The Development of Technology for Melt Processing of Clay/Polypropylene Nanocomposites

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ABSTRACT

Polypropylene is an inexpensive non-toxic polymer and is ideal for food and drink packaging applications. However, its application for enclosures of carbonated liquid containers is unfulfilled due to its inadequate barrier resistance to gases and its low stiffness. The newly merged layered silicate/polymer nanocomposites have the potential to be an effective approach to improve these two properties at low cost. This project has developed the technology for producing clay/polypropylene nanocomposites via direct melt compounding using conventional reactive melt processing equipment.

Several model synthetic methods have been investigated. These methods include direct intercalation between clay and polymers, intercalation between maleic anhydride grafted polypropylene and polypropylene and compatibiliser assisted melt intercalation. In addition, the effects of processing conditions and stabilisers on the melt intercalation were studied. These studies provided a fundamental understanding of the mechanisms of intercalation and their relation to the engineering properties of the nanocomposites.

Based on the understanding obtained in the model synthetic study, two novel synthetic technologies have been developed, these are solid intercalation/melt processing and nylon assisted melt intercalation. The solid intercalation/melt processing utilise the high efficiency of intercalation in in-situ polymerisation and allow the processing to occur in conventional polymer processing equipment. Nylon assisted melt intercalation takes advantage of the easy exfoliation of clay in nylon and then the transfer of the composite structure into polypropylene. This technique also resulted in an important finding that the compatibility between nylon and polypropylene can be improved significantly in the presence of clay. Although the development of these two methods is in a preliminary stage, the results obtained so far already show the advantage of these two technologies over other methods developed. It is anticipated that better quality clay/polypropylene nanocomposites can be developed through the further progress of these two methods.

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Most of all I wish to thank my family for always being there and without whose tremendous sacrifices I could not have finished this work.

I dedicate this thesis

to my

parents and wife

and everyone who has supported me over the years

LIST OF SYMBOLS AND ABBREVIATION

APTES	3-Aminopropyltriethoxysilane
BPO	Dibenzoyl peroxide
CEC	Cation exchange capacity
E-43	Epolyene E-43 Wax
FT-IR	Fourier transform infrared spectrometer
G-3015	Epolyene G-3015
HDT	Heat deflection temperature
HRR	Heat release rate
MAH	Maleic anhydride
MAH-g-PP	Maleic anhydride grafted polypropylene
MFR	Melt flow rate
MMT	Montmorillonite
MTMS	Methyltrimethoxysilane
NCN	Nylon/clay nanocomposites
o-MMT	Organo- montmorillonite
PB300	Polybond®3000
PB3200	Polybond®3200
PP	Polypropylene
PP1	Polypropylene Fina 3228C
PP2	Polypropylene Fina IN419-3-01
PP3	Polypropylene Fina N00-8-1
PPCN	PP/clay nanocomposites
SA	Stearic acid
SB	Sodium benzonate
SIMP	Solid intercalation/melt processing
TEM	Transmission electron microscope
Tg	Glass transition temperature
TGA	Thermogravimetric analysis
XRD	X-ray diffractometry (X-ray)

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CHAPTER 1 INTRODUCTION

1.1 Background of the research

Polypropylene is inexpensive and non-toxic and hence is ideal for food and drink packaging applications. However, its application for enclosures of carbonated liquid containers has not been successful. This is due to its inadequate barrier resistance and stiffness therefore reinforcement of polypropylene is required. Although polypropylene has been successfully reinforced by glass fibers and other inorganic materials, in traditional reinforced composites, the polymer and additives are not homogeneously dispersed in dimensions close to molecular level so adequate barrier resistance could not be achieved. Nanoscience is capable of filling this gap. If nanometer dispersion of individual layers of clay could be achieved, the mechanical properties might be further improved and unexpected new properties may be possible [Giannelis, E.P., 1992]. The work by Toyota on a nylon-6/clay system has demonstrated that dispersion of clay in nano-scale is an effective approach to improve stiffness and barrier resistance of composites at a low cost.

Layered silicates, also called clays, are cheap fillers. When individual silicate layers are dispersed in polymers, the barrier resistance of the polymers can be improved by the formation of tortuous pathways constructed by the impermeable clay layers within the polymer matrix [Kojima, Y. et al., 1993a,c]. The stiffness of polymers is enhanced by the high aspect ratio of individual clay layers, which behave in a similar manner to short fibres [Kojima, Y. et al., 1993b]. However polypropylene is considered to be extremely difficult to intercalate with clays because its non-polar structure makes it incompatible with hydrophilic clays. New methods need to be developed to improve the compatibility between the clays and polypropylene to allow the formation of nano-structured clay/polymer composites. Advances in this field would make a significant breakthrough in nanocomposite synthesis and widen the uses of polypropylene in engineering applications.

1.2 Overall aims and objectives of the project

This project is aimed at the development of melt processing technology to produce clay/polypropylene nanocomposites (PPCN) based on available commercial organoclays and the exploration of the potential to produce nanocomposites directly from original hydrophilic clays with the emphasis on the improvement of mechanical properties.

In order to achieve this, a number of investigations have to be carried out. These include gaining an understanding of the feasibility of using commercially available clays for nanocomposite applications, the development of various synthetic methods for producing clay/polypropylene nanocomposites based on traditional polymer processing equipment, investigating the effects of processing conditions, the properties of clays, the clay loading, compatibilisers and anti-oxidants used in processing, on nanocomposite formation and the mechanical properties of the nanocomposites produced. The mechanisms obtained were utilized to design better synthetic methods for manufacturing clay/polypropylene nanocomposites.

This thesis reviews clay/polymer nanocomposites, their manufacture and characterisation. The experimental section details how clay/polypropylene nanocomposites can be produced from both hydrophilic and organoclays and how the polypropylene can be modified to make it compatible with clays. The results and discussion section has been divided into four chapters. These chapters examine and discuss the problems identified in producing clay/polypropylene nanocomposites by using existing polymer processing methods and ways to overcome these problems through adding stabilisers and compatibilizers are assessed. The influence of processing conditions on the formation of nanostructures during extrusion and the optimisation of these conditions are examined. New synthetic methods of producing nanocomposites are developed and their advantages and limitations are evaluated.

CHAPTER 2 Literature Review

Extensive interests have been shown in clay/polymer nanocomposites over the past decade. Polymer molecules can enter into the galleries in layered silicates, pushing the clay layers apart creating nanocomposites. The significance of nanocomposites is that considerable property enhancements are achievable at very low particle contents, whereas traditional composites might require much higher particle content to obtain the same results. Polypropylene is an inexpensive and non-toxic polymer, and the cost of clay is low, so that compared with conventional fibre-reinforced polymeric composites nanocomposites will be cheaper. Also, clays do not have the same health risks as many short staple fibres do. The newly developed clay/polypropylene nanocomposites would have the potential to be an effective approach to improve polypropylene's inadequate barrier resistance to gases and its low stiffness properties at low cost and would be ideal for food and drink packaging applications.

2.1 The definition of clay/polymer nanocomposites

Nanomaterials are those materials with structural features, particle size or grain size for example, with at least one dimension in the range of 1-100 nm. Nanomaterials can be metals, ceramics, polymeric materials, or composite materials. The idea of structures with nanometer-sized building elements has brought new impetus to material science and technology in the last decade.

Polymer/layered silicate nanocomposites (PLSN) basically consist of a polymer and layered silicates in which at least one dimension of the dispersed particles is no more than 100 nanometers. Owing to the nanometer-sized particles obtained by dispersion, these nanocomposites have a large interface surface and exhibit markedly improved physical properties such as: reinforcement with a low clay loading, improvement of barrier properties, increase in dimensional stability, and enhancement of heat resistance and fire retardancy et al.

2.2 The structure of clays and their polymer nanocomposites

2.2.1 The typical structure of natural hydrophilic clays

The microstructure of layered silicates plays a significant role in enhancing the properties of a polymer. The layered silicates commonly used in nanocomposites belong to the structural family known as the 2:1 phyllosilicates. The crystal lattice consists of two-dimensional layers where a central octahedral sheet of Alumina or Magnesia is bonded into two external silica tetrahedron by the tip so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets. The layer thickness is approximately 1 nm. The lateral dimensions of these layers may vary from 30nm to several microns and even larger depending on the type of silicate. These layers organize themselves to form stacks with regular gaps between them. These gaps are also called galleries. Isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+}, Fe^{2+}, and Li^{+}) generates negative charges that are counterbalanced by alkali or alkaline earth cations situated in the interlayer. As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers is relatively easy [Theng, B.K.G. 1974]. Smectite clays including montmorillonite, hectorite and saponite are the most commonly used layered silicates because of their swelling properties, high cation exchange capacities, high aspect ratio and large surface area [Triantafillidis, C.S.et al., 2002; Pinnavaia, T.G., 1983; Carrado, K.A., 2000 and LeBaron, P.C. et al., 2001]. Montmorillonite has the highest aspect ratios amongst these smectite clays. Their structures are shown in Fig.2.1 [Giannelis, E.P. et al., 1999] and their chemical formula are shown in Table 2.1.

Smectites are characterized by moderate negative surface charges. These surface charges are known as the cation exchange capacity, CEC, and expressed by meq/100 g. The cation exchange capacity of the layer is not locally constant as it varies from layer to layer and must be considered as an average value over the whole crystal. The CEC is contributed by the terminated OH- group, caused by the broken sheet structure. This contribution depends on the crystal size and type of exchangeable cation [Pinnavaia, T.J., 1983]. A small number of the charge balancing cations is located on the external crystallite surface, and the majority of these exchangeable cations are located inside the galleries of the clay crystal. The type of exchangeable cation in clays also affects the interaction between polymer matrix and clay. When the hydrated exchangeable cations are ion-exchanged with organic cations such as bulky alkyammoniums, which will be examined in section 2.2.2, they usually result in larger interlayer spacing.

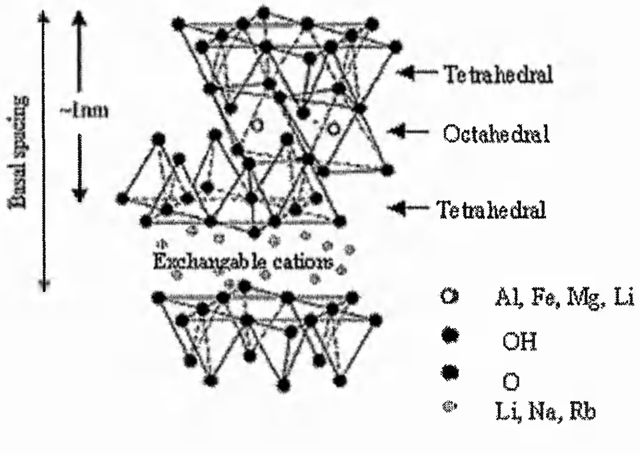


Fig. 2.1. A typical structure of a 2:1 phyllosilicate. [Giannelis, E.P. et al., 1999]

Table 2.1
Chemical structure of commonly used clays [Gianneli, E.P. et al., 1999]

Natural clay	General formula	Aspect Ratio
Montmorillonite	$Mx(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	218
Saponite	$MxMg_6(Si_{8-x}Al_x)\ O_{20}(OH)_4$	165
Hectorite	$Mx(Mg_{6-x}Li_x)\ Si_8O_{20}(OH)_4$	46

M=monovalent cation; x=degree of isomorphous substitution (between 0.5 and 1.3).

2.2.2 The structure of organically modified layered silicates (OMLS)

Natural montmorillonite usually contains hydrated Na^+ or K^+ ions [Brindly, S.W. et al., 1980]. In this original state, layered silicates are only miscible with hydrophilic polymers, such as poly(ethylene oxide) (PEO) [Aranda, P. et al., 1992] or poly(vinyl alcohol) (PVA) [Greenland, D.J., 1963]. To render layered silicates miscible with other polymer matrices, one must convert the normally hydrophilic silicate surface to an organophilic one. The surface chemistry is important, ion exchange reactions with cations, commonly alkyl ammonium or alkyl phosphonium cations, allow the silicate to be compatible with the hydrophobic polymer matrix. The strong interactions between the two materials lead to dispersion at the nanometre level. Substitution of these cations in the montmorillonite (MMT) in this way makes the intercalation of many engineering polymers possible. Generally, this can be achieved by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium (onium) cations. The modified clay is often termed as "organoclay". This intercalation system was firstly used a decade ago in the pioneering work conducted at the Toyota Central Research Laboratories on nylon-6 nanocomposites [Kojima, Y. et al., 1993a]. They generated several commercial products and stimulated a great deal of interest in research which led to the expansion of the technology to other polymers. The modified clay (or organoclay) being organophilic, has a lower surface energy than the natural hydrophilic clays. Alkylammonium or alkylphosphonium cations in organoclays decrease the surface energy of the inorganic host and improve the wetting characteristics of the polymer matrix, resulting in a larger interlayer spacing. Additionally, the alkylammonium or alkylphosphonium cations can provide functional groups that can react with a polymer matrix to make the clay and polymer compatible. In some cases, the polymerization of monomers can also be used to improve the bonding at the interface between the clay and the polymer matrix [Blumstein, A., 1965].

The surface of the organoclay layer has negative charges which originate in the silicate layer. The cationic group of the alkylammonium molecule is attached to the organoclay's surface, leading to the organic tail radiating away from the surface. In a given temperature range, two parameters which were used to define the equilibrium layer spacing of the organoclay were the cation exchange capacity (CEC) of the layered silicate discussed above and the organic chain length of cation. The organic chains were originally thought to lie either parallel to the silicate layer, forming mono or bilayers, or depending on the packing density and the chain length, to radiate away from the surface, forming mono or even bimolecular tilted "paraffinic" arrangement [Lagaly, G., 1986] as shown in Fig 2.2.

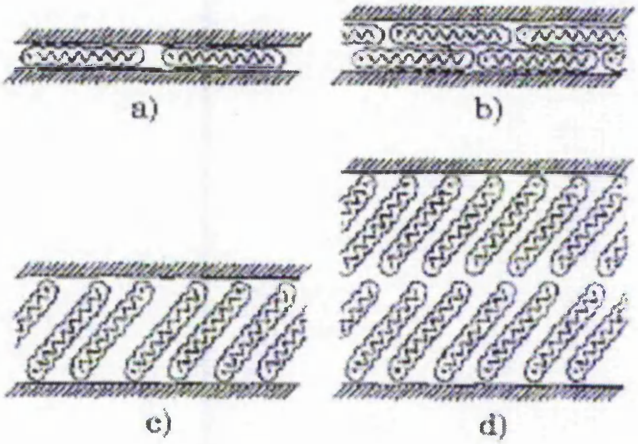


Fig. 2.2. Alkyl chain aggregation in layered silicate: (a) lateral monolayer; (b) lateral bilayer; (c) paraffin-type monolayer; (d) paraffin-type bilayer [Lagaly, G., 1986]

A more realistic description has been proposed by Vaia et al. based on FTIR experiments [Vaia, R.A. et al., 1994]. By monitoring the frequency shifts of the asymmetric CH_2 stretching and bending vibrations of the organoclays, they found that the intercalated chains existed in states with varying degrees of order. In general, as the interlayer packing density or the chain length decreases or the temperature increases, the intercalated chains adopt a more disordered, liquid-like structure resulting from an increase in the *gauche/trans* conformer ratio. When the available surface area per molecule is within a certain range, the chains are not completely disordered but retain some orientational order similar to that in the liquid crystalline state (See Fig. 2.3).

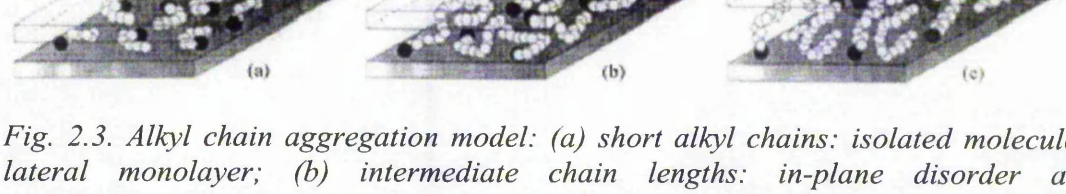


Fig. 2.3. Alkyl chain aggregation model: (a) short alkyl chains: isolated molecules, lateral monolayer; (b) intermediate chain lengths: in-plane disorder and interdigitation to form quasi bilayers and (c) longer chain length: increased interlayer order, liquid crystalline-type environment [Vaia, R.A. et al., 1994].

This interpretation has been recently confirmed by molecular dynamics simulations where a strong layering behaviour with a disordered liquid-like arrangement has been found, that can move towards a more ordered arrangement by increasing the chain length [Hackett, E. et al., 1998]. As the chain length increases, the interlayer structure appears to evolve in a stepwise fashion, from a disordered to more ordered monolayer then "jumping" to a more disordered pseudo-bilayer.

2.2.3 The structure and characterisation of clay/polymer composites

2.2.3.1 The thermodynamics of nanocomposite formation

In general, entropic and enthalpic factors determine the outcome of whether an organically modified montmorillonite (o-MMT) will be dispersed, intercalated or exfoliated in a polymer [Vaia, R. A. et al., 1997a&b; Balazs, A.C. et al., 1998]. Dispersion of MMT in a polymer requires sufficiently favourable enthalpy contributions to overcome any entropic restrictions. Favourable enthalpy of mixing for the polymer/o-MMT is achieved when polymer/MMT interactions are more favourable than surfactant/MMT interactions [Vaia, R.A. et al., 1997; Balazs, A.C. et al., 1998]. For most polar or polarizable polymers, an alkyl-ammonium surfactant, the most commonly used organic modification, is adequate to offer sufficient excess enthalpy to promote nanocomposite formation.

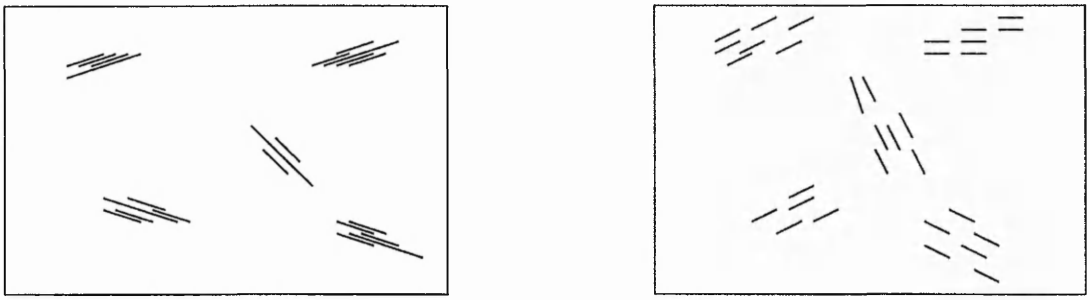
2.2.3.2 General clay/polymer nanocomposites structure

Depending on the fabrication method used and nature of the components used, i.e. layered silicates, organic cations, polymer matrix, four main types of composites can be obtained: conventional composites, intercalated nanocomposites, ordered exfoliated nanocomposites and disordered exfoliated nanocomposites. The structure of these composites is illustrated in Fig.2.4 [Alexandre, M. et al., 2000].

In clays, the distance between a plane in the unit layer and the corresponding plane in the next unit layer is the basal spacing, d_{001}, as defined in Fig 2.1. When the polymer is unable to enter the galleries of silicate layers, d_{001} of clay remains the same and a phase-separated composite is obtained which can be seen in Fig. 2.4A, whose properties stay in the same range as traditional micro-composites. This type of "conventional" composite contains unexpanded clay layers. These composites normally have improved stiffness but lower strength and lower elongation to failure than the base polymer.

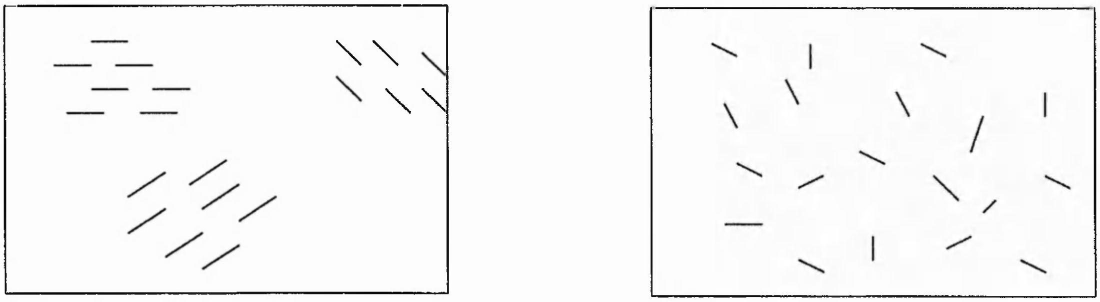
If the polymer enters the galleries causing an increase in d_{001} but the clay layers remain stacked, the composite is "intercalated nanocomposite" which can be seen from Figure 2.4 B. Intercalated structures are self-assembled, well-ordered multilayered structures where the extended polymer chains are inserted into the gallery space between parallel individual silicate layers. The clay layers normally are 1~4 nm. When the clay layers are completely and uniformly dispersed in a continuous polymer matrix, "exfoliated nanocomposite" structures have been formed. In this case, the individual silicate layers are no longer close enough to interact with the adjacent layers' gallery cations [Lan, T. et al., 1994]. The interlayer spacing can be of the order of the radius of gyration of the polymer. Therefore the silicate layers may be considered to be well-dispersed in the organic polymer.

The silicate layers in an exfoliated structure may not be as well-ordered as in an intercalated structure. There are two types of structures in exfoliated



A: Conventional Composite

B: Intercalation Nanocomposite



C: Ordered Exfoilated Nanocomposite

D: Disordered exfoliated Nanocomposite

Fig.2.4 Schematic illustrations of (A) a conventional composite, (B) an intercalated nanocomposite, (C) an ordered exfoliated nanocomposite and (D) a disordered exfoliated polymer-clay nanocomposite.

nanocomposites, namely ordered and disordered structures. These are illustrated in Figs. 2.4 C and 2.4 D. The difference between the two structures is the orientation of the exfoliated clay layers. When clay layers are oriented in preferred directions, the composites are said to have ordered structures. If the layer orientation is random, the composites are said to have disordered structures.

The interlayer spacing d_{001} is a measure of the degrees of intercalation and exfoliation of the clay in the polymers, but it does not directly disclose the proportion of clay that is exfoliated. The typical basal spacing for an intercalated clay is of the order of 1 ~ 4 nm [Tolle, T.B. et al., 2002].

2.2.3.3 The characterization of clay/polymer nanocomposites

Two complementary techniques are commonly used in order to characterize the nano-structures of clay/polymer nanocomposites. These are X-ray diffraction analysis (XRD) and transmission electron microscopy (TEM). X-Ray Diffraction (XRD) is the most commonly used method to examine nanocomposite structures since quantitative assessment can be obtained more easily. For nanocomposites with intercalated structures, the repetitive multiple-layers structure is well developed, allowing the interlayer spacing of the clay layers to be compared with the spacing of the organoclay used. There is a shift in the diffraction peak towards lower angle values as layer expansion occurs. The angle and layer spacing values are related through Bragg's equation: $\lambda=2d\text{Sin}\ \theta$, where λ corresponds to the wave length of the X-ray radiation used in the diffraction experiment; d_{001} is the interlayer spacing between diffractional lattice planes and θ is the measured diffraction angle or glancing angle.

X-ray diffraction (XRD) is successful for measuring partially exfoliated nanocomposites containing small stacks of clay particles, 2-4 layers thick, which are uniformly dispersed in the polymer matrix, as normally obtained. However, XRD is limited as it cannot differentiate between certain types of clay dispersions found in polymers. In composites with disordered exfoliated structure, a periodic stacking sequence does not exist, so the (001) peak of the clay can not be observed in the XRD patterns and observation relies on transmission electron microscopy (TEM).

Transmission electron microscopy (TEM) is a very powerful tool for analyzing the structure and properties of clay/polymer nanocomposites. Transmission electron microscopy allows a qualitative understanding of the internal structure, spatial distribution of the various phases, and views of the defect structure through direct visualization. Transmission electron microscopes are scientific instruments that use a beam of highly electrons through the specimen to examine objects on a very fine scale. Special care must be exercised to guarantee a representative cross-section of the sample. The transmission electron microscopy can clarify not only the atomic arrangement but also the electric and magnetic structure in nano-meter scale. This examination can show the surface features of the clay/polymer nanocomposites and "how it looks". TEM can show the elements and compounds that the composite is composed of and the relative amounts of them, the shape and size of the particles making up the composites and the direct relation between these structures and materials properties etc. The transmission electron microscopy is very useful for understanding the structure and chemistry of composites at the nano-scale and has been widely used in the field of nanocomposites.

2.3 The synthesis of clay/polymer nanocomposites

2.3.1 Compatibility between clay and polymers

Intercalation of polymers in layered hosts, such as layered silicates, has proven to be a successful approach to synthesize layered silicate/polymer nanocomposites. The extent and the homogeneity of the dispersion of the silicate layers within the polymer matrix are very important for the formation of nanostructure and determining physical properties. The dispersion of clay layers into discrete monolayers depends on the compatibility between the polymers and the clays used. The compatibility between clays and the polymers applied is a basic factor to be considered when developing the synthetic methods for producing layered silicate/polymer nanocomposites.

Natural montmorillonite is the most commonly used layered silicate in nanocomposites applications. The layer thickness is approximately 1 nm and its surface is hydrophilic. When hydrophilic polymers such as PVP and PEO are used, intercalation can occur directly with the MMT. However many polymers are hydrophobic, so the dispersion of clay layers into discrete monolayers in these polymers is hindered by the incompatibility between the two components. In this immiscible system, which typically corresponds to conventionally filled polymers, the poor physical interaction between the organic and the inorganic components leads to poor mechanical and thermal properties.

In order to improve the compatibility, the hydrophilic clay surface must be modified to produce organophilic clays. This is often done by exchanging the hydrated cations in the interlayer spacing with cationic surfactants such as alkylammonium or alkylphosphonium (onium) [Vaia, R.A. et al., 1993]. Organoclays have low surface energies and are more compatible with polar polymers. The ability of clay to exchange ion is known as the cation exchange capacity discussed before which is expressed in meq/100g, and is a measure of the clay's negative surface charge. When hydrated cations are ion-exchanged with organophilic cations such as alkylammoniums, it usually results in a larger interlayer spacing for the clay. In general, the longer the chain length of the surfactants and the higher the charge density of the clay, the further apart the clay layers are forced [Lebaron, P.C. et al., 1999].

When the polarity of the organoclay sufficiently matches the monomer or prepolymer, it will intercalate into the galleries and further spread clay layers apart. Strong interaction between the polymer and the modified organoclay in clay/polymer nanocomposites leads to the organic and inorganic phases being dispersed at the nanometer level. As a result, nanocomposites would exhibit unique properties not shared by their micro counterparts or conventionally filled polymers [Okada, A. et al., 1990; Giannelis, E.P., 1996; Giannelis E.P. et al., 1999c; LeBaron P.C. et al., 1999; Vaia, R.A. et al., 1999 and Biswas, M. et al., 2001]. Examples of such systems are ε-caprolactone [Usuki, A. et al., 1993], epoxides [Lan, T. et al., 1995] and polyols [Wang, Z. et al., 1998a]. In the case of long chain onium-exchanged organoclays, the clay galleries swollen by these precursors show a d-spacing indicative of a paraffin monolayer arrangement. This arrangement is thought to be ideal; however these systems may not lead to the formation of true nanocomposites. Only when the clay layers are forced apart and no longer interact through the onium chains is an ideal nanocomposite formed upon polymerization. The complete dispersion, or exfoliation, of the clay nanolayers yields nanocomposites with the highest degree of property enhancement. When the layers keep the repeating layer stacking pattern in which the gallery height is less than two times the onium ion chain length, the final product is said to be an intercalated nanocomposite. These nonocmposites will have regions of very high and very low reinforcement. This non-uniform dispersal of nanolayers limits the stress transfer through the composite, which reduces the reinforcement.

It is imperative that the surface polarities of polymers and clays are matched in order for the polymers to be fully coated by the polymers on the surface. The aforementioned nylon 6 system has achieved this exfoliated state and yielded nanocomposites with remarkable properties. Another important feature of this system is that protonated alkyl amine cations can catalyze the intra-gallery polymerization process. This speeds the intra-gallery reactions relative to the bulk polymer, providing a driving force for nanolayer exfoliation in the final composite. The use of organoclays for nanocomposite application has been used into various polar polymer systems.

Other polymer/clay systems which have been studied with various degree of success are polyurethanes [Wang, Z. et al., 1998b], polyimides [Lan et al., 1994], polystyrene [Vaia, R.A., et al., 1996 and 1997], polyesters [Chang et al., 2002] and polysiloxanes [Burnside, S.D. et al., 1995].

Some polymers such as polyolefins do not have any polar group in their backbone. In these cases the polymers have to be modified into polar polymers in order to improve the compatibility between the polymers and organoclays. The results obtained so far are not generally successful [Usuki et al., 1997; Kawasumi et al., 1997; Kato et al., 1997; Hasegawa et al., 1998]. To produce clay/polypropylene nanocomposites in this area is still a challenge.

2.3.2 Synthetic methods of producing nanocomposites

Several synthetic methods have been developed to produce polymeric nanocomposites. They are normally classified as three main methods. They include in situ polymerisation intercalation, solution intercalation and melt intercalation. Thus the polymers that form clay/polymer nanocomposites can be thermoplastic or thermoset, water soluble or organic solvent soluble.

2.3.2.1 In-Situ Polymerization

In this method, the layered silicate is swollen within a liquid monomer or a monomer solution, for example an aqueous ethylene glycol solution, so the polymer polymerization can occur between the intercalated clay sheets. Polymerization can be initiated either by 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. Although inter-layer polymerization techniques using appropriately modified organoclays or synthetic clays [Blumstein, A., 1965 and Theng, B.K.G., 1979] have long been known, the formation of layered silicate/polymer nanocomposites by in situ polymerization was only started in the early 1990s by the Toyota research centre. Okada and Usuki [Okada, A., 1990 and Usuki et al.,1993] successfully obtained homogenous nanocomposites of nylon 6 and montmorillonite from the polymerization of ε-caprolactam in the interlayer galleries of montmorillonite and dispersion of clay platelets into the nylon 6 matrix. Very low clay loadings resulted in pronounced improvements in thermal and mechanical properties through this method.

The Toyota team also studied the effect of the alkyl chain length of the surfactants used to produce organoclays. They expanded the clay layers in the nanocomposite. The experiments applied protonate α,ω-aminoacid ($^{+}H_3N\text{-}(CH_2)_{n-1}\text{-}COOH$, with n=2,3,4,5,6,8,11,12,18) to modify a montmorillonite. The modified clays were swollen by ε-caprolactam monomer at 100°C. This was followed by the polymerization of the inserted monomer to obtain nylon-6 based nanocomposites [Usuki et al., 1993]. A clear difference in the swelling behaviour was observed. Their experimental data showed that the longer the alkyl chains, the larger degree of layer expansion of modified clay, which is illustrated in Table 2.2.

Table 2.2
Basal spacing on organo-modified montmorillonite in the presence of ε-caprolactam (ε-Cla) at 100°C

$^{+}H_3N\text{-}(CH_2)_{n-1}\text{-}COOH_{(n)}$	Interlayer spacing of the modified clay (Å)	Interlayer spacing when swollen by (ε-Cla) at 100°C (Å)
2	12.7	14.4
3	13.1	19.7
4	13.2	19.9
5	13.2	20.4
6	13.2	23.4
8	13.4	26.4
11	17.4	35.7
12	17.2	38.7
18	28.2	71.2

In situ polymerisation has been widely used in many studies, especially for producing thermosetting polymer/clay nanocomposites. [Triantafillidis, C.S. et al., 2002; Lan, T. et al., 1996 and Chen, J.S. et al., 2002]. The early work on in situ polymerisation has stimulated research activities in the development of other synthetic methods to produce clay/polymer nanocomposites.

2.3.2.2 The solution intercalation method

The solvent intercalation method is based on a solvent system in which polymer or pre-polymer is soluble and the clay is swellable in the solvent. During the synthesis, the clay is first swollen and dispersed in a solvent, such as water, chloroform, or toluene and then blended with the solution of the polymer. When the polymer and clay solutions are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the clay. After solvent removal, the intercalated structure remains, resulting in clay/polymer nanocomposites.

This method is often used for water-soluble polymers, such as poly(vinyl alcohol) [Greenland, D.J., 1963] poly(vinylpyrrolidone) [Francis, C.W., 1973] Poly(ethylene vinyl alcohol) [Zhao, X. et al.,1989] and poly(ethylene oxide) (PEO) [Aranda, P. et al., 1992]. Examples of non-aqueous solvents are the poly(1-lactide)/clay system [Ogata, N. et al, 1997] and the PEO/clay system [Choi, H.J. et al., 2001] in which chloroform was used as a co-solvent, Chen for a polyimide-aluminium nitride system used N-methylprolidinone as the suspension media [Chen, X. et al., 1997] and Joen for high-density polyethylene applying xylene and benzonitrile [Joen H.G. et al., 1998]. Nematic liquid crystal polymer/clay nanocomposites have also been prepared using this method in various organic solvents, such as toluene and dimethyl formamide [Kawasumi, M. et al., 1998]. However, there are some polymeric materials such as poly(imides) which are insoluble in organic solvents. The only possible route to produce nanocomposites with this type of polymer is to use soluble polymeric precursors that can be intercalated in the clay layers and then thermally or chemically converted into the desired polymers [Yano et al., 1993].

In 1992, Aranda and Ruiz-Hitzky [Aranda, P. et al., 1992] reported that the first preparation of PEO/MMT intercalated nanocomposites using this solvent intercalation method. Aranda and Ruiz-Hitzky intercalated PEO in montmorillonite using different solvents: water, methanol, acetonitrile and mixtures (1:1) of water/methanol and methanol/acetonitrile. In this method the nature of the solvent is crucial in facilitating the insertion of polymers between the clay layers, as the polarity of the solvent medium is a determining factor for intercalation in this method.

The selection of an appropriate solvent also has been proved to play a very important role in this solution intercalation method. High solubility of the polymer and good dispersion of clays are the primary criteria used in the solvent selection for good solution intercalation. One example of this is PEO which does not intercalate well into organo-modified bentonite in toluene, but does in chloroform. Also, toluene likewise is a non-polar solvent and does not readily dissolve PEO and thus PEO cannot intercalate well into silicates from toluene [Shen, Z.Q. et al., 2002].

The thermodynamics involved in this solution intercalation method can be explained in the following way. For the overall process, in which polymer is exchanged with the previously intercalated solvent in the clay galleries, a negative variation in the Gibbs free energy is required. The driving force for the polymer intercalation into the clay from a solution is the entropy gained by desorption of solvent molecules, which compensates for the entropy decrease of the confined intercalated polymer chains [Theng, B.K.G., 1979]. This is a good way to intercalate polymers, which have little or no polarity into layered structures, and facilitates the production of thin films of polymer with polymer-oriented clay intercalated layers. However, from the commercial point of view, this method involves the large amount of organic solvents, which are usually environmentally unfriendly and economically prohibitive.

2.3.2.3 Melt intercalation method

Since an environmentally benign and easily removed solvent is not always available, a simple and direct melt intercalation method to produce clay/polymer nanocomposites was developed. This method involves heating a polymer with either an organoclay [Vaia, R.A. et al., 1993] or a natural hydrophilic clay [Akelah, A., 1995] statically or under shear above the melt or glass transition temperature (Tg) depending on the polymer being crystalline [Vaia, R.A. et al., 1993 and 1995] or amorphous [Vaia, R.A. et al., 1996]. If the clay surfaces are compatible with the chosen polymer, the polymer can diffuse into the interlayer spaces of the clays to form either an intercalated or an exfoliated nanocomposite. This technique has great advantages over either in-situ polymerisation or solution intercalation methods. As this method does not require any organic solvents, that makes melt intercalation an environmentally benign and economically advantageous method. Also this method allows the use of many polymers which were previously not suitable for in situ polymerisation or solution intercalation. This method can use current industrial mixing and processing techniques, such as extrusion and injection moulding. Nanocomposites can, therefore, be easily manufactured using traditional industrial processing equipment, such as injection moulding machines or extruders which have led to this process become increasingly popular [Kojima Y et al., 1994 and Giannelis EP., 1999].

Various polymers have been used to produce nanocomposites by this method including polystyrene [Vaia, R.A. et al., 1997; Vaia, et al., 1996], nylon 6 [Tyan, H.L. et al., 1999], polypropylene [Hasegawa, N. et al., 1998; Kawasumi, M. et al., 1997; Kato, M. et al., 1997], Styrene-Butadiene Rubber [Okada, A. et al., 1995], Polydimethylsiloxane (PDMS) [Burnside, S.D. et al., 1995], Nitrile-Butadien Rubber [Okada, A. et al., 1995] and poly(ethylene oxide) [Vaia, R.A. et al., 1995; Fischer, H. et al., 1998].

How the clay is melt processed into the polymers by this method has been well discussed. Most articles focus on the importance of the chemistry used to modify the surface of the clay, usually montmorillonite. Typical work has been done by Vaia et al. on the formation of nanocomposites by direct melt intercalation in organoclays which is schematic illustrated in Fig 2.5. This process involves heating a mixture of the polymer and organoclay above the softening point of the polymer, statically or under the shear. While heating, the polymer chains diffuse from the bulk polymer melt into the clay layers by this technique. A range of nanocomposites with structures from intercalated to exfoliated can be obtained, depending on the degree of penetration of the polymer chains into the clay layers. The experimental results indicate that the outcome of the polymer intercalation critically depends on the clay functionalization and constituent interactions. An optimal interlayer structure of the organoclay with respect to the number per unit area and size of surfactant chains, is most favourable for nanocomposite formation. The polymer intercalation depends on the existence of polar interactions between the organoclay and the polymer matrix. Polymers containing polar groups capable of associative interactions, such as Lewis-acid/base interactions or hydrogen bonding, lead to intercalation. The greater the polarizability or hydrophilicity of the polymer, the easier it is to produce organoclay/polymer nanocomposites by this melt intercalation method.

The effects of processing parameters on the formation of clay/polymer nanocomposites by this method have also been studied recently. The effect of extruder type on the formation of nanocomposites via melt intercalation method was firstly studied by producing organoclay/nylon6 nanocomposites [Cho, J.W. et al., 2001]. In this study organoclay/nylon6 composites were produced via direct melt compounding by using a conventional twin screw extruder and a single screw extruder. The results showed that the organoclay was well exfoliated into the nylon6 matrix when compounded with the twin screw extruder but use of a single screw extruder was far less effective. The mechanical properties of the organoclay nanocomposites produced by the twin screw extruder were significantly better than those produced using the singe screw extruder.

Dennis et al. discussed in detail how the processing conditions (e.g. the configuration of twin screw extruder, residence time and shear rate applied) affected the resulting nylon6/clay nanocomposites [Dennis, H.R. et al., 2001]. They found that increasing the mean residence time in the extruder generally improves the dispersion. However, there appears to be an optimum extent. Excessive shear causes poorer dispersion. Residence time in a low shearing or mildly shearing environment is required to allow polymer to enter the clay layers and expand the platelets apart. The non-intermeshing twin-screw extruder used in this study yielded the best dispersion. Excellent dispersion can be achieved with both co-rotating and counter-rotating, intermeshing types of extruders when a fully optimized screw configuration is used. It is recognized that the extruder process conditions are important parameters that must be optimized to achieve a high degree of clay dispersion in clay/polymer nanocomposites.

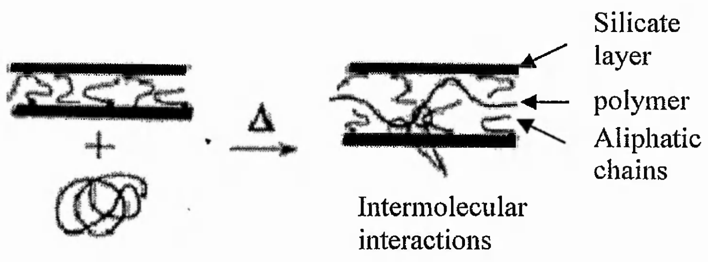


Fig. *2.5. Schematic depicting the intercalation process between a polymer melt and an organoclay [Vaia, R.A. et al., 1997].*

Solid-state intercalation [Gao et al., 2001; Khaorapapong, N. et al., 2001], co-vulcanization [Pinnavaia, T.J. et al., 2000; Okada, A. et al., 1995; Usuki, A. et al., 2002] and sol-gel [Carrado, K.A. et al., 1999 and Musto, P. et al., 2004] methods have also been reported for producing clay/polymer nanocomposites.

Of all these methods, melt intercalation is considered to be suitable for the plastic processing industry to produce clay/polymer nanocomposites due to the absence of organic solvents and the use of traditional polymer processing equipment. Research has been carried out worldwide since 1993, however, at present the development of melt intercalation has been hindered by limited clay layer expansion and exfoliation achieved compared to the in-situ polymerisation. The layer expansion and exfoliation in in-situ polymerisation is greater than in melt intercalation and is more uniform, resulting in a higher efficiency of intercalation. This less effective layer expansion has resulted in lower mechanical properties of the nanocomposites produced by melt intercalation than the composites produced by in-situ polymerisation [Pinnavaia, T.J. et al., 2000]. The design of new effective melt processing technology is necessary to overcome these problems which exist in currently used melt processing. This would make melt processing play a more important role towards commercializing the clay/polymer nanocomposites.

2.4 The enhancement of major engineering properties

Significant enhancement of a wide range of engineering properties can be achieved using clay/polymer nanocomposites with low clay loadings. These properties including higher modulus, increased strength and heat resistance, enhanced barrier properties and fire retardance, and increased biodegradability of biodegradable polymers. This section will discuss these enhancements.

