Crystallization and solid state phase transition of polymer nano-composite and belndsaromatic heterocyclic resin

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**CRYSTALLIZATION AND SOLID STATE PHASE
TRANSITION OF POLYMER NANO-COMPOSITE AND
BLENDS AROMATIC HETEROCYCLIC RESIN:**

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Abstract

Polymer/clay nano-composites have attracted more and more attention from both the scientific and practical point of view. At present, more and more polymer/clay nano-composites have been prepared and investigated. Furthermore, improved properties have been observed. However, the majority of research work around polymer/clay nano-composites and blends has just focused on synthesis and characterization of properties. Although improved properties have been observed, the reason of the improvement as well as some unique phenomena in such nano-composites is still not well understood. On the other hand, the polymorphic behavior is a profound impact on properties of the polymer. However, there are still some great challenges in studying the polymorphism and phase transition of polymer/clay nano-composites. In this study, the crystallization and phase transitions in polymer/clay nano-composites and blends have been investigated. The fundamental analysis and discussion have been presented in this thesis.

Nylon 6/nano-clay nano-composites, Nylon 6/nano-clay/PP-g-MAH blends and SPS/clay nano-composites have been prepared. The peculiar results indicate that in Nylon 6/nano-clay and Nylon 6/PP-g-MAH binary blends, both nano-clay and functionalized polyolefin would favor the formation of γ crystal of Nylon 6. However, the co-existence of both nano-clay and PP-g-MAH in the Nylon 6/nano-clay/PP-g-MAH ternary blends antagonizes each other's promotional effect on γ crystal formation in Nylon 6.

Furthermore, the crystallization temperature should be the intrinsic factor controlling the polymorphism in polymers. The stable phase can only be obtained at higher

crystallization temperature. The metastable phase will be observed at lower crystallization temperature.

Polymer/clay nano-composites provide a good model system to study the metastability theory. The onset or minimum temperature above which the stable phase can be obtained in polymer/clay nano-composites is much higher than that in pure polymers. This is the thermodynamic reason why the addition of nano-clay would favor the formation of metastable phase.

The difference metastability of polymers and polymer/clay nano-composites at normal conditions and in supercritical fluid has been compared in order to get deeper understanding of crystallization and phase transition in polymers.

Chapter 1 Introduction

1.1. Background and Current Challenges

In recent years, polymer/clay nano-composites have attracted more and more attention from both the scientific and practical point of view. Because of the nanoscale structure, nano-composites possess unique properties typically not shared by conventional micro-composites. That is, a relatively small amount of layered silicates gives the possibility to modify drastically mechanical, thermal, optical and chemical properties when compared with virgin polymers or their conventional composites. These improvements can include, for example, increased modulus, strength and heat resistance, as well as decreased gas permeability, thermal expansion, flammability and biodegradability of biodegradable polymers [1, 2].

Therefore, since the initial studies by Toyota research group [3-7], more and more polymer/clay nano-composite systems have been prepared and investigated [1-3]. However, the majority of research work around polymer/clay nano-composites and blends has just focused on synthesis and characterization of physical properties. Although improved properties have been observed, the nature and origin of the improvement as well as some unique phenomena in such nano-composites are still not well understood [7-9].

In addition, polymorphism is a widespread phenomenon in semi-crystalline polymers, which exhibit several polymorphs according to the crystallization conditions [10]. The formation of a particular polymorph depends on both thermodynamics and kinetics. In most cases, the polymorph obtained under given crystallization conditions is controlled by its thermodynamic stability. However, when more than one minimum of free energy is available,

the polymorph obtained is the one crystallized more rapidly, indicating a kinetically controlled process [10, 11].

Furthermore, the polymorphic behavior has a profound impact on the properties of the polymer. The physical properties, e.g., mechanical, thermal, electrical and solvent resistance, of different polymorphic forms for a given polymeric material can be advantageously altered for its potential applications [10, 11].

Although polymorphism has been reported in nano-composites of clay with different polymers, and it is known that the polymorphic behavior of nano-composites is very different from that of the neat polymers [1-3, 8, 9], there are still some great challenges in studying the polymorphism and phase transition of polymer/clay nano-composites.

One of the challenges is to understand the more unique polymorphic behavior of polymer/clay nano-composites and blends. For example, Nylon 6 was often blended with functionalized polyolefin in order to improve its toughness. Meanwhile, the presence of functionalized polyolefin also has a strong effect on the polymorphism of Nylon 6 [10]. However, so far, there is no report on the polymorphism of Nylon 6/clay nano-composites and functionalized polyolefin blends.

In addition, there are still much more research work need to be carried out on polymorphism of polymers. For example, which one is the more significant factor in controlling the formation of α or β crystal for Syndiotactic polystyrene (sPS) without any thermal history,

the crystallization temperature or the cooling rate from the melt? The answer is still under discussion [12, 13].

The most important challenge is how to explain the unique polymorphic behavior of polymer/clay nano-composites. From traditional thermodynamic point of view, thermodynamic states are considered to be of infinite size. However, polymers may have metastability states present due to small phase size [14]. Thus, traditional thermodynamic theory about polymorphism can not be directly applied in polymers. For example, although ordered and disordered models have been used to explain the phase transformations in metals and alloys, they are not applicable to polymers due to many limitations [10].

The theoretical basis of metastability in polymer phase transitions has been thoroughly discussed and examined by Keller and Cheng in 1998 [14]. Metastability theory may be a major step forward toward understanding the mechanism of polymer phase transition. However, due to the experimental limitations [15], there is very few reports [16, 17] to apply this theory to phase transitions in polymers. In fact, it is easy to understand that the large surface area of nano-clay will give rise to constraining effect during the crystallization of a polymer. Nano-clay should provide excellent confinement of polymer crystals. Therefore, we believed polymer/clay nano-composites should be a good model system to apply the metastability theory. Unfortunately, there is still no report on metastability in polymer/clay nano-composites.

