower than that of pure PP1 but it shows higher values in comparison to PPCN. This implies a lower shear strain recovery due to significantly reduced motion of PP molecules in the PPCN structure compared to that of pure PP1. This can be explained since exfoliated clay particles are dispersed homogeneously (as shown in Chapter 6: Preparation and characterisation of PPCN) and interact with PP molecules, resulting in restricted motion of PP chains in the PPCN structure. As a result, elastic recovery of shear strain of PPCN is comparatively lower than that of pure PP1 and PPCC.

On the other hand clay particles in PPCC are not dispersed homogeneously and do not interact with PP molecules and hence motion of PP molecules does not restrict to the same extent as PPCN, resulting in higher swelling ratio than PPCN. This elastic property of polymer melt of PPCN further confirms the morphology of the PPCN structure analysed using TEM, as explained in section 6.4.2





The die swell behaviour of PPCN prepared with 4 wt. % of clay (Figure 7-7) shows a similar pattern as with PPCN prepared with 2 wt % of clay. PPCN showed a lower swelling behaviour compared to both pure PP1 and PPCC.

When PPCN is formed, exfoliated clay particles are dispersed homogeneously and interact with PP molecules. As a result, an interphase is formed with immobile PP molecules. However, when exfoliation is enhanced by the co-intercalation method the total specific surface area of clay particles is also increased and as a result increases the amount of immobile PP molecules within the interphase. These immobile PP molecules cause to lower the elasticity of PPCN, as elasticity is induced by entanglements within the polymer phase, and hence lowers the die swell.

However in PP-clay micro-composites, less specific surface area due to non exfoliation of clay and also weaker interphase is formed due less interaction between clay and PP molecules, resulting in comparatively less immobile PP chains. As a result of this PPCC shows higher elasticity compared to that of PPCN but lesser elasticity than pure PP1.





Since the die swell measurements have shown lower elasticity in PPCN melt, the elastic properties of PPCN melts are also described in terms of elastic modulus in shear using die swell data according to Cogswell method [63], as described in section 5.10.2. Figure 7-8 presents the calculated elastic modulus in shear for PPCN2 and its comparison with pure PP1 and PP-clay micro-composites (PPCC2). It clearly shows that PPCN2 has a higher elastic modulus in comparison to both pure PP1 and PPCC. When PPCN structure is formed exfoliated clay particles interact with PP chains through the compatibiliser (PP-MA) and hence elastic modulus in PPCN melt is increased compared to that of PPCC, in which no significant interaction between clay particles and PP chains takes place. This higher elastic modulus in PPCN is responsible for lowering the recoverable shear strain in capillary rheometry experiments, resulting in a lower die well ratio.



Figure 7-8 Comparison of elastic modulus of PPCN melt with PP1 and PPCC melts

From these elastic responses of PPCN melt further confirm that nanocomposite structure prepared by co-intercalation of PP-MA and AM has improved the clay dispersion and interaction between clay particles and PP chains can be achieved. These elastic property measurements from capillary rheometry experiments can be effectively used to study the clay structure in PP melt and its interaction with PP chains.

7.4.2 Melt fracture of PPCN

The extrudate surface, which was obtained using a long die (16:1 mm), was observed to study the melt fracture behaviour of PPCN and to find out the critical shear stress (corresponding shear rate is critical shear rate) values for the onset of melt fracture. The melt fracture of a polymer melt occurs in a long die when the developed shear stress is beyond the critical stress value. The critical shear stress value of polymer melts is important in polymer processing because it limits the production output, in a given die

Table 7-4 summarises the critical shear stress values and corresponding shear rates for each PPCN prepared with increasing clay loading levels and for pure PP1.

Composite material	Critical shear stress ($ au_{ m c}$) (kPa)	shear rates (γ) (s ⁻¹)
PP1	142.9	500
PPCN2	146.1	700
PPCN4	149.7	700
PPCN6	139.0	900

Table 7-4 Critical shear stress and shear rate values for the onset melt fracture.

The onset of melt fracture of PP1 was observed at shear stress of 143 kPa (critical shear stress) and beyond this critical level the melt fracture of pure PP1 was intensified. When PPCN is prepared by adding 2 wt. % and 4 wt. % of clay the critical shear stress increases slightly up to I46 and 150 kPa respectively. However, the corresponding shear rate values for PPCN are significantly higher in comparison to PP1. This could be due to the reduced viscosity in PPCN compared to PP1 (Figure 7-3). The photographs of onset melt fractured samples of PP1 and PPCN are shown in Appendix K

Melt fracture relates to the melt elasticity and it often occurs when the tensile stress at the die entrance is higher than the rupture strength of the polymer melt. This slightly higher critical stress values for PPCN (PPCN2 and PPCN4) than pure PP1 reveal that the melt strength of PPCN is enhanced slightly compared to that of pure PP1. Polypropylene molecules interact with homogeneously dispersed and exfoliated clay particles in PPCN and hence rupture strength of PPCN melt is likely to be enhanced in comparison to pure PP. As a result of this, PPCN melt can withstand to a slightly higher tensile stress at the die entrance, resulting in comparatively higher critical stress for onset of melt fracture.

However, as shown in Table 7-4, critical shear stress of PPCN6 (critical shear stress 139 kPa) shows a slight reduction compared to that of PPCN2 and PPCN4. This can be explained because AM molecules, which are present as a comparatively higher percentage, are responsible to reduce critical shear stress of PPCN6 since it can act as a viscosity reducer and at the same time it can promote slip at the die wall as well, resulting in a higher critical shear rate.

From these melt fracture results it can be suggested that PPCN delays the onset melt fracture to some extent and as a result during processing operations, the output in a processing operation can be enhanced, in comparison to pure PP. This result offers potential for exploiting commercially, where PPCN can offer improved processing characteristics, in addition to potential increases in solid/physical properties

7.5 Wall slip behaviour of PPCN

Results in previous sections have suggested that wall slip effects may occur if PPCN undergoes shear flow behaviour, due to the presence of amide molecules (AM). Therefore, wall slip experiments were performed using a set of four dies with different dimensions but having the same length to diameter ratio as described in experimental section 5.10.4. Wall slip measurement method [63, 84] has already been explained in literature review section 3.7. In this method, wall slip is measured by plotting a curve of apparent shear rate versus the reciprocal die radius. If there is slip at the die wall, there is a positive gradient of this curve.

Wall slip behaviour of pure PP1 (which does not contain low molecular weight polar additives) and PPCN prepared by co-intercalation of PP-MA and AM was investigated at 200 °C. In order to study the effect of AM on slip behaviour of PPCN, the blend containing PP1, PP-MA and AM was also analysed for wall slip behaviour. The critical stress for the onset of wall slippage was also determined for all above compounds. Figures 7-8 to 7-12 show wall slip analyse of pure PP1, PPCN with 2 and 4 wt. % of clay and their respective blends without clay. Wall slip is indicated if the graph of apparent shear rate plotted against reciprocal of die radius shows a positive gradient for a given shear stress and a zero gradient indicates no slip behaviour. The intercept of the plot gives the true shear rate for each shear stress.

7.5.1 Wall slip in PP

Figure 7-9 shows wall slip analysis for pure PP1 at 200 °C whilst Table 7-5 shows the slip velocity and true shear rates for pure PP1 relating to Figure 7-9. Unmodified PP1 does not slip up to a shear stress of 80 kPa. Unmodified PP1 starts to slip at the die wall at 100 kPa and this is considered as the critical stress value for the onset of wall slip for unmodified PP1 (Table 7-5). At high shear stress (beyond the critical stress value) the slip velocity is further increased and reaches to a 24 ms⁻¹(160 kPa). However, at high shear stress, the slip was accompanied by the melt fracture behaviour since the critical stress value for the onset melt fracture for pure PP1 was observed at 143 kPa.



Figure 7-9 Wall slip analysis for PP1 at 200 °C

Table 7-5 Slip velocities and true shear rates for PP1

Shear stress (kPa)	True shear rate (s ⁻¹)	Wall slip velocity (mms ⁻¹)
60	32.79	0.00
80	65.41	0.00
100	118.27	3.0
120	201.64	6.0
140	331.45	12.0
160	533.06	24.0

Haworth and Khan [6] also reported that the slip effects are detectable for unfilled PP at shear stress levels exceeding 140 kPa. Previous work published [60, 82] for critical shear stress values for linear polyolefins lie in the range between 100 and 200 kPa. In this study finite slip (3 mm s⁻¹) was detected at 100 kPa which represent the critical condition (Table 7-5) for unfilled PP1 and it is in agreement with previous studies

Figure 7-10 shows the wall slip analysis of PP1-AM0.5-PB2 (control sample, with out clay) to study the effect of short chain amide type additive (AM) on slip behaviour and to compare the slip behaviour with PP and PPCN. Figure 7-11 presents the slip velocity changes with shear stress for pure PP1 and PP1-AM0.5-PB2. Wall slip velocity values and true shear rate values for PP1-AM0.5-PB are shown in Appendix L.

When AM and PB were added into PP1, the wall slip velocities are significantly changed in comparison to pure PP1 (Figure 7-10).