2.4.1 Mechanical Properties

Compared to the pure polymer, a polymer filled with a few weight percentage loading of clay has dramatically increased mechanical properties. Toyota scientists reported a typical case for this enhancement of an exfoliated clay/nylon6 nanocomposite over a decade ago. This nylon6 nanocomposite was manufactured by the in situ intercalative ring opening polymerisation of ε–caprolactam with an organoclay, leading to the formation of exfoliated nanocomposites. The properties of the composites can be seen in Table 2.3. Compared with conventional clay/nylon6 composites, the nanocomposite of clay/nylon6 afford remarkable increase in tensile Young's modulus, tensile yielding strength and heat distoration temperature, with little or no loss in impact resistance. As shown in Table 2.3, adding 4.2 wt.% clay resulted in an increase in Young's modulus of 100% and tensile yielding strength of 50% compared to the pure nylon6. However, the impact strength of clay/nylon6 nanocomposite (NCN) was identical to that of pure nylon6.

Table 2.3
Mechanical and thermal properties of Nylon-6/clay composites prepared by in situ polymerization [Usuki et al., 1993]

Composite Type	Clay (wt%)	TensileYielding Strength (Mpa)	Young's Modulus (Gpa)	Charpy Impact Strength(KJ/m^2)
Nanocomposite	4.2	107	2.1	6.1
Microcomposite	5.0	61	1.0	5.9
Nylon 6	0	69	1.1	6.2

Another significant mechanical property enhancement of nylon-6 based nanocomposites produced by a melt processing method was also reported [Cho, J.W. et al., 2001]. In this case good dispersion of the clay layers in the polymer matrix by forming clay/polymer nanocomposites affected the elongation at break compared to the conventional composites enhanced by glass fibres. It can be seen from Table 2.4 that the tensile strength and modulus of the composites were increased in all cases compared to the pure nylon 6. The nylon 6/montomorillonite composites with 5 wt% unmodified natural clay have similar mechanical properties to a nylon 6/glass fibre conventional composite with 5% glass fibres. They have an enhanced tensile yielding strength and tensile modulus but a low elongation at break compared to the pure nylon 6. However, the organoclay/nylon6 nanocomposites formed by only 3.16 wt% organoclay loading had a higher tensile yielding strength and modulus and an almost unchanged elongation at break.

Table 2.4
Mechanical properties of Nylon 6 composites prepared by melt intercalation [Cho, J.W. et al., 2001]

Polymer composites	Mineral content(%)	Izod Impact strength(J/m)	Modulus (Gpa)	Yield Strength(Mpa)	Elongation at break (%)
Nylon 6	0	38±4	2.66±0.2	64.2±0.8	40±8
N6/glass fibre	5	53±8	3.26±0.1	72.6±0.8	14±4
N6/montmorillonite Micro-composites	5	40±2	3.01±0.1	75.4±0.3	14±3
N6/organoclay Nanocomposites	3.16	38±3	3.66±0.1	83.4±0.7	38±19
N6/organoclay/glass fibre	8	44±3	4.82±0.1	95.0±0.9	7±4

The improvement in the mechanical properties of clay/polymer nanocomposites was considered to depend on the extent of dispersion of the clay layers into a polymer matrix. Clay layers in clay/polymer nanocomposites enhancement behave in a similar way to chopped fibres in fibre reinforced polymer composites. Clays that had large surface areas in contact with polymer matrix facilitated stress transfer to the reinforcement phase, resulting in the improvements in the mechanical properties. In the case of nylon 6, there were stronger interactions between the organoclay and nylon6 than between unmodified natural montmorillonite and nylon6. This strong interaction made it easier for the organoclay layers to disperse in the nylon6 matrix which resulted in higher efficiency in intercalation.

The factors that affect the enhancements in clay/polymer nanocomposites' tensile modulus, tensile strength, and elongation at break have been well studied in the last decade and will be discussed here.

2.4.1.1 Tensile Modulus

The tensile modulus of polymers are improved by the nanocomposite approach. The dependence of the tensile modulus (E) measured at 120 °C for exfoliated nylon6 nanocomposites with various clay contents, made by the in situ intercalative polymerization of ε-caprolactam in the presence of protonated aminododecanoic acid-modified MMT (average length: 100 nm) and saponite (50 nm), were studied [Kojima, Y. et al., 1993c]. The results showed that the extent of the improvement of the modulus depends directly upon the aspect ratio of the clay, the ratio between the average length and the average height of the dispersed clay particles. Moreover, the difference in the extent of exfoliation, as observed for nylon6-based nanocomposites synthesized by the in situ intercalative polymerization of ε-caprolactam using Na^+-MMT and various acids [Kojima Y. et al., 1993c], strongly influenced the final modulus of the nanocomposites. Exfoliated layers are the main factor responsible for the stiffness improvement, while intercalated particles having a low aspect ratio, play a minor role in property enhancement.

The same behaviour has been observed for the clay/polypropylene nanocomposites (PPCNs) obtained by melt intercalation when different amount of maleic anhydride-modified PP (MA-g-PP) was added to enhance intercalation and to possibly facilitate exfoliation [Hasegawa, N. et al., 1998]. Maleic anhydride modified PP is normally used to improve the affinity between clay and polypropylene for the synthesis of PPCNs. These results together with the corresponding microcomposite as well as the simple PP/MA-g-PP polymer blends are shown in Table 2.5. In this table the simple blends of PP/PP-MA containing 7wt% and 22wt% PP-MAs are abbreviated as PP/PP-MA7 and PP/PP-MA22. The polypropylene-based microcomposite was abbreviated as PPCC. The PP/clay/MA-PP nanocomposite (PPCN) containing 1:1 clay/MA-PP ratio was abbreviated as PPCN1/1, while the PPCNs with 1:2 and 1:3 clay/MA-PP ratios are abbreviated as PPCN1/2 and PPCN1/3 respectively.

It can be seen that increasing the amount of MA-g-PP (from sample PPCH 1/1 to PPCH 1/3) not only improves intercalation or partial exfoliation, but also increases the modulus value. So the tensile modulus is a function of maleic content, which is to say, the tensile modulus is a function of the extent of exfoliation in clay/polymer nanocomposites. It can also be seen that the tensile modulus of the simple PP/MA-g-PP blends decreased due to the low molecular weight of the MA-g-PPs normally used.

EVA-based nanocomposites obtained by melt intercalation within dimethyldioctadecylammonium-modified montmorillonite also shows a non-linear

Table 2.5
Influence of maleic anhydride-modified polypropylene content on the stiffness of PP matrices and PP/clay nanocomposites [Hasegawa, N. et al., 1998]

Sample	Clay content (wt.%)	PP-MA content (wt.%)	Young's modulus (MPa)
PP	0	0	780
PP/PP-MA7	0	7.2	714
PP/PP-MA 22	0	21.6	760
PPCC	6.9	0	830
PPCH 1/1	7.2	7.2	838
PPCH 1/2	7.2	14.4	964
PPCH 1/3	7.2	21.6	1010

[a] PP=Polypropylene; PP-MA x: polypropylene modified by maleic anhydride (x.wt.% of PP-MA in the blend); PPCC=Polypropylene-based microcomposite; PPCH y/z=polypropylene-based nanocomposite (y/z.weight ratio between y parts of clay and z parts of PP-MA).

increase in the relative tensile modulus as the clay content rises (vol.%). X-ray diffractary and TEM observations for all the nanocomposites produced indicate that both intercalation and exfoliation occurred. A non-linear increase in the relative tensile modulus was observed and may be explained by a decrease in the exfoliated particle fraction as the filler content rose. Another possible explanation would take into account the continuous variation of the mean aspect ratio of the primary particles which decrease when the filler content is increased.

In contrast to the above results, when only intercalated structures (without any exfoliation) occurred, such as for PMMA [Lee, D.C. et al., 1996] based nanocomposites, obtained by solvent intercalation in presence of water-swollen Na^+-montmorillonite, the increase in Young's modulus is relatively weak, ranging, e.g. from 1.21 to 1.30 GPa for pure PMMA and PMMA containing 11.3 wt.% intercalated montmorillonite, respectively. This shows the inefficiency of intercalated structures in improving the stiffness of the nanocomposites.

The influence of clay exfoliation on the increase of tensile modulus has been examined for thermoset polymers. A large increase in the tensile modulus was found for an exfoliated structure but not for an intercalated structure, in amine-cured epoxy systems [Lan, T. et al., 1994 and Lan, T. et al., 1995]. The Tensile Modulus for various amine-cured epoxy-based nanocomposites filled with 2 wt.% montmorillonite previously modified by alkylammonium cations with different length was studied in this case [T. Lan et al., 1995]. It is observed by TEM and XRD that only an intercalated structure was found in the organoclay/epoxy nanocomposites for the montmorillonite modified with butylammonium (Epoxy/MMT4). Three exfoliated structures have been achieved for the organoclay/epoxy nanocomposites with montmorillonite modified by alkylammonium with alkyl chains of 8, 12 and 16 carbons (Epoxy/MMT8, MMT12 and MMT16). The extent of exfoliation increased along with the increase of alkyl chains length. The results showed that the intercalated nanocomposites Epoxy/MMT4 gives a low tensile modulus, while the other three exfoliated nanocomposites with alkyl chains of 8, 12 and 16 carbons had much higher modulus values. However, Zilg et al. [Zilg, C. et al., 1999] have reported small stiffness improvements in the case of some other thermoset systems, such as anhydride-cured epoxy based nanocomposites where exfoliated structures were formed. In this case, the authors think the real key for the anhydride-cured epoxy matrix stiffness improvement resides in the formation of supramolecular assemblies obtained by the presence of dispersed anisotropic laminated clay layers. They also describe a stiffening effect when the montmorillonite is modified by a functionalized organic cation, which can interact with for example carboxylic acid or hydroxyl groups in the matrix during curing.

2.4.1.2 Tensile Strength

The tensile strength of a material is the maximum amount of tensile stress that can be applied to it before it ceases to be elastic. Tensile strength behavior has been shown to be very different in thermoplastic-based nanocomposites and thermoset polymer-based nanocomposites.

In thermoplastic-based intercalated or exfoliated nanocomposites, the tensile strength may vary depending on the nature of the interactions between the matrix and the filler as shown in Table 2.6.

Caution had to be taken when examining these tensile strengths as most of the described nanocomposites were obtained by in situ polymerization so that their properties may be influenced by changes in the matrix molecular weight during their manufacture. The differences observed are usually sufficiently sizeable to draw some conclusions. It can be seen from Table 2.6 that filled polymers such as exfoliated nylon-6 based nanocomposites prepared by different methods [Kojima, Y. et al., 1993a; Kojima, Y. et al., 1993b; Kojima, Y. et al., 1993c] or intercalated PMMA-based nanocomposites exhibit an increase in tensile strength. The presence of polar (PMMA) and even ionic interactions (nylon-6 grafted onto the layers) between the polymer and silicate layers are usually used to explain the increase. The increase appears to be much more pronounced in case of nylon-6, which has both an exfoliated

Table 2.6
Tensile strength for nanocomposites produced from various thermoplastic matrices

Matrix	Matrix Tensile Strength (Mpa)	Clay Content (wt.%)	Nanocomposite type	Nanocomposite Tensile Strength (MPa)
Nylon-6	68.6	4.7	HCH[a]	97.2
	68.6	5.3	L-HCH[b]	97.3
	68.6	4.1	One-pot-NCH[c]	102
PMMA	53.9	12.6	Intercalated	62.0
	53.9	20.7	Intercalated	62.0
PP	31.4	5.0	Intercalated[d]	29.5
	32.6	4.8	Intercalated[e]	31.7
PS	28.7	11.3	Intercalated	21.7
	28.7	17.2	Intercalated	23.4
	28.7	24.6	Intercalated	16.6
	28.7	34.1	Intercalated	16.0

[a] *NCH: exfoliated nanocomposite prepared by in situ intercalative polymerization of e-caprolactam in protonated aminododecanoic acid modified montmorillonite.*
[b] *L-NCH: exfoliated nanocomposite prepared by in situ intercalative polymerization of e-caprolactam inmontmorillonite pre-intercalated with e-caprolactam.*
[c] *One-pot-NCH: exfoliated nanocomposite prepared by in situ intercalative polymerization of e-caprolactam activated by phosphoric acid in Na-montmorillonite.*
[d] *PP added with PP-MA so as a PPCH 1/1 is reached (see Table 2.6).*
[e] *PP added with PP-MA so as a PPCH 1/3 is reached (see Table 2.6).*

structure and ionic bonds with the silicate layers. As far as polypropylene based nanocomposites are concerned [Hasegawa, N., et al., 1998], no or only very slight improvement in the tensile strength has been observed.

This behaviour can be partially explained by the lack of interfacial adhesion between the apolar PP and the polar layered silicates. The addition of maleic anhydride modified polypropylene to the polypropylene matrix has been found to improve the intercalation of the PP chains and maintain the tensile strength at an acceptable level. The tensile strengths of PS intercalated nanocomposites are lower than the original PS. As the clay content of the nanocomposite rises, the tensile strength decreases. This lack of strength is attributed to the fact that only weak interactions exist at the poly(styrene)/clay interface in contrast to the previous compositions in which (stronger) polar interactions may occur which strengthen the clay/matrix interfaces.

Thermoset polymer based nanocomposites, such as epoxy resin-based nanocomposites, exhibit a totally different behavior depending on whether their glass transition temperatures are above or below room temperature.

In epoxy resins with high glass transition temperatures neither intercalated nor exfoliated nanocomposites can lead to an improvement in the tensile strength, they rather make the materials more brittle [Lan, T. et al., 1995; Zilg, C. et al., 1999]. This effect appears to be generally more pronounced for the nanocomposites with intercalated structures than those with exfoliated structures. In contrast, nanocomposites based on epoxies with low glass transition temperature [Lan, T. et al., 1994; Wang, Z. et al., 1998a] and polyurethanes [Wang, Z. et al., 1998b] exhibit a sizeable increase in the tensile strength upon the addition of small quantities of clays. This increase follows qualitatively those observed previously for the Young's Modulus measurements.

The same increase is also observed for silicon rubber-based nanocomposites [Wang, S.J. et al., 1998]. Moreover, in this study, the enhancement in tensile strength in a partially-intercalated and partially-exfoliated organo-montmorillonite/silicon rubber nanocomposite is compared to a composite filled with anisotropic silica nanoparticles (5-20 nm), named as aerosilica. The results indicated that for low glass transition temperature cured nanocomposite materials, the tensile strength increase does not rely upon the aspect ratio of the dispersed particles but on the presence of nanoparticles dispersed in the cross-linked soft matrix.

2.4.1.3 Elongation at break

The effect of nanocomposite formation on the elongation at break has not been well investigated. For thermoplastic polymer based nanocomposites such as intercalated PMMA and PS or intercalated/exfoliated PP, the elongation at break is always reduced compared to their base polymers. In the case of PP/clay composites, the decrease of elongation at break is very significant, 105% decrease compared to pure PP, for the conventional microcomposite with 6.9 wt% non-intercalated clay, while the decrease of elongation at break is 7.5% for the intercalated/exfoliated organoclay/PP nanocomposites with 5 wt% of organoclays. These results showed that nanocomposites approach is less damaging to the elongation at break for the base thermoplastic polymers.

A loss in elongation at break does not occur in the elastomeric epoxy [Wang, Z. et al., 1998a] or polyol polyurethane matrices [Wang, Z. et al., 1998b]. The formation of intercalated and exfoliated epoxy/organo-magadiite nanocomposites facilitated the cross-linked epoxy matrices increased elongation at break. The results showed that, when a conventional magadiite/epoxy composite was prepared (magadiite only exchanged with octadecylammonium cation), a decrease in the elongation at break was observed as expected. While an intercalated organo-magadiite/epoxy nanocomposite, (magadiite modified by trimethyloctadecylammonium cation) tends have a slightly improved elongation at break, but the exfoliated organo-magadiite/epoxy nanocomposite (magadiite modified by methyloctadecylammonium cation) shows a large increase in the elongation at break. The improvement in elasticity may be attributed in part to the plasticizing effect of the gallery oniums and to their contribution to the formation of pendant chains and partly to the conformational effects at the clay-matrix interface. The combination of improved stiffness (tensile modulus), toughness (tensile strength) and elasticity (elongation at break) is quite exceptional and make elastomeric polymer nanocomposites a new family of high performance materials.

Another matrix which exhibits both an increase in strength and elongation at break is poly(imide) (PI) [Yang, Y. et al., 1999]. When PI is filled by montmorillonite exchanged with hexadecylammonium cation, these properties increase with clay loadings of up to 5 wt.%. At higher clay contents, both tensile strength and elongation at break experience a sharp decrease. This behaviour is explained by the formation of non-exfoliated aggregates at higher clay contents, that makes these composites more brittle.

2.4.1.4 Impact Properties

Impact strength is one of the most commonly tested and reported properties of plastics. Impact testing measures the energy required to break a specimen by dynamically applying a load. There are normally two different methods for measuring impact strength — the Izod impact strength and the Charpy impact strength. The Izod impact strength of a material is the amount of energy necessary for a swinging pendulum to break a notched specimen that is secured at one end. While, in the Charpy test, the specimen is simply supported at both ends, and the test measures the amount of energy needed to break a specimen fixed across a 100 mm span.

As the results showed in Table 2.3 and Table 2.4 studied in section 2.4.1, the impact strength (Izod impact strength or Charpy impact strength) of the nanocomposites have been found to either slightly decrease or stay unchanged compared to pure based polymers. The impact properties of nanocomposites have been investigated further and the results showed that the change of impact properties depended on the synthetic methods for producing clay/polymer nanocomposites. The impact properties have been investigated for nylon-6-based nanocomposites prepared by either in-situ intercalative polymerization of ε-caprolactam using protonated aminododecanoic acid exchanged montmorillonite [Kojima, Y. et al., 1993a] and by melt intercalation using octadecylammonium-exchanged montmorillonite [Tyan, H.L. et al., 1999]. Both methods led to exfoliated nanocomposites especially when the clay content did not exceed 10 wt.% (at higher clay levels, melt-intercalation provides partially exfoliated/partially-intercalated materials). The formation of nylon-6-based nanocomposites did not reduce the impact properties greatly, whatever the exfoliation process used. In the case of in-situ intercalative polymerization, the Izod impact strength is reduced from 20.6 to 18.1 J/m when 4.7 wt.% of clay is incorporated in the nanocomposites. Charpy impact testing shows a similar reduction in the impact strength with a drop from 6.21 kJ/m^2 for the original matrix down to 6.06 kJ/m^2 for the 4.7 wt.% nanocomposite. However, it is hard to see a difference in the Izod impact strength of melt-intercalated nylon-6 based nanocomposites over a relatively large clay content range of 1 wt% to 20 wt%.

2.4.2 Thermal Stability

Generally, the incorporation of clay into the polymer matrix was found to enhance thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition.

Blumstein firstly reported the improved thermal stability of a polymer-layered-silicate/nanocomposite that combined poly(methyl methacrylate) (PMMA) and montmorillonite [Blumstein A., 1965]. In this work, the author showed that a 10 wt.% clay intercalated PMMA (produced by free radical polymerization of the intercalated monomer) degraded at a temperature 40~50°C higher than the pure unfilled PMMA. The author proposed that the enhanced thermal stability of the montmorillonite/PMMA nanocomposite is due not only to the different structure of nanocomposites, but also to the restricted thermal motion of the PMMA in the clay layers.

There have been many reports concerned with the improved thermal stability of nanocomposites prepared with various types of organic modified clays and polymer matrices. Burnside and Giannelis [Burnside, S.D. et al., 1995] measured the thermal stability of cross-linked poly(dimethylsiloxane) (PDMS) nanocomposites containing 10 wt.% of exfoliated organo-montmorillonite. Compared to the original cross-linked PDMS, the nanocomposite thermogravimetric analysis (TGA) curve shows a large shift of the weight loss at a higher temperature. This indicates that the nanocomposite is more thermally stable to higher temperatures. Burnside and Giannelis explained their results as the consequence of hindered diffusion paths, formed by the nanocomposites, to volatiles.

In a recent study, Zhu et al. reported the thermal stability of organo-MMT/PS nanocomposites, which were prepared using three different types of new organically modified MMT [Zhu, J. et al., 2001]. Two functionalized ammonium salts modified MMT, Dimethyl-n-hexadecyl-(4-vinylbenzyl) ammonium chloride (VB-16) and Dimethyl-n-hexadecyl -(4-vinylbenzyl) ammonium chloride (OH-16) modified MMT, were used to prepare nanocomposites PS/VB-16 and PS/OH-16. While a phosphonium salt modified MMT, Hexadecyl Triphenyl-phosphonium (P-16) modified MMT, was used to prepare nanocomposite PS/P-16. The results showed that the nanocomposite with phosphonium salt modified MMT, PS/P-16, degraded at a temperature 50°C higher than the pure PS so the thermal stability of the nanocomposite had been enhanced relative to that of pure PS. The degradation mechanism of this phosphonium modified-MMT/PS nanocomposite was explained by the author and found to be different from the others: there is a second step in the degradation. This second step lays around 30% degradation of the nanocomposite PS/P-16, and this must be attributed to some interaction between the clay and the PS that serves to stabilize the nanocomposite. The most likely explanation is that the higher decomposition temperature of the phosphonium modified MMT provides for the formation of char at a more opportune time to retain the PS. In the case of other two nanocomposites with ammonium salt modified MMT, PS/OH-16 and PS/VB-16, char formation occurs earlier and can be broken up by the time the polymer degrades. It is also found the degradation temperature for all these three nanocomposites is a function of the clay content. Even with as little as 0.1 wt% clay loading in the nanocomposite, the degradation temperature of the material was significantly increased.

The study on clay/PS nanocomposites indicated that the actual nature of the thermal degradation mechanism is a key factor that may determine the extent of the thermal stability in nanocomposites. The thermal stability of nanocomposites will depend on the clay, the polymer and the type of nanocomposite formed, and whether the nanocomposites are intercalated or exfoliated. The thermal stability of exfoliated clay/poly(imide) nanocomposites is only enhanced by about 25 °C compared to pure poly(imide), which is much less than the 140 °C jump observed in exfoliated PDMS nanocomposites. Both the structure of the clay/polymer nanocomposites and the degradation mechanisms play an important role in materials thermo stability.

2.4.3 Flame Retardancy

The first mention of the flame retardant properties of nanocompounds appeared in 1976 when Unitika made a patent application on nylon-6 layered-silicate (montmorillonite) nanocomposites as fire retardant materials [Fujiwara S. et al., 1988]. In 1997 Gilman et al. reported detailed investigations on the flame retardant properties of nylon6/layered silicate nanocomposites [Gilman, J.W. et al., 1997]. Subsequently, various types of nanocomposite materials have been investigated and similar reductions in flammability have been reported [Dabrowski, F. et al., 1999; Bourbigot, S. et al., 2000; Gilman, J.W. et al., 2000].

The main parameter used to measure the flame retardant behaviour of materials is the peak of heat release rate (HRR) which is determined by Cone Calorimetry. In a typical experiment, the sample is exposed to a given heat flux, often 35-50 kW/m^2. The heat release rate (HRR) as well as the mass loss rates are recorded as a function of time. The reduction of the peak HRR is evidence of the efficiency of fire retardant material. Moreover, gas and soot production are also measured. Table 2.7 shows the cone calorimeter data of three different kinds of polymer and their nanocomposites with montmorillonite. As shown in Table 2.7, all of the MMT-based nanocomposites exhibit reduced flammability. The peak HRR is reduced by 50-75% for nylon6 (N6), polystyrene(PS) and maleic anhydride grafted polypropylene (MAH-g-PP) nanocomposites [Gilman, J.W. et al., 2000]. According to Gilman, the MMT clay must be dispersed into nanolayers for it to affect the flammability of the nanocomposites. However, it is found that the clay need not be completely exfoliated. In general, the nanocomposite's flame retardancy mechanism mainly involves the formation of high-performance carbonaceous-silicate char layers, which formed through the collapse of the exfoliated and/or intercalated structures and builds up on the surface during burning. This layer of char may act as an excellent insulator and mass transport barrier, slowing down the escape of the volatile decomposition products from the burnt material [Gilman, J.W. et al., 1998; Gilman, J.W. et al., 2000].

Recently, the flame retardancy properties of PS/organo-MMT nanocomposites were also studied by Zhu et al. [Zhu, J. et al., 2001]. Two ammonium salt modified MMT/PS nanocomposites (PS/VB-16 and PS/-16) and one phosphonium modified MMT/PS nanocomposite (PS/OH-16) were prepared as discussed above in the section of Thermal Stability. The study on the peak HRR for PS and all the three nanocomposites showed that as the clay content increases, the amount of char formed increased and it served as a barrier to both mass and energy transport, increases. At the same time, the peak HRR decreased. One of these nanocomposites, PS/OH-16, was the most intercalated and this yielded a slight reduction in the peak HRR compared to the other two nanocomposites which had exfoliated structures. This observation again supports the view that an intercalated material is more effective than an exfoliated material in flame retardancy [Gilman, J.W. et al., 1999].

Table 2.7
Cone calorimeter data of various polymers and their nanocomposites with organoclays [Gilman, J.W. et al., 2000]

Sample (structure)	% residue yield(±0.5)	Peak HRR (KW/m^2)	Mean Hc^a (MJ/Kg)	Mean SEA^b (m^2/Kg)
N6	1	1010	27	197
N6 nanocomposite 2% (exfoliated)	3	686	27	271
N6 nanocomposite 5% (exfoliated)	6	378	27	296
PS	0	1120	29	1460
PS-silicate mix 3% (immiscible)	3	1080	29	1840
PS-nanocomposite 3% (exfoliated/exfoliated)	4	567	27	1730
PSw/DBDPO/Sb2O3) 30%	3	491	11	2580
MAH-g-PP	5	1525	39	704
MAH-g-PP-nanocomposite 2% (intercalated/exfoliated)	6	450	44	1028
MAH-g-PP nanocomposite 4% (intercalated/exfoliated)	12	381	44	968

Hc^a, specific heat of combustion; SEA^b, specific extinction area.

2.4.4 Barrier Properties

In general, polymer/clay nanocomposites have significant reductions in gas and liquid permeability compared to their base polymers. The solvent uptake is also lower. Polymers such as epoxies and siloxanes [Giannelis, E.P. *et al.*, 2000]), and very hydrophilic PVA [Manias, E. et al., 2000], are all improved up to an order of magnitude, for 5-7 wt% MMT loadings. This improvement can be attributed to the formation of tortuous path ways for the diffusing molecules of solvent and gas which is illustrated in Fig2.6.

Generally the high aspect ratio of clay layers in exfoliated nanocomposites has been found to reduce the gas permeability in films prepared from nanomaterials. The permeability to carbon dioxide has been measured for the partially-exfoliated poly(imide)-based nanocomposites prepared by Lan et al. [T. Lan et al., 1994]. The relative permeability values, i.e. Pc/Pp where Pc and Pp stand for the composite and the pure polymer permeability, respectively, have been studied in function of the filler volume fraction. A nanocomposite structure is formed by a 'self-similar clay aggregation mechanism' in which face/face associated and elongated layers are formed in staircase-like fashion. These self-similar structures can exhibit enhanced aspect ratios.

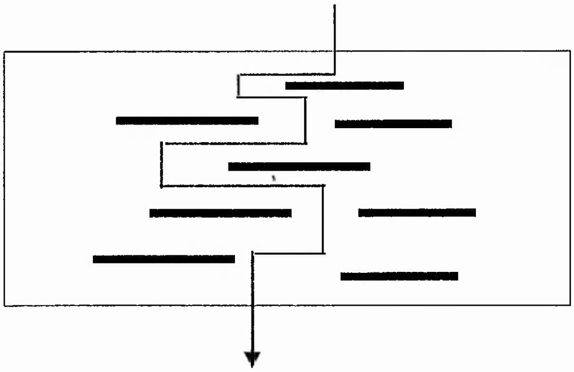


Fig 2.6. Formation of tortuous path in layered silicate/polymer nanocomposites

The water permeability of both partially and totally exfoliated poly(imide)-based nanocomposites has been reported by Yano et al. [Yano, K. et al., 1997]. Organoclays with different layer lengths were used to produce nanocomposites and it was found that there was a clay length dependence of the relative permeability coefficient for the poly(imide) filled with 2 wt.% of organoclays when the clay was either exfoliated, or intercalated. Yano showed that as the length of the clay particles increased, the relative permeability decreased drastically. This indicated that the best gas barrier properties were obtained by fully exfoliated long silicate layers.

Permeability to water vapor has also been investigated for an exfoliated nanocomposite based on poly(e-caprolactone) (PCL), synthesized by in-situ intercalative polymerization of the lactone monomer inside an organo-modified montmorillonite. In order to produce nanocomposite films with different filler contents, PCL nanocomposite containing 15 wt.% (6 vol.%) of exfoliated montmorillonite was prepared and mixed with different amounts of a commercial preformed PCL by co-dissolution in toluene followed by solvent casting. A dramatic drop in the relative permeability of the polymers occurred as the amount of nanofiller increased. An aspect ratio of 70 was found to produce the best reduction in permeability. This is again well below the value expected for exfoliated montmorillonite. The authors explained this apparent discrepancy by the fact that the model was originally developed for particles which were totally oriented parallel to the film plane. However, under the experimental conditions used for the film formation, the silicate layers could not be aligned flat along the film surface and filler aggregation was possible. Bayer has recently commercialized the use of nanotechnology for plastic films for food packaging. They are marketing Durethan1 LPDU 601 which is based on nylon-6 exfoliated nanocomposites with improved gas barrier properties improved transparency and gloss and increased tensile modulus [Scherer, C. et al., 1998].

2.4.5 Ionic conductivity

Nanocomposites have been produced with improved conductivity [Vaia, R.A. et al., 1995]. An intercalated nanocomposite obtained by melt intercalation of poly(ethylene oxide) (40 wt.%) with Li-montmorillonite (60 wt.%) has been shown to have enhanced ionic conductivity at lower temperatures when compared to more conventional PEO/$LiBF^4$ mixtures.

Poly(ethylene oxide) is not able to crystallize when intercalated, hence eliminating the presence of crystallites causing the polymer to be non-conductive. The conductivity of the PEO/ Li-montmorillonite nanocomposite is 1.6×10^{-6} S/cm at 30°C and exhibits weak temperature dependence with an activation energy of 11.76 kJ/mol. The composites have higher ionic conductivity at ambient temperature compared to conventional $LiBF^4$/PEO electrolytes and combined with a single ionic conductor character makes these nanocomposites promising electrolyte materials.

2.4.6 Thermal expansion coefficient

Due to the high aspect ratio of the exfoliated silicate layers, the thermal expansion coefficient of poly(imide)-based nanocomposites prepared by Yang et al. with hexadecylammonium cation exchanged montmorillonite were significantly reduced, from $3.6 \times 10^{-5}\ K^{-1}$ to values as low as $1.55 \times 10^{-5}\ K^{-1}$ when 10 wt.% of clay is added [Yang, Y. et al., 1999].

2.5 The major progress in developing Clay/PP Nanocomposites

The work carried out in this research is focusing on the development of the technology for producing clay/polypropylene nanocomposites via direct melt processing. Below is the review of some of the research work which has been carried out in this area.

2.5.1 The importance and the difficulty for developing clay/PP nanocomposites

Amongst these polymer based nanocomposites discussed previously, polypropylene has great potential for nanocomposite applications. Polypropylene is one of the four major commercial polymers. Breakthroughs in catalyst and process development as well as polypropylene's attractive combination of low cost, low weight, a heat distortion temperature above 100°C, versatility in terms of properties, have allowed polypropylene to be widely used in domestic and engineering applications [Moore, E. P., 1996]. Today polypropylene is competing very successfully with other less environmentally friendly and less versatile plastics [Gramminger, D. et al., 1998]. However, its application for enclosures of carbonated liquid containers is compromised due to its inadequate barrier resistance to gases and its low stiffness. The newly developed polypropylene based nanocomposites have the potential to improve the properties so that they could be used in the food and drink packaging industries where they could replace relatively high cost metal and high-performance thermoplastic polymers.

Several methods have been developed to produce clay/polymer nanocomposites as mentioned before. However, polypropylene is considered to be extremely difficult to intercalate with clays to produce nanocomposites by directly using these methods [Manias, E. et al., 2000]. The reason is that polypropylene does not contain any polar groups in its molecular structure. This makes polypropylene incompatible with both hydrophilic clays and organoclays. To overcome this problem, both the clays and polymer require modifying to produce nanocomposites .[Oya. A. et al., 2000]. Two synthetic methods have been developed and can be classified as in situ polymerization and melt intercalation methods. These two methods will be discussed in detail below.

2.5.2 The synthesis of clay/polypropylene nanocomposites

2.5.2.1 In situ polymerization

A few studies have investigated the production of clay/polypropylene nanocomposites by using the in situ polymerisation method. In this method, the layered silicate is swollen in the solution of monomer propylene, so that the polymerization of propylene can occur between the intercalated clay layer sheets. Polymerization can be initiated by the catalyst, for example a metallocene catalyst, which was fixed inside the interlayer before the swelling occurred. Tudor et al. used the in situ polymerization method for the preparation of clay/PP nanocomposites (PPCN). They demonstrated the ability of using soluble metallocene catalysts to intercalate inside silicate layers and to promote the coordination polymerization of propylene [Tudor et al., 1996]. A synthetic hectorite, Laponite RD, was first treated with methylaluminoxane (MAO) in order to remove all the acidic protons and to increase the interlayer spacing to receive the transition metal catalyst. It should be noted that MAO is commonly used in association with metallocenes to produce coordination catalysts active in olefin polymerizations. During this first treatment step, XRD analysis showed no noticeable increase of the layer spacing. Upon the addition of the metallocene catalyst, a cation exchange occurred between the Na^+ in the MAO-treated hectorite and the metallocene catalyst by an increase in the interlayer spacing of 0.47 nm. The other type of organoclay used in this study was a synthetic fluorinated mica-type silicate. It was deprived of any protons in the galleries and the catalyst inserted itself between the mica layers without the need of MAO pre-treatment. These two modified layered silicates catalysed the polymerization of propylene when the excess of MAO was present and produced PP oligomers. Unfortunately, the structures of the composites were not characterised by the authors so it was not clear if the structure of the composite had been intercalated or exfoliated.

2.5.2.2 Melt synthesis

Most studies reported so far for the preparation of clay/PP nanocomposites used the melt intercalation method. Various ways have been developed for the dispersion of organoclays in the polypropylene matrix in its molten state. The incorporation of organoclays into thermoplastics by conventional polymer melt processing is a promising new approach for forming nanocomposites. This method provided great commercial opportunities for the polymer processing industry to produce clay/polypropylene nanocomposites. If technically possible, melt compounding would be more economical and simple than the in-situ polymerization process. As mentioned before, polypropylene is considered to be extremely difficult to intercalate with clays to produce nanocomposites because polypropylene does not contain any polar group in its molecular structure. If minute amounts of polar functional groups are attached to the polymer in blocks or randomly grafted, polypropylene will be rendered miscible to alkylammonium modified organo-MMT, and nanocomposites could be formed either by direct melt intercalation, or co-extrusion of PP with the organo-montomorillointe. Using this method the traditional processing equipment could be used to manufacture nanocomposites. Reactive melt processing also has the advantage that it does not require any organic solvents and is more environmentally friendly than other methods of producing nanocomposites. It will be very helpful to know the frontier progress that has been made in this research area. The following section will extensively discuss the application of melt processing in producing clay/polypropylene nanocomposites. It will discuss the current problems which exist and examine the possible mechanisms of melt intercalation. This will allow more effective melt processing methods to be designed for commercializing clay/PP nanocomposites.

2.5.2.2.1 Reactive Melt synthesis of PP-g-MAH (or PP-OH)/organoclay nanocomposites

Since PP has no polar groups in the chain, direct intercalation of PP in the organoclays had proved to be very difficult. To overcome this difficulty, Kato used octadecylamine (ODA) modified montmorillonite(ODA-MMT), which was compounded with PP oligomers which were modified with either maleic anhydride groups (PP-g-MAH) or hydroxyl groups (PP-OH) to produce clay/PP nanocomposites [Kato, M. et al., 1997]. Although Transition Electron Microscope images and dynamic mechanical analysis indicated that nanocomposites had been formed, limited information was available regarding to the toughness and stiffness of the polypropylene nanocomposites formed in this study. When PP-g-MAH or PP-OH was melt blended with ODA-MMT under shearing at 200°C for 15 minutes, intercalated nanocomposites were obtained. The interlayer spacing increased from the original 2.17 nm to 3.82 nm and 4.4 nm for the PP-g-MAH and the PP-OH based nanocomposites respectively. It was found that a PP-MA matrix with a lower maleic anhydride content (acid value=7 mgKOH/g for Mw=12,000) did not result in any layer expansion under the same conditions. This illustrated that a minimum functionalization of the PP chains had to be reached for the intercalation to proceed. The authors also examined the effect of clay content on the extent of intercalation. The results showed that intercalated structure was enhanced when clay content was decreased.

Only intercalated structures were obtained in Kato et al.'s study. This method was further developed by Hasegawa et al. [Hasegawa, N. et al., 1998]. The driving force of the intercalation was explained in this study. In his study, Hasegawa described a facile approach for the preparation of PPCN by melt intercalation using a maleic anhydride-modified polypropylene oligomer (PP-g-MAH) and an organically modified clay. In a typical preparative method, PPCN pellets were prepared by melt blending pellets of PP-g-MAH and the powder of stearyl ammonium modified Na^+–montmorillonite (C18-MMT) at 200 °C, using a twin-screw extruder. X-ray diffraction patterns and TEM images showed that the silicate layers were exfoliated and uniformly dispersed in the PP-g-MAH matrix. The possible clay dispersion process in PP-MA-based nanocomposites is schematically illustrated from Fig 2.7. The author concluded that the driving force for the PP-g-MAH interaction originated from the strong hydrogen bonding between the MA groups and the polar clay surface.

Fig 2.7 shows that the extent of layer expansion depends on the bonding between the maleic anhydride group and the oxygen groups of the organoclay. The influence of clay content in clay layers expansion has been studied recently. Nam et al. [Nam, P.H. et al., 2001] prepared PP/MMT nanocomposites using the method as described above. A mixture of PP-g-MAH (0.2 wt% MAH) and stearyl ammonium modified Na^+–MMT (C18- MMT) were melt extruded at 200 °C in a twin-screw extruder. They prepared PPCNs with three different clay contents, 2 wt%, 4 wt% and 7.5 wt%. The XRD patterns and TEM images of C18-MMT, PP-MA and various

PPCNs clearly showed that the nearly disordered exfoliated structure was obtained with 2 wt% clay, while ordered exfoliated nanocomposites and intercalated structure were obtained with clay contents of 4 wt% and 7.5 wt%. This further supported the conclusion of Kato et al that intercalated or exfoliated nanocomposite structures could only be formed by using small amounts of clay [Kato, M. et al., 1997].

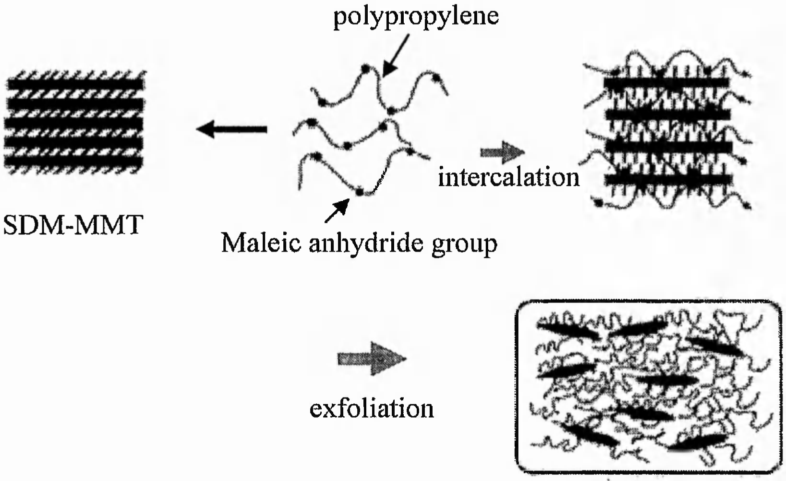


Fig 2.7. Schematic illustration of organoclay dispersion process in PP-g-MAH matrix [Hasegawa, N. et al., 1998].

Although intercalated or exfoliated nanostructures can be formed in PPCNs prepared from PP-g-MAH oligomers and organoclays, the mechanical properties are reduced, because of the low molecular weight of PP-g-MAH oligomers. A new method is required to solve this problem. Research has been done on the melt synthesis of clay/PP nanocomposites by using the functional oligomer (PP-OH) as a compatibilizer [Usuki, A. et al., 1997] investigated by the Toyota research group. Using a functional oligomer PP-OH, as compatibilizer, is expected to increase the compatibility between organoclays and homopolypropylenes. This may lead to an improvement in the engineering properties of the composites compared to PP matrix. In this study, the oligomer PP-OH with polar telechelic OH groups was firstly intercalated between the layers of distearyldimethylammonium modified Na^+–

montmorillonite (DSDM-MMT), and then the PP-OH/DSDM-MMT was melt mixed with homo polypropylene to obtain an intercalated nanocomposite.

Further study by the same group [Kawasumi, M. et al., 1997] reported that the preparation of PP/MMT nanocomposites was obtained by directly melt blending a three components system including PP, a maleic anhydride grafted PP oligomer (MAH-g-PP) and organoclay modified by stearylammonium cations using a twin-screw extruder. Maleic anhydride grafted PP was also used as compatibilizer here. In their study, they used two different types of maleic anhydride modified PP oligomer (MAH-g-PPs) with different amounts of maleic anhydride groups and two types of organically modified clays to examine the miscibility effect of the oligomers on the dispersibility of the organoclay in the PP matrix. They also studied the effect of hybridization on the mechanical properties of the nanocomposites when compared with pure PP and PPCNs without oligomers.