From the above introduction, it is evident that it is necessary to investigate the unique phenomena in crystallization and phase transition of polymer/clay nano-composites and blends. Furthermore, in supercritical fluid (SCF), both thermodynamics and kinetics of phase

transformation are different from those not in SCF [18-20]. Some transformations, which may not occur at normal conditions, will be present in supercritical CO₂ [19, 20]. So investigation of polymorphism and phase transition in supercritical fluid, will help us gain a deeper understanding of the phase transformations in polymers.

1.2 Objectives and Scope of this Research

The main goal of this work is to prepare Nylon 6/clay nano-composites, Nylon 6/nano-clay/PP-g-MAH ternary blends and sPS/clay nano-composites, and to investigate the polymorphism and phase transition of polymer/clay nano-composites and blends. These include:

(1) Unique phenomena of polymorphism in Nylon 6/clay nano-composites and functionalized polyolefin blends

Nylon 6/clay nano-composites and functionalized polyolefin blends have been prepared by melt intercalation. The dispersion of clay was examined by wide angle X-ray diffraction (WAXD) and Transmission Electron Microscopy (TEM). The polymorphic behavior of Nylon 6, Nylon 6/clay nano-composites, Nylon 6/ functionalized polyolefin blends and Nylon 6/nano-clay/functionalized polyolefin blends were investigated by WAXD, Fourier transform infrared spectroscopy (FTIR) and Differential scanning calorimeter (DSC). Furthermore, the interactions in Nylon 6/nano-clay/PP-g-MAH ternary blends have been investigated and discussed in details.

(2) Polymorphism in sPS and sPS/clay nano-composites

The influence of cooling rate from the melt and crystallization temperature, on the formation of α and β form crystals of sPS, were investigated by X-ray diffraction and nonisothermal DSC analysis. Combined these two results, the temperature window in which β crystal (stable phase) can be obtained, was also determined.

Furthermore, sPS/clay nano-composites were successfully prepared by solution intercalation technique using 1, 1, 2, 2-tetrachloroethane (TCE) as the solvent. The dispersion of clay in sPS was also examined by WAXD and TEM. The polymorphism in sPS/clay nano-composites has been investigated by WAXD and FTIR.

(3) Metastability in polymer/clay nano-composites and blends

Polymer/clay nano-composites were used as good model systems to study the metastability phenomenon in semi-crystalline polymers. The polymorphism and metastability in Nylon 6 and Nylon 6/clay nano-composite, sPS and sPS/clay nano-composites, have been investigated by WAXD and DSC.

The crystallization of both the stable and metastable phase of Nylon 6 and sPS with and without the presence of nano-clay was studied systematically through carefully designed annealing experiments. After quantitative analysis of WAXD and DSC results, the onset or minimum temperature, above which the stable phase can be obtained, is compared between the neat polymers and the nano-composites. At the same time, the stability of the 'metastable' phase is assessed. The reason why polymer/clay nano-composites have unique polymorphic behavior was explained and discussed using the metastability theory.

(4) Metastability and phase transition in supercritical fluid

The metastability and phase transition of Nylon 6 and sPS with and without the presence of nano-clay in supercritical CO₂ were investigated. The influence of annealing temperature, pressure and time in the supercritical fluid on the phase transition of polymer was also analyzed and discussed.

1.3 Major Contribution of the Thesis

- Nylon 6/clay nano-composites and sPS/clay nano-composites have been successfully prepared. The polymorphic behaviors of polymer/clay nano-composites have been investigated.
- Nylon 6/nano-clay/PP-g-MAH blends have been prepared. The peculiar polymorphism of Nylon 6 in Nylon 6/nano-clay/PP-g-MAH blends has been reported for the first time. The interactions and the antagonistic effect in Nylon 6/nano-clay/PP-g-MAH ternary blends have been studied and discussed in details.
- The effect of cooling rate from the melt and the crystallization temperature, on the formation of α and β form crystals of sPS, has been investigated in details. The intrinsic factor controlling the formation of α and β form crystals has been defined. The temperature range, at which the stable phase can be obtained, has also been determined.
- Polymer/clay nano-composites have been used as good model systems to apply the metastability theory. The onset or minimum temperature, above which the stable phase can be obtained, has been compared between the neat polymers and the nano-composites. The stability of the metastable phase in neat polymers and polymer/clay nano-composites has also been investigated. The reason why polymer/clay nano-composites

have unique polymorphic behavior has been explained and discussed using the metastability theory.

- The difference in metastability of polymers and polymer/clay nano-composites at normal conditions and in supercritical fluid has been compared. The phase transformation from α crystal to β crystal of sPS, which can not be observed at normal conditions, has been achieved in supercritical CO₂.

1.4 Organization of the Thesis

This thesis contains seven chapters. Chapter one is a brief introduction to the background and challenges of studying the polymorphism of polymer/clay nano-composites and blends. The objectives and the outline of this thesis and the major contribution of this work are also provided in this chapter. Chapter two gives a literature review on the polymer/clay nano-composites and polymorphism of polymer. A brief review on metastability theory and phase transition of polymer in supercritical fluid is also included in this chapter. Chapter three describes the crystallization behavior and the interaction of the Nylon 6/clay nano-composites and functionalized polyolefin blends. Chapter four discusses the effect of crystallization temperature on the polymorphic behavior of sPS and the polymorphism of sPS nano-composites. Chapter five compares the metastability between the neat polymers and the polymer/clay nano-composites. The metastability theory has been used to understand the polymorphic behavior in semi-crystalline polymer/clay nano-composites. Chapter six presents the polymorphism and phase transition of polymers and polymer/clay nano-composites. Chapter seven gives general conclusions of this thesis as well as recommended future work for related research.

Chapter 2 Literature Review

2.1. Polymer/Clay Nano-Composites

2.1.1. Introduction to polymer/clay nano-composites

In recent years, organic-inorganic nanoscale composites have attracted great interest since they frequently exhibit unexpected hybrid properties synergistically derived from two components [21-27]. In polymer nano-composites, particle size of the dispersed phase is at least one dimension less than 100 nm [1]. Amongst all the potential polymer nano-composites, polymer/clay (layered silicate) nano-composites have been more widely studied and investigated, probably due to their easily available raw materials and well studied intercalation chemistry [1, 3].