Figure 7-10 Wall slip behaviour of PP1-AM0.5-PB2

The critical stress value is reduced from 100 kPa to about 50 kPa when AM and PB are blended with PP1. The slip velocity of PP1-AM0.5-PB2 increases gradually with an increase of shear stress above this critical condition and reaches 36 mms⁻¹ at 160 kPa. These higher slip velocities for PP1-AM0.5-PB2 at any given shear stress, in comparison to PP1, indicate that the addition of AM is responsible to induce the slippage at interface between polymer and die wall.

Polymer melt slip occurs at the die wall, when adhesion failure occurs at or close to the polymer-wall interface beyond the critical stress value [82, 83]. When AM is added into PP, it can migrate on to the surface at melt state since this low molecular weight additive containing polar groups is less compatible with bulk PP [32, 58] and as a result, low molecular weight species are concentrated at the Polymer-wall interface. This low molecular weight additive (AM) is caused to adhesion failure at the interface when the stress is above the critical level.



Figure 7-11 Wall slip velocity versus shear stress for pure PP1 and PP1-AM0.5-PB2 at 200 °C

Haworth and Khan [6] proposed a mechanism, based on low molecular weight additives with functional end groups which are present in some of pure PP, for slip behaviour of PP. In their proposed mechanism, short chain additives migrate to the flow boundary and are likely to adhere to the die surface due to the incompatibility of these molecules with non polar PP. It is proposed that cohesive failure occurs within this region. It was further pointed out that slip velocity is critically dependent upon the surface concentration of these polar additives.

7.5.2 Effect of clay on wall slip in PP

When PPCN was prepared by incorporating clay into the PP1-AM0.5-PB2 system, wall slip behaviour of PPCN changes significantly (Figures 7-11 and 7-12: PPCN prepared with 2 and 4 wt. % of clay). Figure 7-13 shows the comparison of slip velocities between PPCN and their matrix with increasing shear stress. The slip velocity values for both PPCN2 and PPCN4 are shown in Appendix L.



Figure 7-12 Wall slip behaviour of PPCN2 at 200 °C



Figure 7-13 Wall slip behaviour of PPCN4 at 200 °C

Both PPCN2 and PPCN4 showed an onset slippage at 80 kPa, indicating a higher critical stress value of PPCN compared to that of their matrix (PP1-AM0.5-PB2). As shown in Figure 7-13, at any given shear stress, wall slip velocity reduces when clay is incorporated into the matrix to make the PPCN2, in comparison to the matrix. This can be explained since, at melt state, most of AM are occupied in clay galleries as a result, no free AM is available in bulk of PP to migrate towards Polymer-wall interface. This observation is consistent with recent data published by Haworth and Khan [6] in which slip velocity attributed to the presence of short chain amide molecules and it was reduced when talc is incorporated into pure PP. Ahn and White [29] also reported the reduction of wall slip velocity attributed to the presence of carboxylic acid, when particulate additives were incorporated into polyethylene.

However slightly higher slip velocities of PPCN were observed than pure PP1 over shear stress range. This could be either due the presence of very small percentage of free AM in the bulk of PP or completely exfoliated clay particles (platelets with 1nm in size) with AM, some of which are close to die wall boundary, promotes the slippage at the die wall surface. This observation is in agreement with the proposed mechanism by Harworth and Khan, in which says that the wall slip velocity is dependent on the surface concentration of short chain amide molecules.



Figure 7-14 Comparison of wall slip velocities between PPCN and their matrix at 200 °C

These wall slip analyses reveal that, when amide molecules are incorporated into pure PP, slip is induced due to the migration of AM to the PP-wall interface. However when PPCN are prepared by incorporating clay, the slip behaviour of PPCN is reduced significantly in comparison to its corresponding blend, especially at low concentration of AM (PPCN2 and PPCN4), since most of the intercalated AM do not migrate on to the Polymer-wall interface during the capillary rheometry experiment.

8 CHAPTER: RESULTS AND DISCUSSION 3: MECHANICAL PROPERTIES OF PPCN

This chapter describes mechanical properties of PP-clay nanocomposites (PPCN) prepared by co-intercalation of functionalised PP based compatibiliser (PP-MA) and short chain amide molecules (AM). As shown from previous sections (Chapter 6 and Chapter 7), this new method of preparing of PPCN significantly improves intercalation and subsequent clay exfoliation in the PP matrix. PPCN can be processed similarly to unmodified PP, and hence in this section, mechanical properties are investigated in order to examine the property improvements that can be achieved in comparison to unmodified PP.

PPCN prepared using a twin screw compounder with different clay loading levels (2-8 wt. %) were extruded into 50 mm wide flat sheets (as described in section 5.11) for mechanical testing. Pure PP1 and PP1-clay conventional type micro-composites (which do not contain either PP-MA or AM) were also extruded into sheets as reference samples. The exact compositions of PPCN as well as PP-clay composites (PPCC) are shown in Table 5-11.

8.1 Structure of extruded PPCN sheets

Extruded PPCN sheets prepared with different clay loading levels (nominal weight percentage; 2-8 wt. %) were analysed using X-ray diffraction and TEM techniques to examine the each nanocomposite structure in terms of intercalation and degree of exfoliation.

Figure 8-1 presents the X-ray diffraction spectra for PPCN prepared with increasing clay loading levels. Table 8-1 summarises the diffraction peak (001) position and interlayer spacing (d spacing) for each nanocomposite structure. As shown in Table 8-1, all diffraction peaks (001) shift to a lower Bragg angle (2θ) in comparison to pure OMMT, due to the co-intercalation of PP-MA and short chain amide molecules (AM). PPCN2 has a 37.44 Å basal spacing and, when the clay concentration increases in nanocomposite structures (PPCN6 and PPCN8), the gallery spacing does not change significantly. However it is not clear why diffraction peak of PPCN4 shifted slightly

to a higher Bragg angle, resulting in a lower gallery spacing (36.17 Å), compared to that of other nanocomposite structures.



Figure 8-1 X-ray diffraction spectra of extruded PPCN sheets prepared with different clay loading levels

These results indicate that the interlayer spacing of clay in these PPCN sheets does not significantly alter by increasing clay concentration (up to 8 %) in nanocomposite structure. This is due to using the same PP-MA and AM ratio with respect to clay (clay 1: PP-MA 1: AM 0.25) content in all PPCN structures. This would suggest that all PPCN extruded sheets have intercalated structures with a similar interlayer spacing. However it can be seen that higher interlayer spacing of clay in extruded PPCN sheets in comparison to twin screw compounded samples (Table 7-1, e.g. PPCN2-300rpm). This implies that when compounded material is extruded into sheets, further intercalation is occurred and as a result, a higher interlayer spacing is achieved in extruded sheets. As shown in Figure 8-1, diffraction peak intensities are increased with an increase in clay concentration and this could be due to the increase of intercalated clay particles concentration in PPCN with increasing of clay loading

levels. Therefore diffraction peak intensities can not be considered as indirect information for the degree of exfoliation of each PPCN structure.

PPCN structures	Bragg angle (2θ) (degrees)	Inter layer spacing (d ₀₀₁) (Å)
OMMT	2.96	30.2
PPCN2	2.36	37.44
PPCN4	2.44	36.17
PPCN6	2.32	38.05
PPCN8	2.30	38.43

Table 8-1 Interlayer spacing (d₀₀₁) for PPCN prepared with increasing clay loading levels

TEM analysis was also performed for all PPCN structures to examine the effect of clay concentration on clay dispersion and degree of exfoliation, which directly affects mechanical properties. Figure 8-2 shows TEM images of PPCN prepared with different clay loading levels. As shown in figure 8-2, when PPCN was prepared with increasing clay concentration, the number of clay particles in TEM images are also increased accordingly, as expected, and theses results are consistent with the X-ray diffraction peak intensities shown in Figure 8-1.

However, the degree of exfoliation in each nanocomposite structure can be qualitatively estimated by considering the clay particle thickness, as this is inversely proportional to the degree of exfoliation. In comparison of PPCN6 (8-2-(c)) and PPCN8 (8-2-(d)), it clearly shows that clay stacks in PPCN8 are comparatively thicker than clay stacks in PPCN6.



Figure 8-2 TEM micrographs of extruded PPCN sheets prepared with different clay loading levels (magnification:50k), (a)PPCN2, (b)PPCN4, (c)PPCN6, (d)PPCN8

This indicates that PPCN6 has a higher degree of clay exfoliation compared to that of PPCN8. From these TEM images, it shows that the degree of exfoliation is decreased with the increase of clay loading level, especially when clay weight percentage is

increased more than 6 wt. %. This can be explained that when a PPCN structure consists of higher percentage of short chain amide molecules (AM), clay particles are not effectively exfoliated because of reduced melt viscosity in PPCN structures (Figure 7-3), resulting less stress generated during the compounding process.

However when TEM images were observed at higher magnification (80k), it can be seen that most of the clay particles consist of single platelet or 2-3 platelets (Figure 8-3).