X-ray diffraction and TEM observations detected the intercalated structures of the nanocomposites produced. On the basis of XRD patterns and TEM images, they proposed a possible mechanism for the dispersion of intercalated clay layers in the PP matrix. Figure 2.8 schematically shows the possible mixing process of the three components i.e. PP, PP-g-MAH, and organoclay to produce clay/PP nanocomposites. The hydrogen bondings between the maleic anhydride group and the oxygen groups of the clay were still believed to be the driving force for the intercalation. The hydrolyzed maleic anhydride polypropylene intercalated into the organoclay, expanded clay galleries, and facilitated the incorporation of polypropylene.

However, only intercalated nanocomposite occurred for this PP/PP-g-MAH/ organoclay system. There are two important factors to achieve the exfoliated and homogeneous dispersion of the layers in the nanocomposites: (1) the intercalation capability of the oligomers in the clay layers and (2) the miscibility of the oligomers with PP. So this showed that the type and content of this oligomer compatibilizer will play an import role in layers intercalation. The effect of compatibilizer content on the nanostructure formation of clay/PP composites was later studied by Hasegawa, N. et al. [Hasegawa, N. et al., 1998]. Formation of an exfoliated structure was observed when a relatively high PP-g-MAH content (typically 22 wt.%) was used. However, the relative content of maleic anhydride could not exceed a given value without increasing the miscibility between PP-g-MAH and PP chains. Compared to the clay dispersion in the PP-g-MAH/organoclay system, no further increase in the interlayer spacing was obtained when too many carboxyl groups were spread along the polypropylene chains (e.g. acid value=52 mg KOH/g).

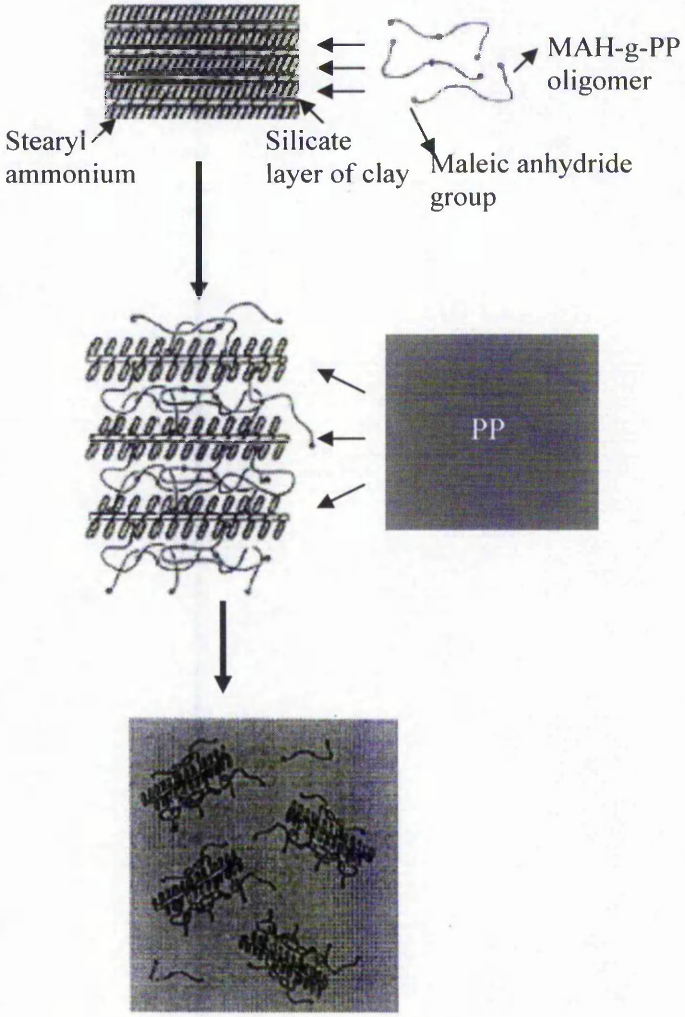


Fig 2.8. Schematic representation of the dispersion process of the organoclay in the PP matrix with the aid of PP-g-MAH [Hasegawa, N. et al., 1998].

2.5.2.2.2 Melt synthesis of PP/organo-clay using swelling agent

Another way to obtain nanocomposites from organoclays and PP has been recently reported [Alexandre et al., 2000]. In this technique, the authors modified a commercially available organoammonium-exchanged montmorillonite using an organic swelling agent, whose boiling point was between 100°C and 200°C, such as ethylene glycol, naphtha or heptane, in order to increase the interlayer spacing. The swollen organo-modified clay was then compounded with PP in a twin-screw extruder at 250°C. The swelling agent was volatised during the extrusion process, leading to the formation of a 'nano' composite which did not have any crystalline reflection in the 2.0-4.0 nm range in XRD patterns.

2.5.2.2.3 PP/clay Nanocomposites prepared by grafting-melt intercalation

Another new method has been recently reported. Propylene/clay nanocomposites were prepared via grafting-melt compounding using a new kind of co-intercalation organophilic clay which had a larger interlayer spacing than the usual organophilic clays which were modified by alkyl ammonium. This new larger interlayer spacing organophilic clay was prepared via an ion exchange reaction in water using alkylammonium. Firstly, Na+-montmorillonite was dispersed into hot water using homogenizer. Then the hexadecyl trimethyl ammonium bromide was also dissolved into hot water separately. The two solutions were blended together for 30 minutes to yield white precipitates. The precipitates were collected and washed by hot water and then were ground to 20um in size after being dried in a vacuum oven. These precipitates were used to prepare a new co-intercalation organophilic clay. The organophilic clay and epoxypropyl methacrylate were mixed for one hour. The initiator of the grafting reaction, dibenzoyl peroxide (BPO), and the grafting agent were dissolved in epoxypropyl methacrylate and then mixed with the clay solution. The larger interlayer spacing and strong interaction caused by grafting improved the dispersion of the silicate layers in the PP matrix. The mechanical properties of this polypropylene/clay nanocomposite were therefore improved. The incorporation of silicate layers gave rise to a considerable increase in the storage modulus stiffness and a decrease of the tan δ value, demonstrating the reinforcing effect of the clay on the PP matrix. The glass transition temperature (Tg) of the PPCN decreased in the presence of the silicate layers. The addition of clay did not change the crystal structure of the PP, however the silicate layers did act as nucleating agents for the crystallization of PP.

2.5.2.2.4 Clay/PP nanocomposites prepared by single-screw extruder

Clay/PP nanocomposites prepared using reactive melt synthesis, were normally extruded by twin-screw extruders. A clay/PP nanocomposite extruded in single-screw extruders has also been examined [Cho J.W. et al., 2001]. The nanocomposite was prepared in two steps. Firstly, a predispersed organoclay masterbatch was prepared by using a twin-screw extruder. Then, the masterbatch was mixed into base PP using a single screw extruder. The effect of single screw mixing on organoclay dispersion and nanocomposite properties was evaluated. The results indicated that the composites obtained from the master batch with a single screw extruder showed better dispersion and better mechanical properties than the composite obtained from the direct compounding with twin screw extruder. Furthermore, rheological study of this single-screw extruded nanocomposite also showed the PP nanocomposite had the same flow characteristics as pure PP, indicating these new materials can be made with existing polymer processing equipment without adding additional cost to end users.

2.5.2.2.5 Exfoliation of clay/PP nanocomposites in an electric field

As discussed above, clay/PP nanocomposites can be easily made by melt processing. However, polypropylene is known to form an exfoliated structure only when maleic anhydride grafted polypropylene (MA-grafted-PP) is added together. However MA-grafted-PP is expensive which prevents its commercial production. To avoid this, a very interesting novel approach to make exfoliated PP/clay nanocomposites in the molten state without adding MA-grafted-PP has recently been reported [Ahn, K.H. et al., 2002]. PP/clay systems compounded by melt processing in a large electric field produce exfoliated structures, which have been confirmed by rheometer and XRD results. As applying electric field is a physical process, similar effects can be expected in other polymer systems that do not show exfoliated structures under normal conditions.

A rheometrics mechanical spectrometer (RMS 800) was used to prepare these nanocomposites in a high voltage electric filed. The melt compounding of PP/clay composites was performed in this mixer. A rotor speed of 50 rpm was used and a mixing time of 10 minutes at 180°C. The clay and polymer samples were dried in a vacuum oven at 80°C for 8 h prior to compounding. However, the mechanism of the exfoliation under electric field was yet to be verified theoretically. The apparatus is schematically illustrated in Figure 2.9.

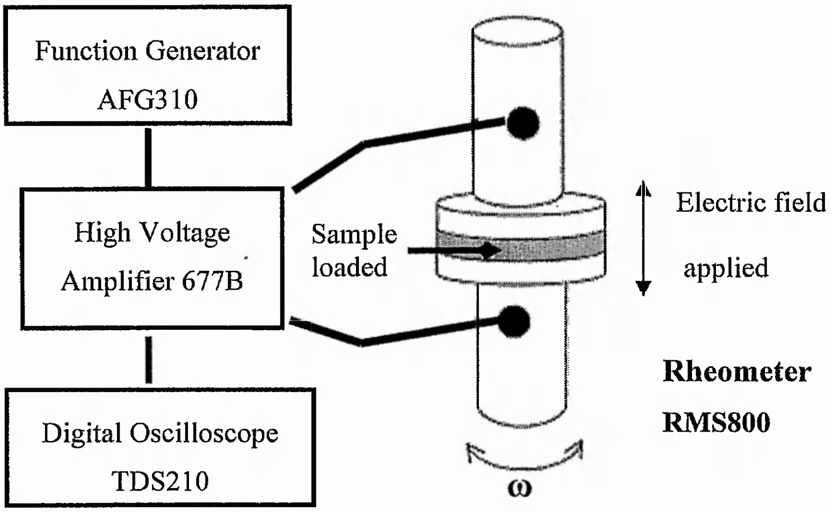


Fig 2.9. Experimental apparatus

2.5.3 Major enhancement of clay/PP nanocomposites

2.5.3.1 Mechanical properties

In the case of PPCNs, most of the PP/MMT nanocomposites studies report tensile properties as a function of clay content characterized by Instron.[Kato, M. et al., 1997; Kawasumi, M. et al., 1997; Hasegawa, N. et al., 1998; Reichert, P. et al., 2000; Manias, E. et al., 2000]. A typical example of a neat-PP/ semifluorinated surfactant modified MMT (f-MMT) exfoliated nanocomposite produced by melt-intercalation processing by extrusion in a twin-screw extruder was compared to a PP/ distearyldimethylammonium modified Na^+–montmorillonite (DSDM-MMT), "conventional" composite, where the DSDM-MMT remained in aggregates while not intercalated or exfoliated with a polymer. The behavior of the PP/f-MMT nanocomposite materials showed that there was a sharp increase in Young's modulus with very small clay loadings (< 3 wt %) followed by a much slower increase when the clay content was more than 4 wt% . As the content of MMT increased, the yield stress did not change markedly compared to that of the pure polypropylene, and there was a small decrease in the maximum strain at break. Polypropylene systems conventionally filled with non-nanometer sized filler PP/ DSDM-MMT do not exhibit such large increases in their Young's Modulus. Improvements in mechanical properties can also be achieved by other layered particulate fillers, however, much higher filler loadings are required. For example, to obtain comparable tensile increase like the ones achieved by the MMT dispersion, 30-60 wt % of talc or mica is often required.

As the polymer/inorganic compatibility is improved when, for example, MAH functional groups are incorporated into the polypropylene, the stresses are much more effectively transferred from the polymer matrix to the inorganic filler, and thus higher increases in Young's Modulus are expected. The enhancement of mechanical properties of such PP-g-MAH/MMT nanocomposites can only be achieved when using the PP-g-MAH with the highest molecular weight. It was reported that there were significant enhancements in the mechanical properties when using maleic anhydride (MAH)-grafted PP as a compatibilizer [Hambir, S. et al., 2001]. The tensile modulus was increased by around 35% and the tensile strength was increased by about 10%. The most interesting outcome of this study was the changes in morphology for PP/clay composites, which was reported for the first time. An optical microscopic study revealed that this PP-g-MAH/clay nanocomposite could be crystallized at higher temperatures than pure PP and that the morphology was altered because of the presence of layers of clay.

The tensile test results obtained from the previous work were not affected by the nanocomposite processing method since the nanocomposite structure did not change markedly within the processing conditions. However, in the absence of favorable thermodynamics for the PP/ organo-montmorillonite (o-MMT) miscibility, the composite structure and the tensile properties were altered by the processing conditions. The work carried out by Reichert et al., a systematic study of the dependencies on compatibilizer functionality and MMT organic modification, revealed that considerable enhancements in tensile properties can be achieved only where appropriate PP-MA "compatibilizers" were used to pretreat the o-MMT in conjunction with specific organic modification of the MMT [Reichert, P. et al., 2000]. Similar materials under different processing conditions showed much smaller improvements in their mechanical properties [Kato, M. et al., 1997; Kawasumi, M. et al., 1997; Hasegawa, N. et al., 1998; Oya, A. et al., 2000].

In the three component clay/PP composite system, PP/PP-g-MAH/MMT, oligomer maleic anhydride modified PP was used as a compatibilizer. As discussed in previous sections, the increase in the interlayer spacing of the PP/PP-g-MAH/MMT nanocomposites was affected by the content of oligomer PP-g-MAH used [Hasegawa, N. et al., 1998]. Further research found that the density of maleic anhydride groups had a significant effect on the final morphology and properties of the composite. The most effective way to form nanocomposites was found to be a mixture of approximately 3:1 by mass of maleic anhydride polypropylene oligomer to organoclay. Compared to pure polypropylene, the nanocomposites exhibited improved storage moduli in the temperature range from the glass transition temperature to 90 °C. However, the significance of nanolayer reinforcement in polypropylene was not as great as in nylon 6.

The enhancement of storage modulus was found for in-situ polymerized nanocomposites [Ma, J.S. et al., 2001]. Polypropylene based nanocomposites were prepared by in-situ polymerization using hexadecyl and octadecyl trimethylammonium chloride modified MMT. The dynamic modulus of the nanocomposites was measured with a dynamic mechanical analyser (DMA-7, Perkin Elmer Cetus Instruments, USA). As clay contents increased, the clay/PP nanocomposites showed a substantial increase in storage modulus, especially at temperatures higher than the polymer's glass transition temperature (Tg). The storage modulus of the nanocomposite above the Tg with 8.1 wt % clay content increased three times compared to the pure PP.

Clay/PP nanocomposites have either intercalated or exfoliated nanostructure which will only occur when small amount of clay are used. This was further supported by a study of the material's mechanical properties, such as stiffness, by Walter et al. [P. Walter et al., 1999]. In comparison to conventional filled polypropylene composites, clay/PP nanocomposites require much lower filler content, as low as 3 wt%, in order to achieve a Young's modulus above 3300 MPa. Commercially, Montell North America and General Motors Research and Development have reported the development of thermoplastic olefin elastomer-based polypropylene nanocomposites, which are considered to compete with Polycarbonate/Acrylonitrile Butadiene Styrene blends and other traditional thermoplastics. Since a low percentage of organophilic layered silicates was sufficient to achieve reinforcement, nanocomposites were lighter than other competitive resins by up to 30%. Moreover, due to low clay content, painted parts were claimed to exhibit better surface appearance [Walter, P. et al., 1999].

2.5.3.2 Heat Deflection Temperature

The nano-dispersion of MMT in the PP matrix not only gives rise to an increase in the mechanical reinforcement of the material, but also promotes a higher heat deflection temperature (HDT). In the case of semifluorinated surfactant modified MMT (f-MMT)/PP exfoliated nanocomposite there is a significant increase of the HDT, from 109°C for the pure polymer to 152°C for a 6 wt% nanocomposite; beyond 6 wt % of f-MMT the HDT of the composite levels off [Manias, A. et al., 2001]. When the pure PP polymer is filled with alkyl-ammonium modified MMT, the HDT is also increased but to a smaller extent. This is due to the lower exfoliation level of the inorganic fillers. Moreover, in the latter case, it was found that there was a strong dependence of the HDT on the processing conditions during the composite formation. A similar HDT improvements were also found for the PP/hexadecyl and octadecyl trimethylammonium chloride modified MMT nanocomposites, which have been reported by Ma J.S. et al using in-situ polymerization. In this case, the HDTs of the nanocomposites increased as the content increased. With 8 wt % organo-clay, the HDT of the nanocomposite increased by 40°C over that of the pure PP [Ma, J.S. et al., 2001]. The increase of HDT due to MMT dispersion is a very important improvement for PP because it is difficult to achieve similar HDT enhancements by chemical modification or reinforcement by other fillers [Karian, H.G., 1999]. This also has significant implications on the industrial applications.

The improvement of the HDT originates from the better mechanical stability of the nanocomposites, compared to the pure PP, rather than any increase in the polymer melting point. In all the PP/MMT hybrids studied, the melting temperature does not change markedly from that of the respective pure polymer. This is different from the behavior of other polymers, e.g. Nylon-6, where the MMT layers stabilize a different crystalline phase which is not found in the pure polymer, which has a higher melting point and also higher HDT [Usuki, A. et al., 1993; Kojima, Y. et al., 1993b].

2.5.3.3 Thermal stabilities

The increase in thermal stability has also been reported for clay/PP nanocomposites by Ma et al. They found that PP based nanocomposites prepared by in-situ polymerization using hexadecyl and octadecyl trimethylammonium chloride modified MMT had significantly increased the thermal stabilities compared to pure PP. The TEM images showed that the clay was exfoliated on a nanometer scale and dispersed uniformly in the PP matrix. The maximum decomposition temperature was increased by 44°C through introducing 10 wt % organoclay [Ma, S.J. et al., 2001]. Similar increases in thermal stability of clay/PP nanocomposites have also been found by Tang et al [Tang, Y. et al., 2003]. The enhancement in the thermal stabilities of clay/PP nanocomposites is believed to be due to the extensive intimate contact between polypropylene and the atoms of the inorganic crystallized clay layers. This contact between the clay and the polymer is greater than that formed in the conventional microcomposites. The layered silicates also played a catalytic role that accelerated the charring process at the beginning of the degradation.

2.5.3.4 Other Properties

Apart from the mechanical and thermal property improvements, nanocomposite formation also enhances some other properties. Because mechanical properties can also be improved by other means [Karger-Kocsis, J., 1995 and Karian, H.G. 1999], the greatest potential for PP/MMT nanocomposites relate to these “other property” enhancements.

Firstly, crystallization rate of clay/PP nanocomposites has shown to be a lot higher than that of microcomposites of PP/$CaCO_3$ samples [C. Saujanya et al., 2001]. It was found that the nucleating efficiency was dependent on the particle size. The optical transparency of the clay/PP nanocomposites was found to be much higher than those containing conventional $CaCO_3$ with the same concentrations, which could be associated with the reduction in the PP crystallite size. Clay/PP nanocomposites could therefore be used in applications where transparency is important.

Secondly, the barrier properties are also improved by nanocomposite formation. The permeability to liquids and gases was reduced by half when 4 wt % MMT was dispersed in the PP matrix or the functionalized polypropylenes. At the same time, the solvent uptake decreased accordingly [Wang, Z.M. et al., 2003]. This unique property makes clay/polypropylene nanocomposites much more attractive for packaging applications where enhanced barrier properties are desired. Another property that is strongly improved affected by these inorganic layered silicates is the sharp increase in the scratch resistance with very moderate loadings of 1-5 wt % organophilic MMT. Montmorillonite-based fillers also promote the flame retardancy of PP. The flammability of a clay/PP-g-MA nanocomposite with 4 wt % distearyldimethylammonium modified Na^+–montmorillonite (DSDM-MMT) is lower than the unfilled polymer by more than 75%. This flame retardant character is traced to the response of a carbonaceous-char layer, which develops on the outer surface during combustion. This surface char has a high concentration of MMT layers and becomes an excellent insulator and a mass transport barrier, which reduces the oxygen supply as well as the escape of the combustion products generated during decomposition.

From a practical viewpoint, because only a few percent of inorganic fillers are needed in the clay/PP nanocomposites, the resulting nanocomposites are lightweight. Moreover, where there exists favorable thermodynamics for organoclay/PP miscibility, the organoclay can be incorporated in the final stages of polymer processing (e.g., extrusion, injection/compression molding) to obtain nanocomposites. Thus, clay/PP nanocomposites are amenable to most of the common processing techniques which allows them to be easily commercialized. Additionally, organophilic clays can be used in conjunction with other PP reinforcements, such as fibers, thus combining the clay/PP improvements and those from the fiber reinforcement in one composite material.

2.6 Outline of the problem posed and work carried out in the PhD study

Although there has been some success in the development of clay/PP nanocomposites, the improvement in the mechanical properties of clay/PP nanocomposites is not as significantly large as compared to other commercial polymers such as Nylon 6. However the demand for PP nanocomposite is high. One of the typical application areas is in enclosures. The application of PP for enclosures has been hindered by its relatively weak stiffness and barrier resistance. The clay/polymer nanotechnology developed at the time of the beginning of this study could not satisfy this requirement. However, the manufacture of clay/polymer nanocomposites has the potential to improve these weaknesses. So developing a new technology for improving the properties of clay/PP nanocomposites without costly capital outlay on new equipment or additional processing costs becomes more and more important to industries. This is the basis of this study. In the following chapters, the technology developed in this project will be described in detail.

CHAPTER 3 Experimental Methods

3.1 Materials studied

This research will concentrate on the development of melt processing technology for improving the properties of clay/PP nanocomposites. The developments will be based on commercial available polypropylenes and clays. Different types of polypropylenes and clays were selected for this study. Their structures and relevant information is described below. Some chemicals, including compatibilizers, stabilizers and monomers, were also used in this study to produce high performance clay/PP nanocomposites. All of the chemicals used were commercially available. The origin and structures of these chemicals are shown in this section.

3.1.1 Clays

All the clays studied are shown in Table 3.1. Most of the clays used were supplied by Southern Clay Products Corporation. Other clays were supplied by Nanocor and Co-Op Chemical Co., Japan.

Table 3.1
The clays investigated in this study

Supplier	Commercial Name	Clay Type
Southern Clay	Cloisite Na^+	Hydrophilic
	Cloisite 15A	Hydrophobic
	Cloisite 20A	
	Cloisite 93A	
	Cloisite 30B	
Nanocor Clay	G-105 PGW	Hydrophilic
Co-Op Chemical	Somasif ME-100	Hydrophilic

The commercial clays, Cloisite Na^+, G-105 PGW and Somasif ME-100 were hydrophilic clays. The other clays studied were organoclays, namely Cloisite 15A, Cloisite 20A, Cloisite 93A, Cloisite 30B supplied by the Southern Clay Products, According to the information provided by the clay suppliers, the organoclays were produced by the ion exchange with different alkyl ammonium salts.

The Cloisite clays from Southern Clay

All the Cloisite clays from Southern Clay are montmorillonites. These Cloisite clays are probably produced from the same natural clay resources. The differences between these clays are due to the differences in the clay modification methods. Cloisite Na^+ may be the precursor of the other four Cloisite organoclays. The information on the physical properties and modification methods for the Cloisite organoclays is listed in Table 3.2.

Table 3.2
Physical properties and modification methods of the Cloisite organoclays

CLAY	ORGANIC MODIFIER	MODIFIER CONCENTRATION	MOISTURE, %	WEIGHT LOSS ON IGNITION, %	SPECIFIC DENSITY, g/cc
Cloisite 15A	[1]2M2HT	125 meg/100gclay	< 2	43	1.66
Cloisite 20A	[1]2M2HT	95 meg/100gclay	< 2	38	1.77
Cloisite 93A	[2]M2HT	90 meg/100gclay	< 2	40	1.88
Cloisite 30B	[3]MT2EtOH	90 meg/100gclay	< 2	30	1.98

Note: [1] *2M2HT -- dimethyl dihydrogenatedtallow ammonium chloride*
[2] *M2HT -- methyl dihydrogenatedtallow ammonium chloride*
[3] *MT2EtOH -- methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium*

The Nanocor Clay

The hydrophilic clay, G-105 PGW, was obtained from Nanocor. Some major physical properties of this clay can be seen from Table 3.3. G-105PGW is a highly pure sodium-based montmorillonite and has a cation exchange capacity (CEC) of 145meq/100g±10%. This clay is white with aspect ratio of 200-400 and a specific gravity of 2.6.

Table3.3. Major physical properties of the Nanocor clay G-105PGW

CLAY	TYPE	COLOUR	AVE. DRY PARTICLE SIZE, μm	SPECIFIC DENSITY, g/cc	MOISTURE, %
G-105 PGW	Hydrophilic clay	White	16~22	2.60	12

The Co-Op chemical clay

The Co-op chemical clay used here is a synthetic hydrophilic mica (Co-op Somasif ME-100). The hydrophilic Somasif ME-100 , layered silicate 26.5 wt% Si; 15.6 wt% Mg; 0.2 wt% Al; 4.1 wt% Na; 0.1 wt% Fe; was produced by heating talcum in the presence of Na_2SiF_6. The negative charge of the layers is compensated by Na^+ ions in the interlayer space. The cation-exchange capacity (CEC) is in a range of 70-80 meq/100g. Its interlayer spacing is 0.95 nm.

3.1.2 Polypropylenes

The commercial polypropylenes investigated were Fina products 3228C, IN419-3-01 and N00-8-1 and were named PP1, PP2 and PP3 respectively in this work for simplicity. The details of these products were not available.

3.1.3 Compatibilizers

Compatibilizers were normally used to improve the compatibility between the clay and polymers.

Maleic anhydride grafted PP oligomers were used as compatibilizer in this study. Four types of commercial maleic anhydride grafted polypropylene (MAH-g-PP) oligomers were used as compatibilisers for clay/PP nanocomposite fabrication.

These were Epolyene E-43 Wax (MA content 5.8 wt%; Mn = 3900; polydispersity index *Mw/M*n = 2.33; Tm = 157 °C), Epolyene G-3015 (MA content 2.96 wt %; Mn = 24,800; polydispersity index *Mw/M*n = 1.90; Tm = 156 °C) supplied by Eastman Chemical, Tennessee and Polybond®3200, Polybond®3000 supplied by Uniroyal Chemicals, Middlebury. The details of Polybond®3200 and Polybond®3000 products were not available.

At the same time, some chemicals were also selected and used as compatibilizers according to their structural compatibility to both organoclays and polypropylenes. They were two types of silanes, 3-Aminopropyltriethoxysilane (APTES) and Methyltrimethoxysilane (MTMS), together with Stearic Acid (SA) supplied from Aldrich.

3.1.4 Stabilizers

Anti-oxidants (or called stabilizers) normally provide protection against degradation caused by oxidation at normal or elevated temperatures during processing, storage or service.Three commercial anti-oxidants were obtained from Cytec Germany. They are coded as CYANOX®2777, CYANOX®2888 and CYANOX®XS4.

3.1.5 The monomer and initiators used for newly developed Solid intercalation/melt Processing technique

An effective melt processing technology for producing clay/PP nanocomposites named Solid intercalation/melt Processing (SIMP) was developed in this study. This method uses the advantages of the high efficiency of intercalation in in-situ polymerisation and the easy processing characteristic of melt processing. The process combines the two techniques together but uses a very small amount of monomer in the in-situ polymerisation. The monomer used must be compatible to polypropylene. Since the amount of monomer used in the in-situ polymerisation is very small, the polymerisation process is carried out essentially in solid clay. Then the intercalated clay prepared by solid in situ polymerization can be used to produce clay/PP nanocomposites together with PP by using a traditional twin-screw extruder.

The monomer used for the solid in situ polymerization is liquid-like glycidyl methacrylate which was purchased from Aldrich. This monomer contains 100 ppm monomethyl ether hydroquinone as an inhibitor and 0.2 wt% epichlorohydrin and 1 wt% glycidol.

The initiator used in this study was dibenzoyl peroxide (BPO) purchased from Aldrich.

3.2 The Characterisation of nano -structures

The nano-structures of clays, polymers and their composites were characterised using X-ray diffractometry (X-ray). The equipment used was a PHILIPS PW 1049/10 X-ray diffractometry, with two radiation sources, CuKα (λ =0.154 nm) and CrKα (λ =0.229 nm).

Samples for the XRD measurement were prepared using different techniques depending on the types of materials studied. Granulated materials were ground into powder using a blender and compressed into discs under 330 MPa pressure at ambient temperature. The discs were then placed in the sample holder.

Film samples were cut into rectangular shapes of 16mm x 20mm and then placed in the holder. The samples were scanned at a scanning speed of 1°/min through the diffraction angle 2θ range of 3 – 70°. The change in interlayer distance of the clay in the nanocomposites was studied by this technique.

3.3 Microscopy

An Olympus stereomicroscope with magnification between 7 to 40 times was used to investigate the 3-D morphology of the samples and their surface structures. The micro structure of clay dispersions were investigated using this optical microscopy.

3.4 Melt intercalation using Twin-Screw Extruder

Most clay/polypropylene composites were extruded using the twin-screw extruder under different operation conditions. A 16-mm PRISM Eurolab twin-screw extruder, with variable L/D ratio (the ratio between the length and the diameter of the screw), 24/1 and 40/1, was used for melt intercalation. The screws can be assembled in various configurations. The configuration used in this study is shown in Fig.3.1.

The extruder screw configuration comprised of three mixing sections. The number of mixing sections used depended on L/D ratio applied during processing. The extruder can be operated in two different L/D ratios, 40/1 and 24/1. The number of mixing sections will be reduced correspondingly from 3 to 2. The main mixing section extruder can be operated in two different L/D ratios, 40/1 and 24/1. The number of mixing sections will be reduced correspondingly from 3 to 2. The main mixing section was arranged in an area close to the die. This enabled effective mixing when 24/1 ratio was used. In this study, experiments were conducted using 24/1 L/D ratio.

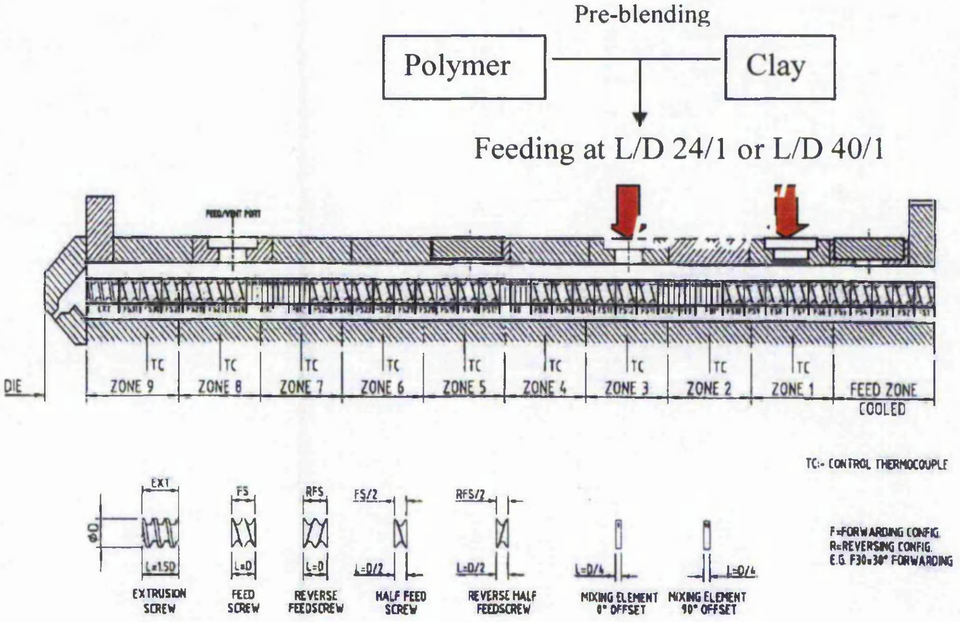


Fig. 3.1 The screw configuration of the twin-screw extruder

Apart from the L/D ratio, there are other parameters controlling melt intercalation. The processing temperature can be varying from room temperature up to 400 °C. The feeding rate can be varying between 3 wt% and 50 wt% and the screw speed can be up to 1000rpm.

Different components were used to produce clay/polymer nanocomposites. These included different polypropylenes, clays, MAH-g-PPs oligomers, compatibilizers and stabilizers. The composites were produced by using different components with different weight concentrations. The required composite mixtures were weighted, and then they were premixed in a sealed plastic bag and shaken. The mixture was added into twin-screw extruder and extruded at different temperatures and shear rates. The obtained strands were pelletized by pelletizer and dried at 80 °C overnight for further mechanical and other properties tests.

3.5 Mechanical Test

The tensile modulus is a measure of how stiff a material is. Tensile strength is, an expression of the maximum stress that can be applied to a material before it ceases to be elastic. The tensile strength and tensile modulus are important concepts that can be used to assess the mechanical property enhancements of newly developed clay/polypropylene nanocomposites. The tensile loading test was used in this study to assess a material's tensile modulus and tensile yielding strength.

The dried pellets were injection-moulded into test bars by using the in-house small scale tensile testing procedure which was developed after several months of mould design and investigation.

The dog-bone shaped tensile loading coupons were produced by using a bench top micro-injection moulding machine. These dog-bone shaped tensile loading coupons were 45 mm long, 15 mm wide and 4 mm thick. The free length of the coupons was 20 mm. The width in the free length is 8 mm. The weight of a sample was ~ 2g. The geometry of those testing samples can be seen in Fig 3.2.

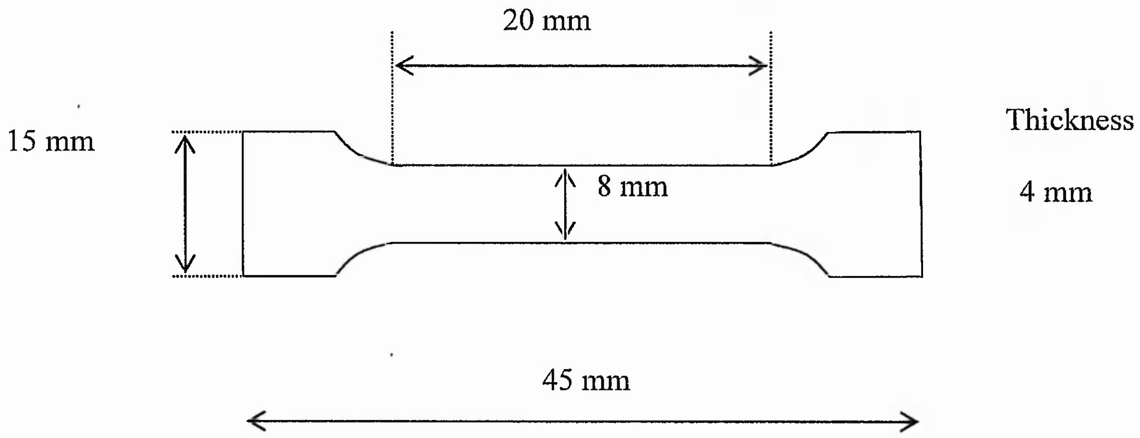


Fig. 3.2 The geometry of testing coupon

The tensile loading test was carried out on MONSANTO TENSOMETER 20 by using the coupons prepared as above. The maximum force applied was 2KN and the loading speed was 15.0mm/min.

3.6 FT-IR analysis

The chemical structures of materials used in this study were characterized by using a JASCO Fourier Transform Infrared Spectrometer (FT-IR). The samples were ground into fine powder and then mixed with potassium bromide (KBr). Care was taken to press all KBr disks under the same conditions to minimize any effect of pressure on peak intensity. A background was run before the sample was scanned. The scanning speed used was 2mm/sec.

3.7 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was conducted with a TA Instrument TGA 2950. Thermograms of the samples were taken under air atmosphere at a heating rate of 10 °C/min and a temperature range of 0~500°C. Approximately 5–15 mg of samples was used to determine the decomposition temperatures.

3.8 Melt Flow Rate

The melt flow rate (MFR) of polymers and their composites were measured by the Davenport Melt Flow Index machine. Melt flow rate can be used to indicate the shear viscosity of polymers and their composites. The MFR data was obtained by cutting off lengths of extrudate which are forced out of the die in a standard time period. Approximately 7 grams of the material was loaded into the barrel of the melt flow index machine which had been preheated to 190 °C. The loaded material was pre-heated for 6 minutes. A 2.16 kg load was then applied and the molten material was forced through the die. The extrudate was cut at 10 minute intervals and weighed. Generally the first and last sections of extrudate were discarded along with any melt which contained bubbles. Melt flow rate values were calculated in g/10 min.

CHAPTER 4 Direct Melt Intercalation

Investigations into the intercalation between clays and polypropylenes were carried out using existing direct melt intercalation technology. Studies of this traditional melt processing techniques will provide an insight into the mechanism of melt intercalation between clay and polypropylene. The mechanisms could then be utilized to design better synthetic methods for manufacturing clay/polypropylene nanocomposites. This chapter examines the effects of different commercially available clays, including natural hydrophilic clays and organoclays, different polypropylenes including grafted polypropylenes, and processing conditions, on the nano- and micro-structure formation of the clay/PP composites produced. The effects of the different clays, polypropylenes and processing conditions on the mechanical properties of the composites produced are also investigated.

The direct melt intercalation process for producing nanocomposites involves heating the polypropylene with either natural hydrophilic clay or an organoclay, under shear, above the melting temperature of the polymer. The manufacturing method for this process is outlined in Fig 4.1. In practice, the clay and polypropylene were initially pre-blended at ambient temperature. The melt intercalation process was then carried out by extruding the clay/polypropylene mixture in a twin-screw extruder. The processing conditions of temperature, feeding rate, screw speed and L/D ratio used in this study were varied and the details of the processing conditions of different formulations are given where appropriate.

The polypropylenes studied were commercial Fina products, Fina®3228C, Fina®IN419-3-01 and Fina®N00-8-1. In this study they were named PP1, PP2 and PP3 respectively. The maleic anhydride grafted polar polypropylenes used were Epolyene Wax E-43 and Epolyene G-3015 from Eastman Chemicals, and Polybond®3200 and Polybond®3000 from Uniroyal Chemicals. The hydrophilic clays used in this study were a natural hydrophilic montmorillonite Cloisite Na^+ from Southern Clay and synthetic hydrophilic mica SOMASIF ME-100 from Co-op Chemical. Three organophilic montmorillonites modified by different alkyl ammonium salts, Cloisite 93A, Cloisite 15A and Cloisite 20A, were also investigated in this study.

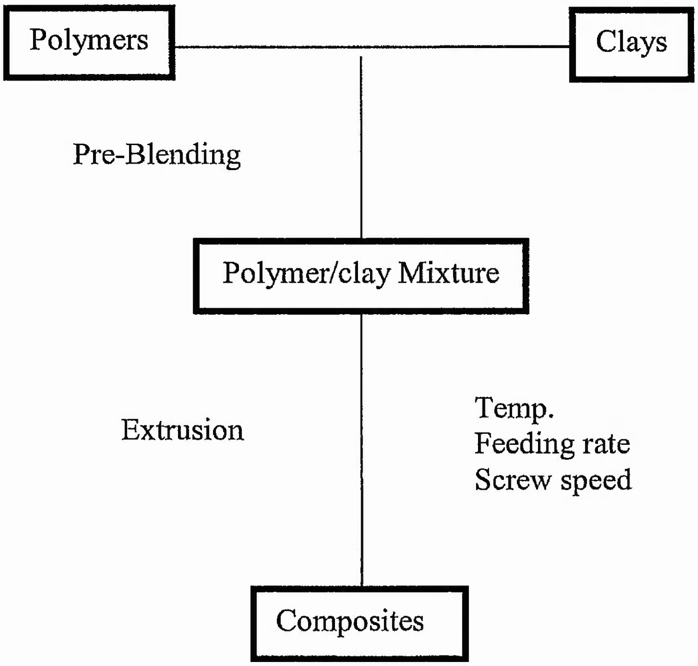


Fig 4.1The fabrication process for direct melt intercalation

The nano- or micro-structures of the clays, polymers and their composites were characterized by using a PHILIPS PW1049/10 X-ray diffractometry (X-ray) and the tensile modulus and yielding strength were tested by a MONSANTO 20 Tensometer.

4.1 Intercalation with hydrophilic clays

Previous researchers in the area of clay/polypropylene composites have found that the compatibility between hydrophobic polypropylene and both natural hydrophilic clays and organophilic clays is poor. As a result little work had been carried out using polypropylene to produce clay/polymer nanocomposites at the time when this study was begun.

The direct intercalation between hydrophilic clays and polypropylenes were investigated in this section. The hydrophilic clay, Cloisite Na^+, was firstly studied. The hydrophilic clay/PP composite was produced from the pure polypropylene PP1 and the Cloisite Na^+. The melt synthesis was carried out using the twin-screw extruder under the conditions of 200 °C extruder temperature, 7% feeding rate, 100 rpm screw speed and 24/1 L/D ratio. The twin-screw extruder used has 40/1 and 24/1 L/D ratios.

The reason for using L/D 24/1 was to avoid the mixture of clay and polymer residing in the extruder for too long before entering the mixing zone of the screw. Two different clay loadings, 5 wt% and 20 wt%, were used to prepare the composites. The dispersion of the hydrophilic clay Cloisite Na^+ in the PP1 matrix was characterized by XRD using Cu as the radiation source. Figure 4.2 shows the diffraction patterns of the composites and the clay. The (001) peaks of the clay have shifted from the original 7.54° (which corresponds to 1.17nm) to 9.24° (which corresponds to 0.96nm) for all the clay loadings. So these results show that the interlayer distance of the clay has decreased from 1.17nm to 0.96nm when the composites have been formed. These results indicate that no intercalation has occurred. The decrease in the interlayer distance may be associated with the release of water absorbed between clay layers of the Cloisite Na^+. The sensitivity of Cloisite Na^+ clay to water and its effect on layer expansion was investigated.