The increasing interest in polymer/clay nano-composites over the last decade has a great deal to do with their demonstrated as well as potential property enhancements, relative to the neat resin [3-7, 28-33]. Because of the nanoscale structure, nano-composites possess unique properties typically not shared by conventional micro-composites. That is, a relatively small amount of layered silicates gives the possibility to modify drastically mechanical, thermal, optical and chemical properties when compared with virgin polymers or their conventional composites. Compared with neat resins, polymer-clay nano-composites, at a lower volume fraction of reinforcement, exhibit increased modulus [6, 30] and heat distortion temperature (HDT) [6, 30] with decreased thermal expansion [32], flammability [33] and permeability [31]. This enhancement in property is related to the high fraction of volume of the interphase

in nano-composites. As a consequence, there are interesting opportunities for the development of new materials [21].

Swellable clay minerals are not nanometer-sized filler themselves, but can produce a nanometer-sized filler in the polymer resin. The layered silicates commonly used in polymer/clay nano-composites belong to the same general family 2:1 phyllosilicates as shown in Figure 2.1 [2]. Their crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesia is fused to two external silica tetrahedrons by the tip so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets. The layer thickness is around 1 nm and the lateral dimensions of these layers may vary from 30 nm to several microns and even larger depending on the particular silicate. Stacking of these layers leads to a regular van der Waals gap between them called the interlayer or the gallery. Isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or by Fe^{2+} , or Mg^{2+} replaced by Li^{+}) generates negative charges that are counterbalanced by alkali or alkaline earth cations situated inside the galleries. As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers is easily available.

Figure 2.1. Structure of 2:1 phyllosilicates [2].

Clay minerals are called layered silicates because of the stacked structure of 1 nm thick silicate sheet with a variable basal distance. These layered silicates can undergo intercalation with various organic molecules such as primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium (onium). The modified clay (or organoclay) being organophilic, its surface energy is lowered and is more compatible with organic polymers. These polymers may be able to intercalate within the galleries. When the hydrated cations are ion-exchanged with organic cations such as more bulky alkylammoniums, it usually results in a larger interlayer spacing. Additionally, the alkylammonium or alkylphosphonium cations can provide functional groups that may react with the polymer matrix, or can in some cases initiate the polymerization of monomers to improve the interface strength between the polymer matrix and the layered silicates [2, 34].

Depending on the strength of the interfacial interactions between the polymer matrix and layered silicate, three main types of composites may be obtained when layered clay is associated with a polymer, a) phase-separated composite, b) intercalated nano-composite and c) exfoliated nano-composites, as seen in Figure 2.2 [2]. The type of the composite obtained can be controlled by varying the nature of the components used (layered silicate, organic cation, polymer matrix) and the method of preparation [1].

Figure 2.2. Scheme of different types of composites arising from the interactions of layered silicates and polymers [1].

When the polymer is unable to intercalate between the silicate sheets, a phase-separated composite (Figure 2.2a) is obtained, whose properties stay in the same range as conventional composites. In conventional composites, the layered silicate tactoids exist in their original aggregated states with no intercalation of the polymer matrix into the galleries [35]. Beyond this kind of composites, two types of nano-composites can be obtained. Intercalated structure (Figure 2.2b) in which a single (and sometimes more than one) extended polymer chain is

intercalated between the silicate layers, resulting in a well-ordered multilayer morphology built up with alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained (Figure 2.2c). Usually, the layered silicate concentration is lower in an exfoliated nano-composite than that in an intercalated nano-composite. However, it must always be remembered that complete or full exfoliation, down to single silicate layer, is an uncommon situation, typically difficult to achieve, but properties enhancements may indeed be seen without perfect exfoliation.

In 1970, Kato reported a “polymer/clay complex” consisting of an organic polymer and a clay mineral [36]. An acrylic acid monomer was intercalated between the silicate sheets and polymerization of the monomer was carried out in situ. This resulted in an increased basal distance of clay from 0.96 to 1.74 nm. However, the first polymer/clay nano-composite was synthesized in a Nylon 6 matrix using a monomer intercalation method by researchers at Toyota’s Central Research and Development Laboratories (CRDL) [4-6]. Since then, more and more polymer/clay nano-composites have been prepared and investigated, including Nylons [7, 37], Epoxy [38, 39], Polypropylene [40, 41], Polyethylene Terephthalate [30, 42] and many other matrices reinforced with organic clay.

2.1.2. Preparation methods and characterization techniques of polymer/clay nano-composites

Polymer/clay nano-composites can be prepared mainly by the following five methods [7]:

- a. Monomer intercalation [4-6]
- b. Monomer modification [43, 44]
- c. Covulcanization [45]
- d. Common solvent [46, 47]

e. Polymer melt intercalation [48, 49]

Among them, monomer intercalation method and polymer melt intercalation method are the two most commonly used methods for the synthesis of polymer/clay nano-composites.

In monomer intercalation method, the layered silicate is swollen by monomers. Then polymerization of monomers occurs in the interlayer of the clay, resulting in an expansion between the layers, leading to further exfoliation and eventually the layers are homogeneously dispersed on nanometer scale at the end of the polymerization. Polymerization can be initiated either by heat or radiation. For example, Nylon 6/clay nano-composites [7] and epoxy/clay nano-composites [38] have been prepared by this method.

In polymer melt intercalation process, the modified clay is mixed with the polymer matrix in the molten state. If the polarity of clay surface is sufficiently compatible with that of the molten polymer, polymer chain can diffuse into the interlayer space and form intercalation structure. Melt intercalation of modified layered silicates is suitable to produce thermoplastic polymer based nano-composites [1, 48, 49], such as Nylon, polystyrene (PS), polypropylene (PP) and ethylene-vinyl acetate copolymer (EVA), poly (styrene-*b*-butadiene) copolymer (SBS) and elastomers (including silicon rubber and nitrile rubber).