Figure 8-3 TEM micrographs of extruded PPCN sheets in higher magnification (80k), (a) PPCN6, (b) PPCN2

This indicates that when Twin Screw compounded PPCN material was extruded into a sheet, clay exfoliation was further occurred during the sheet extrusion and as a result a highly exfoliated nanocomposite structure is formed. The quantification of clay

particles thickness and aspect ratios which directly relates to degree of exfoliation is described in section 8.3 (mathematical modelling of tensile modulus).

8.2 Tensile properties

Tensile testing was carried out on the extruded sheet samples of PPCN and PPCC according to British Standards (BS 2782-3: Method 321 1994), as described in section 5.11.1. For all samples following parameters were determined: tensile modulus, yield stress, and elongation at break. The effect of temperature (80 °C) on tensile properties of PPCN was also studied to establish if PPCN are able to offer good retention of mechanical properties at elevated temperature.

8.2.1 Tensile modulus

Generally polymeric materials are often incorporated with inorganic particulate fillers to improve the stiffness of the composite material [149-152]. Toyota research group has first revealed [11, 118] that polymer clay nanocomposites based on nylon 6 polymer enhanced the tensile modulus by a factor of two, compared to the matrix, with a very little clay content (4.7 wt. %).

Figure 8-4 shows the tensile modulus of PPCN and PPCC as a function of clay loading level at ambient temperature, 20 °C. The raw data for tensile property measurements are shown in Appendix N. All extruded PPCN sheet samples showed a higher tensile modulus in comparison to that of pure PP1. However, the tensile modulus of PPCN increased rapidly with increasing clay content up to 4 wt % and, when clay content increased beyond 4 %, the improvement in tensile modulus is gradually less. When PP1 was reinforced with 2 and 4 wt % clay, the tensile modulus was increased by 23 % and 54 % respectively compared to that of unmodified PP1. However tensile modulus of PPCN6 and PPCN8 was increased by only 61 % and 66 % respectively compared to PP1.

Tensile modulus of PP-clay micro-composites (PPCC) containing similar clay weight percentage as PPCN was also determined for comparison. As shown in Figure 8-4, tensile modulus of PPCC is well below to that of corresponding PPCN and it is not significantly changed with increasing clay content. Poor interfacial interaction between clay particles and PP matrix, due to the absence of compatibiliser (PP-MA), would lead to the formation of non exfoliated and less dispersed larger clay stacks in PPCC structures and hence exhibits a lower tensile modulus in comparison to PPCN.



Figure 8-4 Tensile modulus of extruded PPCN and PPCC sheets with increasing clay loading levels at ambient temperature, 20°C

The improvement of tensile modulus of polymer clay nanocomposite depends on clay aspect ratio, clay mechanical properties and adhesion between polymer matrix and clay [129]. As explained in the preparation and characterization section (Chapter 6, Results and Discussion 1), co-intercalation of PP-MA and AM significantly improves the clay exfoliation and subsequent dispersion. Exfoliation of clay particles into the nano-meter range, resulting in higher aspect ratio, is the key to improvement of tensile modulus for PPCN.

Tensile modulus of PPCN is gradually increased with an increase of reinforcing material (i.e. increase of clay weight percentage). However reduced improvement of tensile modulus beyond 4 % clay could be attributed to that of lower degree of exfoliation at high concentration of clay, especially at 8 wt. % of clay. The lower degree of exfoliation results in a higher number of silicate sheets (clay platelets) per clay stack and hence decreases the effective length to diameter ratio (aspect ratio) of clay stacks. In addition, although the clay concentration improves the reinforcement of PPCN, the reduced crystallinity with an increase of clay content (as shown in section 6.6.3) also has a negative impact on tensile modulus. Another possible reason for the reduced improvement of tensile modulus is the presence of a higher level of free AM at higher clay loading levels (6-8 wt %) and this AM could act as a lubricating agent in PPCN structures.

Similar improvement of tensile modulus of PPCN prepared by conventional method using only PP-MA has been reported by Hasegawa et al. [17]. In their method, highest improvement was achieved with higher concentration of PP-MA (clay to PP-MA ratio is 1:3). Liu and colleagues prepared the polyamide 6-clay nanocomposites with the addition of PP-MA to improve the ductility of nanocomposite and reported that the increased concentration of PP-MA is responsible for reducing tensile modulus [153].

However, tensile modulus of PPCN prepared by the co-intercalation method is increased with a comparatively lower concentration of PP-MA (clay to PP-MA ratio is 1:1) and with the aid of short chain of amide molecules (AM), as shown in Figure 8-4.

Nam et al. [120] also reported a sharp increase in tensile modulus of PPCN for very low clay loading levels (\leq 3 wt. %), followed by much slower increase beyond the clay loading level of 4 wt %.

8.2.2 Yield stress

Yield stress results of PPCN prepared by co-intercalation of PP-MA and AM and PPCC with same clay loading levels are presented in Figure 8-5.

Yield stress of extruded PPCN sheets does not enhance with an increase of clay content. Pure PP1 has a yield stress value of 30 MPa. When clay content was increased in PPCN structures, the yield stress values did not significantly change compared to that of pure PP1. For example PPCN containing 4 and 6 wt % of clay showed yield stress values of 29 and 31 MPa respectively. In contrast to PPCN, yield stress of PPCC showed a decreasing trend with an increase of clay content. However yield stress results of PPCN showed higher values compared to that of PPCC containing level of clay.



Figure 8-5 Yield stress of extruded PPCN and PPCC sheets with increasing clay loading levels at ambient temperature, 20°C

As described in Chapter: 6 (Preparation and Characterization of PPCN), there is no intercalation of polymer molecules into clay galleries and thus no interaction between clay and polymer matrix when conventional type of PP-clay micro-composite (PPCC) is formed. Therefore the strength of the interphase is reduced and hence the stress is

not effectively transferred from the polymer matrix to clay particles, resulting in lower yield stress values compared to that of pure PP1. Yield stress of PPCC continuously decreased with an increase of clay loading levels.

However, on the other hand, when PPCN is formed PP molecules intercalate into clay galleries and exfoliate into smaller clay stacks as shown in X-ray diffraction and TEM results (Figures 8-1 and 8-2). As a result, the effective contact area between PP and clay layers is increased, resulting in a comparatively stronger interphase. This stronger interaction between contact surfaces effectively transfers the stress from polymer to clay particles and therefore PPCN has a comparatively higher yield stress values in comparison to the corresponding PPCC.

The yield stress of PPCN is not changed with an increase of clay content. This could be interpreted that the yield stress is affected with reduced crystallinity with increasing clay content and less degree of exfoliation at higher concentration of clay, since the interaction between clay and polymer depend on the strength and size of the interphase [16, 102, 154].

A similar behaviour of tensile stress of PPCN has been reported in literature [17, 120]. However, these tensile property improvements are not stronger compared to those of nylon 6-clay nanocomposites. This is due to the interfacial adhesion between PP and clay in PPCN being less strong as in nylon 6–clay nanocomposites [11, 119] since polar group in nylon has a better adhesion with clay than non polar PP. However, the addition of PP-MA in to the PP matrix has improved the interaction to a certain level between PP and clay, resulting in acceptable yield stress level in PPCN structures [17]. Xu et al. [139] also reported that PPCN with 2 wt. % clay showed increased tensile yield strength with an increase of PP-MA content. He also pointed out when PP-MA is increased more than 10 wt. %, the yield strength starts to decrease.

8.2.3 Strain at break

The effect of filler loading on the elongation at break of PPCN is shown in Figure 8-6. The addition of clay into PP1 decreases the failure at strain of PPCN compared to that of unmodified PP1. The addition of 4 wt. % of clay into PP1 reduced the elongation at break by about 60 % in comparison to unmodified PP1. However, PPCN8 containing 8 wt. % of clay showed 69 % reduction of elongation at break than pure PP1. This intercalated nanocomposite structure along with comparatively weaker interaction between clay and PP matrix is responsible for this reduced elongation at break in PPCN than pure PP1. However, less reduction of elongation at break at higher clay content could be due to effect of high percentage of AM molecules presence in PPCN structures (PPCN6 and PPCN8) and it could act as a lubricating agent, resulting in enhanced ductility of the nanocomposite structure.



Figure 8-6 Elongation at break of extruded PPCN and PPCC prepared with increasing clay loading levels

However, although PPCN shows a reduction of failure strain with the addition of clay, PPCN remains ductile overall, with failure strain about 400 %. This indicates that the failure mode of PPCN does not change compared to pure PP1 and therefore it fails in ductile manner similar to pure PP1. On the other hand, as shown in Figure 8-6, PP-clay composites (PPCC2, PPCC4 and PPCC6) show very low strain at break compared to that of the corresponding PPCN, resulting in brittle failure. This can be explained since there is no exfoliation of clay that takes place and therefore comparatively larger clay particles act as stress concentrators. As a result of this PPCC fails in brittle mode.

From these strain at break results, although ductility of PPCN is reduced to some extent with increasing clay loading, it reveals that PPCN retain significant degree of ductility in comparison to PPCC.