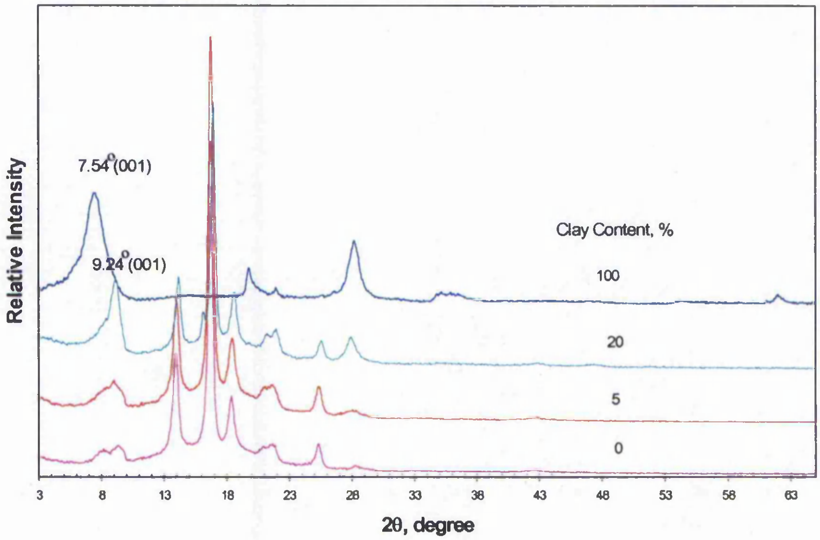


Fig. 4.2 XRD patterns of the extruded products produced from PP1 and the hydrophilic clay, Cloisite Na^+, with different clay loadings under the condition of 200°C temperature, 7% feeding rate, 100 rpm screw speed and 24/1 L/D (Cu radiation source).

The XRD pattern of the as received Cloisite Na^+ montmorillonite was measured initially. The influence of moisture content on the interlayer spacing was examined by heating the sample in an oven at 105 °C for two hours and then exposing the sample to air for various times to allow the clay to absorb water from the atmosphere. The XRD diffraction patterns of the Cloisite Na^+ sample with different amounts of absorbed water are shown in Figure 4.3 and the interlayer spacings are given in Figure 4.4. The undried clay had an interlayer spacing of about ~1.2 nm. The clay in this sample will be saturated in water for the atmospheric conditions it has been stored in.

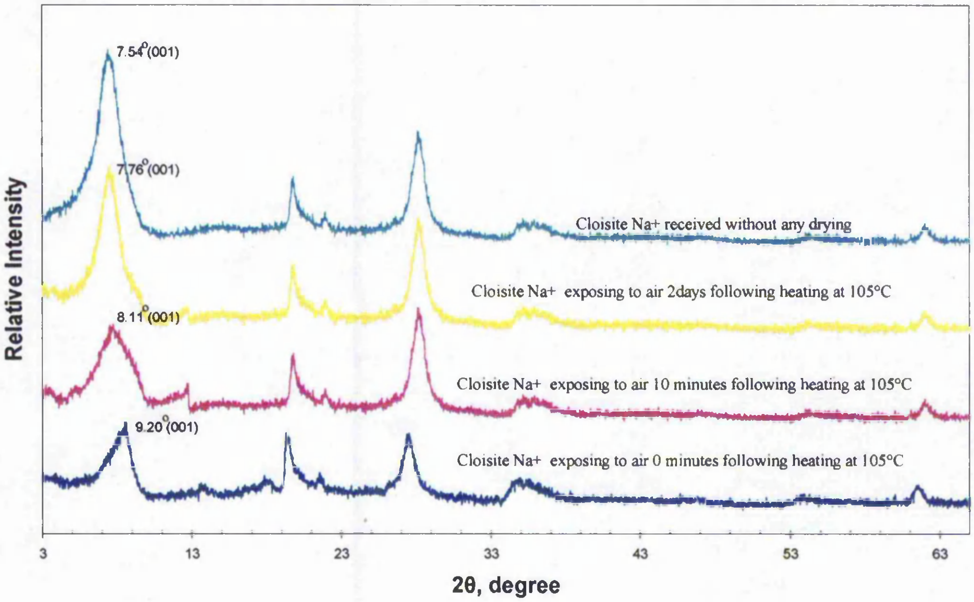


Fig. 4.3 XRD patterns of the hydrophilic Cloisite Na^+ montmorillonite with different exposure time to air following heating at 105^oC in oven (Cu radiation source).

The results for the clay sample after it had been dried and then exposed to air for varying lengths of time, to absorb moisture from the atmosphere, show that the interlayer spacing increased as the exposure time increased. The interlayer spacing of the dried Closite Na^+ is approxiamately the same as that of the Closite Na^+/

polypropylene composites which confirms that the loss of water from the clay is why the composites interlayer spacing is lower than that of the undried clay. Also as the distance between the clay layers in the composite and dried clay layer are the same, it can be concluded also that no intercalation between the polymer and the clay has occurred.

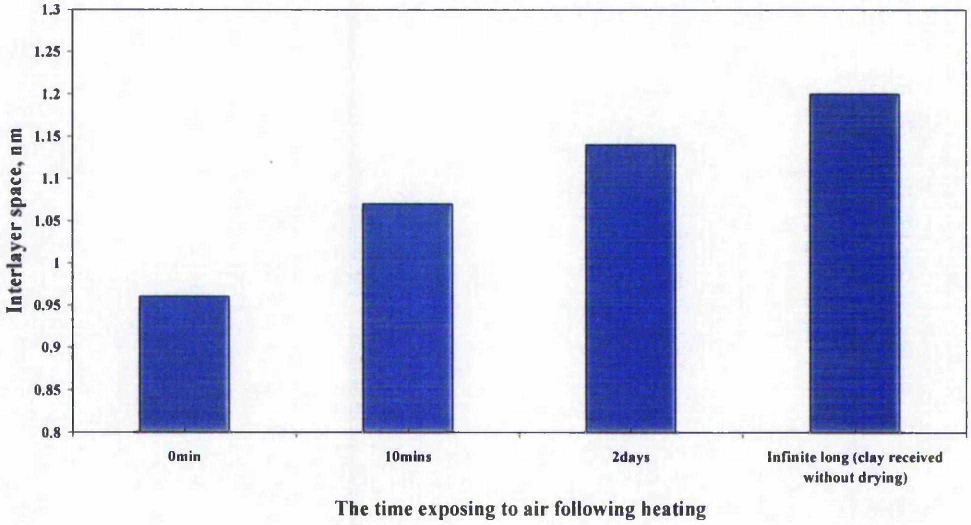


Fig. 4.4.The change of the interlayer space of Cloisite Na$^+$ with the time exposed to air following heating at 105°C (in oven) (Cu radiation source).

The other hydrophilic synthetic mica, SOMASIF ME-100 was processed with polypropylene under the same conditions as the Closite Na$^+$. The SOMSIF ME-100 was not dried before extruding and loadings of 3, 5 and 7wt% of the clay were used. The XRD patterns of the composites are illustrated in Fig 4.5. They show that the clay layers have not been expanded in any of the composites. The interlayer spacing of the initial clay is ~1.01nm and ~0.96nm for the composites. The results indicate that the hyrophilic SOMASIF ME-100 and the hydrophobic polypropylene were unable to intercalate at all.

Extrusion of the hydrophilic clays Cloisite Na$^+$ and SOMASIF ME-100 and polypropylene, produced conventional composites, where the clay is still in aggregates, and not nanocomposites.

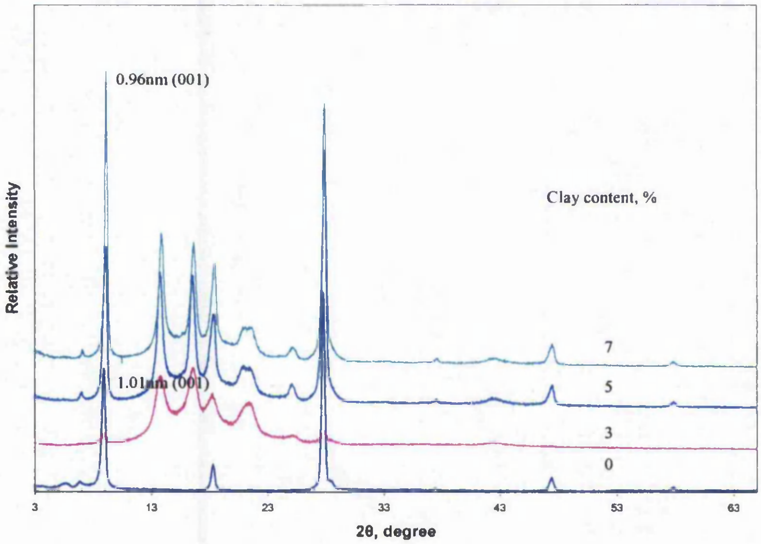


Fig.4.5 XRD patterns of the extruded products produced from PP1 and the synthetic hydrophilic clay, SOMASIF ME-100$^+$, with different clay loadings under the same condition as indicated in Fig.4.2 (Cu radiation source).

4.2 Intercalation with organoclays

4.2.1 Intercalation with organoclay Cloisite 93A

The experiments with Cloisite Na$^+$ and SOMASIF ME-100 showed that there was no interaction between polypropylene and hydrophilic clays. An investigation into commercially produced organoclays was undertaken.

The organoclay Cloisite 93A, produced via ion exchange with methyl dihydrogenatedtallow ammonium chloride, and the polypropylene PP1 were extruded by twin screw extruder under the conditions of 200 ^{o}C barrel temperature, 7% feeding rate, 100 rpm screw speed and an L/D ratio of 24/1. Different organoclay loadings between 3 –10wt% were used in this study. Figure 4.6 shows the XRD patterns of the extruded products using Cr as radiation source. In all the Cloisite 93A/polypropylene composites clay layer expansion occurred. This was demonstrated by the shift in the (001) peak to angles below 3 ^{o}. The interlayer spacings of clay layers were expanded from 2.22nm, the clay layer spacing for the pure organoclay, to 3.42nm, 3.47nm and 3.47nm for clay loadings of 10wt%, 7wt% and 5wt% respectively. The interlayer spacing for the sample with a clay loading of 3wt% could not be measured as the shift in the angle was below 3 ° and could not be measured. Changes in the interlayer spacing are an indication that polymer has been incorporated within interlayers of the clays during melt extrusion. Therefore, intercalation or even partially exfoliation has occurred between the clay and PP1, resulting in significant layer expansion.

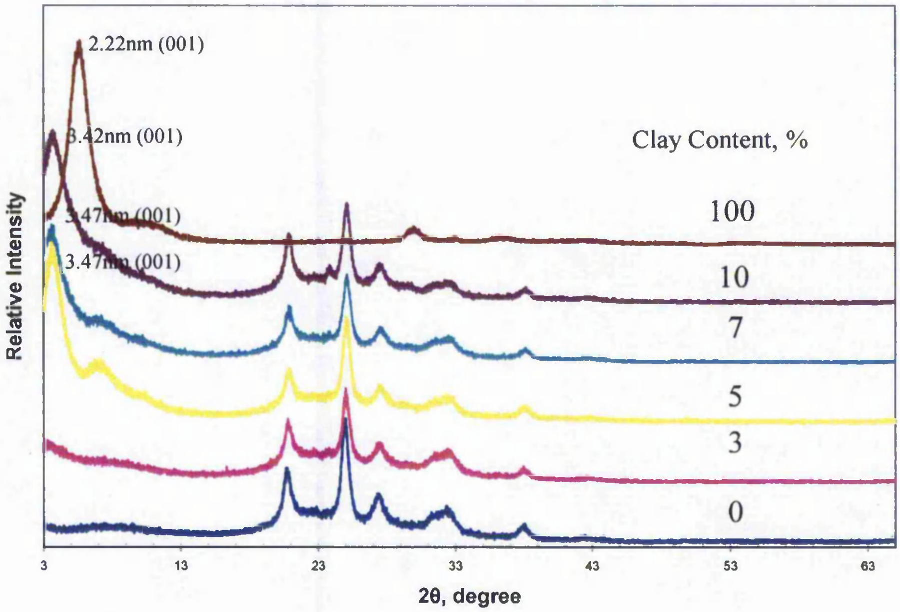


Fig. 4.6 XRD patterns of the extruded products produced from the original polypropylene and the organoclay Cloisite 93A with different clay loadings under the condition of 200 °C temperature, 7% feeding rate, 100 rpm screw speed and 24/1 L/D ratio (Cr radiation source).

Intercalated nanostructures may occur for the composites containing 5wt%, 7wt% and 10wt% clay loadings because the (001) peaks of clay Cloisite 93A have been moved to lower angles. However the extent of the layer expansion of the composite containing 3wt% clay is more significant than those of the other composites and this suggests that this composite has a partially exfoliated nanostructure. If the composite had a fully exfoliated structure the tail of the (001) peak would not be visible in XRD trace.

There are no reports in the literature to indicate that the intercalation could occur between polypropylene and organophilic clays by using direct melt intercalation when this research was carried out. The results obtained in this study found that intercalation could occur for some commercial available polypropylenes. This study also supported the conclusion reached by other researchers that intercalation is more successful when low clay loadings are used to produce composites.

4.2.2 Intercalation with other organoclays

Two other commercially available Cloisite organoclays were studied to investigate the effect of clay structure on nanocomposite formation in order to select the ideal organoclay for producing clay/PP nanocomposites. They were Cloisite 15A and Cloisite 20A obtained from Southern Clay Corporation.

The interlayer spacing of the Cloisite organoclays 15A, 20A and 93A were investigated by X-ray diffractometry using Cr as radiation source. The XRD patterns of these three Cloisite organoclays are shown in Fig 4.7. There are similarities in XRD patterns in these Cloisite organoclays. Cloisite 15A however has the highest extent of layer expansion with an interlayer spacing 3.31 nm. The (001) peaks of other two clays are very similar. This can be explained by the molecular structure of the organoclays.

All the Cloisite organoclays studied here, Cloisite 93A, Cloisite 15A and Cloisite 20A, were produced via ion exchange with quaternary ammonium chlorides from the same natural Na^+ montmorillonite. Among them Cloisite 15A and 20A were modified using the same ammonium salt, dimethyl dihydrogenated-tallow ammonium chloride. The molecular structure of the ammonium ion is illustrated in Fig 4.8, where HT is hydrogenated tallow comprising ~65% C18, ~30% C16 and ~5% C14. The difference between Cloisite 15A and 20A is the content of the

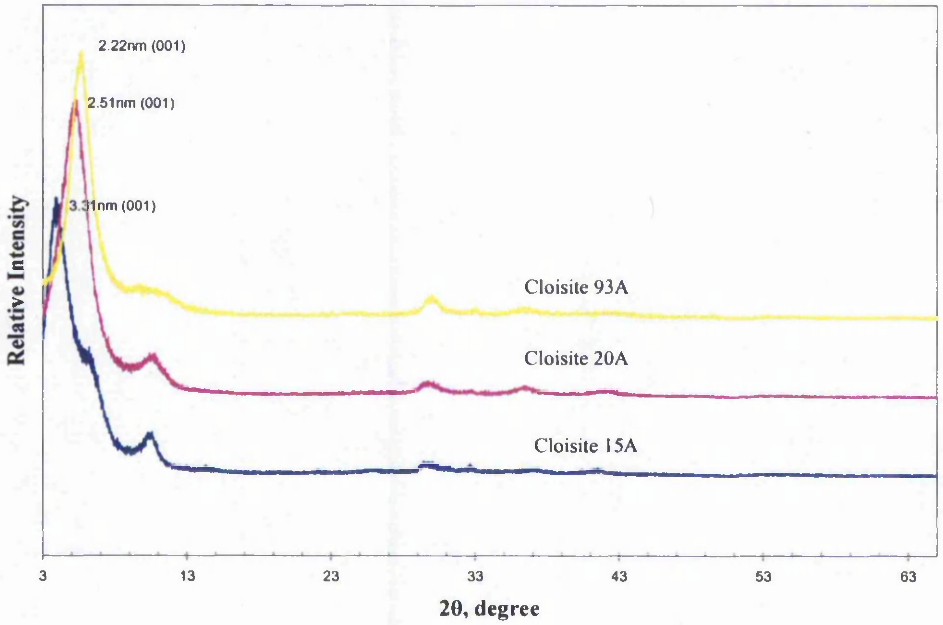
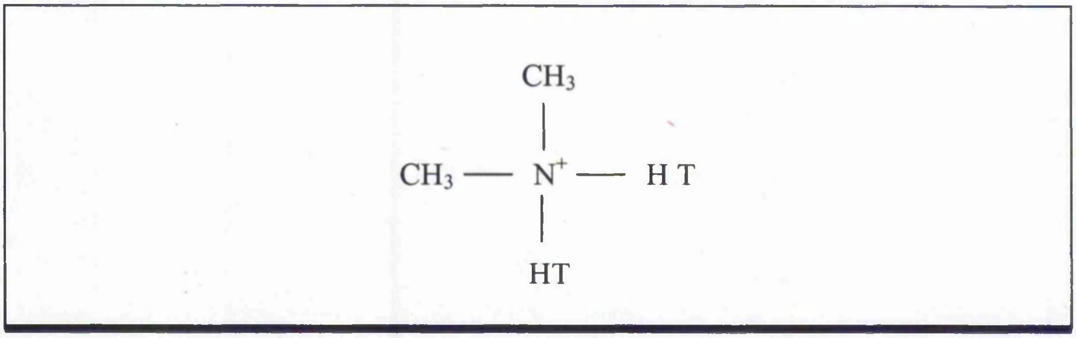


Fig 4.7 XRD patterns of the organophilic clays obtained from the Southern Clay Products (Cr radiation source).

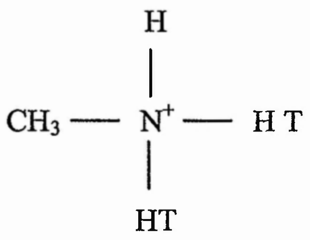
ammonium ions inserted between the clay layers. Cloisite 15A contains more ammonium ions, a consequence of this is that it has a higher weight loss when heated and has a lower density.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle HT}{N^+}}-HT$$

Fig 4.8 The molecular structure of the ammonium ion in Cloisite 15A & 20A

The organoclay Cloisite 93A was produced by modifying Na^+ montmorillite with methyl dihydrogenatedtallow ammonium chloride. The structure is shown in Fig 4.9. When this ion structure is compared with that used to produce Cloisite 15A and 20A, it can be seen a methyl group has been replaced by a hydrogen in Cloisite 93A. Therefore the hydrophobic of Cloisite 93A should be weaker than that of the other clays. The XRD studies show that the organoclays Cloisite 15A and 20A are more hydrophobic than 93A, as their interlayer spacings are larger, and therefore should intercalate better with polypropylene. So it is necessary to investigate the effect of organoclays Cloisite 15A and 20A on nanocomposite formation by direct melt intercalation with raw polypropylene.



$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & | & & \\ \mathrm{CH_3} & — & \mathrm{N^+} & — & \mathrm{HT} \\ & & | & & \\ & & \mathrm{HT} & & \end{array}$$

Fig 4.9 The molecular structure of the ammonium ion in Cloisite 93A

Polypropylene PP1 and organoclay Cloisite 20A were extruded, with 3wt% and 5wt% of clay, under the same extrusion processing conditions that were used for

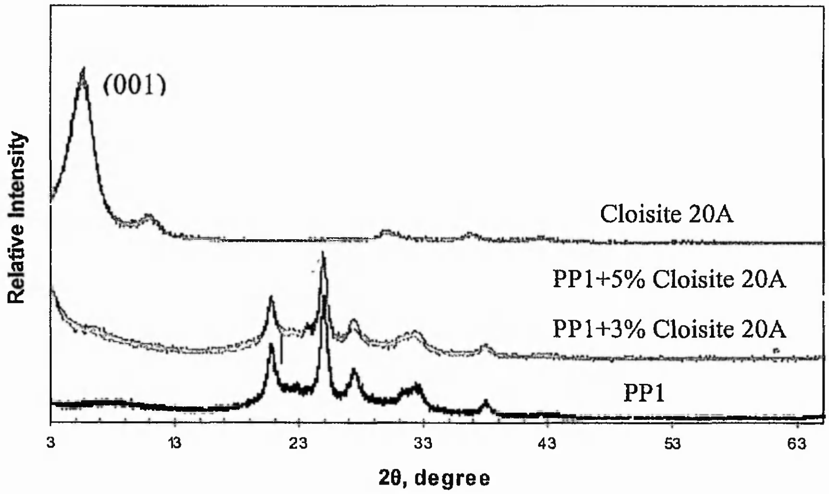


Fig. 4.10 XRD patterns of the extruded products produced from PP1 and the organophilic clay Cloisite 20A with different clay loadings under the same condition as indicated in Fig.4.6 (Cr radiation source).

Cloisite 93A. The dispersion of Cloisite 20A into PP1 matrix was investigated by X-ray diffractometry using Cr as radiation source. Figure. 4.10 shows the XRD patterns of the extruded products. Intercalated nanocomposites were obtained for composites. However the results were not significantly different to those obtained for Cloisite 93A. Cloisite15A was extruded with polypropylene PP1 with the same experimental conditions as Cloisite 20A and 93A. Two loadings of clay were used 3wt% and 5wt%. The XRD patterns were measured for both composites and are shown in Fig 4.11. These results are similar to those of the Closite 20A.

From these experimental results it appears that in all cases intercalated materials have been produced but the extent of exfoliation cannot be determined by XRD. The mechanical properties of these materials will be examined in Section 4.4.2 to determine how the dispersion of these clays in the polypropylene has affected the polymer's strength.

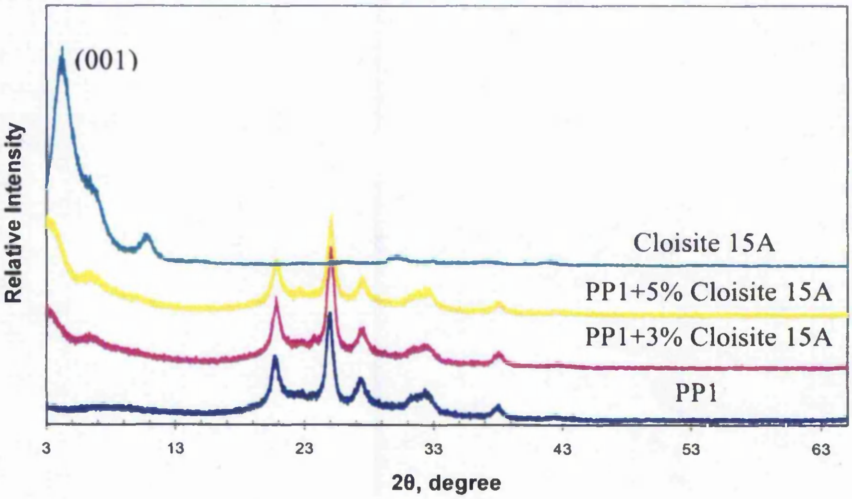


Fig 4.11 XRD patterns of the extruded products produced from PP1 and the organophilic clay Cloisite15A with different clay loadings under the same condition as indicated in Fig.4.6 (Cr radiation source).

4.3 The influence of different polypropylenes on intercalation

4.3.1 The effect of different commercial raw polypropylenes on the intercalation

Investigations with the commercial polypropylene PP1 and organoclays produced intercalated composites. Examination of two other commercial polypropylenes was undertaken to see if they could intercalate with organoclays. The polypropylenes were Fina PP IN419-3-01 and N00-8-1, designated PP2 and PP3, respectively. The compatibility between the three polypropylenes and the organoclay Cloisite 93A was examined. Direct melt synthesis was carried out using a twin-screw extruder under the condition of 200 °C barrel temperature, 7% feeding rate, 100 rpm screw speed and 24/1 L/D ratio. A clay loading of 5wt% was used. The XRD patterns of the extruded products were characterized by X-ray diffractometry using Cu as radiation source. In figure 4.12 the (001) peak position of clay does not change in the extruded material of PP2 and PP3 which indicates that no intercalation has taken place and conventional composites had been produced. In comparison the (001) peak of the clay has moved to an angle below 3 ° in the Cloisite 93A/PP1 composite and only the tail of the peak is visible. This indicates that the polypropylene PP1 has produced a nanocomposite.

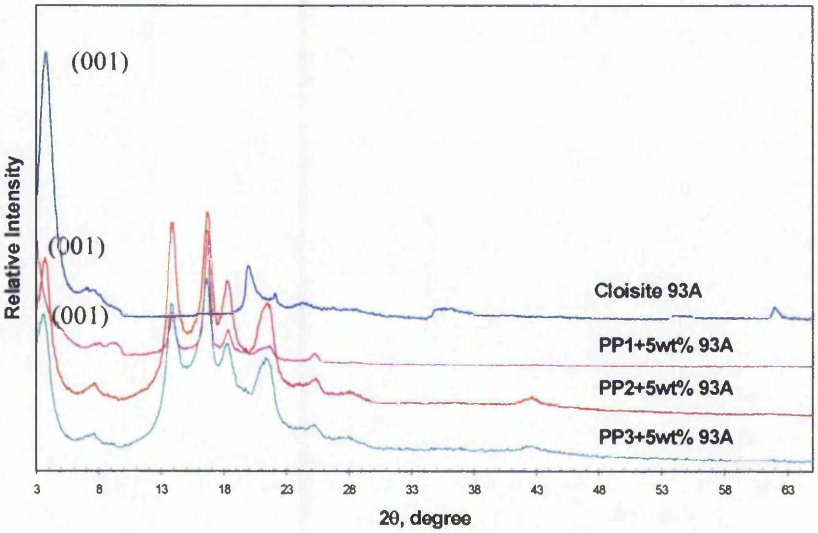


Fig. 4.12 XRD patterns of the extruded products produced from the three commercial polypropylenes and 5wt% organoclay Cloisite 93A under the condition of 200°C temperature, 7% feeding rate, 100 rpm screw speed and 24/1 L/D ratio (Cu radiation source).

In order to find out why the polypropylene PP1 had intercalated with the clay, while the other two had not, the chemical structures of the polypropylenes were studied using Fourier Transform Infrared Spectrometer (FT-IR). The samples for FT-IR characterization were ground into fine powder and then mixed with potassium bromide (KBr). The FT-IR spectra of the three polypropylenes are shown in Fig 4.13. There is little difference in most of the regions of the spectra. However differences can be identified in the region between 1600cm^{-1} and 1800 cm^{-1}. The polypropylenes PP1 and PP2 have absorption peaks at 1651 cm^{-1} and 1725 cm^{-1} which are not visible in the spectrum of PP3. These two peaks are associated with the C=O stretch of the

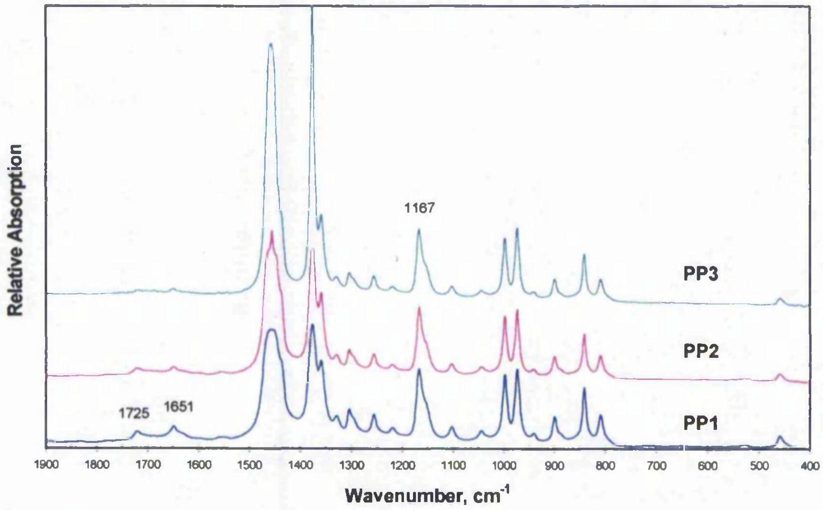


Fig. 4.13 FTIR spectra of the three commercial polypropylene products.

carbonyl bonds. The peak position of the stretch varies in this region depending on the functional groups bonding to the carbon atom of the carbonyl groups. Although it is difficult to compare the peak intensities between different samples when using the KBr method, the ratios of the carbonyl peaks and the CH_3 peaks at 1167 cm^{-1} should give an indication of how many carbonyl groups are in the polypropylene. The higher ratio (approximately 5:1) found for PP1 indicates that PP1 has more carbonyl groups in its structure and is less hydrophobic than PP2 and is therefore more compatible to the organoclay. The FT-IR results indicate that the polypropylene PP1 was likely to be the best of the three commercial polypropylenes for intercalation with clays and was selected for further research.

4.3.2 The effect of maleic anhydride grafted polar polypropylenes on melt intercalation

Only intercalated nanocomposites were produced from Cloisite organoclays and PP1 through direct melt intercalation. The clay layers cannot be uniformly exfoliated into the PP1 matrix using this method. This was thought to be due to inadequate surface compatibility between the polymer PP1 and the polar clay surface, even though PP1 was found to be less hydrophobic than initially thought and more compatible to the organoclay than expected. There is insufficient bonding between the surface of the PP1 and the organoclays to allow enough expansion of the clay layers to occur so that exfoliated nanocomposites can be formed. In order to overcome this problem, polypropylene is often modified via grafting a polar monomer to polypropylene to improve the polymer clay compatibility. There are several commercial grafted polypropylenes available.

4.3.2.1 The materials studied here

The materials investigated here were four types of commercial maleic anhydride grafted polypropylenes (MAH-g-PP) including Epolene E-43 Wax (E-43) and Epolene G-3015 (G-3015) supplied by the Eastman Chemical Company and Polybond®3000 (PB3000) and Polybond®3200 (PB3200) supplied by the Uniroyal Chemical. The major engineering properties of these products were not available but according to James Lee's recent publication [Svoboda, P. et al., 2001], E-43 is an ultra low molecular weight wax with 5.8 ^{wt}% MAH content. This information was used as the basis for calibration of MAH content in other materials.

The MAH-g-PP products were characterised using FTIR to assess the extent of grafting. Fig. 4.14 shows the FTIR spectra of the MAH grafted products. All these materials have absorption at 1790 cm^{-1} which is the characteristic peak of carbonyls from five-membered cyclic anhydrides [Svoboda, P. et al., 2001]. The peak at 1167 cm^{-1} is the characterisctic peak of CH_3 groups and is proportional to the amount of PP

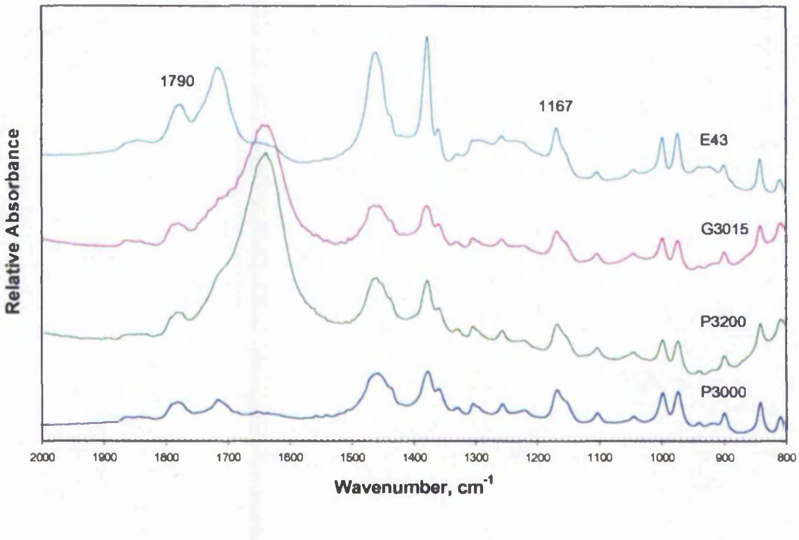


Fig. 4.14 FTIR spectra of MAH-g-PP products obtained using the KBr disk method

[Svoboda, P. et al., 2001]. These spectra were obtained using a traditional KBr method. Although this method is difficult to apply quanitatively, the ratio of the intensities at the two wavenumbers, A_{1790}/A_{1167}, will give the relative proportion of MAH in the grafted polypropylenes. When the MAH content in E-43 is used as a reference, the MAH contents of the other grapfted polypropylenes can be calculated. The MAH content in the commercial products is given in Table 4.1. The data shows that the MAH content in E-43 is much higher than in other three products which all have similar MAH contents, which are below 3wt%.

Table 4.1
MAH content in the grafted products calculated using the FTIR spectra

MAH-g-PP Product	**Supplier**	**A_{1790}/A_{1167}**	**MAH content, wt%**
E-43	Eastman Chemical	0.893	5.80[a]
G-3015	Eastman Chemical	0.455	2.96
P-3200	Uniroyal Chemical	0.428	2.78
P-3000	Uniroyal Chemical	0.404	2.62

[a] :[P. Svoboda et al., 2001]

4.3.2.2 The direct intercalation between clay and MAH-g-PP

The potential of using polar polypropylene, MAH grafted polypropylene, to produce nanocomposites was investigated via direct reactive melt extrusion using the twin-screw extruder. The investigations in this section cover the influences of clay type and concentration, MAH content in PP, and processing temperature on nanostructures formation.

The structure of the extruded composites produced from E-43 and PB3200, with the organoclay, Cloisite 93A, at two different clay loadings were characterized by X-ray diffractometry using Cu as the radiation source. The melt synthesis was carried out using the twin-screw extruder under the conditions of 130 °C barrel temperature, 15% feeding rate, 200 rpm screw speed and 24/1 L/D ratio. The composites were examined by XRD. The XRD traces in Fig 4.15 and Fig 4.16 show that the extent of layer expansion of the clay is much greater when using MAH grafted PP compared to the results obtained when PP1 alone was used to produce clay/PP composites (Fig 4.6). When the MAH grafted PPs have been used the (001) peak of the clay has been moved to angles below 3° and only the tail of the peak is observed. The gradient of the tail of the Clositie 93A/PB3200 composite is steeper than that of the Cloisite 93A/E-43 composite, this indicates that the (001) peak of the 93A/PB3200 composite is at a larger angle than that of the 93A/E-43 composite. These results indicate that the degree of layer expansion of the clay is greater when the MAH content in the composite is higher. Exfoliated nanocomposites may have been formed for the composites containing E-43 and PB3200 which suggests that grafting of MAH onto PP does improve nanostructure formation.

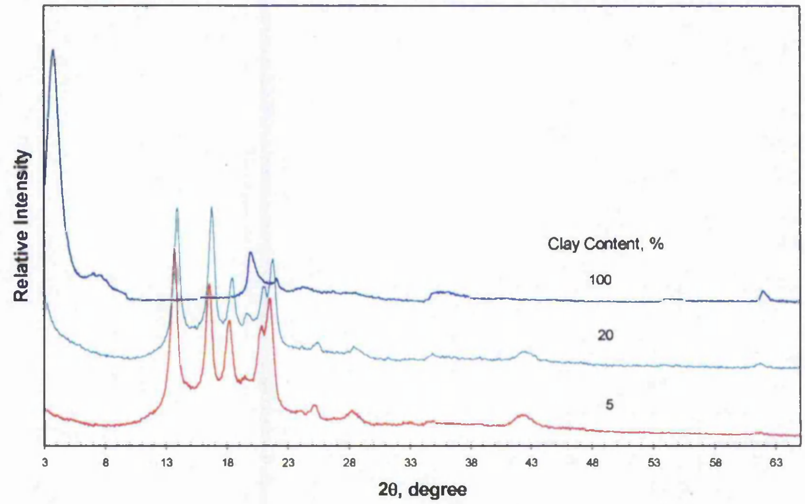


Fig. 4.15 XRD patterns of the extruded products produced from E-43 with different loadings of Cloisite 93A under the extrusion condition of L/D ratio 24/1, temperature 130 °C, feeding rate 15% and screw speed 200 rpm (Cu radiation source).

Other than E-43, composites produced using the three other grafted products, with the same MAH content, of around 3%, processed under the same conditions, were similar to those for PB3200 therefore it was decided to use PB3200 in further experiments. The interactions between the organoclay Cloisite 93A and the MAH-g-PPs, PB3200 at different processing temperatures 130 °C and 220 °C, were examined and compared with the results for an E-43 nanocomposite prepared at 130°C Composites with 5% Cloisite 93A and MAH –g-PP were produced by extrusion in a twin screw extruder with a L/D ratio 24/1, a feeding rate 15% and a screw speed 200 rpm. The dispersion of the clay Cloisite 93A in grafted PP matrices was investigated by X-ray diffractometry using Cu as radiation source. The XRD results show that layer expansion has occurred in both composites as the (001) peak of the clay has moved to a lower angle than 3°.

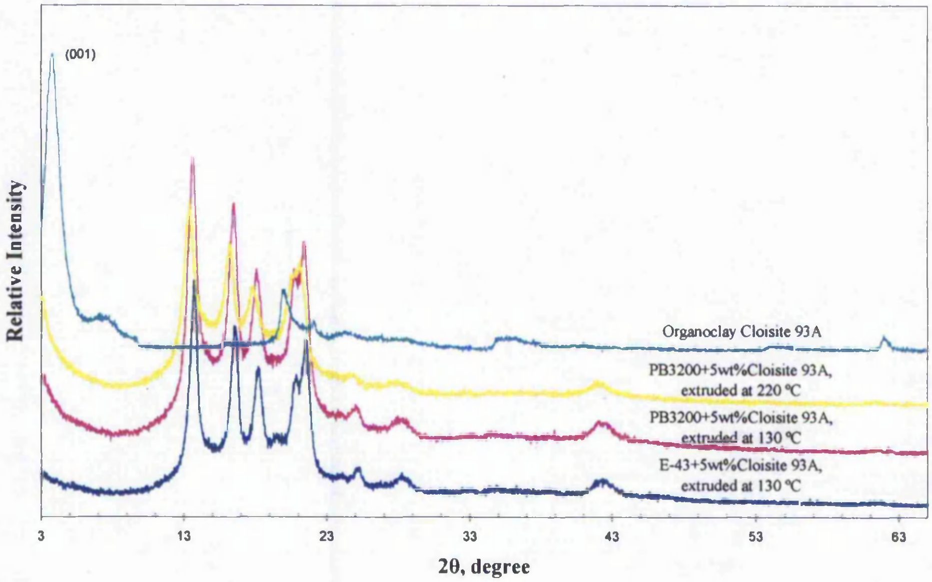


Fig. 4.16. XRD patterns of the extruded products produced from PB3200 with 5wt% Cloisite 93A under the extrusion conditions of L/D ratio 24/1, feeding rate 15%, Screw speed 200 rpm and two different temperatures, 130 °C and 220 °C (Cu radiation source).

A difference was found when the extrusion was carried out at the different processing temperatures. The slope of the (001) peak of the extruded product processed at 220 °C was much steeper than that of the product extruded at 130 °C. The extent of the layer expansion obtained using the higher processing temperature is lower than that for the lower processing temperature. This could be associated with the decomposition of the quaternary ammonium ions inserted between the Cloisite organoclay layers and poor shear resistance of individual clay particles during processing. A Thermogravimetric Analysis (TGA) of the organoclay Cloisite 93A is shown in Fig. 4.17. This shows that decomposition begins at 190 °C, which means that the organoclay is already degrading when the organoclay/PB3200 composite is being extruded at 220 °C. This explains why the visible slope of the (001) peak of the extruded product was much steeper for the composite processed at the higher temperature. The partial loss of the aliphatic ammonium ions and any organic volatile vapours generated between the clay layers, due to degradation, would reduce the distance between the clay layers and reduce the amount of molten polymer flowing into the clay layers and intercalating with the clay. However these are not the only factors affecting the interaction of the polymer. The capillary effect and the compatibility between the polymer and the remaining organophilic structure of the clay promote the polymer flowing into the clay layers. There will be a balance between these factors and this balance will change with polymer type, the organophilic structure between the clay layers and the processing conditions. In the case studied, the final balance or the extent of the intercalation depends on the extent of clay degradation.

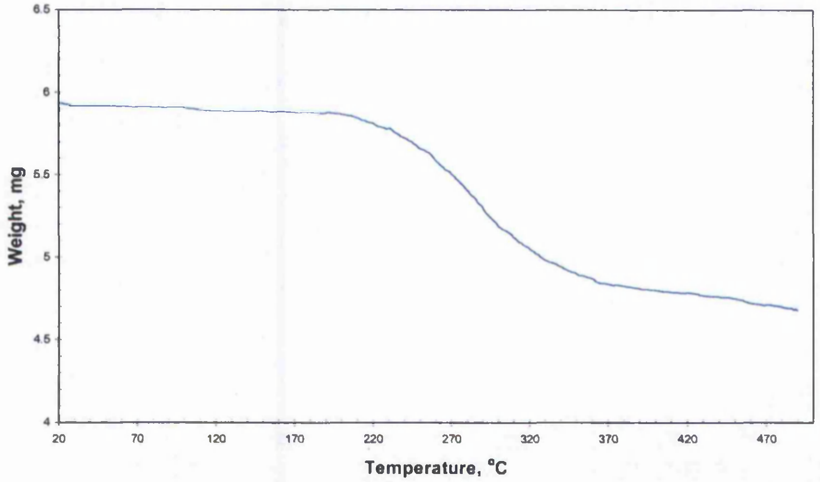


Fig. 4.17 weight loss of Cloisite 93A in air at the heating rate of 10 °C/min

The direct intercalation between the grafted polar PP and hydrophilic clay was also investigated. The natural hydrophilic clay Cloisite Na^+ was used in this study to produce E-43/Cloisite Na^+ composites by twin-screw extruder under the processing condition of 130 °C temperature, 15% feeding rate, 200 rpm screw speed and 24/1 L/D ratio. The X-ray diffraction analysis data are shown in Fig. 4.18 using Cu as radiation source. This result is significantly different from the results obtained by using the same hydrophilic clay and unmodified raw polypropylene PP1 which can be seen in Fig. 4.2. In the previous case, melt extrusion of PP1 and Cloisite Na^+ could not result in any layer expansion. However, when applying grafted PP, the layer of the hydrophilic clay expanded from 1.2 nm to 1.62 nm, 2θ at 5.4°, for the composite with 5wt% Cloisite Na^+. The clay sample in Fig. 4.18 contained moisture. According to the data in Fig.4.4, the interlayer distance of the original dry Cloisite Na^+ montmorillonite is estimated to be 0.96 nm. The intercalated nanocomposite has been obtained in this study. Such an expansion is significant. It has been never reported elsewhere that intercalation could occur between MAH grafted PP and a hydrophilic clay when this research was carried out.