Two complementary techniques, wide angle X-ray diffraction (WAXD) analysis and transmission electron micrographic (TEM), have been widely used to characterize the structure of polymer/layered silicate nano-composites [2]. Due to its simplicity and availability, WAXD is most commonly employed to probe the nano-composite structure. It is a good way to evaluate the spacing between the layered silicate sheets. By monitoring the

position of the basal reflections from the distributed silicate layers, the nano-composite structure (intercalated or exfoliated) may be identified based on the Bragg's relation.

According to Bragg's equation [50], the basal spacing of clay can be calculated by X-ray diffraction (XRD) analysis.

$$\lambda = 2d \sin \theta \quad 2.1$$

where λ corresponds to the wave length of the X-ray radiation used in the diffraction experiment, d is the spacing between diffractive lattice planes and θ is the measured diffraction angle or glancing angle.

For clay powder, diffraction peak can be seen at around $2\theta = 9^\circ$, which corresponds to basal distances of about 1 nm. When exfoliated structure is tested, no more diffraction peaks are visible in the XRD diffractograms, either because of a much larger spacing between the layers, normally exceeding several nanometers in the case of ordered exfoliated structure, or because the loss of ordering in the nano-composite.

The advantage of this method is that the sample preparation is relatively easy and the X-ray analysis can be performed within a few hours. However, lack of the sensitivity and limits of the equipment can lead to wrong conclusions about the nano-composite structure [51]. In addition, the depth of penetration of X-rays is inversely proportional to the diffraction angle. It means that X-ray analysis, at low angle, will only reflect the structure present in a thin layer close to the surface (typically 0.1mm for polymers) [50].

Transmission electron microscopy (TEM) is a complementary to XRD, especially WAXD,

which is used widely in polymer based nano-composites. TEM gives a direct observation and measurement of the spatial distribution of the layers. Although TEM allows a qualitative understanding of the internal structure and spatial distribution of the various phases, special care must be exercised to guarantee a representative cross-section of the sample. Also TEM is time-intensive, and only gives information on a small localized region, while low angle peaks in WAXD patterns allow quantification of changes in layer spacing. Therefore, combination of WAXD and TEM is necessary when the nano-composite structure need to be analyzed.

In addition to WAXD and TEM, atomic force microscopy (AFM) has also been used by some researchers to determine whether the layered silicates are truly dispersed. However, this technique is also problematic because the images obtained are highly dependent on selecting the proper imaging parameters and having a very clean and sharp AFM tip. Only an experienced operator is able to get reliable results.

2.1.3. Properties of polymer/clay nano-composites

Polymer/clay nano-composites have demonstrated significant enhancements in a number of physical properties and there are great potentials for further exploitation [6, 30-33]. Compared with traditional resins, polymer/clay nano-composites exhibited increased modulus [6, 30], heat distortion temperature (HDT) [6, 30] and barrier properties [31] with decreased thermal expansion [32]. Polymer/clay nano-composites are also finding new applications due to their reduced flammability [33], improved resistance to UV [52] and oxidative degradation [53], and improved ablative performance [54]. In contrast to composites filled with micron sized fillers, such as talc, carbon black, silica or mica, which normally require loadings of 20 wt% or higher, polymer/clay nano-composites achieve enhanced properties with as little as 5 wt% addition of a dispersion of 1 nm thick

aluminosilicate layers with diameters typically between 20 (laponite) and 500 nm (montmorillonite) [55]. The low percentage of reinforcing phase allows the resins to be processed using conventional techniques, and yet maintain a high degree of optical clarity.

Mechanical properties

The enhancement in mechanical properties of polymer nano-composites can be attributed to the high rigidity and aspect ratio together with the good affinity between polymer and organoclay. For instance, stronger interface interactions significantly reduce the stress concentration upon repeated distortion, which easily occurs in conventional composites reinforced by glass fibers and thus lead to weak fatigue strength [56].

The unprecedented mechanical properties of nylon 6/clay nano-composite synthesized by in-situ polymerization were first demonstrated by researchers at the Toyota Central Research Laboratories [57]. Such nano-composites exhibit significant improvement in strength and modulus, namely, 40% in tensile strength, 60% in flexural strength, 68% in tensile modulus, and 126% in flexural modulus. The RTP Company has reported equivalent property enhancement of nylon 6/clay nano-composites synthesized by direct melt intercalation [58]. The increase in modulus is believed to be directly related to the high aspect ratio of clay layers as well as the ultimate nanostructure. Moreover, a dramatic increase was also observed in exfoliated nanostructures, such as MMT based thermoset amine-cured epoxy nano-composite and magadiite-based elastomeric epoxy nano-composite [59]. The effects of clay loading on tensile modulus [48, 60] and yield strength [61] of some polymer nano-composites have been investigated. In contrast, a relatively small increase was reported for the intercalated nano-composites such as those from clay and polymethylmethacrylate (PMMA) and PS [56].

The interaction strength at the interface would greatly affect the mechanical properties of polymer nano-composites. For example, polar PMMA and ionic nylon 6 interacts with clay layers, which may explain the stress increase for intercalated PMMA nano-composites and exfoliated nylon 6 nano-composites respectively. In the case of polypropylene (PP) nano-composite [56], the slight enhancement in tensile stress is attributed partially to the lack of interfacial adhesion between apolar PP and polar clays, which may be improved by adding maleic anhydride modified PP to the matrix.

In thermoset nano-composites, the exfoliation of clay minerals can also result in substantial property improvement, including enhanced mechanical properties, dimensional stability, thermal stability, chemical stability, resistance to solvent swelling, excellent transparency, together with high barrier property and reduced flammability [1-3, 56].

Thermal stability and flame-retardant properties

Other interesting properties exhibited by polymer/clay nano-composites are their increased thermal stability and their improved flame retardancy at quite low level of nano-clay through the formation of insulating and incombustible char [1]. Thermal stability stated here includes the heat distortion temperature (HDT), thermal degradation and glass transition temperature (T_g) of the materials.