8.3 Effect of temperature on tensile properties of PPCN

The effect of temperature on tensile properties (tensile modulus and tensile stress) for extruded PPCN sheets prepared with co-intercalation of PP-MA and AM was also studied to examine the retention of tensile properties at elevated temperature. Tensile property measurements were carried out with dumbell shaped samples at 80 ± 5 °C, as described in section 5.11.1

Figure 8-7 shows tensile modulus with respect to clay loading level, when tensile measurements were carried out at a higher temperature (80 °C). As expected tensile modulus values of PPCN at higher temperature are lower than the modulus of PPCN at room temperature.

As shown in Figure 8-7, all PPCN have higher tensile modulus compared to that of pure PP1, indicating a significant retention of reinforcement at elevated temperatures. When PPCN was prepared with increasing clay loading levels, the tensile moduli at high temperature (80 °C) shows an increasing trend, similar to the tensile moduli at room temperature. The 60 % increase in tensile modulus with increasing clay content (PPCN8) at high temperature (80 °C) is achieved compared to 67 % increase in tensile modulus at room temperature (20 °C). This increase in modulus of PPCN implies that the intercalated and exfoliated clay structure in the PP matrix reinforces effectively at this temperature, resulting in a higher modulus. At high temperature tensile modulus shows slightly a lower degree of enhancement with increasing clay content in comparison to tensile modulus at room temperature.

As shown in section 6.6.3 (Results and Discussion 1: Preparation and characterisation of PPCN), crystallinity reduces with increasing clay concentration. This reduced crystallinity with increasing clay content would lead to an increase the rubbery amorphous phase content and as a result, the tensile modulus would tend to reduce at each temperature.



Figure 8-7 Tensile modulus of PPCN at ambient (20 °C) and high temperatures (80 °C) with increasing clay weight percentages (2-8 %)

In addition to the reduced crystallinity, short chain amide molecules (AM) could also have an effect on the tensile modulus at elevated temperature (80 °C) since the melting temperature of AM is 82 °C (Table 5-4). At high temperature, amide molecules will become more mobile in nanocomposite structure resulting in a lubricating effect in PP molecules and hence tensile modulus may be affected as a result.

Figure 8-8 shows the effect of temperature on tensile yield stress of PPCN prepared with different clay loading levels (2-8 wt. %) and tensile yield stress values at room

temperature for comparison. A similar retention of tensile yield stress, at high temperature, is achieved for PPCN in comparison to unmodified PP1. However, tensile yield stress values of PPCN, at high temperature, show a slight reducing trend with an increase of clay loading levels whereas at room temperature, similar strength characteristics for PPCN are achieved, compared to PP1.



Figure 8-8 Tensile yield stress of PPCN at ambient (20°C) and high (80°C) temperature and with increasing clay weight concentration (2-8 %)

As explained in Chapter 6, short chain amide molecules (AM) intercalate with PP macro molecules and interact with clay layers during the compounding process. The AM percentage is also increased according to the clay content in PPCN structures. However at high temperature (80°C), these intercalated amide molecules (AM) could influence the polymer-clay particle interphase of PPCN and, as a result, yield stress decreases slightly in comparison to pure PP1. At high concentration of clay, there are more AM molecules and this will tend to reduce the tensile yield stress at high temperature.

From these results it is clear that relatively a high degree of retention of tensile properties can be achieved in PPCN. However, the reduced crystallinity and amide molecules (AM) may have a negative impact on tensile properties at higher temperature (80 °C).

8.4 Modelling of tensile modulus data

Predicting tensile properties such as tensile modulus, yield stress and elongation to failure using mathematical models is increasingly common for conventional particulate/fibre filled composites, for example CaCO₃ filled PP composites and talc filled PP composites. These composite models have proved successful in predicting mechanical properties of conventional polymer composites. However, very few studies predicting mechanical properties using mathematical models have been reported for clay containing polymeric nanocomposites.

8.4.1 Theory

Numerous micromechanical models have been developed to predict elastic modulus of conventional composites such as the Nielson equation [155], the Ishai-Cohen equation [156], and the Halpin-Tsi equation [157]. These models generally depend on individual component properties such as matrix and filler modulus, filler volume fraction, filler aspect ratio and filler orientation.

However, very few studies have been reported in literature for modelling the mechanical properties of clay containing polymeric nanocomposites [128, 129, 158-162]. Fornes and Paul [128] modelled the reinforcement of nylon 6-clay nanocomposites using the composite theories of Halpin-Tsai and Mori-Tanaka. Brune and Biccerano [154] also showed that the Halpin-Tsai equation can be used to model modulus of fully exfoliated nanocomposite structure. Halpin–Tsai theory has been used in most of studies to model the elastic modulus of polymer clay nanocomposite since it has been developed by considering particle aspect ratio.

In this section the Halpin-Tsai model has been used to predict the tensile modulus of PPCN prepared with co-intercalation of PP-MA and AM and to examine how these
predicted values of PPCN agree with the experimental results of PPCN prepared with increasing clay loading levels.

The Halpin-Tsai equation is given as follows:

$$\frac{E_{composite}}{E_{matrix}} = \frac{1 + 2A_f\eta\phi}{1 - \eta\phi}$$
[8.1]

where E_{composite} and E_{matrix} are composite and matrix elastic moduli respectively.

Aspect ratio,
$$A_f = \frac{l}{t}$$
 [8.2]

l = particle length

t = particle thickness

 ϕ = volume fraction of particles

The parameter η is given by:

$$\eta = \frac{E_r - 1}{E_r + 2A_f}$$
[8.3]

The relative modulus, E_r is given by:

$$Er = \frac{Eclay}{Epp}$$
[8.4]

E_{clay} = clay particle modulus

 $E_{PP} = modulus of pure PP$

A number of assumptions are made for this Halpin-Tsai approach:

• The filler is perfectly oriented and uniform in shape and size

• The filler and matrix are well bonded and there are no particle-particle interactions.

8.4.2 Clay particle parameters

This section describes determination of clay particle parameters (i.e. clay volume fraction, clay particle dimensions, clay particle modulus) which are needed to apply the Halpin-Tsai theory for PPCN.

(A) Clay particle volume fraction

Experimental results of elastic modulus for PPCN were plotted (Figure 8-4) in terms of clay weight percentage of clay. However, this model describes the elastic modulus with respect to filler volume fraction (ϕ). Therefore the actual clay weight percentage (hence weight fractions) obtained from ashing analysis was converted into clay volume fractions (ϕ) using the following equation [129].

$$\phi = \frac{W_c / \rho}{W_c / \rho + (1 - W_c) / \rho_m}$$

 ρ : density of clay, 1.660 kg m⁻³

 $\rho_{\rm m}$: density of PP, 0.905 kg m⁻³

Table 8-2 shows the actual clay weight fractions (Wc) of PPCN prepared with increasing clay loading levels and corresponding clay volume fractions (ϕ) calculated using equation 8.5.

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[8.5]

Composite material	Clay weight fraction (Wc)	Clay volume fraction (ϕ)
PPCN2	0.0187	0.0103
PPCN4	0.0360	0.0197
PPCN6	0.0522	0.0286
PPCN8	0.0724	0.0434

Table 8-2 Clay volume fractions (to 3 significant figures) of PPCN prepared with different clay loading levels

(B) Clay particle modulus

The clay particle (MMT) modulus was estimated elsewhere [128] and the value given for modulus was 178 GPa. This elastic modulus value is for clay platelet, which is complete exfoliation. However Brune and Bicerano [154] showed that when exfoliation is not completed (intercalated structure), the clay stack modulus is altered with respect to the number of platelets per stack (i.e. highest modulus, 178 GPa, can be achieved with a single platelet). However in our system (PPCN, prepared by cointercalation of PP-MA and AM), as shown in TEM images (Figure 8-3) and image analysis data (Appendix P), a higher degree of exfoliation was achieved. For all PPCN structures about 50% of clay particles are less than 10 nm thick and 80% of clay particles are less than 20 nm thick (image analysis data are shown in Appendix P). Therefore 178 GPa is a reasonable approximation to the clay particle modulus for these PPCN structures and this has been used in the model prediction.

(C) Clay morphology and determination of clay aspect ratio

The sectioning for TEM analysis was done as shown in section 5.4.3 to see both clay particle length and thickness. Clay dimensions (length and thickness of clay particles) were measured using Image-Pro Plus software as described in section 5.4.3. The raw data for clay dimensions obtained from image analysis software is shown in Appendix

N. Table 8-3 shows clay particle dimensions obtained from image analysis software. However, as shown from Table 8-3, clay particle length shows very high variation in each PPCN structure and this would suggest that clay particle length are not uniform in same size or that they are not aligned in the extrusion direction as a result complete clay particle length could not be seen from TEM sectioning. However average clay particle length is considered for the calculation of clay aspect ratio.