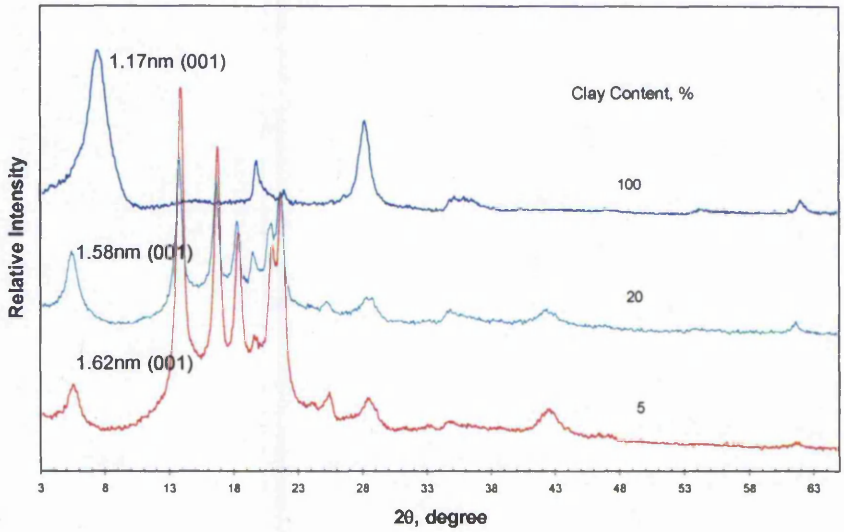


Fig. 4.18 XRD patterns of the extruded products produced from E43 with different loadings of natural hydrophilic clay Cloisite Na^+ *under the extrusion condition of temperature 130 °C, feeding rate 15%, screw speed 200 rpm and L/D ratio 24/1 (Cu radiation source).*

The interactions between hydrophilic clay and other three MAH-g-PPs containing lower MAH content compared to E-43 was studied as well. Again, the results obtained using other three grafted products are similar, so MAH-g-PP PB3200 was demonstrated here as a representative. The natural hydrophilic clay Cloisite Na$^+$ was used to produce PB3200/Cloisite Na$^+$ composites with 5wt% clay loading under the same extrusion condition with E-43. The results are shown in Fig. 4.19. The clay sample in Fig 4.19 contained moisture. According to the previous discussion, the interlayer spacing of the dried clay Cloisite Na$^+$ is approximately 0.96 nm. The (001) peak of the composite in Fig. 4.19 corresponds to 1.20 nm. It is apparent that the extent of the layer expansion in this case is less significant than that obtained using E-43. Again, the extent of the layer expansion obtained using the product with lower MAH content is not as great as using E-43

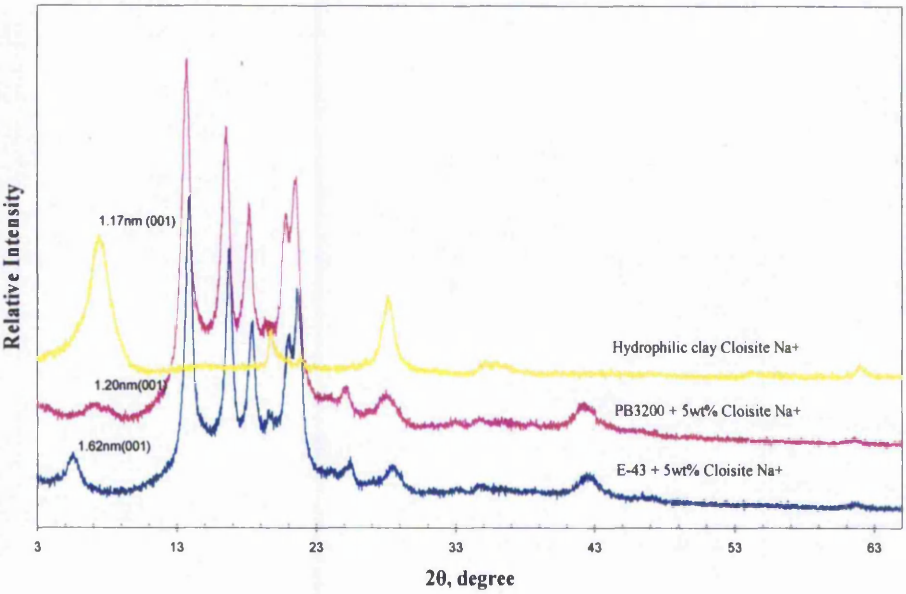


Fig. 4.19 XRD patterns of the extruded products produced from P3200 with 5wt% Cloisite Na$^+$ under the extrusion condition of L/D ratio 24/1, feeding rate 15%, Screw speed 200 rpm and temperature 130 ^{o}C (Cu radiation source).

4.4 Mechanical properties of the composites produced

The influence of nanostructure on the improvement of mechanical properties of the composites was examined by tensile testing.

4.4.1 The mechanical properties of hydrophilic clay/PP composites

The effect of the natural hydrophilic clays on the mechanical properties of the composites, Cloisite Na^+/PP and ME-100/PP, produced by the direct melt intercalation were studied and compared with those of pure PP1. Table 4.2 shows the tensile yielding strength and tensile Young's modulus of the materials produced. The tensile Young's modulus is a measure of the stiffness of a material, while the tensile yielding strength of a material indicates the maximum amount of tensile stress that can be applied to it before it ceases to be elastic. It can be seen from Table 4.2 that there are no improvements in the yielding strengths or the Young's modulus for the composites of PP1 using hydrophilic clays. In general, adding hydrophilic clays to the polymers results in a decrease in their mechanical properties. This is because the direct blending method is almost the same as traditional additive melt processing when hydrophilic clays are used. Intercalation of the clays and polymers does not occur. Only conventional composites have been obtained by the direct blending method and the clays still stay as aggregates inside the polypropylene matrix.

Table 4.2
Tensile yielding strength and modulus of hydrophilic clay/PP1 composites

Material	Yielding Strength, MPa			Relative Young's Modulus, GPa		
	Average	σ*	n**	Average	σ	n
PP1	33.55	0.87	6	1.00	0.12	6
PP1+5% Na^+	31.16	0.98	6	0.64	0.05	6
PP1+20% Na^+	31.09	0.69	6	0.77	0.35	6
PP1+3%ME-100	34.43	1.09	6	0.87	0.17	6
PP1+5%ME-100	33.11	0.98	6	0.67	0.12	6
PP1+7%ME-100	32.27	1.23	6	0.70	0.21	6

*Note: *σ - standard deviation, **n – number of specimens tested*

4.4.2 The mechanical properties of organophilic clay/PP nanocomposites

The mechanical properties of the intercalated nanocomposites obtained when the organoclays, Cloiste 15A, Cloisite 20A and Cloisite 93A, were extruded with PP1 by twin-screw extruder at 200°C were examined. Table 4.3 shows the yielding strength and Young's modulus of the materials studied. The results indicate that there is no improvement in the yielding strengths and the Young's modulii for the intercalated nanocomposites when the results are compared with polypropylene PP1 This suggests that the formation of intercalated nanostructure with low extent of layer expansion does not improve the mechanical properties of a composite. The marginal decrease in the mechanical properties when the organoclays were added to the polymer could be associated with the breakdown of the quaternary ammonium ions inserted between the clay layers and poor shear resistance of individual clay

Table 4.3
Tensile yielding strength and modulus of organoclay/PP1 nanocomposites

Material	**Yielding Strength, MPa**			**Relative Young's Modulus, GPa**		
	Average	**σ***	**n****	**Average**	**σ**	**n**
PP1	33.84	0.97	6	1.000	0.18	6
PP1+3% Cloisite 93A	33.42	1.01	6	0.926	0.12	6
PP1+5% Cloisite 93A	32.83	1.08	6	0.923	0.35	6
PP1+3%Cloisite 20A	31.82	1.45	5	0.801	0.31	5
PP1+5%Cloisite 20A	31.64	2.45	5	0.948	0.51	5
PP1+3%Cloisite 15A	32.57	1.14	6	0.884	0.19	6
PP1+5%Cloisite 15A	32.48	1.27	6	0.990	0.24	6

*Note: *σ - standard deviation, **n – number of specimens tested* particles. The Thermogravimetric Analysis (TGA) of Cloisite 93A has shown previously (Fig. 4.17) that the decomposition of the clay commences at around 190 °C. The thermal stability of organoclay Cloisite 15A and 20A was also investigated and it was found that all the commercial organoclays studied here begin to degrade at about 190 °C. This means the organoclay is degrading at the processing temperature of the organoclay/polypropylene composites

The influence of clay loading on the mechanical properties of the composites can be seen in Table 4.3. The tensile yielding strength of nanocomposites containing 3 wt% organoclay, for all the clay types, showed a slight increase compared to the nanocomposites containing 5 wt% organoclay in all cases. At the higher clay content, aggregation of the organoclay may occur. As a consequence, the mechanical properties of the nanocomposites with higher clay content may decrease.

Compared to the composite containing 3 wt% Cloisite 93A, both yielding strength and Young's modulus have been shown a slight decrease in the intercalated nanocomposites with 3 wt% Cloisite 15A and Cloisite 20A, although Cloisite 15A exhibits the highest extent of layer expansion. The reason has not been well understood yet. It may be associated with some unknown additives inside modified organoclays Cloisite 15A and 20A. These additives have low molecular weights and therefore result in a decrease in their composites mechanical properties.

4.4.3 The mechanical properties of composites produced from an organoclay and different polypropylenes

The mechanical properties of the composites produced from the organoclay Cloisite 93A and different polypropylenes were studied. The XRD studies of the composites found that layer expansion occurred when the polypropylene PP1 was used while clay aggregates remained in the composites of the polypropylenes PP2 and PP3. The tensile yielding strength and the Young's modulus of the conventional composites produced by PP2 and PP3 are significantly lower than the polypropylenes they are produced from (Table 4.4). The nanocomposite of PP1 and the organoclay had mechanical properties which were very similar to the pure polypropylene PP1. The clay layers were intercalated but the changes in the mechanical properties were not as expected. This may be due to the Cloisite 93A decomposing at the temperature at which the composite was being extruded resulting in interaction but not exfoliation.

Table 4.4
Tensile yielding strength and modulus of composites produced by organoclay Cloisite 93A and different pure polypropylenes

Material	**Yielding Strength, MPa**			**Relative Young's Modulus, GPa**		
	Average	**σ***	**n****	**Average**	**σ**	**n**
PP1	33.84	0.97	6	1.000	0.18	6
PP1+3% Cloisite 93A	33.42	1.01	6	0.926	0.12	6
PP2	32.29	1.69	6	1.000	0.15	6
PP2+3%Cloisite 93A	31.15	1.09	6	0.652	0.14	6
PP3	32.69	0.18	6	1.000	0.07	6
PP3+3%Cloisite 93A	30.58	1.45	6	0.748	0.24	6

*Note: *σ - standard deviation, **n – number of specimens tested*

4.4.4 The mechanical properties of Clay/MAH-g-PP nanocomposites

Both exfoliated nanocomposites and intercalated nanocomposites were produced when MAH-g-PPs were melt extruded with an organoclay and a hydrophilic clay. However, the mechanical properties of the extruded nanocomposites could not be measured because all the maleic anhydride grafted products studied had low molecular weights which resulted in their mechanical properties being too low to be measured on the testing equipment.

4.5 Conclusions

In conclusion, only one of the commercially available polypropylenes PP1 was capable of forming intercalated nanostructures with organoclays. Infra red results indicated that this was due to the presence of carbonyl groups in the polypropylene's structure. The intercalated structures obtained by direct melt intercalation did not enhance the mechanical properties of the polypropylene because of the organoclay degradation and inadequate compatibility between the organoclay and the pure polypropylene.

Grafting maleic anhydride onto polypropylene improved the intercalation between clays and polymers. High degrees of intercalation or exfoliation can occur if

MAH-g-PPs with a high MAH content (~5%) are used. The mechanical properties of these types of composite are very low because of the low molecular weight of the MAH-g-PP products used.

CHAPTER 5 Effect of Stabilizers, Compatibilizers and Processing Conditions on Melt Processing of Clay/PP nanocomposites

Intercalated nanocomposites have been obtained by the direct melt extruding polypropylene and the organoclay as discussed above. However the non-uniform dispersal of clay layers in the polypropylene matrix limits the reinforcement of the major engineering properties. The study in this section was intended to use a small fraction of different stabilizers and compatibilizers in unmodified PP1 and organoclay mixtures to achieve further intercalation via the direct melt intercalation processing method. An extensive study on the effects of stabilizers and compatibilizers on the extent of clay dispersion in polypropylene matrix has been carried out and tested by X-ray diffractometry (X-ray). The enhancement of mechanical properties has been examined by tensile loading testing. Two different radiation sources, CuKα (λ =0.154 nm) and CrKα (λ =0.229 nm), were also used in the XRD analysis. The influences of melt processing parameters, such as the role of shear and residence time, on the nanostructure formation in the melt processing of clay/polymer nanocomposites have also been examined.

5.1 The effect of stabilizers on the formation of clay/polypropylene composites

5.1.1 The materials studied

Stabilizers, also called anti-oxidants, are traditionally used to prevent the degradation of polypropylene during melt extrusion processing. The effect of stabilizers on the formation of nanocomposites was investigated. Three commercial anti-oxidants were obtained from Cytec Germany. They were coded as CYANOX®2777, CYANOX®2888 and CYANOX®XS4. The first two are essentially phenolic / phosphite mixtures while the third one is an amine substance. The chemical structure of the first two products are shown in Fig 5.1. They are a mixture of tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-s-triazine-2,4,6-(1H,3H,5H) trione and tri(2,4-Di-t-butyl phenyl) phosphite. But the ratio of phenolic / phosphite is different. The ratio of phenolic / phosphite is 1:2 in CYANOX®2777 while the ratio of phenolic / phosphite is 1:3 in CYANOX®2888. However, there was no relevant data available for the product CYANOX®XS4.

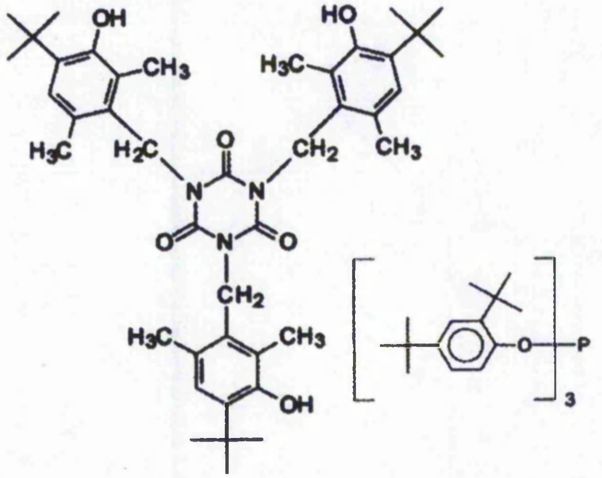


Fig 5.1 The chemical structure of CYANOX®2777 and CYANOX®2888

5.1.2 Structure of the composites produced from organoclay, PP1 and different stabilizers

The polypropylene PP1 with 3 wt% organoclay Cloisite 93A and 0.2wt% each of the stabilizer, were extruded using the twin-screw extruder at 210°C with a 12% feeding rate, 24/1 L/D ratio and 500 rpm screw speed. The colour of the composites produced is shown in Fig. 5.2.

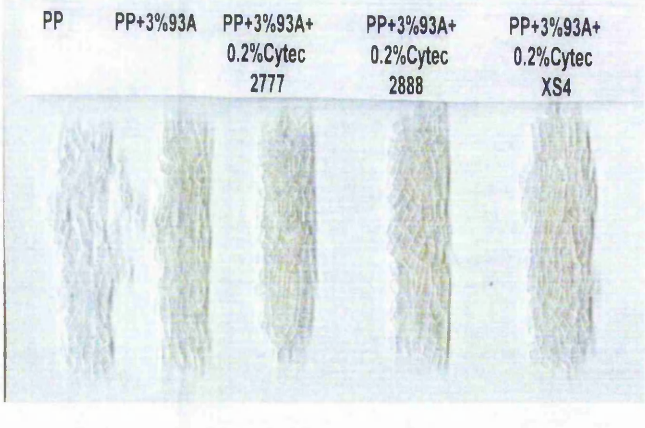


Fig 5.2 The colour of Clay/PP composites containing different stabilisers

Any change of colour should indicate the degree of degradation. The photographs show that there is little difference in colour between the composites with and without anti-oxidants.

In order to explain this, the change of molecular weight of nanocomposites obtained compared to the neat polypropylene was examined. Normally, the average molecular weight of linear polymers is related to the shear viscosity at a low shear rate. Therefore the nanocomposites containing different stabilizers were investigated and studied using a low shear rate melt flow index (MFI) test. The materials were tested at 190oC with a standard weight of 2.16 kg. The change in melt flow index (MFI) would give the indication of the change in molecular weight of the polypropylene by degradation. The changes in MFI can be seen from Table 5.1.

The results show that there is little change in MFI data by using the stabilizers. The data agree with the results on colour change. The stabilisers are not effective in the current clay/polypropylene system. Only slight improvements have been made in the layer expansion by the stabilizers. The commercial available stabilizers were developed for preventing PP degradation rather than preventing organoclay degradation. The effective stabilisers for clay/PP nanocomposites system have not yet been available in commercial market and are required to be developed.

Table 5.1
The change in molecular weight

Material	**MFR, g/10min**
PP	1.117
PP+3%93A	1.097
PP+3%93A+Cytec2777	1.016
PP+3%93A+Cytec2888	1.043
PP+3%93A+CytecXS4	1.101

The dispersion of the organoclay in the composites produced was evaluated by X-ray diffractometry (X-ray) using Cr as the radiation source. The XRD patterns of the samples in Fig 5.3 show that intercalated nanocomposites have been obtained in all the samples. The interlayer spacing has been expanded slightly by adding those three anti-oxidants compared to the sample with no anti-oxidants.

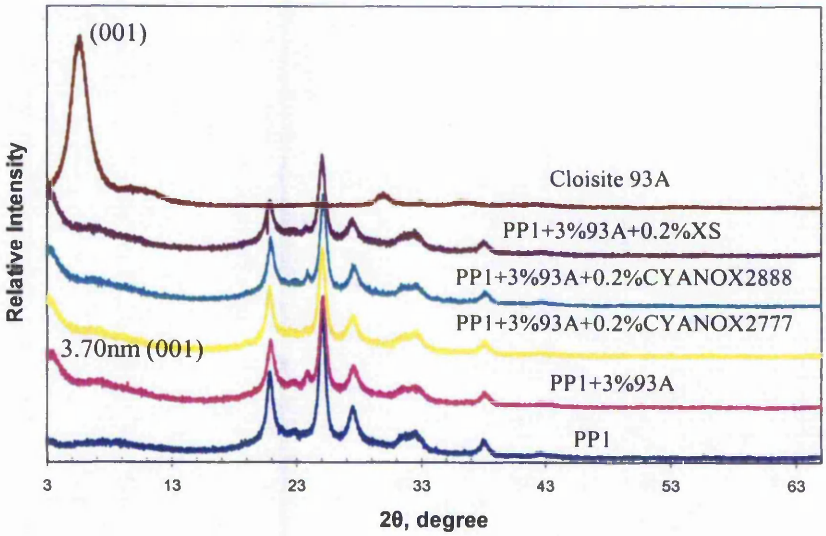


Fig 5.3. XRD patterns of the extruded products produced from unmodified PP1, 3% clay Cloisite 93A and 3 anti-oxidants, CYANOX®2777, CYANOX®2888 and CYANOX®XS4, were extruded under the extrusion condition of L/D ratio 24/1, temperature 210 °C, feeding rate 12% and screw speed 500 rpm.

The anti-oxidants investigated are a few of the most effective products for traditional PP melt processing. However the data from the studies here indicate that these anti-oxidants are not effective in the current clay/polypropylene system. Only slight improvements have been made in the layer expansion by the anti-oxidants which suggest intercalation of the polymer and clay has not been greatly improved. The lack of efficiency of stabilizers is associated with the fact that they were developed according to the polymer structure rather than allowing for other additives in the system. In clay/polymer nanocomposite processing the ammonium salts degrade first and cause degradation of polymer. It appears that the mechanism applied in preventing PP from degradation can not be applied to PP/organoclay nanocomposites system. The effective approach should be the mechanism for preventing organoclay degradation rather than PP degradation. This idea should be investigated in further work.

5.2 The effect of compatibilizers on melt processing of Clay/PP nanocomposites

The commercially available polypropylene PP1 is less hydrophobic than expected due to carbonyl groups in its structure which make it capable of forming intercalated nanostructure with organoclays. However the extent of layer expansion in this nanocomposite is quite low due to the inadequate compatibility between the non-polar polypropylene backbone and the organoclays. Further study on the grafting of maleic anhydride onto the polypropylene much improved the intercalation between the clay and the polymer. High degrees of intercalation or exfoliation may be possible when using MAH-g-PP with a high MAH content. However the mechanical properties of these nanocomposites are very weak because of the low molecular weight of the MAH-g-PP products. In this section, an innovative method has been developed to produce clay/polypropylene nanocomposites by using low molecular weight maleic anhydride grafted polypropylene oligomers (MAH-g-PPs) as compatibilizers in this study. Three chemicals, 3-aminopropyltriethoxysilane (APTES), methyltrimethoxysilane (MTMS) and stearic acid (SA), were also selected as compatibilizers to produce clay/PP nanocomposites according to their structural compatibility.

5.2.1 The effects of adding MAH-g-PPs as compatibilisers

This method was intended to use a small fraction of MAH-g-PP in unmodified PP and organoclay mixtures to achieve intercalation via direct melt blending. The MAH-g-PP was used as the compatibilizer to improve the interfacial interaction with the clays and introduce polar functionality onto the polymer backbone. The melt intercalation process to produce this composite was a organoclay/MAH-g-PP/PP three components system as illustrated from Fig 5.4.

The MAH-g-PP oligomers investigated here were the four types of commercial maleic anhydride grafted polypropylenes discussed above including Epolene E-43

Wax (E-43), Epolene G-3015 (G-3015), Polybond®3000 (PB3000) and Polybond®3200 (PB3200).

5.2.1.1 The effect of using MAH-g-PP E-43 on the nanostructure formation and mechanical properties of the composites

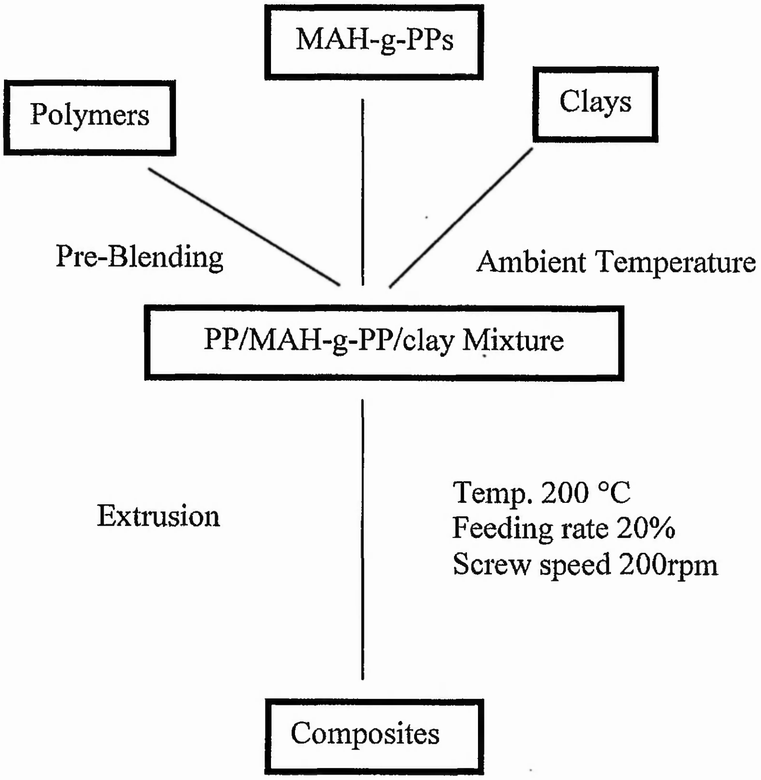


Fig 5.4 The fabrication of organoclay/MAH-g-PP/PP via direct melt intercalation

Maleic anhydride grafted PP Epolene E-43 has the highest MAH content amongst the four commercial grafted polypropylenes and hence theoretically is more efficient in intercalation. Thus Epolyene E-43 was firstly used as the compatibilizer to investigate the potential of using this method to produce nanocomposites. The original polypropylene PP1, organoclay Cloisite 93A and the MAH-g-PP E-43 were extruded to produce composites using the twin-screw extruder under the conditions of 200°C, 20% feeding rate, 24/1 L/D ratio and 200 rpm screw speed. Two different clay loadings, 3 wt% and 5wt% of compatibilizer E-43 were used to prepare this three component composites system. The colour of the composites was dark yellow. The dispersion of the organoclay in the composites produced was studied by X-ray diffractometry using Cu as a radiation source. The XRD patterns of the extruded nanocomposites produced by melt-mixing of the three components are shown in Fig 5.5. The materials in the chart include the original PP1, the organoclay Cloisite 93A and the composites with 3 and 5 wt% clay loadings. It can be seen that layer expansion occurred in all cases as the (001) peak shifted gradually to angles below 3 °. The interlayer spacings of clay layers were expanded. Changes in the interlayer spacing are an indication that polymer has been incorporated within interlayers of the clays during melt extrusion. The driving force for this kind of intercalation is thought to originate from the maleic anhdride group, or the -COOH group generated by the hydrolysis of the maleic anhydride group and the oxygen groups of the organoclays. However it appears that small amounts of MAH-g-PP may not be sufficient to exfoliate the composites. Only intercalated nanocomposite structure with a low extent layer intercalation can be obtained because the tails of the (001) peak of the extruded products are still visible. There is little difference in the intercalation levels between 3wt% and 5wt% clay loadings because the tails of the (001) peak of these two products are quite similar.

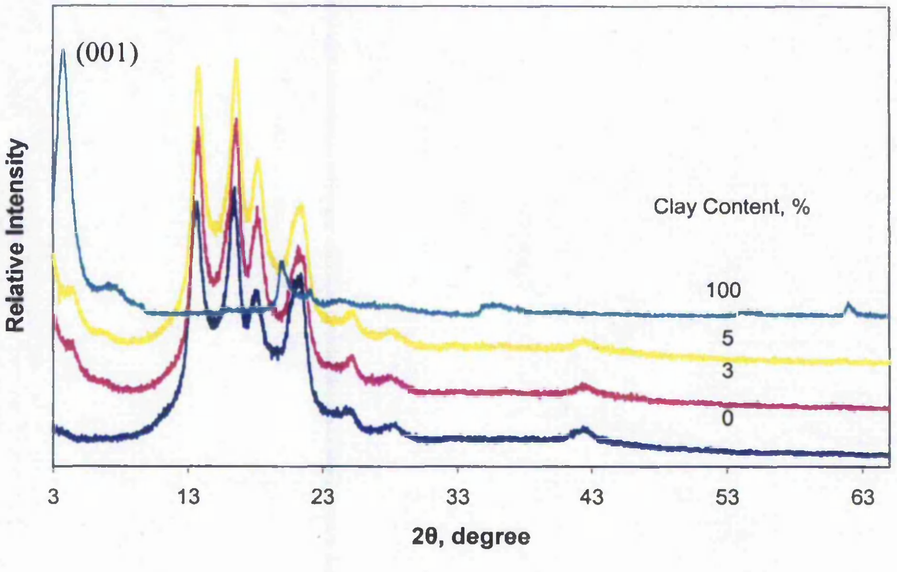


Fig.5.5. XRD patterns of the extruded products produced from unmodified PP1, 5% E-43 and different loadings of organoclay Cloisite 93A under the extrusion condition of L/D ratio 24/1, temperature 200 °C, feeding rate 20% and screw speed 200 rpm (Cu radiation source).

The intercalation between the maleic anhdride and the oxygen groups of the organoclay is the driving force for clay layer expansion. Therefore the content of MA-g-PP would play an important role in intercalation. Following the melt extrusion of small amounts of E-43 as compatibilizer to produce clay/PP nanocomposites, the influences of different MAH-g-PP loadings on nano-structure formation were investigated.

In order to find out the most suitable MAH-g-PP concentration for nanostructure formation with a high extent of layer expansion, the polypropylene PP1 with 3 wt% organoclay Cloisite 93A and different E-43 loadings were extruded to produce organoclay/MAH-g-PP/PP1 composites. Three MAH-g-PP E-43 loadings, 5%, 20% and 23.5%, were used in this study. The melt synthesis was carried out using the twin-screw extruder with the conditions of 200°C, 20% feeding rate, 24/1 L/D ratio and 200 rpm screw.

The dispersion of Cloisite 93A in the composites produced was studied by X-ray diffractometry using Cu as radiation source. The materials in Fig 5.6 include the original PP1, the organoclay Cloisite 93A and the composites with 3 wt% organoclay and different E-43 loadings. The XRD diffraction patterns show that clay expansion has occurred in all the cases because all (001) peaks of Cloisite 93A shifted gradually to angles below 3 °. Epolyene E-43 has acted as the compatibiliser here and the interlayer spacing in the composites increases as the E-43 loading is raised.

It appears that there is little difference in the intercalation levels for the composites containing 5wt% and 20wt% MAH-g-PP E-43 loadings because the slopes of the (001) peak of these two products are quite similar. Only intercalated nanocomposites structure with a low extent of layer intercalation are obtained for these two products because the tails of the (001) peak of the extruded products were still visible. However, exfoliated structures maybe achieved when adding 23.5 wt% MAH-g-PP E-43. In this case, the (001) peak has been shifted to the angles below 3° and the slope of the tail of (001) peaks in the 3° region is much flatter than for the other sample. This suggests that the angle of the (001) peaks is much smaller in the nanocomposite containing 23.5 wt% compatibilizer E-43. These results show that the higher the compatibilizer content, the higher the layer expansion of the clays in this polypropylene, organoclay and MAH-g-PP three component nanocomposites system.

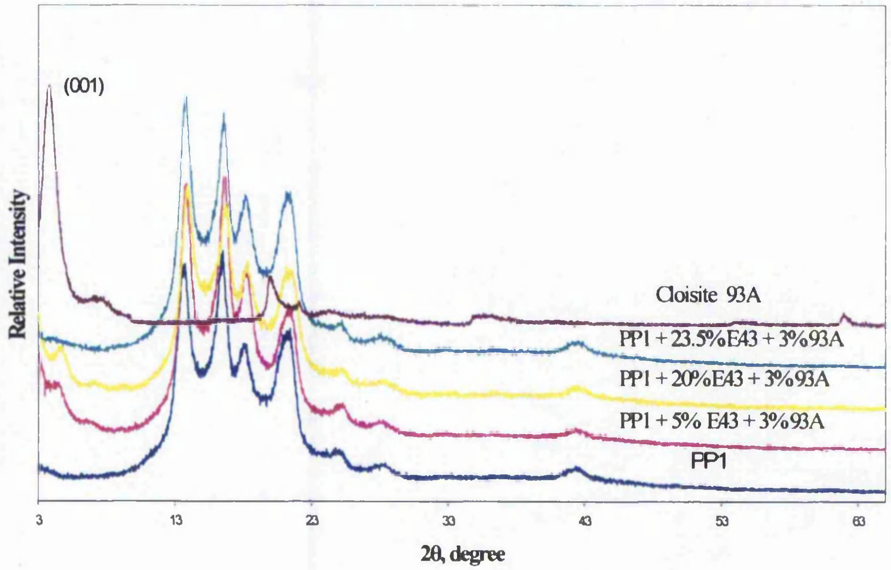


Fig. 5.6. XRD patterns of the extruded products produced from unmodified PP1, 3% organoclay Cloisite 93A and different E-43 loadings under the extrusion condition of L/D ratio 24/1, temperature 200 °C, feeding rate 20% and screw speed 200 rpm (Cu radiation source).

The tensile yielding strength of the materials produced previously was studied by tensile testing. Figure 5.7 shows the tensile yielding strengths of the nanocomposites produced from the unmodified polypropylene, PP1 and composites produced with different E-43 loadings. It can be seen that there is no improvement in the tensile yielding strength for the nanocomposites produced compared to the original PP1. The yielding strength decreased as the compatibilizer E-43 loadings increased within 0 wt% to 20 wt%. Some improvement can be seen when a high MAH-g-PP content, 23.5 wt%, was used to produce PP1/3wt% Cloisite 93A/E-43 nanocomposite. However, compared to original PP1, the tensile yielding strength of this nanocomposite is still very low. It should be noted as well that all the nanocomposites produced here were dark yellow.

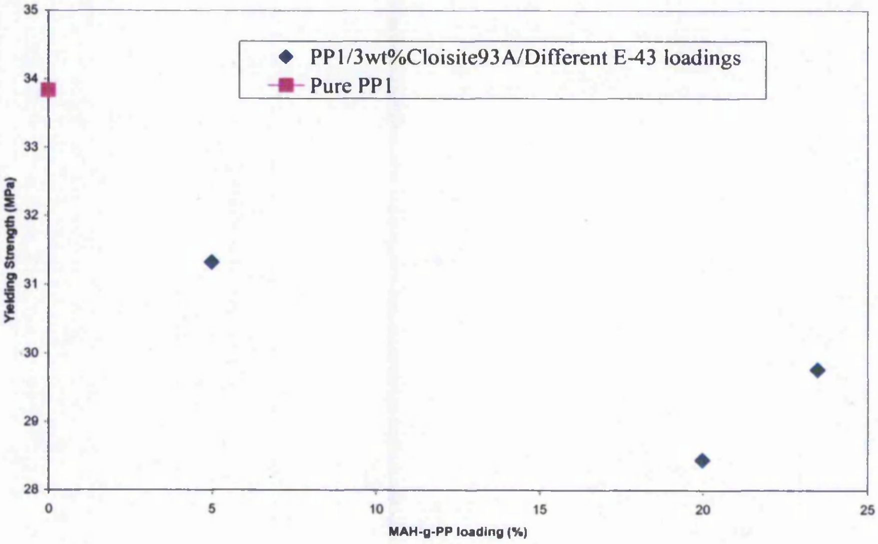


Fig5.7. Tensile Yielding Strength vs different MAH-g-PP E-43 loadings in PP1/ 3wt%Cloisite93A /E-43 nanocomposites prepared under the extrusion condition of L/D ratio 24/1, temperature 200 °C, feeding rate 20% and screw speed 200 rpm.

This approach did not improve the yielding strength of polypropylene. The reason is that adding low molecular weight grafted PP tends to reduce the yielding strength. Epoxylene E-43 has a relatively high MAH content but a lower molecular weight compared to the other commercial MAH grafted PPs. Although improvement can be made by the formation of exfoliated nanocomposites when higher E-43 concentration are used, the reinforcement made by the well dispersed clay layers could not compensate the reduction caused by the low molecular weight of the polymer. These results are different from the work published by the Ohio Group and Mülhaupt's Group at Freiburger [Svoboda, P.et al., 2001; Reichert, P. et al., 2000]. In their case, the tensile yielding strength was reported to be significantly improved.

5.2.1.2 The effect of using different MAH-g-PPs on the nanostructure formation and the mechanical properties of the composites

Epolyene E-43 has a very low molecular weight and a high MAH content of 5%. In contrast, the other commercial MAH-g-PPs have lower MAH with higher molecular weight. A study of the maleic anhydride grafted polypropylenes with higher molecular weights was undertaken using the same method as for the E-43 in the previou section. The polyproplene PP1 and 5wt% of the MAH-g-PPs, Epolene G-3015 (G-3015), Polybond®3000 (PB3000) and Polybond®3200 (PB3200), were examined with 3wt% and 5wt% of Cloisite 93A respectively to produce Cloisite 93A/MAH-g-PP/PP1 composites. The melt processing was carried out using the twin-screw extruder at 200°C, 20% feeding rate, 24/1 L/D ratio and 200 rpm screw.

The dispersion of the organoclay in the composites produced was studied by X-ray diffractometry using Cu as radiation source. The XRD patterns are shown in Figs 5.8 and Fig 5.9 and the results are compared with these extruded composites with Epolyene E-43. It can be seen from Fig 5.8 that layer expansion has occurred in all cases as the (001) peak shifted gradually to angles below 3 °. The interlayer spacings of clay layers were expanded. Only intercalated nanocomposites have been obtained for all the products produced because the tails of the (001) peak of extruded products

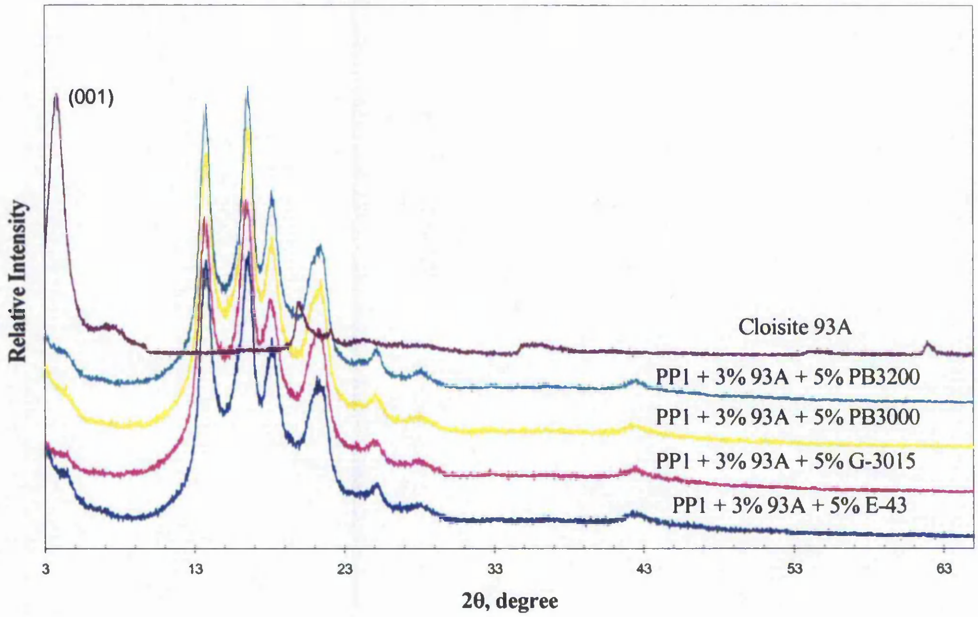


Fig 5.8 XRD patterns of the extruded products produced from unmodified PP1, 3 wt% clay Cloisite 93A and 5 wt% different MAH-g-PPs under the extrusion condition of L/D ratio 24/1, temperature 200 °C, feeding rate 20% and screw speed 200 rpm(Cu radiation source).

are still visible in all the cases. However it looks as though the extent of the layer expansion of the nanocomposite containing 5wt% MAH-g-PP G-3015 is higher than those of the composites containing 5wt% MAH-g-PPs E-43, PB3000 and PB3200. This is because the slope of the tail of (001) peak in the 3° region in nanocomposite containing G-3015 is slightly flatter than the other samples. The reason why choosing G-3015 with less MAH content cause a higher extent layer expansion in this PP1/organoclay/MAH-g-PP three components nanocomposites system has not been well understood yet.

When 5wt% clay loading was applied to produce three components composites PP1/MAH-g-PP/Cloisite 93A, intercalated nanocomposites with a low extent of layer expansion have been obtained for all the cases when different MAH-g-PPs were applied. This can be seen from Fig 5.9, where all the (001) peaks of the composites produced shifted to angles below 3°. In general, there is little difference between nanocomposites by adding different MAH-g-PPs when a higher clay content was used. At higher clay contents, aggregation of the organoclay may occur.