The thermal stability of polymer composites is generally estimated from the weight loss upon heating due to the formation of volatile products. The improved thermal stability in polymer nano-composites is due to the clay platelets which hinder the diffusion of volatiles and assist

the formation of char after thermal decomposition. Blumstein [62] first reported the thermal stability improvement in PMMA nano-composites, which showed that intercalated PMMA containing 10% clay degraded at about 40 – 50°C higher than unfilled PMMA. Recently, there have been great deals of reports on the improved thermal stability of nano-composites made with various organoclays and polymer matrix [56].

Another thermal behavior is the heat resistance upon external loading which can be measured from the heat distortion temperature (HDT). The HDT of nylon 6 nano-composites reported by Toyota researchers is increased from 65°C of pristine nylon to 145°C [58]. The increase in HDT has also been observed in clay-based nano-composites for other polymer systems such as PP and polylactide (PLA) [56]. Such an increase in HDT is very difficult to achieve in conventional polymer composites reinforced by micro-particles.

Glass transition temperature (T_g) of the material is one of the most important thermal properties. It determines the upper temperature limit of the materials. T_g of the nano-composites prepared from polymers and clay has been studied for some systems including elastomers such as Nylon 6 [3, 9, 56], nitrile rubber (NBR) [63], polyurethane (PU) [64], thermoplastics such as PMMA [65], PS [66] and thermosetting polymers such as epoxy [67-69], PI [70-72], cyanate [73-75], polybenzoxazole [76, 77]. There are different effects (increasing, decreasing or unchanging) of clay on T_g of various polymers. Normally, T_g of the system was increased for the elastomers due to the restraining effect of clay on the rubber chain and also the rigidity of the clay particles. This increase in T_g can also be observed in most of thermoplastic and thermosetting polymer based clay nano-composites. However, no consistent conclusion was obtained as to the influence of the layered silicates on the T_g of

epoxy resin [56].

From the previous studies, it seems that the interfacial condition may play an important role in determining the effect of layered silicates on T_g of the system. The stronger interfacial interaction between clay and polymer normally leads to increase T_g . When the interaction between clay and polymer is too weak, there is almost no effect of clay on T_g of the system [56]. Therefore, it is important to study the effect of clay layers on the glass transition temperature of polymers under investigation.

Flame retardancy and mechanical properties are both improved in clay-based polymer nano-composites while the mechanical properties are always degraded in polymer composites with conventional flame retardants. Such fire resistance of polymer nano-composites is attributed to the carbonaceous char layers formed when burnt and the structure of clay minerals. The multilayered clay structure acts as an excellent insulator and mass transport barrier. Char formation and clay structure impede the escape of the decomposed volatiles from the interior of a polymer matrix [56]. The flame retardancy has been recently reviewed by Gilman [78]

Barrier properties

Polymer nano-composites have excellent barrier properties against gases (e.g., oxygen, nitrogen and carbon dioxide), water and hydrocarbons. Studies have showed that such reduction in permeability strongly depends on the aspect ratio of clay platelets, with high ratios dramatically enhancing gaseous barrier properties. The water permeability of exfoliated polyimide (PI) nano-composites as shown in Figure 2.3 has been reported by Yano et al [79] through the use of organoclays with different aspect ratios. The best gas barrier

properties would be obtained in polymer nano-composites with fully exfoliated clay minerals. Moreover, the aspect ratio of clay platelets was observed to affect greatly the relative permeability coefficient for PI filled with 2% of organoclay. The permeability to water vapor of exfoliated poly(caprolactone) (PCL) nano-composites decreases dramatically with the increase of nanometer clay platelets [56]. In addition, polymer nano-composites have also shown better barrier properties against organic solvents such as alcohol, toluene and chloroform.

Figure 2.3. Effect of clay aspect ratio on relative permeability coefficient of polyimide nano-composites [79].

The enhanced barrier properties of polymer nano-composites may be explained by the labyrinth or tortuous pathway model as proposed in Figure 2.4 [79]. When a film of polymer nano-composites is formed, the sheet-like clay layers orient in parallel with the film surface. As a result, gas molecules have to take a longer way around the impermeable clay layers in polymer nano-composite than in polymer matrix when they traverse an equivalent film

thickness. It is interesting to note that the enhancement of barrier properties does not arise from the chemical interactions since it does not depend on the type of gas or liquid molecules.

Figure 2.4. Proposed model for the tortuous zigzag diffusion pathway of a gas through clay-based polymer nano-composites [79]

Optical properties

Despite their microns lateral size, clays are just 1 nm in thickness. Thus, when single layers are dispersed in a polymer matrix, the resulting nano-composite is optically clear in the visible region. Manias and co-workers [80] investigated the UV/vis transmittance of the nano-composites of neat PP/f-mmt and PP-r-MA/2C18-mmt. There was no marked decrease in the clarity due to the clay. One had to load approximately 20.0 wt. % of 2C18-mmt in 3-mm thick films of PP-r-MA before haze is observable by the naked eye. They suggested that achieving a fully exfoliated structure should lead to nano-composites as optically clear as the initial polymers. They also studied the optical properties of PVA/clay nano-composites [81] by UV/vis transmission spectroscopy and showed that the visible region (400-700 nm) was not affected at all by the presence of the silicate and retained the high transparency of the PVA. In addition, poly (vinyl chloride) (PVC)/clay nano-composites were investigated by

Wan and co-workers [82]. They indicated that below 5.0 wt% of clay content, even though the light transmission values of the nano-composites were less than that of pure PVC, the nano-composites still have good optical clarity. Actually, the optical properties of the nano-composites based on epoxy resins attracted more attention in these years. Wang and co-workers [83] demonstrated that magadiite nano-composites based on an epoxy matrix were much more transparent than corresponding smectite nano-composites at the same loading.