PPCN	Particle thickness (nm)		Particle length (nm)			
	min.	mean. (SD)	max.	min.	mean (SD)	max.
PPCN2	3.47	10.9 (7.08)	32.0	52.2	130 (69.0)	288
PPCN4	3.59	15.4 (11.0)	49.7	43.3	157 (83.5)	402
PPCN6	3.62	9.91 (4.83)	25.2	45.1	139 (79.4)	328
PPCN8	3.82	17.7 (10.4)	54.2	69.0	173 (72.6)	318

Table 8-3 Clay particle dimensions (particle length and thickness) in PPCN

As shown clay particle morphology statistics data for each of the PPCN structures (Table 8-3) shows that, clay particle thickness is not same for all PPCN structures and as a result of this, different clay particle aspect ratios exist for each PPCN structure. However if maximum exfoliation is achieved, clay particle thickness approaches a minimum particle thickness. Therefore maximum achievable clay particle aspect ratio was calculated (Equation 8.2) from clay particle dimensions (i.e. minimum particle thickness and average particle length) in order to predict the maximum tensile modulus according to the Halpin-Tsai theory. Table 8-4 shows the maximum clay aspect ratios for each PPCN structure.

PP-clay nanocomposites	Maximum clay particle aspect ratio		
	$(\mathbf{A}_{\mathbf{f}})$		
PPCN2	38		
PPCN4	44		
PPCN6	39		
PPCN8	45		

Table 8-4 Clay particle aspect ratios for PPCN

8.4.3 Modelling using Halpin-Tsai theory

The Halpin-Tsai theory has been used to model the tensile modulus of extruded PPCN sheets prepared by co-intercalation of PP-MA and AM. Experimental results (shown in Figure 8.4) were compared with the predicted values.

This theory assumes constant particle aspect ratio (uniform shape and size) as described in section 8.4.1. However, as shown in Table 8-4, maximum clay particle aspect ratio is not same for all PPCN. Therefore an average clay particle aspect ratio (42) was considered for the Halpin-Tsai theory. Figure 8-9 shows the prediction of maximum tensile modulus of PPCN according to Halpin-Tsai theory with the experimental results of PPCN modulus, at 20 °C.

As shown in Figure 8-9, Halpin-Tsai predicts the increase of tensile modulus with an increase of clay volume fraction linearly. It can be seen that actual tensile modulus values of PPCN are generally tally with predicted values, at lower clay volume fraction. However actual values show a significantly lower tensile modulus, at higher clay volume fraction, than the maximum tensile modulus values predicted from the theory.



Figure 8-9 Modelling results (theoretical/actual) for tensile modulus of PPCN at 20 °C

The experimental data fitting with predicted values at lower clay volume fraction indicate that clay particles are fully exfoliated and as a result, fully exfoliated nanocomposite structure is likely to be achieved. However, at higher clay addition, experimental data reveals the existence of more intercalated clay particles and therefore there is a significant variation in clay particle sizes in PPCN structures, resulting in different clay aspect ratios in nanocomposite structure. Hence, there is significant number of clay particles that have a lower aspect ratio than a maximum value, as a result the actual values show a lower tensile modulus than the predicted values. The reduction of crystallinity with an increase of clay percentage, as explained in 6.6.3, also tends to lower the tensile modulus of PPCN, especially at higher clay volume fraction. In addition to these factors, clay particles could not be well bonded to PP matrix and may not align in the extrusion direction (as assumed in Halpin-Tsai theory) and these factors are also responsible for the lower values than those predicted from the Halpin-Tsai theory.

However, at higher clay volume fractions (more than 0.02), the experimental values approach towards a limiting value. This can be explained since clay particle concentration may have a negative effect on the degree of exfoliation, resulting in a lower aspect ratio. This can be explained due to the presence of high percentage of short chain amide molecule molecules (AM) in PPCN, especially at higher clay volume fraction, resulting in lower melt viscosity (Figure 7-3), as explained in section 7.2. As a result of this, the degree of exfoliation may be reduced due to the lower stress generated during the compounding process. However, this factor is not considered in the Halpin-Tsai theory (i.e. constant particle aspect ratio). It is not possible to find an appropriate relationship between clay aspect ratio and clay volume fraction from the clay morphology data obtained from this analysis since they were obtained from a single TEM micrograph. Therefore more TEM images are needed for an accurate measurement.

This modelling data shows that the Halpin-Tsai theory predicts tensile modulus correctly for PPCN with a lower clay volume fraction. It further suggests that at higher clay volume fraction, the PPCN has not achieved the maximum improvement of tensile modulus since the PPCN structure contains not only fully exfoliated clay layers but also intercalated clay particles.

8.5 Impact behaviour of PPCN

Extruded sheet samples of pure PP1 and PPCN prepared with increasing clay loading levels were used to study the impact resistance using an instrumented free-falling dart method as described in section 5.11.3. The peak force, peak energy, deflection at failure and failure energy were measured for all compounds. Figures 8-10 to 8-13 present impact properties for PPCN, measured at laboratory temperature (16 °C).



Figure 8-10 Peak force for PPCN with increasing clay loading levels,



Figure 8-11 Peak energy of PPCN with increasing clay loading levels

Figures 8-10 and 8-11 show the peak force and peak energy results for pure PP1 and PPCN prepared with increasing clay loading levels (actual clay weight percentages). Appendix P shows raw data traces obtained from impact measurements for PP1 and PPCN samples.

Both peak force and peak energy values were normalised by dividing by the sample thickness values. Peak force and Peak energy show same trend in PPCN. Unmodified PP1 shows higher peak values compared to that of PPCN. The energy absorbed at peak force is significantly reduced in PPCN with 2 wt. % of clay compared to pure PP1 and further increase of clay loading shows a slight decreasing trend in peak values. This indicates that PPCN absorbs less energy when fracture initiates.

Figure 8-12 presents the effect of clay loading on deflection at failure of PPCN. Deflection at failure was reduced when 2 wt. % of clay was added in to pure PP1 to form nanocomposite structure due to changes in failure mode. The increase of clay concentration in PPCN further shows gradual reduction of failure deflection.



Figure 8-12 Deflection at failure of PPCN prepared with increasing clay loading levels

The total energy absorbed at failure for PPCN is shown in Figure 8-13. The energy absorption data show a similar trend as deflection at failure results (Figure 8-12). Pure PP1 absorbed a comparatively higher level of energy at failure (2.68 J/mm). However, when clay was added into pure PP, the energy absorb at failure was reduced significantly and it decreases gradually with increasing clay loading.



Figure 8-13 Failure energy of PPCN prepared with increasing clay loading levels

These impact parameters show a reduction in impact resistance with increasing clay loading levels. As shown in Appendix P, Pure PP1 fails by a mixed, brittle-ductile mode and as a result, absorbs comparatively higher energy before it fails (Figure 8-13) compared to PPCN. In order to confirm this failure mode, the failure surface was observed using a scanning electron microscope (Figure 8-14) as explained in section 5.2.5. Scanning electron microscopic (SEM) images of a failure surface (Figure 8-14) shows mainly brittle morphology with evidence of fast crack growth. However, small scale yielding can also be seen due to the absorption of energy during the crack propagation process. When failure occurs in unmodified PP1, the crack propagates

through polymer but energy is also absorbed by a limited yielding process on a small scale.



(a) x 50

(b) x 260

Figure 8-14 Scanning electron micrographs of fracture surface of PP1 at different magnifications

From these SEM images of failure surfaces and impact energy results (Figure 8-13, Appendix P), it confirms the brittle-ductile mixed failure mode of this semicrystalline (59 %, Table 6-3) unmodified PP1 under impact energy at this temperature (16 $^{\circ}$ C).

However, when clay is added into PP1 to make PPCN, the energy absorbed at failure decreases significantly (Figure 8-13), indicating the changes in failure mode (Appendix P). For example, failure energy was reduced from 2.68 J/mm (failure energy for PP1) to 1.41 J/mm when PPCN8 fails under impact loading. Photographs of fractured samples of PPCN are shown in Appendix P, showing brittle failure.

Figure 8-15 shows the fracture surface of PPCN prepared with 4 wt. % of clay. This shows a mainly brittle morphology with more localised crack paths compared to PP1 and there is less small scale yielding observed in this fracture surface. This SEM image (Figure 8-15) together with impact measurement data (Appendix N) suggests that PPCN4 fails in a predominantly brittle manner in comparison to unmodified PP1 and as a result, less energy is absorbed during the fracture process (Figure 8-13). However, clay particles are not visible on this fracture surface (Figure 8-15). This could be due to either the low volumetric concentration of clay or that clay particles are exfoliated to very small stacks (nano-meter range) and hence adhesion to PP appears to be good since exfoliated clay layers are more compatible with PP through the functionalised PP-MA compatibiliser. As a result of this, cracks propagate through PP and therefore clay does not delaminate from PP and particles are not visible on the surface.



(a) x 50

(b) x 260

Figure 8-15 Scanning electron micrographs of fracture surfaces of PPCN4 at different magnifications

In contrast, Figure 8-16 (SEM micrographs of the fracture surface for PPCN prepared with 8 wt. % of clay) shows clay particles on the fracture surface. This can be explained since when clay concentration is increased in PPCN structure the degree of exfoliation reduces, resulting in comparatively larger clay stacks (sub micron level: 200-400 nm) which do not adhere to PP so effectively. When cracks propagate in PPCN8 structure, clay particles do not transfer the load effectively to PP due to the lower adhesion to PP matrix and hence brittle failure is more intensified.