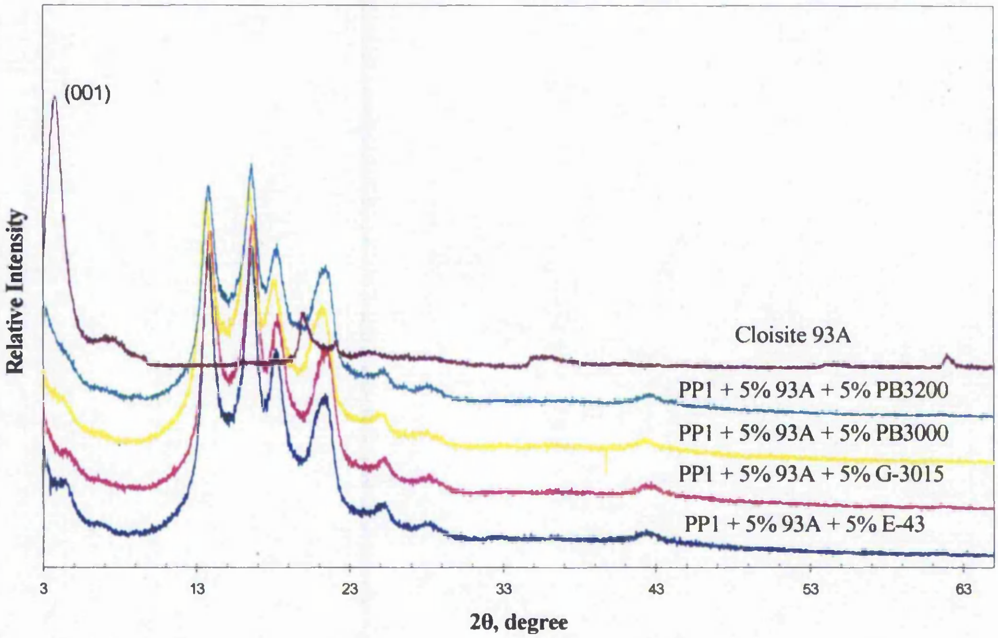


Fig 5.9 XRD patterns of the extruded products produced from unmodified PP1, 5 wt% clay Cloisite 93A and 5 wt% different MAH-g-PPs under the extrusion condition of L/D ratio 24/1, temperature 200 °C, feeding rate 20% and screw speed 200 rpm(Cu radiation source).

The tensile yielding strength of the nanocomposites produced by adding different MAH-g-PPs were investigated by tensile testing. The results are shown in Fig. 5.10. The materials in Fig 5.10 include the polypropylene PP1, PP1/MAH-g-PP composites without any clay and PP1/MAH-g-PP/Cloisite 93A three components nanocomposites with 3 wt% and 5 wt% clay loadings respectively. When the polypropylene PP1 is compared with the PP1/MAH-g-PP/Cloisite 93A three components nanocomposites produced either with 3 wt% or 5wt % clay loadings the yielding strength is lower than that of the original polypropylene. However, 3 wt% clay loading, in general are more effective at maintaining the mechanical properties than 5 wt% clay loadings. The highest tensile yielding strength, for the nanocomposites produced by the three component system, was exhibited by the nanocomposite comprising of 5 wt% G-3015 with 3 wt% of the organophilic clay Cloisite 93A. This result is in agreement with the result obtained previously where the nanocomposite containing 5 wt% G-3015 and 3 wt% organoclay Cloisite 93A has the highest extent layer expansion.

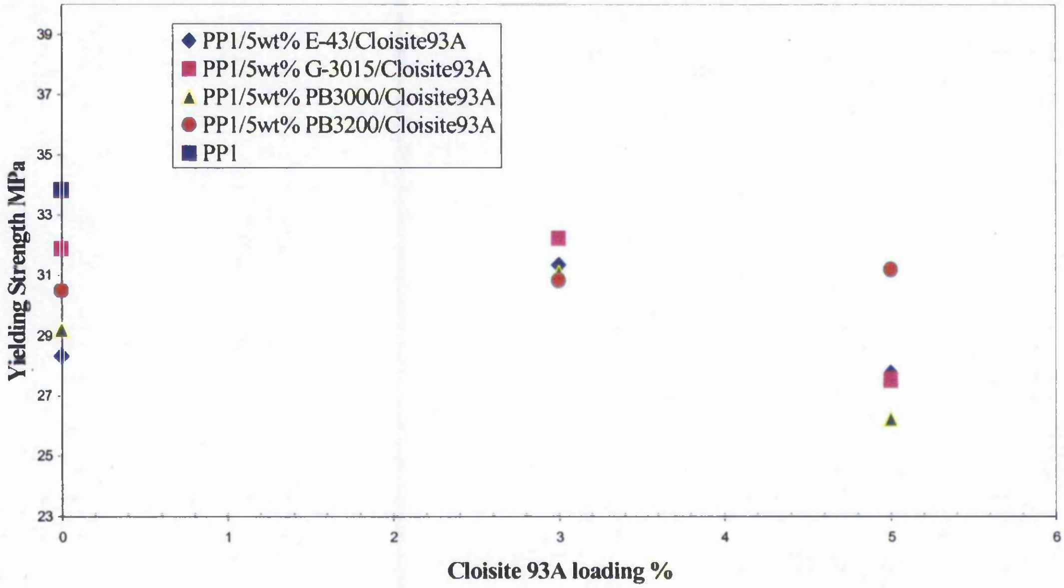


Fig5.10. Effect of clay content on Tensile Yielding Strength in different PP1/MAH-g-PP/Cloisite93A composites prepared under the extrusion condition of L/D ratio 24/1, temperature 200 °C, feeding rate 20% and screw speed 200 rpm.

5.2.1.3 The use of Cloisite 15A to prepare PP1/MAH-g-PP/organoclay composites

As discussed above, the intercalation of organoclay Cloisite 93A does not occur when low concentrations of less than 5% MAH-g-PP are used to produce PP1/MAH-g-PP/organoclay nanocomposites. Examination of a number of organoclays found that Cloisite 15A had the best hydrophobic surface and the largest layer expansion of all the commercial clays examined (Section 4.2.2). For these reasons an investigation was carried out using Cloisite 15A to determine whether it could be used to form composites with high extents of clay layer expansion when low MAH-g-PP loadings was used. The difference in structure between Cloisite 93 A and Cloisite 15A is that a hydrogen atom in the ammonium salt used to make Cloisite 93A has been replaced by a methyl group in Closiste 15A, resulting in the Cloisite 93A being less hydrophobic than Cloisite 15A.

Two maleic anhydride grafted polypropylenes were used in this study. They were Epolyene E-43 with very low molecular weight but the highest MAH content and Polybond 3200 with a relatively high molecular weight but low MAH content. The original polypropylene PP1, organoclay Cloisite 15A and the two MAH-g-PPs were extruded to produce composites via direct melt intercalation by using the twin-screw extruder under the conditions of 200°C, 20% feeding rate, 24/1 L/D ratio and 200 rpm screw speed. The concentration of Cloisite 15A used was 3 wt% and the content of MAH-g-PP used was 5 wt% in this study.

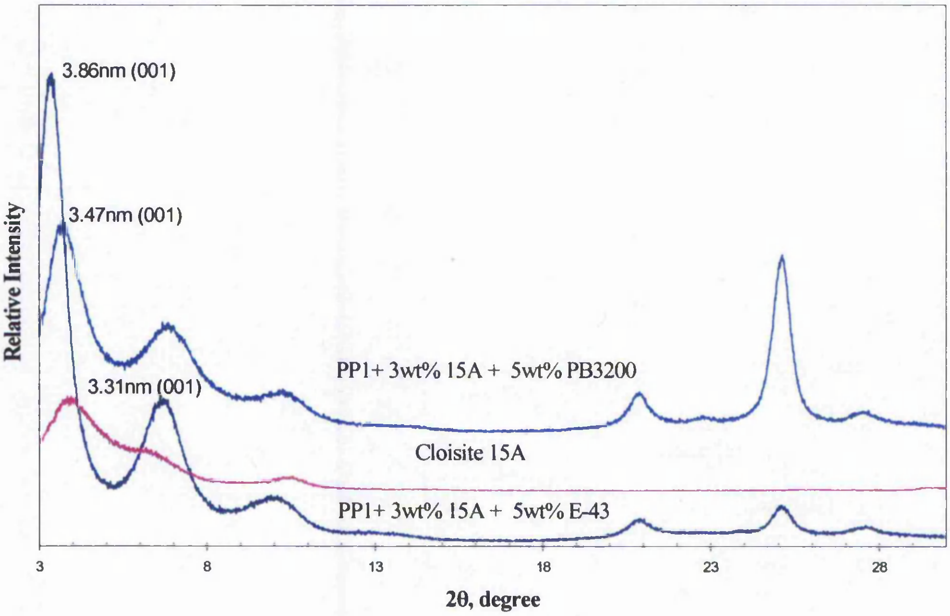


Fig 5.11 XRD patterns of the extruded products produced from unmodified PP1, 3wt% clay Cloisite 15A, 5wt% Epolyene E-43 and Polybond 3200 under the extrusion condition of L/D ratio 24/1, temperature 200 °C, feeding rate 20% and screw speed 200 rpm (Cr radiation source).

Figure 5.11 shows the XRD patterns of the extruded products using Cr as radiation source. It can be seen that all the samples with MAH-g-PP loaded samples from E-43 to PB3200, layer expansion occurred in all cases as the (001) peak shifted gradually to angles below 3 °. The interlayer spacings of the clay layers were expanded from 3.31nm for the pure organoclay Cloisite 15A to 3.47nm and 3.86nm respectively. The highest extent of layer expansion in this study was found when applying MAH-g-PP with a high MAH content (E-43). Slight changes in the interlayer spacing are an indication that only intercalated nanocomposites has been formed. Small amounts of MAH-g-PP were also found to be insufficient to help exfoliate Cloisite 15A in the polypropylene matrix. The mechanism is not fully understood but it may be associated with some unknown additives inside modified organoclays Cloisite 15A and 20A. These additives have low molecular weights and therefore result in a decrease in their composites mechanical properties.

Table 5.2 shows the tensile yielding strength and Young's Modulus of the intercalated nanocomposites obtained. The mechanical properties decreased in both cases. The tensile yielding strength of the nanocomposite containing Epolyene E-43 is a little bit higher than that of nanocomposite containing Polybond 3200. This agrees with the results obtained above that the dispersed clay layers do exhibit a reinforcement effect and these mechanical properties are low due to the low molecular weights of the MAH-g-PPs. The results indicate that small amounts of grafted polypropylene with high malaeic anhydride content do benefit the intercalation of the polymer and Cloisite 15A but do not improve the mechanical properties. Further clay expansion using maleic anhydride grafted polypropylenes with high maleic anhydride content and relatively high molecular weights are necessary to achieve enhancement in polypropylenes mechanical properties.

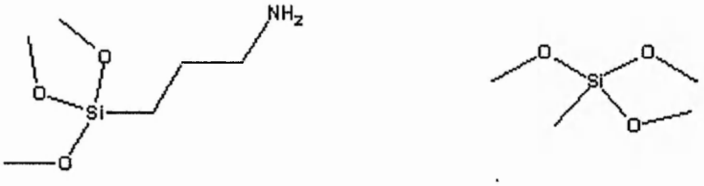
Table 5.2
Tensile yielding strength and modulus of raw polypropylenes with organoclay Cloisite 15A and different MAH-g-PPs

Material	Yielding Strength, MPa			Relative Young's Modulus, GPa		
	Average	σ*	n**	Average	σ	n
PP1	33.55	0.54	5	1.000	0.11	5
PP1+3%Cloisite 15A+5%E-43	31.82	0.68	5	0.546	0.01	5
PP1+3%Cloisite 15A+5%PB3200	31.47	0.63	5	0.615	0.08	5

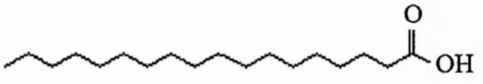
*Note: *σ - standard deviation, **n – number of specimens tested*

5.2.1.4 Investigation of some other chemicals used as compatibilizers

Previous studies found that blending organoclays, MAH-g-PP and unmodified PP together can produce clay/polypropylene nanocomposites. However the extent of intercalation is not great. This may be because the grafted polypropylenes and the polypropylenes are not completely compatible. In order to improve the compatibility between the PP, MAH-g-PP and organoclays, some other chemicals were also selected as compatibilizers to produce clay/PP nanocomposites because their functional groups are compatible to both the organoclays and polypropylenes. Three commercially available chemicals, 3-aminopropyltriethoxysilane (APTES), methyltrimethoxysilane (MTMS) and stearic acid (SA), were investigated. Their structures are shown in Fig 5.12.



(A) APTES (B) MTMS



(C) SA

Fig 5.12 The structure of three commercially available chemicals: (a) 3-Aminopropyltriethoxysilane (APTES); (b) Methyltrimethoxysilane (MTMS); (c) Stearic Acid (SA)

The composites produced contained 3 wt% organoclay Cloisite 93A, 4 wt% MAH-g-PP Polybond 3200, 1 wt% chemical used, and polypropylene PP1. They were extruded by the twin-screw extruder under the conditions of 210 °C, 15% feeding rate, 24/1 L/D ratio and 500 rpm screw speed. The clay dispersions in the composites were characterized by X-ray diffractometry using Cr as radiation source. The XRD patterns are shown in Fig 5.13.

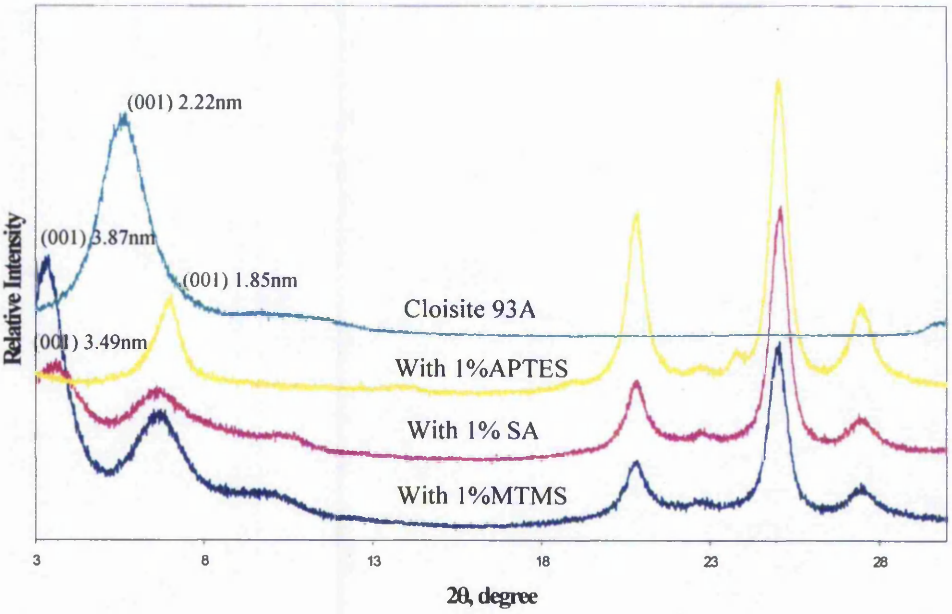


Fig 5.13 XRD patterns of the extruded products produced contained different chemicals under the extrusion condition of L/D ratio 24/1, temperature 210 °C, feeding rate 15% and screw speed 500 rpm (Cr radiation source).

It can be seen that the layer expansion has occurred for the composites contained 1wt% stearic acid (SA) and 1 wt% methyltrimethoxysilane (MTMS). The interlayer spacings of clay layers were expanded from 2.22nm for the pure organoclay to 3.49nm for the composite containing SA and 3.87nm for the composite containing MTMS respectively. The slight changes in the interlayer spacing are an indication that intercalated nanocomposites have been obtained for the composites containing MTMS and SA. However, for the composite containing 1 wt% *3*-aminopropyltriethoxysilane (APTES), the interlayer distance of the clay decreased from 2.22nm to 1.85nm. There is no intercalation occurred. The decrease of the interlayer distance may be associated with the release of the water absorbed between clay layers since the organoclay Cloisite 93A was used as received without drying. The XRD patterns show that the order of efficiency in intercalation is as following: MTMS >SA>APTES.

The colour of the extruded products was also studied. The photographs of the extruded products are shown in Fig. 5.14. The composite with the APTES has the darkest colour. This result matched the XRD data that adding APTES resulted in a low efficiency of intercalation. The degradation of the animo-group in APTES during melt processing may be responsible for the low efficiency in intercalation.

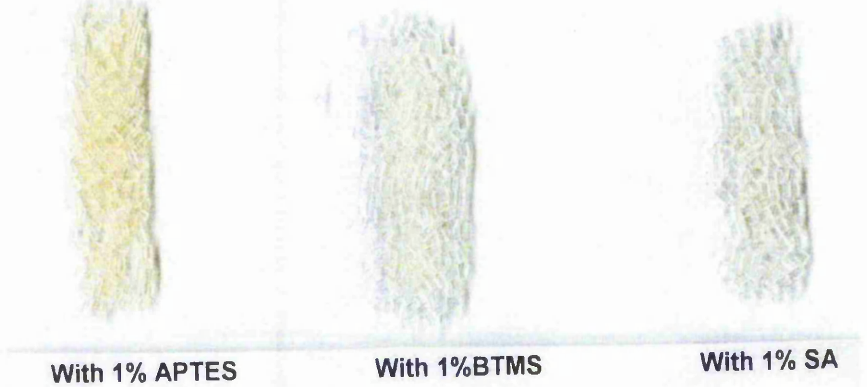


Fig 5.14. The colour changes in the composites contained different chemicals

The extent of intercalation is not large when either the MTMS or the SA was used to improve the compatibility between both the organoclay and PP. The colour of the extruded polypropylene did not change when MTMS and SA were added.

This investigation demonstrates that "compatibilizer" plays an important role in intercalation and exfoliation of clay in PP and the choice of "compatibilizer" can affect the colour of the product. However the organoclay, Cloisite 93A, selected in this study may not be compatible with methyltrimethoxysilane or stearic acid since Cloisite 93A does not contain any –OH groups. Similar results would be expected for Cloisite 15A for the same reason.

5.3 The effects of processing conditions on intercalation

All the work studied previously was focused on the importance of the different clays, polypropylenes used and the compatibility and chemical interactions between the clay and the polymers, without including the role of processing. This section will discuss the influences of melt processing parameters, specifically on the role of shear and residence time, on nanostructure formation during the melt processing of clay/polypropylene nanocomposites.

The materials selected for this study were capable of forming nanostructures but the quality of the nanocomposites was not important. Blends of polypropylene, PP1, maleic anhydride grafted polypropylene Epolyene Wax E-43 and the Na^+ based hydrophilic montmorillonite Nanocor clay G-105PGW were used for the experiments. The clay G-105PGW was used as received. Intercalated nanocomposites with an extent of layer expansion of the clay between 1.2 nm and 1.7 nm, depending on the concentration of the PP-g-MAH, were produced.

To investigate the role of processing parameters on the nanostructure formation, the twin-screw extruder and the melt flow index (MFI) test equipment were used for melt processing experiments. The two techniques have significant differences in mixing, melt flow and shear rate. Hence the data obtained may be applicable to wide range of melt processing techniques.

To investigate the role of shear in the nanostructure formation, the original polypropylene PP1, 5wt% clay G-105PGW and 5wt% MAH-g-PP E-43 were extruded together to produce composites using both the MFI equipment and the twin-screw extruder at different extruder speeds but at the same processing temperature. The processing temperature used was 200°C. A feeding rate of 10% and L/D ratio of 24/1 were used on a twin-screw extruder. Two different extruder screw speeds, 200 rpm and 500 rpm, were used to produce the composites by using twin-screw extruder. The Melt Flow Index test was carried out at 200°C with a 2.16kg load. The shear rate for the MFI test is very low. The dispersion of clay was studied by X-ray diffractometry using Cu as radiation source. The XRD patterns of the PP/ MAH -g- PP /clay composites are shown in Fig 5.15. The extent of layer expansion is shown to be independent of the processing method and shear rate. In all cases, the (001) peak shifted from the original 7.38° to 6.76°. The intensity of the peak is influenced by shear rate. The increase of shear rate tends to reduce the peak intensity. A similar tendency has been found in other experiments for processing a poly(styrene/acrylic) system [Vaia et al., 1993]. These results demonstrate that the role of shear during processing is to reduce the stacking height of tactoids rather than the enhancement of layer expansion.

The influence of residence time on the nanostructure formation was studied by extruding the material a number of times using both the MFI equipment and the twin-screw extruder.

The same materials extruded in different cycles by twin-screw extruder under the conditions of 200°C, 10% feeding rate, 24/1 L/D ratio and 200 rpm screw speed have the same extent of layer expansion. There is little difference in the layer stacking height between the materials extruded in different cycles using the twin-screw extruder. However, differences can be seen for the samples extruded at low shear rate using the MFI equipment. Figure 5.16 shows the the XRD patterns of the composites extruded using the MFI facility in different cycles. These results show that the low shear rate of the MFI test will reduce the stacking height of tactoids to the levels achieved by the extruder but require longer residence times to do so.

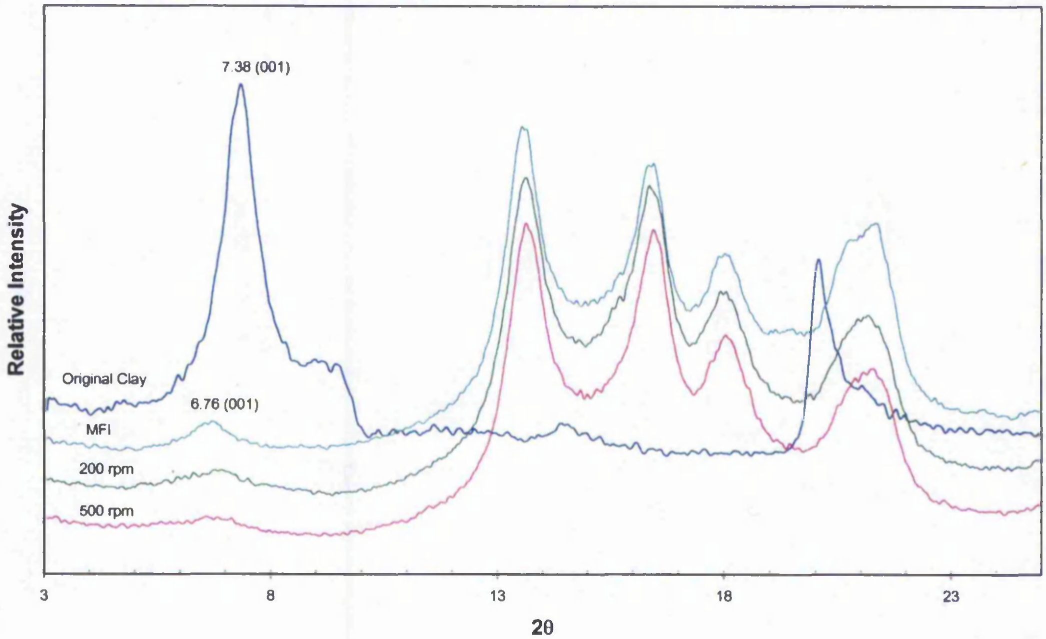


Fig. 5.15. XRD patterns of PP/PP-g-MAH/clay composites produced using MFI and the twin-screw extruder (Cu radiation source).

The results obtained show that the expansion of clay layers, during melt processing, is still mainly determined by the compatibility and chemical interactions between the clay and the polymers. Melt processing allows the molten polymer to flow into the capillary channels of the clays and this occurs at very early stage in the melt processing. The major action of the extruder in processing is to break down the large clay particles into smaller tactoids with higher aspect ratios. Improving the compatibility between clay and polymers to enable the polymer to flow into the clay galleries is still a major problem.

To check the validity of the results all the experiments described were repeated. The results achieved were found to be reproducible.

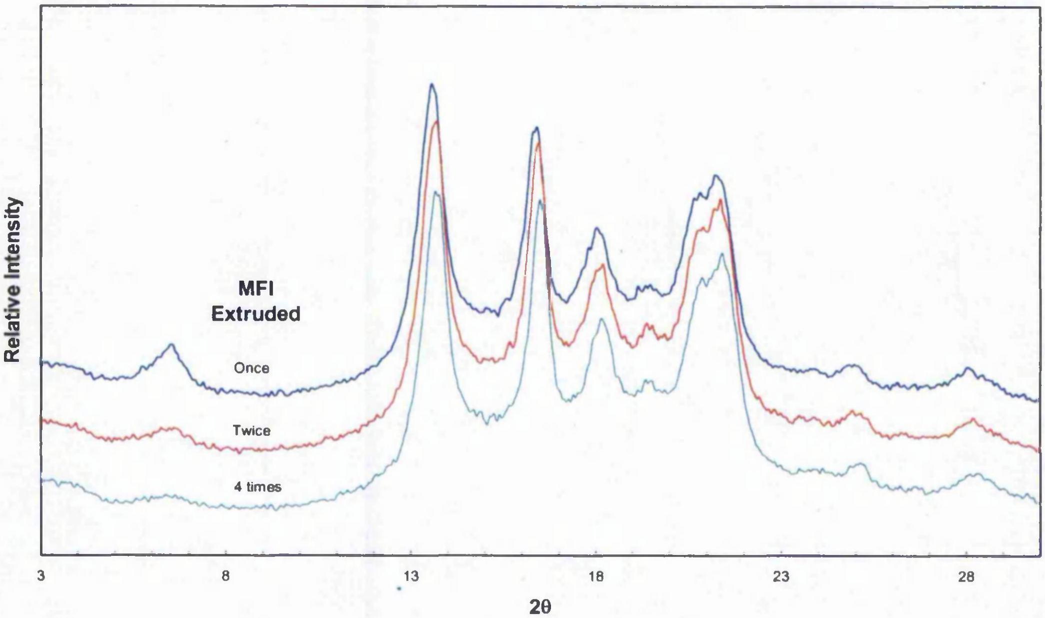


Fig.5.16. XRD patterns of PP/PP-g-MAH/clay composites extruded using MFI in different cycles (Cu radiation source).

5.4 Conclusion

The effects of stabilizers, compatibilizers and processing conditions on melt processing of clay/PP nanocomposites have been extensively studied. The study on adding stabilizers to organoclay/PP1 nanocomposites, via direct melt intercalation, showed only slight improvements in the layer expansion of the clay. The lack of efficiency of stabilizers in intercalating with the clays is due to the fact that the stabilisers did not contain suitable functional groups. In clay/polymer nanocomposite processing, the ammonium salts in the organoclays degrade first and cause degradation of the polymer. The effective approach to prevent this should be the mechanism for preventing organoclay degradation rather than PP degradation or for producing organoclays that are more thermally stable. None of the stabilizers examined have produced nanocomposites with enhanced mechanical properties compared to polypropylene. The stabilizers examined have not enhanced intercalation of the clays in the polymer, however careful choice of the stabilizer could prevent the composite discolouring during processing.

Using MAH-g-PP as compatibilizer to blend clay, MAH-g-PP and unmodified PP together is a solution to producing clay/polypropylene nanocomposites. This approach is capable of introducing intercalation and the dispersed clay layers could exhibit reinforcement effects. However these reinforcement effects are negated because commercial PP-g-MAHs, with relatively high MAH contents, normally are low molecular weight materials which when blended with polypropylenes, suitable for commercial forming, produce composites with inferior mechanical properties. As a consequence, no improvement in the mechanical properties can be made.

The study on processing parameters showed that melt processing alone provides suitable conditions which allows the polymer melt to flow into the capillary channels of the clays. This occurs at very early stage in melt processing. The major action of the extruder in processing is to break down the large clay particles into smaller tactoids with high aspect ratios. Layer expansion of clay in melt processing is still mainly determined by the compatibility and chemical interactions between the clay and the polymers.

CHAPTER 6 Solid Intercalation/Melt Processing Technique

The above study in producing clay/PP nanocomposites by using existing technology investigated several model synthetic methods. These methods include direct intercalation between clay and polymers, intercalation between maleic anhydride grafted polypropylene and polypropylene, and compatibiliser assisted melt intercalation. In addition, the effects of processing conditions and stabilisers on the melt intercalation were studied. These studies provided a fundamental understanding of the mechanisms of intercalation and their relation to the engineering properties of the nanocomposites. Based on the understanding obtained in the model synthetic study, a new synthetic technology, solid intercalation/melt processing, has been developed. Solid in-situ polymerization/melt processing utilises the high efficiency of intercalation in in-situ polymerisation and allows processing using conventional polymer processing equipment.

6.1 The methodology used for solid intercalation/melt processing

The mechanical and physical properties of composites are determined by the structure of the materials. The limited mechanical improvement in the composites studied so far in this thesis is mainly due to the limited interlayer spacing expansion achieved using the current methods for producing clay/polypropylene nanocomposites. In order to achieve high-performance composites, it is necessary to further expand the clay layers in the clay/polymer composites. Researchers in this field have found that more effective layer expansion and exfoliation can be achieved by in-situ polymerisation compared to melt intercalation [Pinnavaia, T.J. et al., 2000]. The layer expansion and exfoliation in in-situ polymerisation are more uniform than when using melt processing, resulting in higher efficiency of intercalation. However, it is difficulty to apply in-situ polymerization in industry due to the time-intensive preparation process, relatively complicated processing procedures and environmental pollution which increase the application costs.

Based on this analysis, a new concept called Solid Intercalation/Melt Processing (abbreviation SIMP) was developed in this study to produce clay/polypropylene nanocomposites. This concept utilised the advantages of the high efficiency of intercalation in in-situ polymerisation and the easy processing characteristics of melt intercalation. The process combines the two techniques together but uses a very small amount of monomer in the in-situ polymerisation. The monomer used can have a different structure to the monomer of the polymer but it must be compatible to the polymer. Since the amount of monomer used in the in-situ polymerisation is very small, the polymerisation process can be carried out essentially in solid clay.

Compared to the traditional in-situ polymerisation, the solid intercalation/melt processing technique does not require expensive in-situ polymerisation equipment and has little health and safety concerns. In a real manufacturing process, the solid in-situ polymerisation can be carried out in a traditional blender plus wind tunnel to transport the raw materials into the extruders. The advantages of this technique over traditional melt intercalation should be that organoclay degradation could be avoided, the master batch produced can be used in relative high temperatures and high efficiencies in intercalation should be achieved.

The design of this method, in a real manufacturing process, is illustrated in Fig 6.1. The in-situ polymerisation is carried out in a traditional blender in solid clay by introducing small amounts of monomer and initiator. The master batch produced and the PP can be transported into the extruders through wind tunnels. This method will be suitable for existing extrusion equipment without expensive upgrading because in-situ polymerisation equipment is not required.

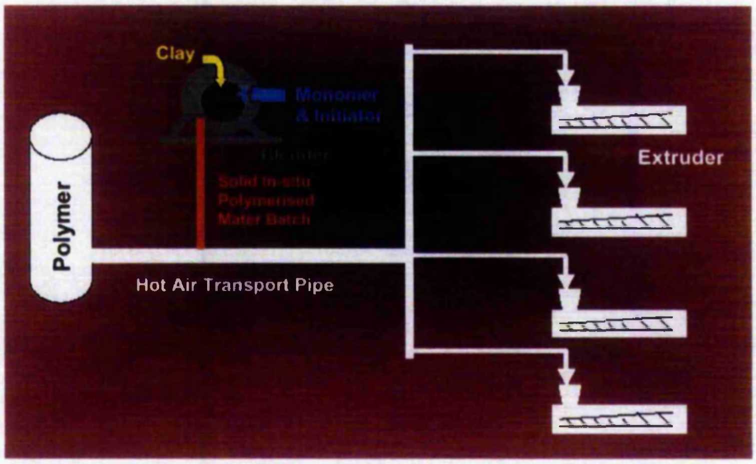


Fig 6.1. An example of solid intercalation/melt processing in a real manufacturing process.

6.2 Details of the processing method

Laboratory experiments were used to verify the feasibility of the solid intercalation/melt processing technique. A liquid monomer which was, inexpensive, readily available and compatible with polypropylene was required. Glycidyl methacrylate was selected for this study. The monomer contains 100ppm monomethyl ether hydroquinone as inhibitor and 0.2% epichlorohydrin and 1% R-glycidol.

The method developed in this study is outlined in Fig 6.2. The method comprises of the master batch preparation by in-situ polymerization in solid clay and melt intercalation of the master batch and PP. The master batch was firstly prepared and used for the newly developed solid intercalation/melt processing technique (SIMP). In this master batch production, the organoclay and monomer were blended in a plastic bottle containing stainless steel balls. The bottle was rotated in a co-rotating twin-roller machine at 30 rpm for 20 minutes. Dibenzoyl peroxide (BPO) was added as the polymerisation initiator and the bottle was further rotated for 1 hour. The mixture was finally reacted in a vacuum oven overnight at 60 °C. The Organoclay Cloisite 93A, monomer glycidyl methacrylate and initiator BPO were used to produce the master batches for this technique. The content of monomer used was 15 wt% while the content of BPO used is in a range between 0.3 wt% and 3.0 wt%. The content of BPO which delivered the best results in this study was 0.8 wt%. The master batch thus produced was in powder form, which appeared similar to the original organoclay.

This master batch was then used in melt processing of polypropylene. The polypropylene used was original polypropylene PP1. The polymer and master batch were pre-mixed in a plastic bag and then extruded using the twin-screw extruder at 235 °C, 5% feeding rate, 500 rpm screw speed and 24/1 L/D ratio.

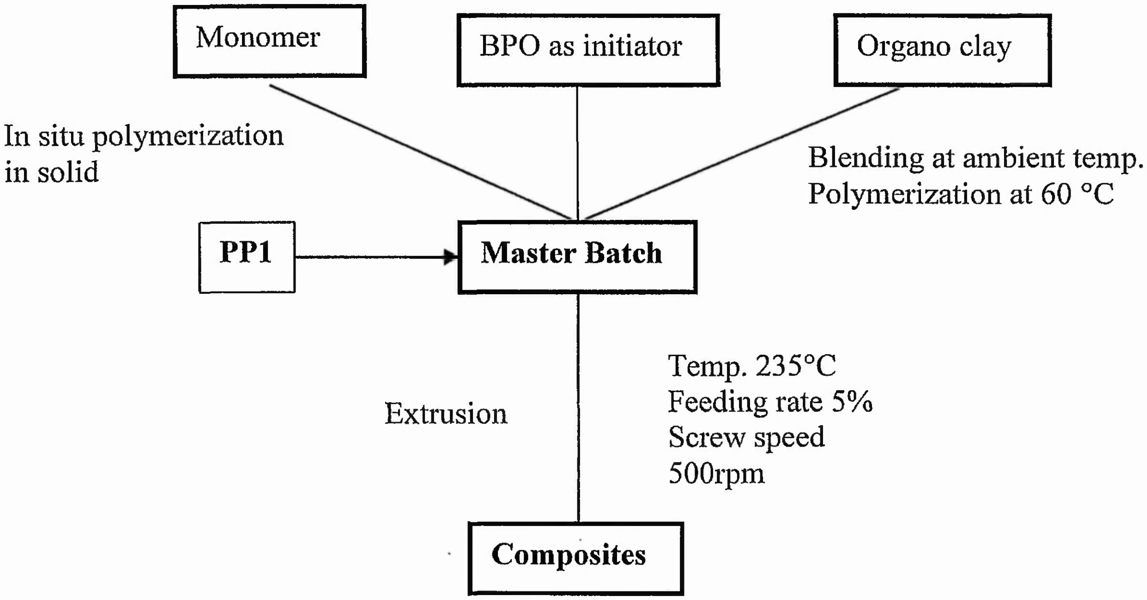


Fig. 6.2. Solid intercalation/melt processing method developed in this study

6.3 Nanostructure formation of the composites produced by SIPMP

The effect of different master batch loadings on the formation of nanocomposites using the SIPMP method was investigated. Three composite materials were produced. These composites contained 3 wt%, 5 wt% and 10 wt% Cloisite 93A based master batches respectively and were extruded by twin-screw extruder under the conditions of 235 °C, 500 rpm screw speed, 5% feeding rate and 24/1 L/D ratio. The nanostructure of the extruded materials together with the master batch was characterised by X-ray diffractometry using Cu as radiation source. The results are shown in Fig. 6.3. The layer expansion occurred in the solid intercalation/melt processing process. According to the (002) peak of the master batch sample, the interlayer spacing changed from the original 2.2 nm for organoclay to 3.2 nm for master batch. For the three extruded composite products containing 3 wt%, 5 wt% and 10 wt% master batches, the (001) peak completely disappeared. The X-ray diffractometry had a minimum scanning angle at 3°. Previous experiments have shown that it is difficult to find any (001) peaks using wider or smaller angle XRD equipment if no tail of the (001) peak can be observed using this equipment at 3°. Based on this knowledge, it appears that nanocomposites with a high extent of exfoliation may be obtained by using this SIPMP method.

The solid intercalation/melt processing method has great potential for producing nanocomposites with high efficiency in layer expansion. The master batch produced may become a good "media" for the further incorporation of PP into organoclay layers. The weak bonding between the layers of the organoclay was broken by the in-situ polymerisation. The monomer, glycidyl methacrylate, used is compatible to the polypropylene PP1. So the polymerized poly(glycidyl methacrylate) intercalated into the organoclay during solid in-situ polymerisation, expanded clay galleries, and facilitated the incorporation of polypropylene via melt processing by twin-screw extruder.

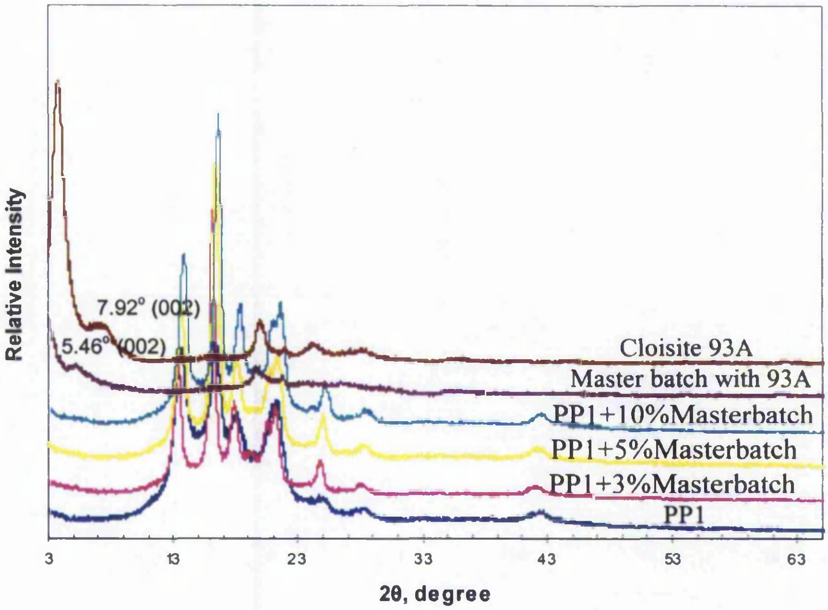


Fig 6.3. XRD patterns of organoclay Cloisite 93, the master batch produced by solid in-situ polymerisation and the extruded composites produced from PP1 and the master batch with different loadings under the extrusion condition of L/D ratio 24/1, feeding rate 5%, Screw speed 500 rpm and temperature 235 °C (Cu radiation source).

It should also be pointed that the colour of the extruded products did not change during processing up to temperature of 235 °C. In previous experiments, using the Cloisite 93A, the extruded products became significantly darker when processed above 220 °C. The master batch prepared is more thermally stable than Cloisite 93A and this suggests that organoclay degradation is not a problem for such composites produced by this new technique.

The nanocomposite products were subjected to tensile testing. Fig 6.4 shows the yielding strength of the nanocomposites produced. The tensile yielding strength of the nanocomposites was improved compared to the original polypropylene. There was about 10% improvement in the yielding strength when 3 wt% of the master batch was used in the composite but little improvement made with 5 wt% master batch. At higher concentrations of master batch the tensile strength of the composites decreased.

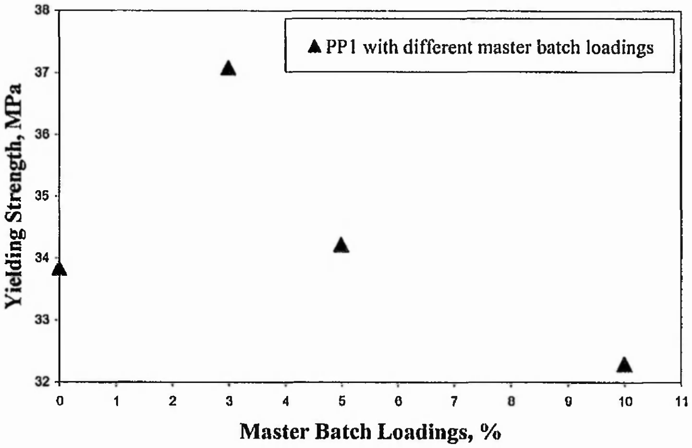


Fig. 6.4. Yielding Strength behaviour of the composites produced by the solid intercalation/melt processing with different master batch loadings.

The increase in tensile yielding strength may originate from the homogeneous dispersion of the clay layers in the nanocomposites and the possible avoidance of clay degradation at the high processing temperature. The thousands of dispersed layers acted as reinforcing components in this nanocomposite. The highest extent of layer expansion was achieved for the nanocomposite containing 3 wt% master batch. This may be because the clay is able to disperse better in the polymer and form composites with exfoliated clay layers. The tensile yielding strength of the nanocomposites decreased as the master batch loadings increased because the clay layers have insufficient space to exfoliate and form intercalated structures instead. When producing the master batch by in-situ polymerisation, the monomer has to get into the clay layers before it is polymerised. The size of the molecule and how it is transported into the clay layers will affect the molecular weight of the polymer. If the monomer can get between the clay layers and evenly coat the clay before polymerisation it would be expected that the length of the polymer chains could be similar, however if this does not happen a large range of molecular weights for the polymer chains may result.

The Young's modulus of the material was also investigated and the results are shown in Fig 6.5. The Young's modulus of these nanocomposites produced by PP1 and different master batch loadings via SIPMP was not improved. This might be due to the low extent of chain extension during polymerisation of the glycidyl methacrylate, resulting in a low molecular weight of poly(glycidyl methacrylate) during in-situ polymerisation. This will be investigated further in section 6.4 by adding different amounts of initiator in the monomer for master batch preparation.