Electrical conductivity

Clay minerals exhibit unique electrical properties, which is mainly attributed to their ionic conductivity. Although the clay layers can be regarded as insulators, the hydrated interlayer cations and their mobility ensure a significant ionic conductivity of the system. Moreover, the intercalation of neutral species could affect the hydration shells of interlayer cations and therefore significantly modifies the ion mobility, electrical conductivity and other electrical parameters. The ionic conductivity of crown ether-clay was reported to be several orders of magnitude higher than that of corresponding clay [84]. In addition, it increases with temperature up to a maximum value, depending on the nature of the intercalated crown ether. Further improvement in conductivity is expected by intercalating electroactive polymers into clay minerals.

Nano-composites based on the intercalation of polymer electrolyte (e.g., polyethylene oxide, PEO) into clay minerals are an attractive substitute of conventional polymer-salt compounds. The ionic conductivity of the latter is strongly affected by the crystallinity of the material, the ion-pair formation as well as high mobility of counter-ions [84]. In contrast, the ionic conductivity of the former avoids the mobility of the anions (negatively charged clay layers). For instance, PEO/clay nano-composites show higher ionic conductivities than the clays,

increasing with temperature until a maximum at around 600 K [84]. Moreover, the maximum conductivity in the direction parallel to the clay layer is in the range of 10.5–10.4 S/cm. Similar nano-composite was also reported by direct melt intercalation of PEO into Li-MMT [85]. This nano-composite has shown to enhance the stability of the ionic conductivity at lower temperature when compared to more conventional PEO/LiBF₄ mixture. Such stability enhancement is explained by the fact that intercalation of PEO avoids its crystallization and thus eliminates the presence of non-conductive crystallites.

Nano-composites with conjugated conducting polymers have also been reported, including polymers such as PANI [86], polypyrrole (PPR) [87] and polythiophene (PTP) [87].

Other properties

Polymer nano-composites also show significant improvement in some other polymer properties. For example, scratch resistance is strongly enhanced by the incorporation of layered silicates [88]. The polymer nano-composites can be used in highly technical areas to improve the ablative properties in aeronautics [89].

Although improved properties have been obtained, the reason why polymer/clay nano-composites achieved these features is not full understood [7-9]. However, it is believed to be related to the clay's enormous surface area and multilayer structure and the extent of dispersion or exfoliation of the clay in the matrix. The commercial potential has made polymer/clay nano-composites one of the focuses of current polymer composite research. Most studies pay attention to the effect of the nano-clay on the properties such as mechanical properties, thermal resistance and other properties, and the structures of the polymers, like the crystallization, or nano-composites, exfoliation and intercalation. There are also a few

studies on the influence of the processing methods on the properties and the structures. More recently, there is an increasing interest in the barrier properties and flame retardant properties of the thermoplastic polymer/clay nano-composites, which provide a new class materials and a new concept for flammability materials.

2.1.4 Nylon 6/clay nano-composites

Nylon 6/clay nano-composites are the first polymer/clay nano-composites studied and also the first polymer/clay nano-composite commercialized. Researchers at Toyota CRDL reported the synthesis a Nylon 6/clay nano-composite in two steps [4-7]. They first obtained an aminododecanic acid-clay complex with an enlarged basal distance through an ion exchange reaction between the sodium ion in the interlayer of clay and a protonated acid. In the second step, ϵ -caprolactam was intercalated into the interlayer of the complex and then polymerized in situ. Using this method, exfoliated structure was obtained which is verified by wide angle X-ray diffraction (WAXD) and Transmission electronic spectroscopy (TEM). Later, Nylon 6/clay nano-composites prepared by polymer melt intercalation method were also reported [28, 48, 90]. Direct blending of Nylon 6 with octadecylammonium-clay in melting state using a twin screw extruder can also form Nylon 6/clay nano-composites.

However, because of differences in raw material, method for the synthesis and process, the properties of Nylon 6/clay nano-composites obtained by different researchers show a wild variation. For example, few researchers have got increased impact strength [6, 48]. However, most results showed Nylon 6/clay nano-composites were more brittle than Nylon 6 [7, 8, 28, 30, 37, 90-92]. Therefore, the relationship between the structure and properties of polymer/clay nano-composites is still under discussion [7, 8].

The Nylon 6/clay nano-composite developed by Toyota CRDL group formed through ring opening polymerization was found to have considerably improved properties, as compared with ordinary Nylon 6. Selected important properties of Nylon 6/clay nano-composite are shown in Table 2.1.

Table 2.1 Properties of Nylon 6/clay nano-composite [7]

Properties	Nylon 6	Conventional reinforced Nylon 6	Nylon 6/clay nano-composite
Filler type	-	Talc	clay
Filler content (wt%)	-	4	4
Specific gravity	1.14	1.15	1.15
Elongation (%)	4	4	4
Flexural strength (MPa)	108	125	158
Flexural modulus (GPa)	3.0	3.0	4.5
Heat distortion temperature (°C)	65	-	150

Compared with neat Nylon 6, Nylon 6/clay nano-composite with 4 wt% clay had about 45% higher flexural strength, 50% higher flexural modulus. Further, one of the more interesting results is that heat distortion temperature (HDT) raised substantially from 65°C to 150°C. However, the reason why Nylon 6/clay nano-composites achieved these features is not well understood [7-9].

As commercial Nylon 6/clay nano-composites, the properties of Nanomor™ production are listed in Table 2.2.

Table 2.2 Properties of Nylon 6/clay nano-composite of Nanomor™ production [90]

	Nylon 6	Nano-composites	Nano-composites	Nano-composites
Filler content (wt%)	0	2.5	5	7.5
Tensile Strength (MPa)	79	88	88	79
Flexural strength (Mpa)	124	133	128	131
Flexural modulus (GPa)	3.1	3.6	3.8	4.3
Notched Impact (ft-lb/in)	1.1	0.6	0.5	0.4
Heat distortion temperature (°C)	62	79	98	99

Thermoplastic polymer/clay nano-composites often exhibit increased mechanical properties, thermal resistance, barrier properties and flame retardancy. However, the toughness of the polymer is almost always decreased due to the presence of clay [7, 8, 28, 30, 37, 90-92]. Therefore, how to prepare reinforced nano-composites without decreasing the toughness is also a challenging problem.