(a) x 50

(b) x 2300



From these impact strength results together with the fracture surface images, it can be concluded that the impact resistance of PPCN decreases in comparison to unmodified PP since PPCN fails in a predominantly brittle manner in comparison to the brittleductile (mixed) failure mode of unmodified PP. The increased clay concentration in the PPCN structure further intensifies the brittle failure mode due to the poor adhesion of clay to the PP matrix.

9 CHAPTER: CONCLUSIONS

This chapter describes the conclusions drawn from this research project. The overall objective of this research project was to study the effect of low molecular weight polar additives, which are present in some commercial PP grades, on PP-clay nanocomposite (PPCN) structure and to develop a new method to prepare PPCN based on the incorporation of short chain amide molecules (AM) with improved intercalation and exfoliation. Exfoliation of clay particles into single platelets is thought to be the key factor to achieving improved material properties of PPCN. Processability (based on rheological characterisation) and mechanical properties of PPCN prepared by this new method, based on co-intercalation of PP-MA and AM, have also been studied in detail.

In summary, the first section of this research study covered the effect of a functionalised PP-based compatibiliser (PP-MA) and low molecular weight polar additives on PPCN structure, in terms of intercalation and degree of exfoliation. PPCN was prepared by co-intercalation of PP-MA and AM and the nanocomposite structure was characterised using different characterisation techniques (X-ray diffraction, TEM, contact angle, MFI, DSC and TGA). The second main section described the rheological characterisation relevant to commercial processes, including shear flow behaviour, die swell, melt fracture and wall slip behaviour of PPCN prepared by co-intercalation of PP-MA and AM. The role of AM on shear flow behaviour of PPCN was also discussed in this section. The final section investigated the mechanical properties of extruded products based upon this new material which were compared with the equivalent mechanical properties of conventional micro-scale PP-clay composites (PPCC).

The most important conclusions drawn from this research project are summarised below, under separate headings.

9.1 Preparation and characterisation of PPCN

(A) Mixing time

It was shown that compounding time is an important factor when PPCN is prepared since not only the compounding temperature but also compounding residence time affects the thermal stability of the organic modifier on the clay. Six minutes is the optimum mixing time to prepare PPCN using a Haake Rheometer, within a temperature range 185-200 $^{\circ}$ C.

(B) Effect of PP-MA and low molecular weight polar additives on PPCN structure.

The effect of PP-MA and its characteristics (molecular weight and maleic anhydride content) on PPCN structure was evaluated using two different PP-MA grades (PM and PB) in terms of intercalation and exfoliation behaviour. From X-ray diffraction and TEM analysis the following important conclusions can be made:

- The low molecular weight and higher maleic anhydride (MA) containing PP-MA grade (PB) is more suitable for the preparation of PPCN since it improves the intercalation as well as clay dispersion in PPCN structure.
- PP-MA concentration (PP-MA to clay ratio) also plays an important role to disperse clay particles in PPCN structure. A high concentration of PP-MA (3: 1 ratio of PP-MA to clay) is more effective for clay dispersion in the PP matrix, as it improves the compatibility between clay and PP. These results are consistent with previous results reported in the literature.
- The experimental results showed that short chain organic molecules containing polar end groups (amide type slip additive; erucamide and antistatic agents; glycerol monostearate), which are present in commercial PP grades, are able to intercalate into clay galleries, resulting in a higher interlayer spacing. As a result of this, exfoliation of clay is enhanced in the PP matrix.

(C) Effect of short chain amide molecules (AM; erucamide)

PP was melt blended with clay and short chain amide molecules (AM) in the absence of PP-MA to evaluate the effect of AM on intercalation and exfoliation behaviour of clay. The following important conclusions can be made from the experimental results.

- AM intercalates into clay galleries during the compounding process and hence increases the interlayer spacing, allowing PP molecules to diffuse into clay galleries
- The maximum interlayer spacing is achieved with a low concentration of AM (4: 1 ratio of clay to AM) and a further increase in AM concentration is not effective in terms of interlayer spacing.
- Contact angle and MFI results confirmed the intercalation of AM into clay galleries and the interaction with silicate layers.
- The addition of AM alone does not exfoliate or disperse clay homogeneously in the PP matrix, resulting in intercalated but non-homogeneously dispersed clay particles in PP matrix. Therefore we propose to refer our new technique as a "Co-intercalation" method (see below).

(D) Preparation of PPCN by co-intercalation of PP-MA and AM

Since the addition of AM alone does not exfoliate clay particles to a nanometre scale, PPCN was prepared by the addition of both PP-MA and AM.

- The addition of both PP-MA and AM remarkably enhance the clay exfoliation and dispersion in PP, in comparison with conventional type PPCN prepared with only PP-MA.
- This study has demonstrated a new way of synthesising PPCN by cointercalation of PP-MA and AM and the resultant nanocomposite structures have improved clay dispersion.

- This new method of preparing PPCN significantly reduces the PP-MA concentration required in the nanocomposite structure. In this system PP-MA to clay ratio: 1:1 is sufficient to achieve homogeneous dispersion of clay.
- The driving force to intercalate AM into clay galleries is hydrogen bonding between the polar -CONH₂ groups and the silicate layers. Based on this, a new mechanism has been proposed for the co-intercalation of PP-MA and AM.
- Quantitative analysis of clay exfoliation performed on TEM micrographs using image analysis software has confirmed that a higher degree of exfoliation can be achieved from this new co-intercalation method, although a fully exfoliated structure is yet to be formed.

(E) Characterisation of PPCN prepared by co-intercalation method.

PPCN structures prepared by this method were characterised and the following important findings were made.

- Normalised melt flow index (n-MFI) results showed that PP molecules intercalate into clay galleries and interact with them and as a result of this, clay particles are exfoliated into smaller stacks resulting in a higher aspect ratio during the compounding process.
- Contact angle measurements showed that, at low loading levels of clay, the surface free energy of PPCN was not significantly changed, since most of the AM intercalates into clay galleries without migrating onto the surface of PPCN. However, at higher clay loading levels, the surface energy of PPCN is changed, since some of AM migrates onto the surface.
- Thermal stability of PPCN prepared by co-intercalation of PP-MA and AM is significantly enhanced compared to that of pure PP. This enhanced thermal stability further confirms the formation nanocomposite structures with an improved exfoliation and dispersion of clay.

 DSC data show that, although clay particles initiates crystallisation at slightly a higher temperature, crystallinity of PP in PPCN decreases with an increase of clay content

9.2 Rheological characterisation of PPCN

Rheological characterisation of PPCN prepared by co-intercalation of PP-MA and AM and the effect of AM on flow properties at high shear rates were examined by capillary rheometry.

- Shear flow behaviour of PPCN showed shear thinning, pseudoplastic behaviour similar to pure PP (i.e. power law index of PPCN is equivalent to PP) and the effects of exfoliated clay particles are less significant on shear viscosity, over the measured shear rate range which is comparatively high.
- At high loading levels of clay (PPCN6 and PPCN8), excess AM induces slippage at the die wall and acts as a viscosity reducing agent. Therefore AM significantly affects the measured shear viscosity leading to an apparent reduction of the shear viscosity of PPCN.
- Reduction of die swell for PPCN shows that melt elasticity of PPCN is significantly reduced in comparison to pure PP and PP-clay micro-composites. Shear modulus data confirms the reduced melt elasticity in PPCN. This elasticity response in PPCN melt further confirms the interaction between PP molecules and well-dispersed clay particles in the PPCN structure.
- The onset melt of fracture of PPCN is delayed compared to that of pure PP and as a result, processing output can be increased in commercial processes.
- Wall slip is induced when AM is incorporated into pure PP but slip velocity at
 a given shear stress is reduced significantly in PPCN, especially with a low
 concentration of clay, since most of the AM interacts with the clay particles
 rather than migrating to the die wall surface.

9.3 Mechanical properties of PPCN

Mechanical properties, including tensile and impact properties, of extruded PPCN sheets were examined in order to investigate the property improvements that can be achieved in PPCN prepared by this new co-intercalation method. The property changes for PPCN in comparison to pure PP and PPCC are summarised as follows:

- The improvement of tensile modulus in PPCN shows the reinforcement effect of exfoliated smaller clay stacks when PPCN is formed with co-intercalation PP-MA and AM. However, when clay is increased more than 6 wt. % the tensile modulus of PPCN does not significantly increase. The reduced PP crystallinity in PPCN with increasing clay content appears to have a negative impact on improving tensile properties of PPCN, especially at high concentration of clay.
- Modelling of tensile modulus using Halpin-Tsai approach shows that experimental data fits with predicted values at low volume fraction of clay. However, the deviation of experimental results form predicted values at higher clay volume fractions suggests that the model is lacking a parameter to account the effect of clay concentration on clay aspect ratio.
- Strength (yield stress) of PPCN (from 0 clay volume fraction to 0.04) is similar to that of pure PP and it is unaffected by increasing clay loading level over this range.
- Elongation at break results show that, although the ductility of PPCN is reduced with increasing clay loading level, a significant degree of ductility is retained in PPCN compared to that of PPCC. As a result the tensile failure mode does not change, in comparison to pure PP.
- Falling weight impact properties of PPCN show decreasing trend since clay stacks are not fully exfoliated. Impact properties of PPCN are dependent on clay loading levels and PPCN fails in a more brittle manner in comparison to unmodified PP.