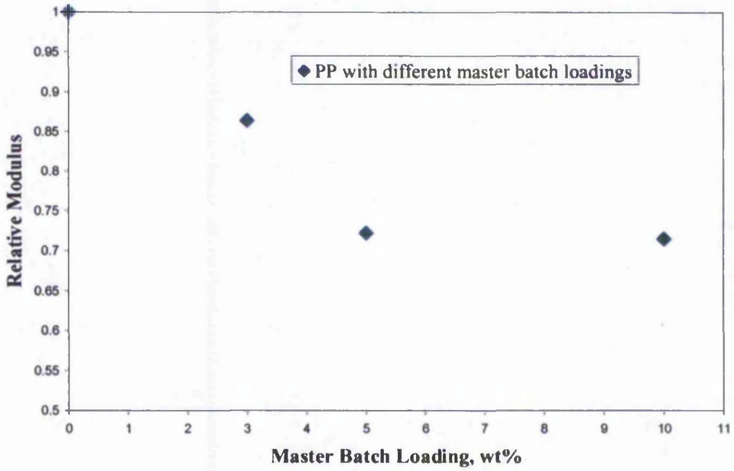


Fig. 6.5. Young's Modulus of the composites produced by solid intercalation/melt processing with different master batch loadings.

6.4. The effect of initiator concentration

In order to find out the reasons why the modulii of the nanocomposites produced by SIPMP method decreased, different composites were synthesised and investigated by adding different contents of the initiators. The purpose of this study was intended to control the molecular weight of poly(glycidyl methacrylate) during the solid in-situ polymerisation for preparation of the master batch.

The monomer glycidyl methacrylate, organoclay Cloisite 93A and initiator BPO were used to produce master batches in this section. The monomer concentration in clay was 15wt%. The concentration level of the initiator in the monomer was 0.3 wt%, 0.5 wt%, 0.8 wt%, 1.2 wt%, 2.5 wt% and 3.0 wt% respectively. The master batches were produced as described before in section 6.2. The original polypropylene used was PP1. PP1 and 3 wt % master batch were pre-mixed and then extruded using a twin-screw extruder under the extrusion condition as used previously in section 6.3.

The XRD patterns and the tensile properties of the composites were measured. The XRD patterns shown in Fig 6.6 indicate that there is very little difference between

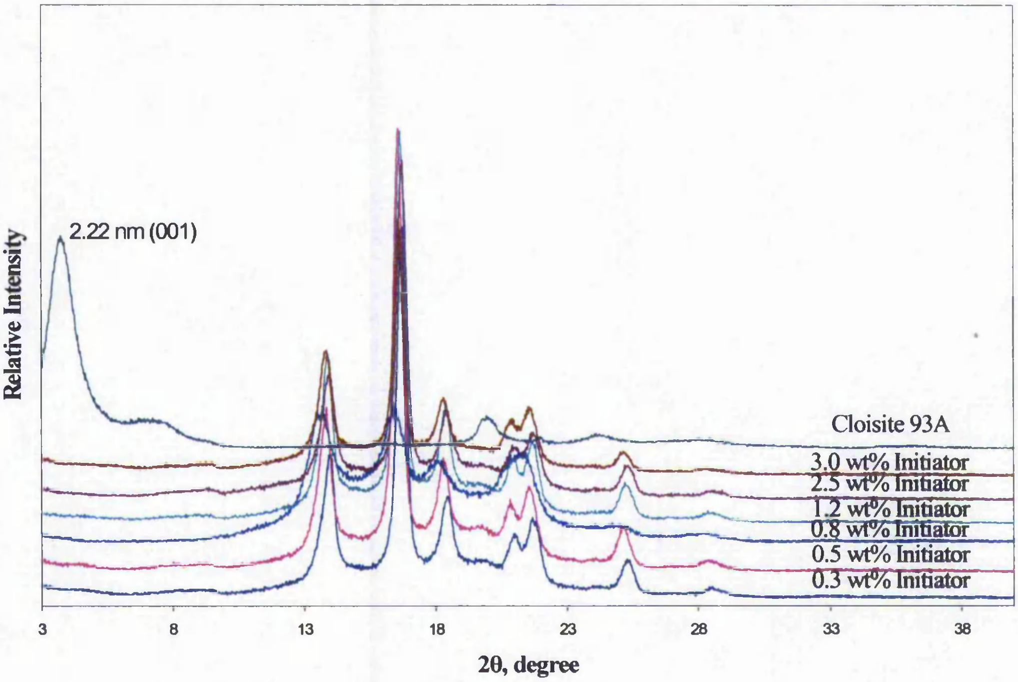


Fig 6.6. XRD patterns of organoclay Cloisite 93A and the extruded composites produced from PP1 and 3 wt% master batch with different concentrations of initiators under the same extrusion condition applied in section 6.3 (Cu radiation source).

the composites prepared with different initiator loadings from 0.3 wt% to 3.0 wt%. The (001) peak completely disappeared for all the extruded composites. The nanocomposites with a high extent of exfoliation structure may be obtained in all cases by the SIPMP method. The molecular weight of poly(glycidyl methacrylate) during the solid in-situ polymerisation is different due to different initiator concentrations. The differences in molecular weight of poly(glycidyl methacrylate) could have an influence on the extent of layer expansion in the nanocomposites produced. However, the (001) peak of clay cannot be observed in the XRD patterns for such nanocomposites with high extent layer expansion.

Table 6.1 shows the yielding strength and Young's modulus of the materials studied. The tensile yielding strength of these nanocomposites increases as the concentration of initiator increases up to 0.8 wt%, above this initiator concentration the tensile strength decreases. The Young's modulii of the composites are similar but lower than the value of the original polypropylene PP1. It appears that the mechanical properties of the composites are a function of the molecular weight of the polymerised

Table 6.1
Tensile yielding strength and modulus of the composites produced by SIPMP with different initiator concentrations

Material	**Yielding Strength, MPa**			**Relative Young's Modulus, GPa**		
	Average	**σ***	**n****	**Average**	**σ**	**n**
PP1	32.70	0.97	6	1.000	0.18	6
PP1+3%Master Batch(0.3%initiator)	31.86	0.98	6	0.785	0.02	6
PP1+3%Master Batch(0.5%initiator)	35.63	1.92	6	0.742	0.07	6
PP1+3%Master Batch(0.8%initiator)	37.08	1.25	8	0.742	0.02	8
PP1+3%Master Batch(1.2%initiator)	33.13	0.76	6	0.760	0.07	6
PP1+3 wt% Master Batch(2.5%initiator)	31.53	2.13	6	1.071	0.05	6
PP1+3 wt% Master Batch(3.0%initiator)	32.52	1.09	6	0.725	0.05	6

Note: *σ - standard deviation, **n – number of specimens tested.

products during solid in-situ polymerisation. When the initiator concentration increases up to 0.8wt% the size of the polymer chains may increase leading to the improvement of the tensile yielding strength. This may occur because there are larger polymer chains between the clay layers which increases the compatibility of the polypropylene with the clay and improves the exfoliation of the clay. However, further increases in the initiator concentrations may cause cross-linking and this will make it more difficult for the polypropylene to expand the clay layers further. The result of this being that the yielding strength is reduced.

The termination reactions of the free radical polymerisations are usually by combination of two free radicals or disproportionation, the former being the most common. During the polymerisation reaction the monomer will be used up and the polymer chains will terminate by combination of two free radicals, providing two are close enough together. The termination reactions can produce cross-links between polymer chains particularly when the free radicals are constrained, which may be the case between the clay layers. A full study of the mechanism of this in-situ polymerisation has not been undertaken and the effect of the clay on the reaction. Further work in this area may help resolve some of the problems encountered.

The results suggest that the modulus of the material could be improved if the polymerised product, poly(glycidyl methacrylate), formed in the solid in-situ polymerisation has sufficient large molecular weight without cross linking. Based on this investigation, it seems that it is very difficult to avoid cross-linking occurring when high initiator concentrations are simply added under the current polymerisation conditions. In order to achieve high molecular weight polymerised products, the effect of different master batch synthesis conditions was studied.

6.5 The effect of the processing conditions on master batch synthesis

The possibility for improving the extent of chain extension during polymerisation of monomer glycidyl methacrylate was explored. The aim was to produce high molecular weight poly(glycidyl methacrylate) during the solid in-situ polymerisation. Different experimental conditions were used to produce the master batch.

The organophilic clay, monomer and a range of monomer concentrations were used. The same clay as before, Closites 93A, was used for master batch production.

The concentration of the initiator in the monomer was 0.8wt%. The technique used to produce the master batch was the same as the conditions discussed in the previous sections. The master batch mixture was prepared by blending a mixture of clay, monomer and initiator at ambient temperature for 1 hour. Three different sets of conditions were applied to control the polymerisation of the monomer. Under condition A, the mixture of clay, monomer and initiator were placed in the vacuum oven immediately after blending on a co-rotating twin-roller machine and reacted at 60 °C for sixteen hours under high vacuum. These experimental conditions were used in the previous tests. For condition B, the blended mixture was left at room temperature for 72 hours in a lidded container before being placed in a vacuum oven and dried under vacuum at 60 °C for sixteen hours. In Condition C, the blended mixture was heated in the oven without any vacuum at 60 °C for 2 hours.

The purpose of using different conditions for master batch production is to control the molecular weight of the polymerised products. The Conditions A were used in previous experiments but there was concern that unreacted monomer may have evaporated under the high vacuum conditions used. Under vacuum at elevated temperatures the monomer will have a reduced boiling point and could be lost, reducing the amount of polymerisation occurring in the master batch. So the design of Conditions B were used to allow the polymerisation to proceed at ambient temperatures for 72 hours to try to improve the degree of polymerization before the evaporation of unreacted monomer under high vacuum at 60 °C. The use of condition C is intended to allow polymerization to occur in air at 60 °C for a short time without any vacuum to avoid the evaporation of monomer.

The original polypropylene PP1 and the master batches produced using different conditions were extruded using the twin-screw extruder under conditions described in section 6.3. Their structures can be seen in Fig 6.7. The (001) peaks

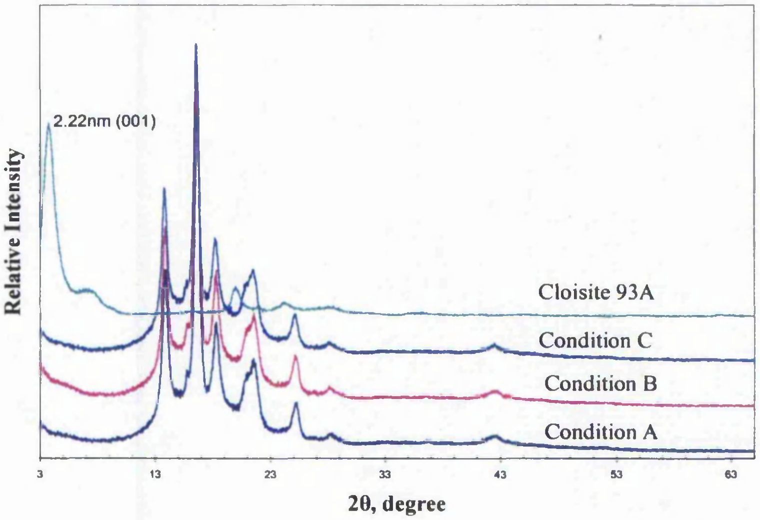


Fig 6.7. XRD patterns of organoclay Cloisite 93A, the extruded composites produced from PP1, 3 wt% master batch produced by different master batch preparation conditions under the same extrusion condition applied in section 6.3 (Cu radiation source).

of all the samples completely disappeared and there is very little difference between the XRD patterns of the composites. It appears that nanocomposites with a high extent of exfoliation might be obtained for all the extruded composites produced from PP1 and the 3 wt% master batches produced using different master batch preparation conditions by this SIPMP method.

However the effect of the different conditions for master batch synthesis can be found in the mechanical properties of the composites. The tensile yielding strength and Young's modulus of these extruded nanocomposites can be seen in Table 6.2. The material containing the master batch produced under Conditions A show the best tensile yielding strength. There is a small decrease for the nanocomposite containing the master batch produced by Conditions B while the nanocomposite containing the master batch produced under Conditions C has similar values to the base polypropylene.

Table 6.2
Tensile yielding strength and modulus of raw polypropylenes and their clay composites

Material	**Yielding Strength, MPa**			**Relative Young's Modulus,GPa**		
	Average	**σ***	**n****	**Average**	**σ***	**n****
PP1	31.90	01.73	6	1.000	0.02	6
PP1+3%Master Batch(condition A)	37.08	1.25	8	0.864	0.02	8
PP1+5%Master Batch(condition B)	34.74	1.50	6	0.733	0.01	6
PP1+3%Master Batch(condition C)	31.84	0.80	5	0.658	0.01	5

*Note: *σ - standard deviation, **n – number of specimens tested.*

Condition A: The mixture of master batch was heated at 60 °C in the oven with vacuum for 16hrs;

Condition B: The mixture of master batch was left at room temperature for 72 hrs before heated in the oven with vacuum further 16 hrs;

Condition C: The mixture was heating in the oven without vacuum for only 2 hours.

During the production of the master batch produced under conditions B some of monomer may have evaporated from the clay during storage for 72 hours at room temperature so that there was very little monomer left to polymerise at 60 °C. Alternatively it could be an effect of chemical reactions in the system. The monomer had an inhibitor added. The inhibitor would prevent premature polymerisation of the monomer and any free radicals in the system would be removed by it. Once the inhibitor had been used up any free radicals formed would allow polymerisation of the monomer to occur. If polymerisation occurred in this way there would have been very little monomer left to polymerise when heated to 60°C. There are also the possibilities of other reactions between the organoclays and the free radicals which could affect the propagation and termination reactions of this system, and depending on the reaction energies required could affect the molecular weight of the polymer produced. Any of these factors may have resulted in low molecular weight polymerized polymer and a decrease in the mechanical properties of the nanocomposite produced.

The mechanical properties of the nanocomposite containing master batch produced under "condition C" decreased dramatically. This may be due to the monomer not being fully blended into the clay so that when polymerisation occurs the monomer is on the clay surface and has not penetrated into the clay layers. The inhibitor would be used up rapidly at elevated temperatures and the polymerisation would occur rapidly so that polymerisation was limited to the exposed surfaces of the clay.

Vacuum appears to be very important during polymerisation processing. When a monomer is heated under vacuum at elevated temperatures its boiling point is reduced, which in a polymerisation would result in a loss of monomer and a reduction in the molecular weight of any polymer formed. Vacuum will remove oxygen from the system which might otherwise cause premature termination of the polymerisation reactions and result in low molecular weight products.

The results of the mechanical properties for the composite produced under Conditions A appear to balance the detrimental effects of vacuum and premature termination with the advantages of allowing the monomer to be well blended into the clay so it can penetrate into the clay layers.

The Young's modulus of these nanocomposites has still not been improved due to the low molecular weight of polymerized product during the solid in-situ polymerisation. Optimization of the polymerisation reaction is critical to the success of this technique.

6.6 The effect of the removal of inhibitor from the monomer glycidyl methacrylate

As discussed above, the initiator concentration of 0.8 wt% has been shown to be the best condition for application in this method so far. But the degree of polymerisation is not enough to improve the material's Young modulus. By adding a high initiator concentration, the cross-linking is unavoidable. If the degree of the polymerisation can be further increased, the tensile yielding strength and Young modulus should both be improved further. The "inhibitor" inside the monomer will always prevent the monomer's polymerisation. Removal of the inhibitor in the monomer during solid in-situ polymerisation may lead to higher degrees of chain extension during the polymerisation process. The inhibitor inside the monomer glycidyl methacrylate, monomethyl ether hydroquinone, was removed by 4wt% sodium hydroxide solution.

6.6.1 The removal of inhibitor in monomer

A 100ml of the monomer glycidyl methacrylate was shaken with an equal volume of dilute sodium hydroxide solution (4 wt% by weight) in a separating funnel. The sodium hydroxide was decanted off and the monomer washed twice with equal volumes of deionised water. The monomer was dried by shaking in a stoppered conical flask with anhydrous sodium sulphate. The inhibitor free monomer was then used in the polymerization reaction.

6.6.2 The nano structure of the composites produced by removing inhibitor

The inhibitor free monomer was used in order to achieve high degree of chain extension during the solid in-situ polymerisation process. The organoclay, Cloisite 93A, 15 wt% inhibitor free monomer, glycidyl methacrylate, and 0.8 wt% initiator BPO were used to produce master batch using "Conditions A" as discussed above. Original PP1 and 3 wt % master batch were then extruded using the twin-screw extruder as the same processing conditions as used previously. The layer dispersion of organoclay in the composites produced by PP1 and 3 wt% master batch with and without the removal of the inhibitor in the monomer was characterized by X-ray diffractometry using Cr as radiation source. The XRD patterns are shown in Fig 6.8.

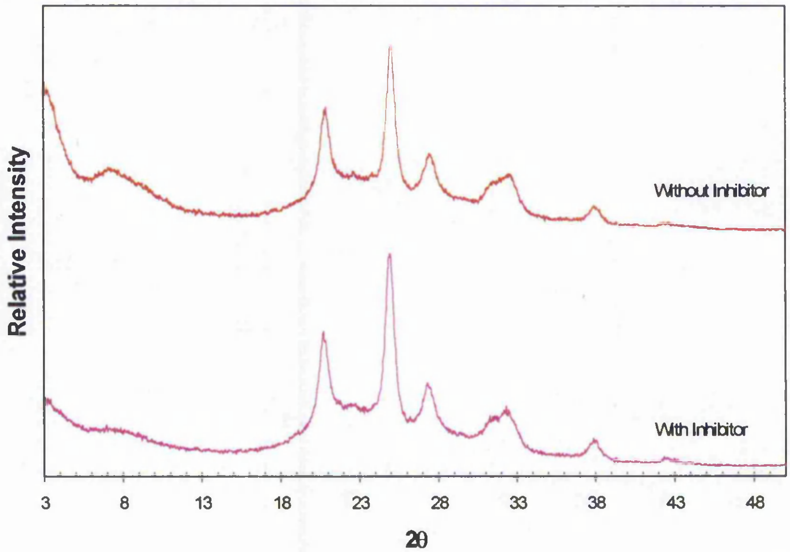


Fig 6.8. XRD patterns the composites produced from PP1, 3 wt% master batch loading produced using in situ polymerisation/melt processing with and without the removal of inhibitor in the monomer as the extrusion conditions discussed above (Cr radiation source).

Intercalation has occurred in both cases as the (001) peak of these two composites has moved to angles below 3°. The results show that better layer expansion/exfoliation was achieved in the nanocomposite without removing the inhibitor because the slope of the tail is quite flat. Removing the inhibitor did not result in better improvement in clay intercalation because the tail of the (001) peak is still visible. This may be associated with the polymerisation rate. The rate of the polymerization reactions was too rapid after the removal of inhibitor in monomer glycidyl methacrylate. The monomer did not have time to penetrate into the clay layers before it was polymerised therefore the efficiency of exfoliation was then affected.

6.7 The use of organoclay Cloisite 15A to produce clay/PP nanocomposites by SIPMP

The organoclay Cloisite 15A has the higher extent of layer expansion than Cloisite 93A. However, the clay layer of Cloisite 15A was found difficult to expand by using direct reactive melt intercalation as discussed in section 4.2.2 and 5.2.1.3. Cloisite 15A was thought to be strongly bonded between the clay layers and hence is difficult to expand further to reinforce the mechanical properties of the nanocomposites produced by the direct melt intercalation method. The solid intercalation/melt processing technique, has the potential to break the strong bondings between clay layers in Cloisite 15A and lead to a property enhancement of the composites. The potential of using Cloisite 15A to produce clay/PP nanocomposites by SIPMP is studied in this section.

A master batch was prepared by sold in-situ polymerisation of organoclay Cloisite 15A and monomer glycidyl methacrylate. The monomer concentration used in clay was 15wt% and the concentration of the initiator in the monomer was 0.3 wt %, 0.8 wt % and 1.2 wt % respectively. Polypropylene PP1 and 3 wt % master batch were then extruded using the twin-screw extruder as the same processing conditions as described in section 6.3.

The XRD patterns of the organoclay Cloisite 15A and the extruded composites produced from PP1 and 3 wt% master batch with different initiator concentrations can be seen in Fig 6.9. It is difficult to find any tail of (001) peak of the composites. This

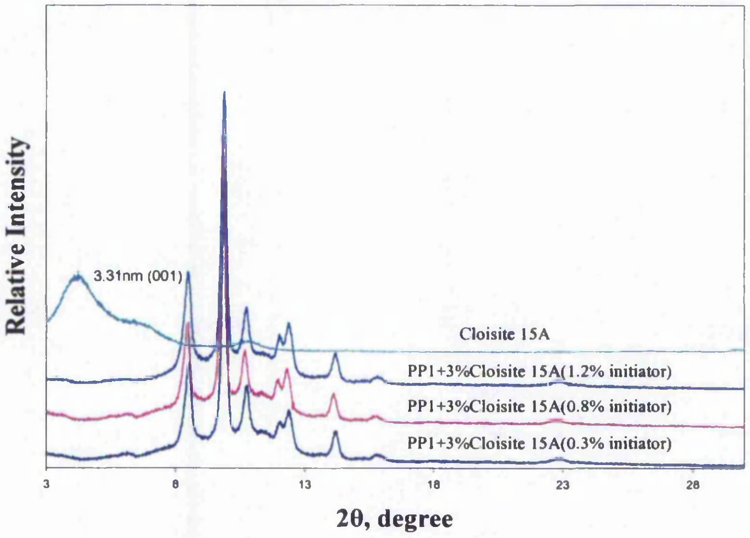


Fig 6.9. XRD patterns of organoclay Cloisite 15A, the extruded composites produced from PP1, 3 wt% master batch produced by different initiator concentrations under the extrusion condition of L/D ratio 24/1, feeding rate 5%, Screw speed 500 rpm and temperature 235 °C (Cr radiation source).

indicates that a high extent of exfoliation has occurred in the nanocomposites produced. The mechanical properties of the composites have been investigated. The results are shown in Table 6.3.

There is a little improvement in the mechanical properties compared to the polypropylene PP1 when 0.8wt% initiator is used for Cloisite 15A master batch synthesis. The nanocomposite produced with 0.8% initiator was still produced the best composite.

The mechanical properties of polypropylene PP1, Cloisite 15A/PP1 nanocomposites produced by the direct melt processing technique, Cloisite 15A master batch/PP1 nanocomposite using solid intercalation/melt processing

Table 6.3
Tensile yielding strength and modulus of nanocomposites produced by Cloisite 15A via solid intercalation/melt processing.

Material	**Yielding Strength, MPa**			**Relative Young's Modulus, GPa**		
	Average	**σ***	**n****	**Average**	**σ***	**n****
PP1	32.70	1.49	6	1.000	0.12	6
PP1+3%Cloisite15A	32.48	1.14	6	0.884	0.19	6
PP1+3%Master Batch(0.3% initiator)	30.73	1.99	6	0.746	0.05	6
PP1+3%Master Batch(0.8% initiator)	33.71	2.15	6	0.705	0.01	6
PP1+3%Master Batch(1.2% initiator)	32.15	1.45	6	0.676	0.07	6

*Note: *σ - standard deviation, **n – number of specimens tested.*

technique (SIPMP) and Cloisite 93A master batch/PP1 nanocomposite using SIPMP were compared and the results have been shown in Fig 6.10.

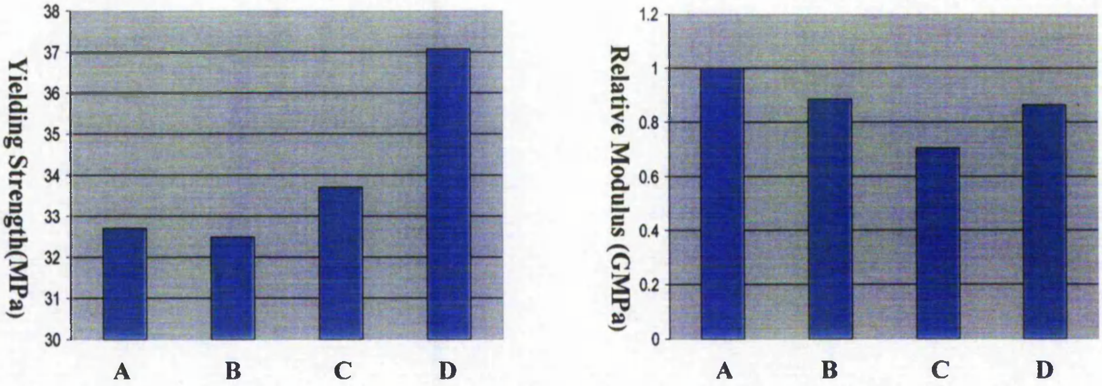


Fig 6.10 The comparison of mechanical properties at the same extrusion conditions: (A) Original PP1; (B) PP1+3 wt% Cloisite 15A (Direct Melt Intercalation); (C) PP1+3 wt% Cloisite 15A Master Batch(0.8 wt% initiator)(SIPMP technique); (D) PP1+3 wt% Cloisite 93A Master Batch(0.8 wt% initiator)(SIPMP technique).

The results show that the SIPMP method is able to produce nanocomposites with improved yielding strengths that are better than that of the original polymer. The SIPMP method produces better composites than the direct intercalation method. However, the improvement in the nanocomposites containing the organoclay Cloisite 15A is not as good as the improvement in the composites containing organoclay Cloisite 93A. The bonding between Cloisite 15A clay layers is very strong and even the solid intercalation/melt processing intercalation can not achieve any further expansion of the clay layers. Cloisite 93A is still the best of the current clays available for producing by the SIPMP method.

The results have also shown that neither the direct reactive melt processing technique or the newly developed solid intercalation/melt processing technique can be effective in reinforcing material's Young's modulus. The polymerisation conditions applied have not reached the optimum. A high extent of polymerisation will form a cross linked polymer, which will not benefit to clay/polypropylene intercalation. A low extent of polymerisation will form low molecular weight structures leading to a decrease in the mechanical properties of clay/polypropylene nanocomposites. Further optimisation is required and there is a need to find an alternative monomer for using in the solid intercalation/melt processing technique.

6.8 Conclusion

The solid intercalation/melt processing technique has produced composites with improved nanostructure and tensile yielding strengths by using the monomer glycidyl methacrylate. This promising approach offers high efficiency in intercalation at relatively low processing costs. The successful application of this method depends on the monomer used and the control of in-situ polymerisation reaction. The lower Young's modulus may be associated with control of the polymerisation reaction and its effect on the molecular weight of the polymer. Optimisation of this reaction is critical to developing this method commercially.

CHAPTER 7 Nylon Assisted Melt Intercalation Technique

7.1 The method of Nylon Assisted Melt Intercalation Technique

In addition to solid intercalation/melt processing (SIMP), another technology has been developed. This technology was named the Nylon Assisted Melt Intercalation. The principle of this technology is to use the advantage of easy exfoliation of clay in nylon and to transfer the exfoliated structure into polypropylene. The process developed is shown in Fig 7.1.

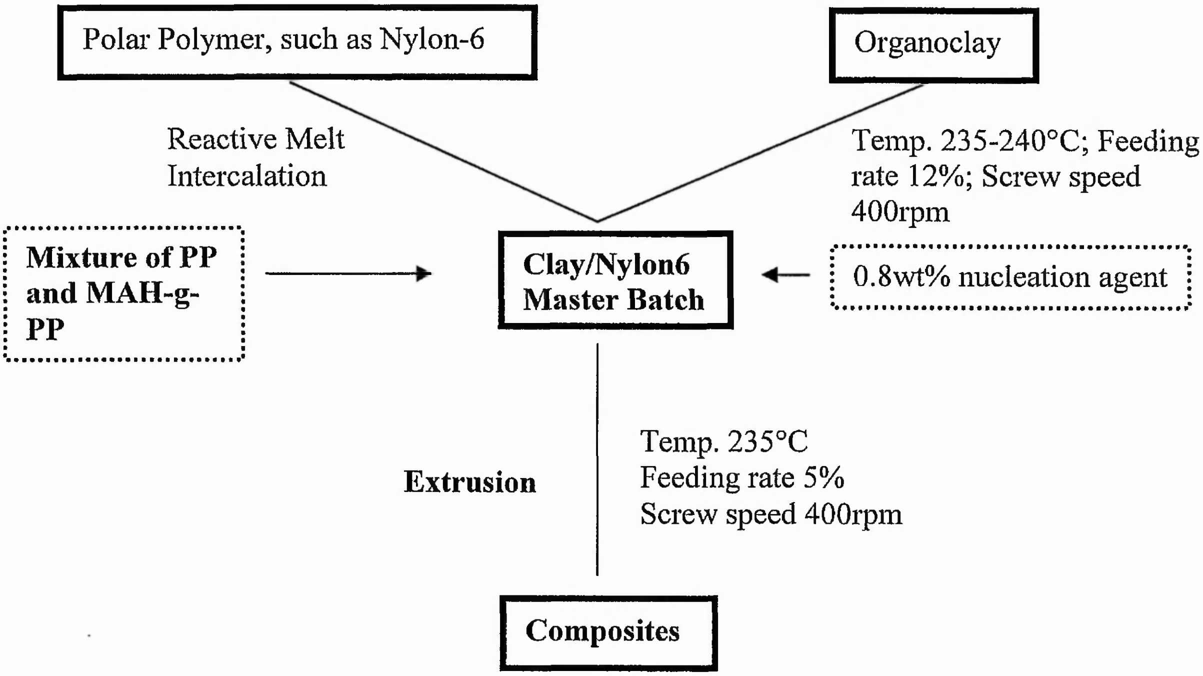


Fig 7.1 Schematic illustration of Nylon6 Assisted Melt Intercalation Technique

This nylon assisted melt intercalation method comprises of the clay/nylon6 master batch preparation and melt intercalation of the clay/nylon6 master batch with polypropylene. Nylon 6 is a wildly used and relatively inexpensive material. Clay/nylon 6 nanocomposites with exfoliated structures can be easily produced from organoclays modified by ammonium cations and nylon 6 using both in-situ polymerization and reactive melt intercalation methods [Okada, A. et al., 1990;

Kojima, Y. et al., 1993 (a) and 1993 (b); Dennis, H.R. et al., 2001; Usuki, A. et al., 1993]. A clay/nylon nanocomposite was used as master batch to produce clay/PP nanocomposites in this study. The exfoliated structure was transferred into the polypropylene through the clay/nylon master batch. The master batch was produced from quaternary ammonium chloride modified Cloisite organoclays and a commercial nylon 6 supplied by BASF AG using direct reactive melt extrusion. The melting range of the nylon 6 was between 220°C and 280°C. The clay/nylon 6 master batch was produced using a 16 mm twin-screw extruder with 24/1 L/D ratio. The processing temperature varied between 235°C and 240°C from the feeder to the die and the screw speed was 400 rpm. A pelletiser was used to produce composite pellets. Different Cloisite organoclays and different clay loadings were used to produce clay/nylon 6 master batches.

This clay/nylon6 master batch produced was then used in melt processing of polypropylene. The polypropylene used was polypropylene PP1. Maleic anhydride grafted PP MAH-g-PP was used to improve the compatibility between the surface of polypropylene and the clay/nylon6 master batch. Different MAH-g-PP concentrations were investigated in order to improve the compatibility between the polypropylene and the master batch. The nucleation agent, sodium benzonate (SB) with a concentration of 0.8wt%, was used in this study to control the crystallization of polypropylene during melt extrusion. The clay/nylon/PP composites were produced using a 16 mm twin-screw extruder under the extrusion conditions of 235°C, 5 % feeding rate, 400 rpm screw speed and 24/1 L/D ratio.

7.2 The clay/nylon-6 master batch

From processing details discussed above, it can be seen that in this nylon assisted melt intercalation, the concentration of clay in the clay/nylon 6 master batch would influence the nanostructure formation and its mechanical property enhancements of the clay/nylon/PP composites produced. If high clay contents are used to produce the clay/nylon 6 master batches, aggregation of the organoclay may take place. The consequence of this would be that, exfoliated nanostructures may not be formed in the master batch. This non-uniformly dispersed master batch structure may not be able to enhance the mechanical properties of the clay/nylon 6/PP composites. Also if the clay concentrations in the master batches are too low they may have insufficient clay to produce good clay/nylon/PP composites. The nylon concentration in the clay/nylon/PP composite needs to be controlled because the nylon matrix and polypropylene are incompatible so too much nylon may lead to a significant decrease in mechanical properties of the final products.

The effect of clay loading on clay layer expansion and exfoliation in nylon matrix was studied. Clay/nylon 6 master batches with 3wt%, 5wt% and 10wt% clay loadings were produced using reactive melt extrusion. The organoclay studied here is Cloisite 93A. The extrusion conditions are described in section 7.1.

The change of the organoclay structure in the polymer following melt extrusion was studied using X-ray diffraction using Cu as radiation source. The original nylon 6 was also extruded for comparison purposes. Figure. 7.2 shows the XRD patterns of the organoclay 93A, extruded nylon 6 and clay/nylon 6 master batches with 3wt%, 5wt% and 10wt% clay contents respectively. The organoclay has a characteristic (001) peak at 3.96° which corresponds to interlayer spacing 2.22 nm. Following the extrusion, the (001) peak moved to angles below 3° in all the composites. As discussed previously, the XRD equipment has a limit of 3° and cannot examine peaks lower than this. However the tail of the (001) peak of the clay for the composite with 10wt% can be seen very clearly, this suggest there must be a peak which cannot be seen. This may indicate that only an intercalated nanostructure was obtained with 10wt% organoclay Cloisite 93A. The small tail of the (001) peak of the clay for the composite with 5wt% clay loading may indicate that this composite comprises intercalated structure, possibly with a combination of both exfoliated and intercalated structures. Exfoliated nanostructure may have been obtained for the composite with 3wt% clay content because the tail of (001) peak of the clay is not visible in the XRD pattern.

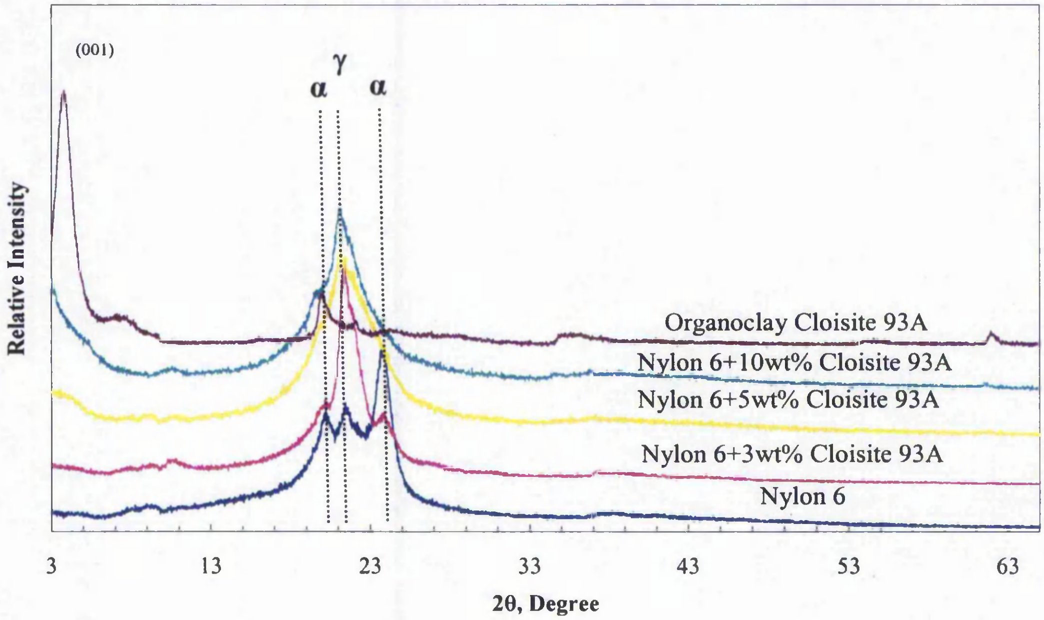


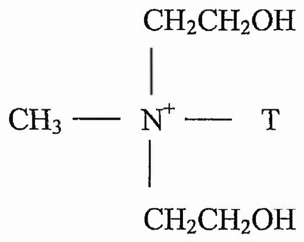
Fig 7.2. XRD patterns of the composites produced from Nylon, 3 wt% , 5 wt% and 10 wt% Cloisite 93A under the condition of L/D ratio 24/1, feeding rate 12%, Screw speed 400 rpm and temperature 235-240 °C. (Cu source)

This XRD patterns also show the change of crystal structure of the materials. There are three peaks in the XRD pattern of the extruded nylon-6. The two peaks at 20.3° and 24° are the characteristic peaks of the α phase of the crystalline polymers structure while the peak at 21.5° is associated with the γ phase. For the composites with 3wt%, 5wt% and 10wt% clay loadings, the intense peaks of the α phase disappears, merging with the γ peak to form a broadened peak with high intensity at 21.5° in the XRD patterns. Similar results have been obtained by a number of researchers for clay/nylon 6 nanocomposites produced by both in situ polymerisation and melt processing. The change of the crystal structure from α to γ phase was explained to be the consequence of conformational changes of the polymer chains due to intercalation with clays and the limited formation of H-bonded sheets.

Based on the results obtained from Fig 7.2, the clay content used to produce clay/nylon 6 master batches should not exceed 10 wt% because aggregation of the clay may take place. A clay/nylon 6 master batch with 3 wt% clay loading would be ideal for the reinforcement of PP because uniformly exfoliated nanostructures have been obtained for this master batch. However, almost a 40 wt% master batch is required to produce clay/nylon 6/PP composites in order to keep 1.2 wt% clay content level in the clay/nylon 6/PP composites. The pure nylon 6 matrix content thus might be too high in this clay/nylon 6/PP composite. In order to minimize the content of nylon 6, high clay loadings are necessary to produce the clay/nylon 6 master batch.

7.3 The effect of clay type on the exfoliation of clay/nylon 6 master batch

Other than Cloisite 93A, another clay was studied to see its potential to produce exfoliated master batch structures. This was the organoclay Cloisite 30B. The molecular structure of Cloisite 30B organic modifier can be seen from Fig 7.3. The structure is different from organoclay Cloisite 93A as Cloisite 30B was modified using a different ammonium salt, methyl tallow bis-2-hydroxyethyl ammonium chloride. Theoretically organoclay Cloisite 30B should be more compatible with hydrophobic polymers than organoclay Cloisite 93A because organoclay Cloisite 30B has two hydroxyethyl groups that can react with polar polymers.



$$\begin{array}{ccccc} & & CH_2CH_2OH & & \\ & & | & & \\ CH_3 & — & N^+ & — & T \\ & & | & & \\ & & CH_2CH_2OH & & \end{array}$$

Fig 7.3 The molecular structure of the ammonium ion in Cloisite 30B

The effect of using organoclay Cloisite 30B on clay layer expansion and exfoliation was initially examined. Clay/nylon master batches with 3wt% and 5wt% clay loadings were produced using reactive melt extrusion. The processing conditions used to produce Cloisite 30B/nylon master batch was the same as the conditions discussed above for producing Cloisite 93A master batches. The structure of the clay/nylon 6 master batches and Cloisite 30B were characterised using X-ray diffractometry (XRD) using Cr as radiation source. The exfoliation of the different organoclays, Cloisite 93A and Cloisite 30B by nylon with different clay concentrations can be seen in Fig 7.4. The organoclay Cloisite 30B has a characteristic (001) peak at 7.06° which corresponds to interlayer spacing 1.86 nm. The (001) peaks of the master batches produced from Cloisite 30B and nylon 6 with both 3wt% and 5wt% clay loadings have moved to angles below 3°. Significant layer expansion has occurred.

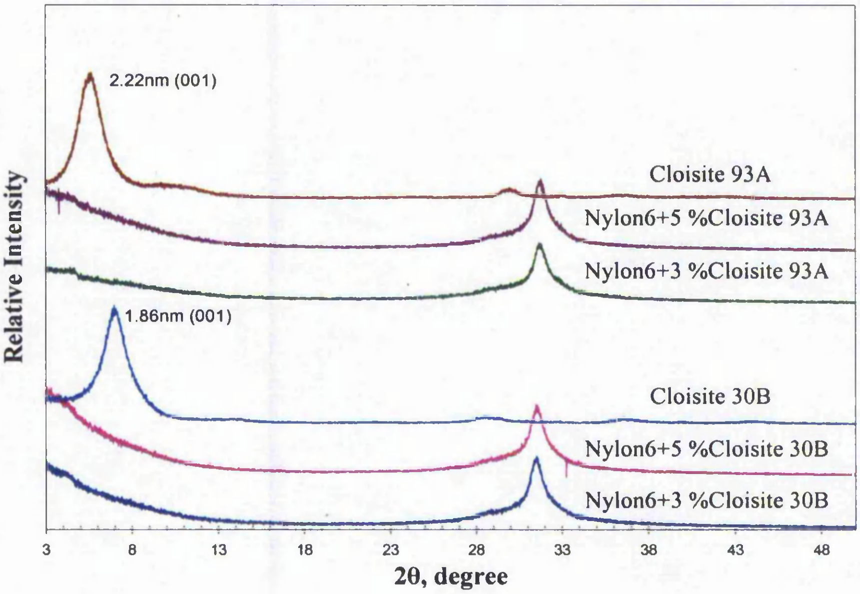


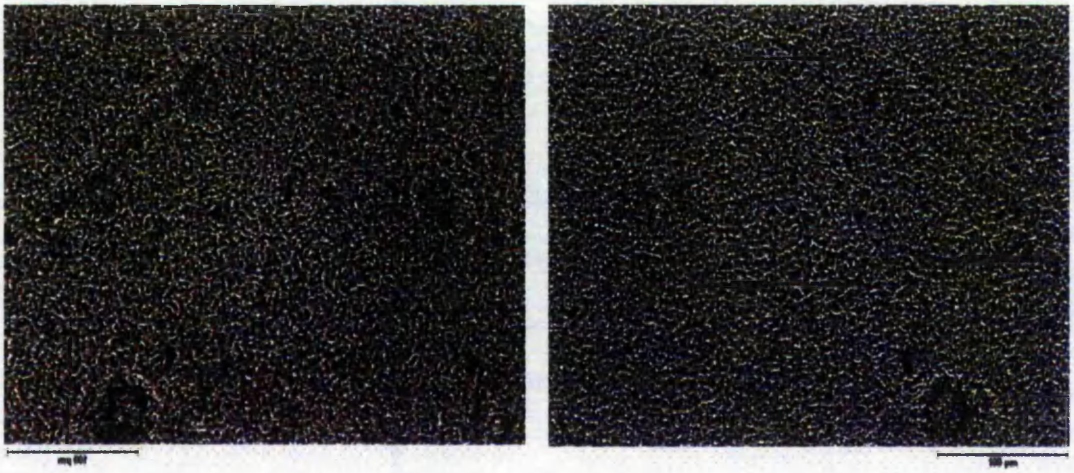
Fig 7.4 XRD patterns of clay/nylon master batches produced by nylon and 3wt%, 5wt% organoclays Cloisite 30B and Cloisite 93A using a twin-screw extruder under the same conditions discussed in Fig 7.2 (Cr source).