In order to improve the toughness, polypropylene-grafted-maleic anhydride (PP-g-MAH) was used to blend with Nylon 6/clay nano-composite, as it was done with neat Nylon 6 [37, 91]. The mechanical properties of Nylon 6/clay nano-composites and PP-g-MAH blend containing 5 wt% clay and 10 wt% PP-g-MAH are summarized in Table 2.3 [37].

Table 2.3 Properties of Nylon 6/nano-clay/PP-g-MAH blends [37]

Properties	Nylon 6	Nylon 6/clay nano-composites	Nylon 6/nano-clay/PP-g-MAH blends
Clay content (%)	0	5	5
PP-g-MAH content (%)	0	0	10
Tensile strength (Mpa)	52	89	85
Tensile modulus (GPa)	1.8	2.5	2.4
Flexural strength (Mpa)	85	139	129
Flexural modulus (GPa)	1.6	2.9	2.7
Notched Izod impact strength (J/m)	39	23	61

The results showed that, with the addition of PP-g-MAH, tensile strength, tensile modulus, flexural strength and flexural modulus of Nylon 6/nano-clay/PP-g-MAH blends decreased slightly. But compared with Nylon 6, the Nylon 6/nano-clay/PP-g-MAH blends still exhibit substantially improved properties. At 10 wt% of PP-g-MAH, the notched Izod impact strength of Nylon 6/nano-clay/PP-g-MAH blend (61 J/m) is higher than that of Nylon 6 (39 J/m), let alone Nylon 6/clay nano-composites (23 J/m). PP-g-MAH was identified as an effective toughener for Nylon 6/clay nano-composites.

Because of the excellent properties, Nylon 6/clay nano-composites and blends have been used widely in the field of precision injection molding [7, 90]. The examples of application include engine covers, timing belt covers, oil reservoir tanks and fuel hoses in automobile and various connectors in electric and electronic industry. Other potential applications have taken advantage of the improved barrier properties and transparency of the nano-composites [7].

2.1.5 Syndiotactic polystyrene/clay nano-composites

Syndiotactic polystyrene (sPS) has received considerable attention as the potential engineering plastic, due to its high melting temperature, fast crystallization rate and good chemical resistance [93]. Since Ishihara *et al.* [93] first obtained syndiotactic polystyrene, more and more studies [93-95] have been carried out on the synthesis and copolymerization of sPS.

In recent years, polymer/clay nano-composites have also attracted great interests from industries and academic. However, at least two important factors need to be considered to achieve the homogeneous dispersion of the clay layers in sPS. First, the surfactant should be intercalated between silicate layers of clay through ionic bonding. Second, the hydrophobic tail of the surfactant molecule should be partially compatible or interacted with sPS molecules [96, 97]

sPS/clay nano-composites were mainly prepared by solution intercalation method [96-101]. It was impossible to fabricate the sPS/clay nano-composites by direct melt intercalation method [99-101]. In general, silicate should be modified with alkyl ammonium for the polymer to penetrate easily into the silicate layer because alkyl ammonium makes the hydrophilic silicate surface organophilic. However, the interaction between alkyl ammonium and the silicate layer is not thermally stable enough to resist the high-melt processing temperatures of sPS (about 270°C), which makes the melt intercalation of sPS into the clay gallery very difficult.

There are only a few papers on sPS/clay nano-composites [96-101]. These nano-composites have markedly improved thermal stability in comparison with pure sPS [96, 97]. Also,

sPS/clay nano-composites exhibit higher mechanical properties such as strength and stiffness than the matrix polymer [98, 99].

It is clear that clay minerals are cost-effective and versatile raw materials for polymer nano-composites, due to their unique layered structure, rich intercalation chemistry, high aspect ratio, high in-plane strength and stiffness, as well as abundance in nature and low cost. As presented above, clay based nano-composites from various polymers have been reported in the past decade. These polymer nano-composites have demonstrated significantly improved properties, including mechanical, thermal, gas and liquid barrier, flame retardancy, optical, electrical and biodegradable properties. In addition, the very low level of clay loading makes the overall density similar to neat polymer and also greatly improves their processing capability for film or fibers, which is unlikely in conventional polymer composites. As a result, clay based polymer nano-composites have been produced as energy-saving and environment-friendly automotive parts and packaging materials [1, 2, 56]. Their future markets will further expand from current automotive, packaging and containers, coatings and pigments to other industries such as appliances and tools, electro-materials, building and construction. Moreover, clay-based polymer nano-composites have shown promising applications in the biomedical and bioengineering fields [2, 56].

However, in spite of these efforts and some successes in commercial development of clay based polymer nano-composites, their design, manufacturing and applications are often empirical and large scale productions are still in its infancy. This is mainly due to the limited theoretical knowledge on such novel nanostructure materials, such as a basic guideline for the selection of surfactants and the modification of clays for the targeted polymer matrix, the mechanisms of superior reinforcement observed as compared with their micro-counterparts,

and the establishment of a simple processing-structure-property relationship for such nano-composites. Therefore, further development of polymer/clay nano-composite materials depends largely on our understanding of the above fundamentals in relation to their formation, processing, property prediction and design.

2.2 Polymorphism and Phase Transition in Polymers

2.2.1 Polymer crystals

Polymers are partly crystalline. As high molecular weight, the polymer chains were calculated to be much longer than the crystallites. Hence, it was assumed that they passed in and out of many crystallites. This is the basis of the fringed-micelle model [102].

It is proposed that a semi-crystalline polymer consists of small crystalline regions (crystallites or micelles), each having a precise alignment, which are embedded within the amorphous matrix composed of randomly oriented molecules. According to this model, the crystallites are about 10 nm long [102]. The disordered regions separating the crystallites are amorphous. The fringed-micelle model was accepted for many years and was used with great success to explain a wide range of behaviors in semi-crystalline plastics.