 Fracture surface morphology has been studied using SEM; at low clay loading levels, classical brittle failure is observed. However, when clay is added at 8 wt. % the surface is significantly different, showing poor adhesion between clay and the PP matrix due to the less degree of exfoliation, resulting in more sub micron level clay particles

10 CHAPTER: SUGGESTIONS FOR FUTURE WORK

(A) Other low molecular weight functional species

This investigation has revealed that low molecular weight polar additives have a positive and significant impact on PP-clay nanocomposite structure in terms of intercalation and exfoliation. However in this study, we examined in detail only the effect of short chain amide molecules (AM; erucamide) on PPCN and hence it is interesting to study the effect of other low molecular weigh polar additives with other functional groups and changes in aliphatic chain length on nanocomposite structure.

(B) Additive synergy

Although this new co-intercalation method results in a PPCN structure with improved clay dispersion, complete exfoliation from this co-intercalation method has not yet been achieved. Exfoliation of clay particles into single platelets is the key factor in PPCN to achieve improved material properties. The experimental results suggest that both amide type slip additive and antistatic agents, which are present in some commercial PP grades, intercalate into clay galleries. Therefore it is important to examine whether the combination of these two additives can be used to prepare PPCN and to see how the degree of exfoliation can be enhanced.

(C) Mechanism of co-intercalation

More studies are needed to confirm the exact mechanism of co-intercalation of PP-MA and AM. For example, the formation of imide groups during co-intercalation could not be experimentally proven from FTIR technique used in this study. Therefore some other advanced analytical techniques could be used to examine the formation of imide bonds (and other secondary effects) and their interaction with silicate layers.

(D) Improvement in mechanical properties

The mechanical properties of PPCN prepared by co-intercalation of PP-MA and AM were enhanced compared to pure PP. However, at higher clay loading levels, mechanical properties were not always improved, probably due to the significant negative impact from free AM and the reduced level of PP crystallinity. Therefore it

is important to develop a method to keep the AM concentration comparatively low (avoiding 'free' AM in the bulk PP) and to achieve the same degree of exfoliation by improving the other parameters, for example processing conditions.

(F) Nucleation

It is important to do more studies on microstructure of PPCN and to include a more effective nucleating agent (external) to control PP crystallinity better since experimental results show that this additive combination reduces PP crystallinity in PPCN

(E) Rubber toughening

Incorporation of rubber phase (e.g. EPDM) into PPCN could be an important step as a toughening material since experimental results showed that impact properties were not improved in PPCN. Improving the overall balance of properties (modulus, strength and toughness) is a very important aspect, for commercial PP grades.

(F) Suitable applications

PP-clay nanocomposites (PPCN) are widely being researched for applications in the automotive industry and packaging industries. Therefore it is important to study the structure and properties of injection moulded products of PPCN prepared by this co-intercalation method. It is important to examine the barrier properties of PPCN films which is one of the most important property improvements for packaging applications.

11 PUBLICATIONS

1. U.N. Ratnayake, B. Haworth., 'Polypropylene-clay nanocomposites: Influence of low molecular weight polar additives on intercalation, exfoliation and rheological behaviour', *Conference Proceedings*, '*Polymer Nanocomposites 2005' Third International Symposium on Polymer Nanocomposites Science and Technology*, Bouchervile, Qubecc, Canada (September 28-30, 2005).

2. U.N. Ratnayake, B. Haworth, 'Polypropylene-clay nanocomposites: Influence of low molecular weight polar additives on intercalation exfoliation behaviour', *Polymer Engineering and Science* **46** (8), 1008 (2006).

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13 LIST OF APPENDIXES

- A Technical specifications for PP grades
- B Rheographs for PPCN prepared using a Haake Rheometer
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Appendix A: Technical specifications for PP grades

TF 1009 18.08 2003 Ed.4



Polypropylene HB671TF

Polypropylene Homopolymer for Thermoforming

Description

HB671TF is a nucleated polypropylene homopolymer intended for extrusion and thermoforming featuring very good processability and melt stability. The formulation of HB671TF makes it especially suitable for both in-line and off-line thermoforming.

Products manufactured from HB671TF are characterised by excellent clarity, a very good stiffness, high heat resistance and sufficient impact properties. HB671TF has a very high crystallisation temperature allowing high de-moulding temperature as well as reduced cooling time.

Applications

HB671TF is successfully used in the following applications

- High transparent trays and cups (incl. hot filling and sterilisable applications)
- Houseware and thin wall packaging -
- Margarine tubs and yoghurt cups
- Blister packaging

Physical Properties**

		Typical Value*	Unit	Test Method	
Density		905	kg/m ²	ISO 1183	-
Melt Flow Rate	(230°C/2.16 kg)	2	g/10 min	ISO 1133	
Melting Temperature	(DSC)	162-168	*C	ISO 3146	
Flexural Modulus	(5 mm/min)	1650	MPa	ISO 178	
Tensile Stress at Yield	(50 mm/min)	38	MPa	ISO 527-2	
Tensile Strain at Yield	(50 mm/min)	8.0	%	ISO 527-2	
Tensile Modulus	(1mm/min)	1700	MPa	ISO 527-2	
Charpy Impact Strength, notched	(+23°C)	4.5	kJ/m ²	ISO 179/1eA	
Heat Deflection Temperature	(0.45 MPa)	103	*C	ISO 75-2	

Data should not be used for specific work. Values determined on injection moulded specimens acc. to ISO/DIS 1873-2 (54)

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3

Technical specifications for PP1 (HB671)


Polypropylene Homopolymer for Compression Moulding

Description

HB306MO is a low melt flow rate homopolymer polypropylene for caps and closures. It is specially formulated to provide the necessary lubrication level to meet the opening torque requirements for screw caps on all types of beverage bottle

HB306MO combines a good balance of stiffness and impact strength with good processability and melt stability. It is also formulated to provide anti-static protection.

Applications

HB306MO is particularly suitable for production of closures by the compression moulding process. It does not require any further lubrication addition by masterbatch.

HB306MO should only be used for closures containing a liner in contact with the contents of the package.

Physical Properties

		Typical Value*	Unit	Test Method	
Density		908	kg/m ³	ISO 1183	
Melt Flow Rate MFR	(230°C/2.16 kg)	2	g/10 min	ISO 1133	
Tensile Modulus	(1 mm/min)	1450	MPa	ISO 527-2	
Tensile Stress at Yield	(50 mm/min)	34.5	MPa	1SO 527-2	
Tensile Strain at Yield	(50 mm/min)	9	%	ISO 527-2	
Charpy Impact Strength, notched	(+23°C)	7	kJ/m ²	ISO 179/1eA	
Hardness, Rockwell		90	R-scale	ISO 2039-2	
Heat Deflection Temperature	(0.45 MPa)	88	°C	ISO 75-2	

* Data should not be used for specification work.

Processing Guidelines

HB306MO can be processed under normal conditions on all compression moulded closure production equipment. HB306MO is well stabilised and can withstand temperatures up to 300°C, for a short time, without any serious degrading.

 Melt temperature
 180 - 260°C

 Shrinkage
 1 - 2%, depending on wall thickness and moulding parameters

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Technical specifications for PP2(HB306)

"Moplen" HP510M data provided by IDES

Page 1 of 2

basell
 Polyolefins

Moplen HP510M

Friday, December 05, 2003

Basell	Polyo	lefins -	Poly	propy	lene	Homo	nol	vmer
				Pri - Pr J				

Unite	SI	

Actions

ASTM Data Sheet

MSDS
 E-mail a Basell Data Sheet

Product Description

"Moplen" HP510M is a polypropylene homopolymer particularly suited for the extrusion of cast film. It is formulated with a general purpose stabilisation package and does not contain any slip or antiblocking agents. Main applications are film for packaging foodstuffs such as pasta, snacks, biscuits, bakery products and confectionery, film for packaging for flowers, books stationery, blankets, shirts, knitwear and hosiery. "Moplen" HP510M is suitable for food contact.