However, the tail of the (001) peak of the Cloisite 30B can still be seen very clearly for the master batches. The tail of the (001) peak of the Cloisite 93A can only be seen for the master batch produced with 5wt% of Cloistie 93A while the (001) tail for the master batch containing 3wt% Cloisite 93A cannot be seen. The results suggest that Cloisite 30B's clay layers do not expand as much as those of Cloisite 93A. This result is not as expected. Theoretically Cloisite 30B should be more compatible to hydrophobic nylon 6 than Cloisite 93A because Cloisite 30B it has two hydroxyethyl groups that can react with nylon 6. The results suggest that for some reason the nylon cannot penetrate into the clay layers effectively. One reason may be that some unknown additives inside the commercially available nylon are not compatible to organoclay Cloisite 30B. This study was a preliminary one and further work is needed to understand the mechanism of the reactions between the Closiste 30B and the nylon.

7.4 The compatibility between nylon and polypropylene

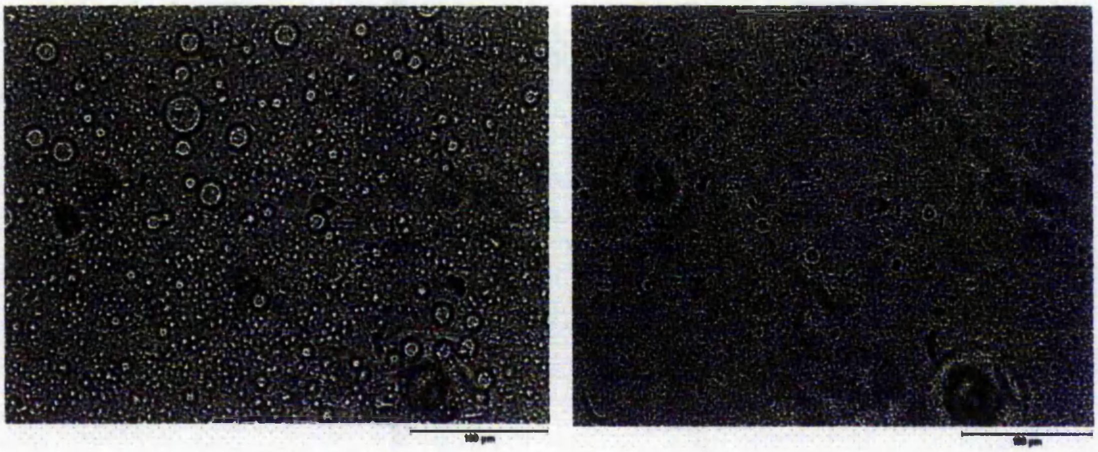
The compatibility between nylon 6 and PP was investigated. Optical microscopic images of the polypropylene PP1, pure nylon 6, a mixture of the pure PP/ pure nylon6 and a composite produced from the polypropylene PP1 and the clay/nylon 6 master batch with 10wt% MAH-g-PP PB3200, were examined using a Leica optical microscope. The micrographs can be seen in Fig 7.5. The PP/nylon 6 mixture and the composite were all extruded by twin-screw extruder using the extrusion conditions of 235°C, 5 % feeding rate, 400 rpm screw speed and 24/1 L/D ratio.

The incompatibility between pure PP and pure nylon 6 can be seen from Fig 7.5 (C) .There are two separate phases in the mixture of polypropylene and nylon 6 which can be seen. However, the compatibility between PP and nylon 6 was improved when the Cloisite 93A/Nylon master batch with the compatibiliser added, the structure is a lot finer as can be seen from Fig 7.5 (D). This suggests that the clay and the compatibiliser break up the nylon and polypropylene matrices so the two polymers are more intermingled.



(A) Pure PP1

(B) Pure nylon



(C) PP1 + nylon6

(D) PP1 + master batch (5%clay+nylon) + 10wt% MAH-g-PP

Fig 7.5 The optical microscopy observations of original polypropylene (A); pure BASF ultramide nylon6 (B); the mixture of PP/nylon (C); the clay/nylon/PP composite produced by clay/nylon master batch and PP1 with adding 10wt% MAH-g-PP Polybond PB-3200 (D) .

Why the formation of exfoliated clay/nylon master batch can help to improve the compatibility of PP and nylon is not fully understood. The exfoliation of clay/nylon master batch and adding compatibilizer Polybond PB-3200 are both thought to have an effect on the improvement in compatibility of the polymers.

7.5. The methodology applied to improve compatibility between nylon and PP

The compatibility between nylon and polypropylene is very important in enhancing the major engineering properties of the composites produced. This is because the presence of immiscible phases will lead to poor mechanical and thermal properties. There are two ways that can be used to improve the compatibility between nylon and polypropylene in this clay/nylon master batch filled clay/nylon/PP composite system. One way is to improve the degree of clay dispersion in the clay/nylon master batches. The dispersion of the clay layers in the clay/nylon master batch will mainly depend on the clay type and the clay concentration used. The type and concentration of the clay may also have effect on the compatibility between nylon and PP in the composites produced. The other way is to use a compatibilizer, for example MAH-g-PP, to improve the compatibility between the nylon 6 and the polypropylene. Maleic anhydride grafted polypropylene was used in this study as a compatibilizer to improve the compatibility between the polypropylene and the clay/nylon master batches. The following study focuses on these two methods to improve the compatibility between nylon and polypropylene.

7.6 The nanostructure formation and mechanical properties of clay/nylon/PP composites produced by nylon assisted melt intercalation

7.6.1 The effect of clay/nylon 6 master batch

The effect of clay content on the compatibility between nylon and PP was examined. Cloisite 93A was used to produce clay/nylon 6 master batches with clay contents of 3 wt%, 4wt%, 5wt%, 7wt% and 10wt%. The effects of these different master batches on the formation of clay/nylon/PP nanocomposites were investigated. In order to keep the sufficient clay content inside the composites, the amount of clay/nylon 6 master batch used to make the clay/nylon/PP composite was 25 wt%. The clay concentrations in the final clay/nylon/PP composites were about 0.75wt%, 1.0wt%, 1.25wt%, 1.75wt% and 2.5wt%. The polypropylene PP1, 25wt% master batch, 10wt% MAH-g-PP Polybond PB-3200 and 0.8wt% nucleation agent sodium benzoate were extruded by the twin-screw extruder using the extrusion conditions discussed in section 7.1.

The nanostructure of the composites was characterised using X-ray diffractometry (XRD) which used Cr as the radiation source. The results show that significant layer expansion and exfoliation occurred in all the cases because all the (001) peaks of the composites produced are not visible in the XRD pattern. The results in Fig 7.6 show that the nylon assisted melt intercalation was effective in layer expansion. All the clay layers appear to have been uniformly dispersed in the polypropylene-nylon 6 matrices. Nanocomposites with high degrees of layer expansion have been obtained for all the composites produced by this method. It is difficult to see any differences in the nanostructures formed from the XRD patterns for the nanocomposites containing different clay concentrations.

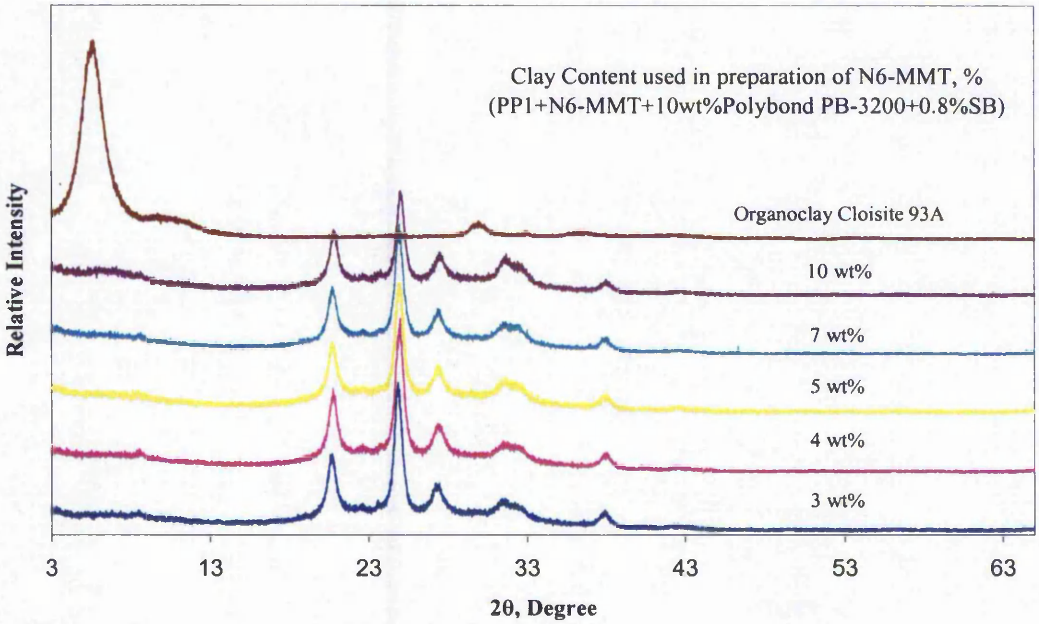


Fig 7.6. XRD patterns of the clay/nylon master batches containing different Cloisite 93A concentrations for the formation of clay/nylon/PP1 nanocomposites extruded by twin-screw extruder with 10wt% MAH-g-PP Polybond PB-3200 and 0.8wt% nucleation agent sodium benzoate under the extrusion condition of L/D ratio 24/1, feeding rate 5%, Screw speed 400 rpm and temperature 235 °C. (Cr radiation source)

The mechanical properties of the nanocomposites produced containing different clay contents were measured and the results are tabulated in Table 7.1. The tensile yielding strength and the relative Young's modulus of the nanocomposites have been improved for the nanocomposites produced from polypropylene and the clay/nylon6 master batches with clay concentrations up to 7%. However both the tensile yielding strength and Young's modulus have been found a decrease for the nanocomposite containing 10wt% Cloisite 93A. This maybe associated with the formation of an intercalated nanostructure for the clay/nylon 6 master batch containing 10wt% Cloisite 93A. As discussed in section 7.2, exfoliated nanostructure of clay/nylon 6 master batch can only be obtained when low clay loadings are used to produce this kind of master batch. When high clay loadings are used, for example 10 wt%, only intercalated nanostructures can be formed in the master batch.

Table 7.1.
Tensile yielding strength and modulus of nanocomposites produced by PP1 and clay/nylon master batches with different clay loadings

Material	**Tensile Yielding Strength (MPa)**			**Relative Young'sModulus (GPa)**		
	Average	**σ***	**n****	**Average**	**σ***	**n****
PP1	33.77	0.96	6	1.000	0.01	6
PP1+25wt%N6-MMT (3wt%Cloisite93A)+10wt% PB-3200+0.8wt%SB	34.13	1.20	3	1.040	0.01	3
PP1+25wt%N6-MMT (4wt%Cloisite93A)+10wt% PB-3200+0.8wt%SB	35.16	0.04	3	1.040	0.003	3
PP1+25wt%N6-MMT (5wt%Cloisite93A)+10wt% PB-3200+0.8wt%SB	36.93	0.30	3	1.080	0.005	3
PP1+25wt%N6-MMT (7wt%Cloisite93A)+10wt% PB-3200+0.8wt%SB	34.40	0.45	3	1.020	0.006	3
PP1+25wt%N6-MMT (10wt%Cloisite93A)+10wt% PB-3200+0.8wt%SB	33.38	0.35	3	0.865	0.010	3

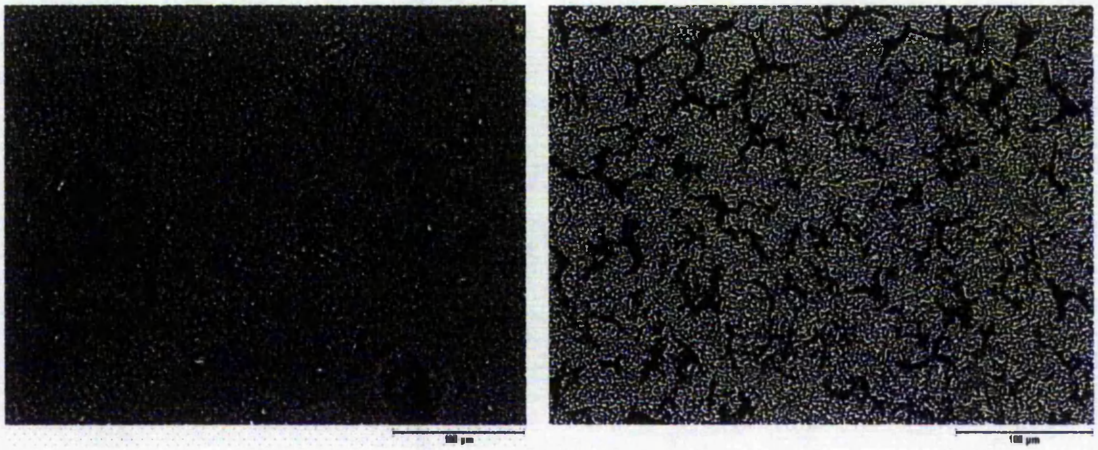
*Note: *σ - standard deviation, **n – number of specimens tested.*

In order to further explain the decrease of mechanical properties of the nanocomposites containing high clay contents, optical microscopic images of the nanocomposites produced from polypropylene and the master batches containing 5wt% and 10% Cloisite 93A clay loadings were examined (Fig 7.7). The same magnification was used as for the previous micrographs. The micrographs show that in the case of the composite with 10 wt% Cloisite 93A, degraded clay particles can be clearly seen. (Fig 7.7 (B)). This suggests this composite is a microcomposite with some intercalated clay. The presence of clay particles may be related to the fact that in the masterbatch the clay had been intercalated not exfoliated into the nylon 6, which has led to the master batch being less thermally stable than the other master batches which contained lower clay loadings. The consequence of this being that the organoclay has degraded during the melt processing to produce the polypropylene composites.

In contrast the structure of the nanocomposite of polypropylene with clay/nylon 6 master batch with a 5wt% Cloisite 93A concentration has a more integrated structure (Fig 7.7(A)). This is probably due the fact that the organoclay was fully exfoliated in the clay/nylon 6 master batch and was therefore more thermally stable and compatible to polypropylene. In this case when the polypropylene was extruded with the clay/nylon master batch degradation of the organoclay did not occur and a better exfoliated nanaocompoiste was formed. The compatibility between PP and nylon 6 can be much improved when exfoliated clay/nylon 6 master batch can be formed. Also the mechanical properties of the nanocomposites are better when exfoliated clay/nylon6 master batch were used.

It also can be seen that there is an optimum clay content for a clay/nylon 6 master batch to enhance the mechanical properties of a clay/nylon/PP nanocomposite. Although a fully exfoliated nanostructure has been obtained in the clay/nylon 6/PP composite using a master batch with 3wt% of Cloisite 93A, the mechanical properties of this nanocomposite are lower than for the nanocomposite produced with a master batch containing 5wt% of Cloisite 93A. The master batch with 5 wt% of clay had sufficient clay dispersed in the nylon 6 to achieve maximum reinforcement of the polypropylene nanocomposite. When the clay loadings in the master batches are high, for example 10wt%, the composite reinforcement is lower probably due to the clay being intercalated and not exfoliated in the nylon 6. Degradation of the organoclay during processing may also play a role in reducing the mechanical properties.

A clay loading of 5wt% Cloisite 93A was selected as the optimum clay concentration to be used in clay/nylon 6 master batches to produce better quality clay/nylon 6/PP nanocomposites when using this nylon assisted melt intercalation.



(A) FinaPP+25wt%(5wt%93A+Nylon6)+ 10wt%PB3200+0.8wt%nucleation agent

(B)FinaPP+25wt%(10wt%93A+Nylon6)+ 10wt%PB3200+0.8wt%nucleation agent

Fig 7.7 The optical microscopy observations of the clay/nylon/PP nanocomposite produced by PP1 and clay/nylon master batch containing 5wt% clay Cloisite 93A (A) and the clay/nylon//PP nanocomposite produced by PP1 and clay/nylon master batch containing 10wt% clay Cloisite 93A (B).

The effect of clay type on the compatibility between nylon and PP has also been examined. The clay/nylon/PP composites produced from Cloisite 30B were compared to the composite containing Cloisite 93A.The PP1, 25wt% clay/nylon6 master batch containing 5wt% Cloisite 30B, 10wt% MAH-g-PP PB3200 and 0.8wt% nucleation agent were extruded by the twin-screw extruder under the same extrusion condition used to produce the nanocomposites of Cloisite 93A. The nano-structures of the composites produced were characterised using XRD (Cr as radiation source) and the XRD patterns can be seen in Fig 7.8. Significant layer expansion and exfoliation occurred for both clays however it is impossible to see structural differences between the two composites because the (001) peaks are below the detection limit of the XRD.

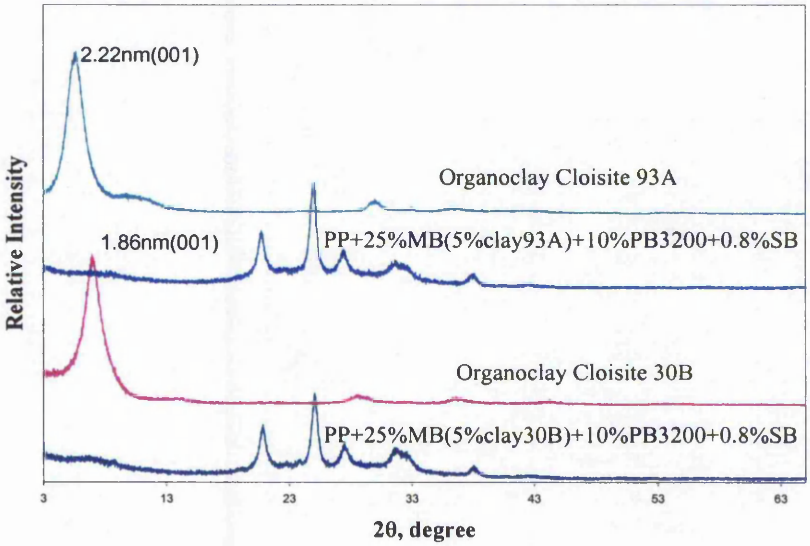


Fig 7.8 XRD patterns of clay/nylon/PP prepared by different organoclays via nylon assisted melt intercalation under the same extrusion condition discussed at Fig7.6 (Cr source).

Table 7.2 summarizes the tensile yielding strength and tensile relative Young's modulus of these clay/nylon6/PP nanocomposites. The results show that both the tensile yielding strength and the Young's modulus of clay/nylon/PP nanocomposite produced with Cloisite 30B are lower than those of the nanocomposite made by Cloisite 93A and the original polypropylene. This result agrees with the result obtained in section 7.2 that Cloisite 30B is not effective for producing Cloisite 30B/nylon 6 master batches to use to make polypropylene nanocomposites. Further mechanistic studies on Cloisite 30B are required to understand why this clay is not as compatible as Cloisite 93A with nylon 6 despite it having two hydroxyethyl groups in its structure.

Organoclay Cloisite 93A has proved to be the best of the commercial clays available, at the present time, for producing clay/nylon6/PP nanocomposites by the nylon assisted melt intercalation method.

Table 7.2
Tensile yielding strength and modulus of composites produced PP1 and clay/nylon6 master batch containing different organoclays

Material	**Yielding Strength (MPa)**			**Relative Young's Modulus (GPa)**		
	Average	**σ***	**n****	**Average**	**σ***	**n****
PP1	33.77	0.96	6	1.000	0.11	6
PP1+25wt%N6-MMT (5wt%Cloisite30B)+10wt% PB-3200+0.8wt%SB	31.61	1.14	3	0.875	0.015	3
PP1+25wt%N6-MMT (5wt%Cloisite93A)+10wt% PB-3200+0.8wt%SB	36.93	0.30	3	1.080	0.005	3

*Note: *σ - standard deviation, **n – number of specimens tested.*

7.6.2 The effect of MAH-g-PP on nylon assisted melt intercalation

The effect of MAH-g-PP concentration on the compatibility between nylon and PP was initially examined. Clay/nylon/PP composites with different concentrations of the compatibilizer PB3200 were produced using the nylon assisted melt intercalation technique. The clay Cloisite 93A at a concentration of 5wt% was used to produce the clay/nylon 6 master batch. This master batch was extruded with MAH-g-PP and polypropylene to produce the nanocomposites. The extrusion conditions used were the same as discussed in section 7.6.1. The concentrations of PB3200 used were 5 wt%, 10wt% and 20wt% respectively.

The XRD patterns (Cr source) of the composites produced can be seen in Fig 7.9. All the (001) peaks of the composites produced are not visible in the XRD patterns. Significant layer expansion and exfoliation has occurred in all the cases.

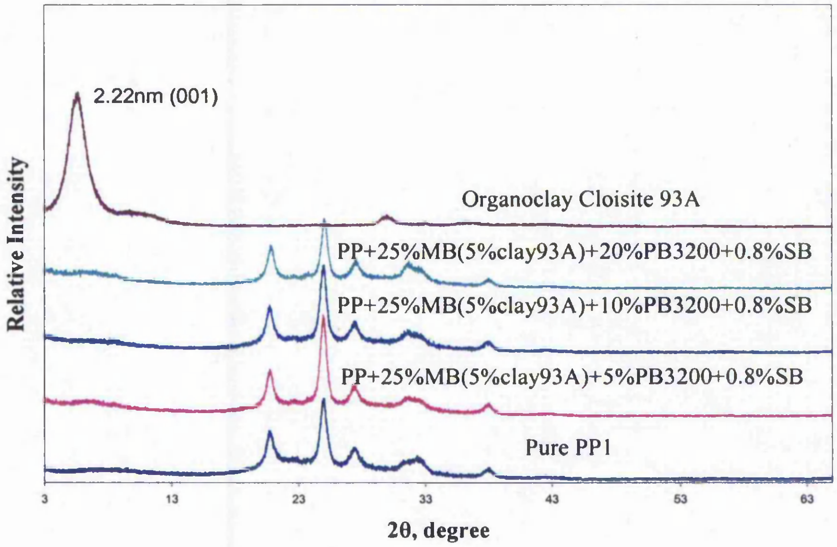


Fig 7.9 XRD patterns of clay/nylon6/PP composites with adding different MAH-g-PP contents produced by using nylon assisted melt intercalation under the same extrusion condition discussed at Fig7.6 (Cr source).

The difference in mechanical properties can be seen in Table 7.3. There are significant improvements in the mechanical properties for the composites produced with the compatibilzer, PB3200. All the composites with Polybond 3200 have similar or better mechanical properties compared with original polypropylene. This improvement maybe associated with the improved compatibility between the different components in the composite. The mechanical properties of the nanocomposites are dependent on the MAH-g-PP concentration and the best composites were formed when 10wt% of PB3200 was added. The reduction of the mechanical properties for the nanocomposite with 20wt% of PB3200 may be due to the high concentration of the low molecular weight molecules from the compatibilzer as discussed in Chapter 5. The compatibilizer used appears to work in a positive way with the nylon 6 master batch, to allow better exfoliation of the clay in the polypropylene.

The results show that the compatibilizer MAH-g-PP plays a very important role in the enhancement of mechanical properties of composites using this nylon assisted melt intercalation technique. A maleic grafted polypropylene with both a high

MAH content and a high molecular weight would be the ideal compatibilizer to use. The high MAH content can improve the surface compatibility between the organoclay and hydrophobic polymers, while the high molecular weight can make contributions for improving materials physical properties.

Table 7.3
Tensile yielding strength and modulus of composites produced by adding MAH-g-PP via nylon assisted melt intercalation

Material	**Yielding Strength (MPa)**			**Relative Young'sModulus (GPa)**		
	Average	**σ***	**n****	**Average**	**σ***	**n****
PP1	33.77	0.96	6	1.000	0.11	6
PP1+25wt%N6-MMT (5wt% Cloisite93A) +0.8wt% SB	28.22	0.80	3	0.896	0.01	3
PP1+25wt%N6-MMT (5wt%Cloisite93A)+5wt% PB-3200+0.8wt%SB	33.88	0.68	3	0.948	0.005	3
PP1+25wt%N6-MMT (5wt%Cloisite93A)+10w% PB-3200+0.8wt%SB	36.93	0.30	3	1.080	0.005	3
PP1+25wt%N6-MMT (5wt%Cloisite93A)+20w% PB-3200+0.8wt%SB	33.70	0.09	4	0.969	0.009	4

*Note: *σ - standard deviation, **n – number of specimens tested*

An second MAH-g-PP was investigated. This was Epolene Wax G-3015. A clay/nylon 6 master batch which contained 5wt% of Cloisite 93A was used. The clay/nylon/PP composite was produced by extruding the master batch with polypropylene and 10wt% of Epolene Wax G-3015 .The composites were produced by using twin-screw extruder under the same extrusion as discussed above. The nano-structure of the composites was characterised by XRD (Cr as radiation source) and the mechanical properties of these composites were measured. The results were compared with those for PB3200.

The XRD patterns of these composites are shown in Fig 7.10. Layer expansion and exfoliation occurred in both composites. There is a significant difference in the composites' mechanical properties. The composites were tested on different dates. So polypropylene samples prepared at the same time as the composite and kept under the same conditions were used for comparison. The results are summarized in Table 7.4. The nanocomposite containing Epolene G-3015 enhanced polypropylene's physical properties especially the Young's modulus. The tensile yielding strength of the composite using Epolene G-3015 was 38.02 MPa compared to 35.51MPa for the polypropylene. The tensile Young's modulus of this composite has improved by about 22% compared to the polypropylene PP1 while there was only about 8% increase for the composite by using Polybond PB-3200 as compatibizer.

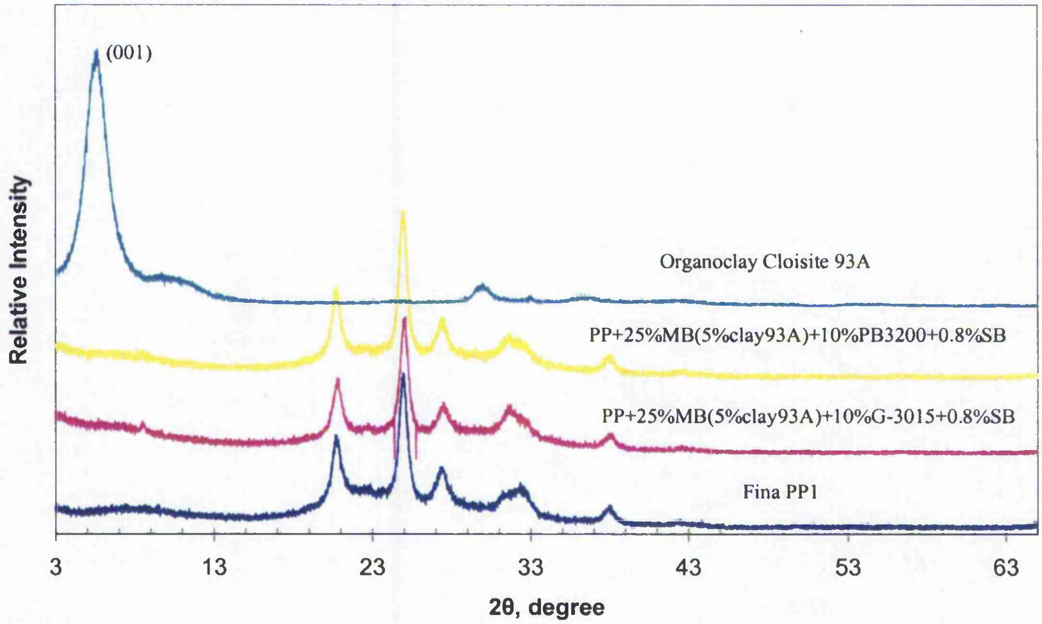


Fig 7.10. XRD patterns of clay/nylon6/PP1 nanocomposites extruded by twin-screw extruder with 10wt% MAH-g-PP Polybond PB-3200, Epolene G-3015 and 0.8wt% nucleation agent sodium benzoate under the same extrusion condition discussed in Fig 7.6 (Cr source).

Table 7.4
Tensile yielding strength and modulus of composites produced by different MAH-g-PPs via nylon assisted melt intercalation

Material	**Yielding Strength (MPa)**			**Relative Young's Modulus (GPa)**		
	Average	**σ***	**n****	**Average**	**σ***	**n****
PP1	33.77	0.96	6	1.000	0.11	6
PP1+25wt%N6-MMT (5wt%Cloisite93A)+10wt % PB-3200+0.8wt%SB	36.93	0.30	3	1.080	0.005	3
PP1	35.51	0.86	5	1	0.004	3
PP1+25wt%N6-MMT (5wt%Cloisite93A)+10wt % G-3015+0.8wt%SB	38.02	0.39	4	1.22	0.014	4

*Note: *σ - standard deviation, **n – number of specimens tested*

The reason for the enhancement of the nanocomposites properties when compatibilisers are added is not fully understood as there is very little information supplied about the compatibilisers structure In order to find why enhancement of the composites occurred. The MAH grafting content of the MAH-g-PP products was examined by FTIR spectroscopy and the melt flow characteristics of these materials were investigated here using a melt flow index test. The results of the melt flow index test will give an indication of the molecular weight of the compatibilizer. The results are tabulated in Table 7.5. The experimental tests show that Epolene Wax E-43 has the highest MAH concentration of all the maleic anhydride grafted polypropylenes. Its melt flow index could not be measured, as its melt viscosity was too low. This suggests that Epolene Wax E-43 has a very low molecular weight. All the other maleic anhydride grafted polypropylenes had similar MAH concentrations but their melt flow index was very different.

Table 7.5
The MAH contents and their corresponding melt flow index data of commercially available MAH-g-PPs

MAH-g-PP Products	Supplier	MAH content (wt %)	MFI* (g/10min)
Epolene Wax E-43	Eastman Chemical	5.80	----**
Epolene Wax G-3015	Eastman Chemical	2.96	68.8
Polybond PB-3200	Uniroyal Chemical	2.78	12.0
Polybond PB-3000	Uniroyal Chemical	2.62	54.3

**Using Melt Flow Index; pre-heating time 6 minutes; 2.16 kg load used as standardized weight on the piston and processing temperature is 170 °C*
*** melt flow index is too high to be recorded*

The Epolene Wax G-3015 has a slightly higher MAH content than Polybond PB-3200 but its melt flow index is a lot higher which means the molecular weight of the wax is significantly lower than that of the Polybond PB-3200. The Polybond PB-3000 has a lower MAH content than the other maleic anhydride grafted polypropylenes and a relatively high melt flow index. These results indicate that the Epolene Wax G-3015 does not have a higher molecular weight than the Polybond P3200 as its melt flow index is high. A possible explanation for this could be that the ability of the compatibilizer to work effectively depends on the distribution of the maleic anhydride groups along the polymer chains. Further work is needed to understand why adding Epolene Wax G-3015 improved the compatability between nylon 6 and polypropylene and the mechanical properties of the composites more successfully than the Polybond 3200.

7.7 Conclusion

The nylon assisted melt intercalation technique produced clay/nylon6/PP composites with exfoliated structures. The mechanical properties of the composites were improved. The tensile strengths were similar or better than the original polyropylene and improvements in the Young's modulus of the composites has been made. The use of compatibilizers in the nylon assisted melt intercalation method has produced nanocomposites with tensile yielding strengths and Young's modulii higher than the original polymer. The mechanical properties have not been improved to a satisfactory degree yet and further work is required to optimise the current commercial compatibilizers and develop new ones. However these results show that nylon assisted melt intercalation technique has great potential to achieve significant enhancement of the engineering properties of polypropylene using clay/polymer nanotechnology.

CHAPTER 8 Conclusion

Various novel processing techniques have been developed to produce clay/polymer nanocomposites. These include solid intercalation/melt processing and nylon melt assisted intercalation methods. These technologies were developed based on the investigation of several basic model clay/PP systems to gain a fundamental understanding of clay/PP intercalation and its relation to processing and mechanical properties. Although these developments are still in a preliminary stage, the study has paved the way for further development of these technologies to achieve significant enhancement of the engineering properties of polypropylene using clay/polymer nanotechnology. The major findings are discussed in detail below.

- **Problems in producing clay/PP nanocomposites by using existing technology**

A feasibility study for producing clay/polypropylene nanocomposites, directly using commercially available polypropylenes was undertaken. Several commercial polypropylenes were investigated and it was found that the polypropylene FinaPP 3228C was capable of forming intercalated nanostructures with organoclays by using direct melt intercalation. Among the Cloisite organoclays examined, Cloisite 93A exhibited higher extents of layer expansion and was more compatible to polypropylene than other available Cloisite organoclays. However, the Cloisite organoclays and the polypropylene were not completely compatible and the organoclays decomposed at lower temperatures than those used to process the polypropylene. The intercalated structures obtained by direct melt intercalation were unable to enhance the mechanical properties of polypropylenes because of the non-uniform dispersal of clay layers. The grafting of maleic anhydride groups (MAH) onto polypropylene improved the intercalation between clay and polymers. High degrees of intercalation or exfoliation were only possible when using maleic anhydride grafted polypropylenes (MAH-g-PP) with high MAH contents (~5%). However the mechanical properties of the nanocomposites produced using this method were very low due to the low molecular weight of the MAH-g-PP products used.

- **The way to overcome these problems through adding stabilisers and compatibilizers, and some insights on the influences of processing parameters**

The clay degradation and non-uniform dispersal of clay layers in clay/PP1 intercalated nanocomposites constrain the enhancement of the major engineering properties of polypropylene. A small fraction of stabilizers and compatibilizers were used in order to prevent the degradation of clay/PP nanocomposites produced and to improve the compatibility between clays and polymers. Some commercially available stabilizers, also called anti-oxidants, were used to try to avoid the degradation of the polypropylene during high temperature melt processing. However, the results showed that the methods that are usually used to prevent PP from degrading can not be applied to organoclay/PP nanocomposites system because all the commercial stabilisers were developed according to polymer structure rather than any other additives in the system. In clay/polymer nanocomposite processing the ammonium salts used to produce the orgaonoclays degrade first and cause degradation of the polymer. This suggests that the most effective approach to produce clay/PP nanocomposites should be by preventing organoclay degradation rather than PP degradation.

As discussed above, a high degree of intercalation or exfoliation could be obtained when MAH-g-PP was directly used to produce clay/MAH-g-PP nanocomposites but their mechanical properties were very low. To solve this problem, MAH-g-PP was used instead as a compatibilizer to improve the compatibility between organoclay and unmodified polypropylene. In this case, clay, MAH-g-PP and the polypropylene, PP1, were blended together to produce clay/PP nanocomposites. The results showed that this approach was capable of introducing intercalation and the dispersed clay layers also exhibited reinforcement effects. However, commercial MAH-g-PPs with relative high MAH contents normally are low molecular weight products. The reduction in the mechanical properties of the composites is due to the introduction of these low molecular weight materials whose effects are more significant than the reinforcement of the composite by the dispersed clays. As a consequence, little improvement in the mechanical properties of polypropylene was achieved. Degradation during processing was significant and the colour of the final products was not satisfactory.

The influences of melt processing parameters, such as shear and residence time, on nanostructure formation in the melt processing of clay/polymer nanocomposites have also been studied. It was found that melt processing only provided melt flow of polymers into the capillary channels of the clays and this occurred at a very early stage in melt processing. The major action of the extruder in processing was to break down the large clay particles into smaller tactoids with higher aspect ratios. Layer expansion of clay in melt processing was still mainly determined by the compatibility and chemical interactions between the clays and the polymers.

- **Advantages of the new technology developed and its limitations**

This study has built up some basic model clay/PP systems. These model systems have helped to gain a fundamental understanding of clay/PP intercalation and its relation to processing and mechanical properties. The knowledge was utilized to design better synthetic methods for manufacturing clay/PP nanocomposites with enhanced major engineering properties. A solid intercalation/melt processing technique (SIMP) and a nylon assisted melt intercalation technique have been developed.

This work shows that this newly developed solid intercalation/melt processing technique has a great potential for producing better quality clay/PP nanocomposites. With this method, there is little organoclay degradation during processing. Extrusion can be carried out at relatively high temperatures and the colour of the material does not change during processing. Exfoliated nano-structures are produced by this technique. This technique does not require an additional processing for melt grafting, which will reduce the processing costs and the cost of using grafted products. The tensile yielding strength of the nanocomposites produced was also improved. The Young's modulus of the nanocomposite however decreased and this decrease may be due to the low degree of polymerisation in the in-situ polymerisation phase of the process. The mechanical properties of the composites could be further improved if the degree of polymerization could be increased. It was found that the success of this technique will depend on the monomer used and control of the solid in-situ polymerization reaction.

In the nylon assisted melt intercalation technique, the clay/nylon master batches were produced and used to form the clay/nylon/PP nanocomposites. The principle of this technology is to take the advantage of easy exfoliation of clay in nylon and to transfer the exfoliated structure into polypropylene. The results showed that compatibility between nylon and polypropylene could be significantly improved by using the nylon assisted melt intercalation approach. The clay/nylon 6 master batches produced contained clay with intercalated and exfoliated clay in them which were more thermally stable and more compatible to polypropylene than the ordinary organoclay which was only modified by alkyl ammonium ions. Furthermore, the clay/nylon 6 master batches became easier to further intercalate with polypropylene when a compatibilizer of maleic anhydride grafted polypropylene, was added before extrusion. The clay/nylon/PP composites produced had exfoliated structures and there was some improvement in the tensile yielding strengths and a significant increase in Young's modulii for some of the composites compared to the original polypropylene. Although the mechanical properties have not improved to a satisfactory degree due to the use of the low molecular weights of the commercial compatibilizers available, this nylon assisted melt intercalation technique has demonstrated that it has a great deal of potential to achieve significant enhancement of the engineering properties of polypropylene.

Although these new technologies for producing clay polypropylene nanocomposites are still being developed, this research has demonstrated that significant improvements in the mechanical properties of the nanocomposites can be achieved using the techniques described. The processing methods use conventional polymer processing equipment which will allow clay/PP nanocomposites to be produced inexpensively, and will open up many opportunities for the commercial development and applications of these materials.

CHAPTER 9 FUTURE WORK

The fundamental understanding of the mechanisms of intercalation and their relation to the engineering properties of the nanocomposites should be further investigated based on the results obtained from the model synthetic study. Low molecular weight commercial compatibilizer, maleic anhydride grafted polypropylene, and clay degradation are identified to be the major problems so the development of new compatibilizers with high molecular weight and thermally stable organoclays are required for the future work.

Alternative monomers and optimised polymerization conditions should be investigated for solid intercalation/melt processing technique to increase the molecular weight while the polymer remains to be thermal plastic. Solid in-situ polymerisation process can also be combined with the nylon assisted melt intercalation technique to further improve the efficiency.

For nylon assisted melt intercalation, some new organoclays which are more compatible to nylon should be explored. The purpose of this is to increase the concentration of clay in nylon without the sacrifice of exfoliation during master batch processing. This can help to minimize the content of pure nylon used and to keep the clay content in a satisfactory level in the clay/polypropylene nanocomposites. Other "master batches" with exfoliated clay structures should be explored using thermally stable polymers. These "master batches" produced should be more thermally stable and more compatible to PP than ordinary organoclays which were modified by ammonium salts.

Using hydrophilic clays might be an alternative way to avoid organoclay degradation during melt processing, but the use of original hydrophilic clay was limited by the incompatibility between hydrophilic clays and hydrophobic polypropylene. Compatible organophilic polymers should be used to solve this problem. This organophilic polymer assisted melt intercalation technique would help to prevent organoclay degradation during melt processing and to transfer the exfoliated composite structure into polypropylene.

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LIST OF PUBLICATIONS & PRESENTATIONS

- F.G. Gao, S.J. Chen, **Z.H. Han** and J.B. Hull, *A Screening of the microstructure of Major Commercial Clays for Nanocomposite Application*, Nanocomosites, 2003, ECM, San Francisco, California, 10-12, November, 2003.
- J. B. Hull, **Z.H. Han** and F.G. Gao, *A Mechanistic Understanding of Melt Processing of Clay/Polymer Nanocomposites,* In Proc. Mechanics in Design II Conference, Nagoya, Japan, 5- 8 June 2002.
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