Commercial: Active		
Australia Pacific Rim Africa Asia Latin America Europe Middle East		
ISO ASTM		
Homopolymer Food Contact Acceptable		
 Packaging, Food Film 		
Pellets		
Film, BlownFilm, Cast		
	Australia Pacific Rim Arrica Asia Latin America Europe Middle East ISO ASTM Homopolymer Food Contact Acceptable Packaging, Food Film Pellets Film, Blown Film, Cast	

Physical	Nominal Values (SI)	Test Method
Density	0.900 g/cm ^a	ISO 1183
Melt Mass-Flow Rate (MFR) (230°C/2.16 kg)	9.0 g/10 min	ISO 1133
Mechanical	Nominal Values (SI)	Test Method
Tensile Modulus (1 mm/min)	1500 MPa	ISO 527-1, -2
Tensile Stress at Yield (50 mm/min)	34.0 MPa	ISO 527-1, -2
Tensile Strain at Yield (50 mm/min)	13 %	ISO 527-1, -2
Hardness	Nominal Values (SI)	Test Method
Shore Hardness (Shore D)	71	ISO 868
Thermal	Nominal Values (SI)	Test Method
HDT B (0.45 MPa) Unannealed	85.0 °C	ISO 75B-1, -2
Vicat Softening Temperature (A50 (50°C/h 10N))	154 °C	ISO 306

Additional Properties

Elongation at Yield, ASTM D882, 500 mm/min, 50 µm cast film: 5% Coefficient of Friction, ASTM D1894, Static: >0.5

Coefficient of Friction, ASTM D1894, Dynamic: >0.5

Notes

¹ Typical properties; not to be construed as specifications.

Regional Sales Offices: France +33 1 49 64 58 00 Benelux +31 168 384 400 Spain +34 934 96 4240

http://icatalog.ides.com/datasheet.asp?I=614&M=7&SM=7&SFP=5&FP=5&E=5463... 05/12/2003

Technical specifications for PP3 (HP510)





Torque and temperature variation during the compounding process of PPCN and PPCC



SAMPLE DEFLECTION





SAMPLE DEFLECTION



12

A = energy at peakA+B = energy at faliure





```
Molecular weight distributions for PP1, PP2 and PP2
```



Appendix E: DSC traces for PP and PP-MA

DSC thermogram for PP3



DSC thermogram for PP-MA (PB)



DSC thermogram for PP-MA (PM)











FTIR spectrum of PP1-AM0.5-2



FTIR spectrum of PP1-AM1.5-2



FTIR spectrum of short chain amide molecules (AM)



FTIR spectrum of amide treated organically modified clay (AM-OMMT)





Diiodomethane contact angles for PPCN prepared with increasing clay concentration.

Surface energy results of PPCN prepared with increasing clay loading levels

	Surface energy,		
PP-clay Nanocomposites	Dispersive component	Total S.E	Surface polarity (%)
PP1	26.51	26.62	0.4
PP1-AM0.5-PB2-2	26.72	26.87	0.56
PP1-AM1-PB4-4	26.07	26.38	1.2
PP1-AM1.5-PB6-6	24.57	25.11	2.2
PP1-AM2-PB8-8	23.71	24.36	2.6

Surface polarity values of PP1-AM blends

ity (%)

Appendix I: DSC traces for PPCN



DSC thermogram for PP1-2



DSC thermogram for PP1-AM0.5-PB2-2



DSC thermogram PP1-AM1-PB4-4



DSC thermogram for PP1-AM1.5-PB6-6



Appendix J: Derivate thermogravimetric curves for PPCN

Derivate thermogravimetric (DTG) curves for PP1 and PPCN

Appendix K: Melt fracturing of PPCN



PP1







PPCN4

Melt fractured samples for PP1, PPCN2 and PPCN4

Appendix L: Wall slip analysis

Shear stress (kPa)	True shear rate (/s)	Wall slip velocity (mm/s)
60	20.94	3.0
80	51.41	7.0
100	107.88	12
120	204.01	18
140	358.17	26
160	594.64	36

Slip velocities and true shear rates for PP1-AM0.5-PB2

Slip velocities and true shear rates for PPCN2

Shear stress (kPa)	True shear rate (/s)	Wall slip velocity (mm/s)
60	41.62	0
80	83.9	3.0
100	153.78	6.0
120	266.15	11
140	443.35	16
160	718.75	22

Shear stress (kPa)	True shear rate (/s)	Wall slip velocity (mm/s)
60	34.47	0
80	74.67	3.0
100	141.83	6.0
120	247.38	11
140	405.91	17
160	635.47	24

Slip velocities and true shear rates for PPCN4

Appendix M :Tensile property measurements

Tensile Me	odulus		_					
	1	2	3	4	5	6	Avg.	S.D
PP1	1721	1629	1395	1515	1557		1563	122
PPCN2	1643	1929	2066	2417	2140		2039	284
PPCN4	2479	2360	2471	2297	2498	2320	2402	89
PPCN6	2779	2330	2430	2530			2516	193
PPCN8	2363	2560	2875	2664	2530		2599	189
PPCC2	1258	2223	2255	1685	1874		1859	412
PPCC4	2042	2280	2099	1682			2025	251
PPCC6	1721	1735	1910	2263	1924		1910	218

Tensile modulus for PPCN and PPCC

Tensile Yield stress for PPCN and PPCC

Tensile yi stress	eld							
	1	2	3	4	5	6	Avg.	S.D
PP1	30.18	31.91	27.59	28.84	31.84		30.07	1.88
PPCN2	27.82	34.12	31.94	28.07	30.89		30.49	3.07
PPCN4	29.79	28.13	29.31	28.26	29.32	28.56	28.87	0.81
PPCN6	31.91	28.81	32.25	29.56			30.64	1.7
PPCN8	30.37	27.81	29.47	31.82	29.46		29.82	1.46
PPCC2	28.1	27.66	27.166	25.89			27.2	1
PPCC4	23.81	25.81	22.99	24.25	24.86		24.34	1.06
PPCC6	24.75	25.43	20.46	22.92	22.45		23.2	1.97

Strain at failure for PPCN and PPCC

Strain at I	Failure							
	1	2	3	4	5	6	Avg.	S.D
PP1	716	1296	1280	1084	944		1094	243
PPCN2	912	800	928	788	880		861	64
PPCN4	436	357	338	504	504	394	422	72
PPCN6	712	824	512	440			622	177
PPCN8	386	333	355	341	344		352	21
PPCC2	136	91.1	123	207			139	49
PPCC4	22.68	20.48	11.2	7.08	20.2		16.33	6.79
PPCC6	6.2	15.3	13.8	16.64	8.98		12.18	4.42

Appendix N: Raw data for clay particles dimensions

PPCN2:



TEM image of PPCN2 (80k)



Histogram of clay particles width

Histogram clay particles length

Thickness (nm)	Bin Counts	Percentage
9	12	52.2
15	7	30.4
21	1	4.35
27	2	8.70
33	1	4.35

Distribution of clay particles width in TEM image of PPCN2

Distribution of clay particles length in TEM image of PPCN2

Length (nm)	Bin Counts	Percentage
110	15	65.2
170	3	13.0
230	2	8.70
290	3	13.0
350	0	0

Statistics of clay particles thickness and length

Analysis Statistics	thickness (nm)	Length (nm)
Minimum	3.47	52.2
Maximum	32.0	288
Mean	10.9	130
Std. Dev.	7.08	69.0





TEM image of PPCN4



Histogram of clay particles width

Histogram of clay particles length

Thickness (nm)	Bin Counts	Percentage
13	11	50
23	6	27.3
33	3	18.2
43	1	4.55
53	1	4.55

Distribution of clay particles width in TEM image of PPCN4

Distribution of clay particles length in TEM image of PPCN4

Length (nm)	Bin Counts	Percentage
120	7	31.8
200	10	45.5
280	4	18.2
360	0	0
440	1	4.55

Statistics of clay particles thickness and length

Analysis	Thickness	Length
Statistics	(nm)	(nm)
Minimum	3.59	43.3
Maximum	49.7	402
Mean	15.4	157
Std. Dev.	11.0	83.5

PPCN6:



TEM image of PPCN6



Histogram of clay particles width

Histogram of clay particles length

Distribution of clay particles width in TEM image of PPCN6

Thickness (nm)	Bin Counts	Percentage
10	19	67.9
16	7	25
22	1	3.57
28	1	3.57
34	0	0

Distribution of clay particles length in TEM image of PPCN6

Length (nm)	Bin Counts	Percentage
120	14	50
200	8	28.5
280	4	14.3
360	2	7.14
440	0	0

Statistics of clay particles width and length

Analysis Statistics	Thickness	Length	
	(nm)	(nm)	
Minimum	3.62	45.1	
Maximum	25.2	328	
Mean	9.91	139	
Std. Dev.	4.83	79.4	

PPCN8:



TEM image of PPCN8



Histogram of clay particles width

Histogram of clay particles length

Thickness (nm)	Bin Counts	Percentage
15	15	48.4
27	11	35.5
39	4	12.9
51	0	0
63	1	3.23

Distribution of clay particles width in TEM image of PPCN8

Distribution of clay particles length in TEM image of PPCN8

Length (nm)	Bin Counts	Percentage
120	9	29.0
180	9	29.0
240	6	19.4
300	5	16.1
360	2	6.45

Statistics of clay particles width and length

AnalysisStatisticsMinimumMaximum	Thickness (nm) 3.82 54.3	Length (nm) 68.8 319			
			Mean	17.7	174
			Std. Dev.	10.43	72.6





Force deflection curves for unmodified PP1 and PPCN at 16 °C



Fractured samples of PPCN