More recently, investigations centered on polymer single crystals grown from dilute solutions. These crystals are regularly shaped, thin platelets (or lamellae), approximately 10-20 nm thick, and on the order of 10 μm long. Frequently, these platelets will form a multilayered structure. It is theorized that the molecular chains within each platelet fold back and forth on themselves, with folds occurring at the face. This led to the folded-chain model, illustrated in Figure 2.5.

Figure 2.5 The chain folded structure for a polymer crystallite [102, 103]

When a polymer crystallizes from the melt, the most commonly observed structure is the spherulite. As implied by the name, each spherulite may grow to be spherical in shape [103].

The spherulite consists of an aggregate of ribbon-like chain folded crystallites (lamellae) approximately 10 nm thick that radiate from the center outward. The individual chain folded lamellae crystals are separated by amorphous material. Tie-chain molecules that act as connecting links between adjacent lamellae pass through these amorphous regions [14, 102].

Usually the spherulites are really spherical in shape only during the initial stages of crystallization. Spherulites form by nucleation at different points in the samples and grow as spherical entities. The growth of the spherulites stops when impingement of adjacent spherulites occurs.

As the crystallization of a spherulitic structure nears completion, the extremities of adjacent spherulites begin to impinge on one another, forming more or less planar boundaries. When the spherulites are nucleated simultaneously, the boundaries between them are straight. However, when the spherulites have been nucleated at different times, they are different in size when impinging on one another, their boundaries form hyperbolas [102].

Normally, the size of the spherulites may be larger than 100 μm [102]. However, with the addition of fillers, the size of the spherulites will decrease [104]. This is because the growth of the spherulites must stop when impinging the surface of fillers. The detailed structure of polymer spherulites can be studied by electron microscopy. Up to now, there is no report on the influence of nano-clay on the size of spherulites [7].

Spherulites are considered to be the polymer analogue of grains in poly-crystalline metals and ceramics. However, as discussed above, each spherulite is really composed of many different lamellae crystals and, in addition, amorphous phase.

The crystallization of polymers is of enormous technological importance. The presence of the crystals has an important effect upon polymer properties. There are many factors which can affect the rate and extent to which crystallization occurs for a particular polymer. They can be processing variables such as the rate of cooling, the presence of orientation in the melt and the melt temperature. Other factors include the tacticity and molar mass of the polymer, the amount of chain branching and the presence of any additives such as nucleating agents.

Melt-crystallized polymers are never completely crystalline. Because there are an enormous number of chain entanglements in the melt and it is impossible to form a 100% crystalline polymer during crystallization. The degree of crystallinity can be measured by several methods. For example: density method, wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) [102, 103].

2.2.2 Theory of nucleation

- Homogeneous nucleation

At temperature below a material's equilibrium melting temperature, the driving force for crystallization is the difference in Gibbs free energy between the liquid and the solid. When a crystal is formed, Gibbs free energy of the system will decrease. It might be expected that the liquid phase would spontaneously crystallize. In fact, at the same time, there is another energy term to be considered, the surface energy [105, 106]. When a crystal is formed, the surface energy of the system will increase. The sum of these two terms initially increases, goes through a maximum, and then decreases (shown in Figure 2.6). The radius at which the Gibbs free energy curve is at a maximum is defined as the critical radius r^* for a nucleus of solid in liquid. A viable nucleus which leads to spontaneous crystal growth must have a radius greater than or equal to r^* .

Figure 2.6 Gibbs free energy of nuclei as a function of radius [106]

- Heterogeneous nucleation

Under practical crystallization condition, nuclei of the solid can be formed on surfaces that catalyze crystallization, such as fillers, inclusions in the material, or the walls of the container. The analysis of the energies involved in heterogeneous nucleation follows the same method as the one used for homogeneous nucleation. One thing we must noted is, for heterogeneous nucleation, the surface energy term involves the surface energy between the solid nucleus and the liquid, and the change in surface energy of the catalyst surface as it is coated by the nucleus [105, 106].

Figure 2.7 Plot of ΔG versus radius for homogeneous nucleation and heterogeneous nucleation [106]

Figure 2.7, a graph of ΔG as a function of radius of the nucleus, shows the difference between homogeneous nucleation and heterogeneous nucleation.

From this figure, it can be seen that the critical radius, r^* , does not change when the nucleation because heterogeneous. However, the critical Gibbs free energy, ΔG^* , is greatly decreased. A lower value of ΔG^* means a lower activation energy to be overcome in nucleation. In other words, nucleation takes place more easily. That is why the addition of filler will favor the crystallization of polymer.

In fact, neither the filler concentration, nor the particle size appears to have an influence on the nucleation of polymer [9, 104, 107]. Recently, some results [108] show that the presence

of nano-clay displays a higher propensity to nucleate polymer crystallization than other fillers. The behavior of nucleation depends on the different nano-clay contents slightly.

2.2.3 Introduction to polymorphism and phase transition in polymers

Polymorphism is a widely observed phenomenon in polymers and almost all crystalline polymers are polymorphic, if proper conditions for crystallization of the different forms can be met [10]. Polymers may exhibit several polymorphs depending on factors including crystallization conditions, mechanical stress, plastic deformation and temperature/pressure change [10, 11].

In most case, the formation of a particular polymorph under given crystallization conditions is controlled by its thermodynamic stability. In some special cases, when more than one minimum of free energy is available, the form obtained is the one crystallized more rapidly, indicating a kinetically controlled process.

Under certain conditions, phase transition can occur between different polymorphs. Because this transition takes place directly (there is no indication that a transition is from one polymorph to the amorphous state first, then to another polymorph), it is also called solid state phase transition [10, 12]. The thermodynamic transition between different forms as described above is normally discontinuous. The difference between polymorphs is given by a different metrical description of the corresponding lattices [10].

Such transitions are first-order transitions and can be induced thermally, mechanically or chemically [10, 11]. The polymorphism and phase transitions between polymer crystals caused by several different factors are summarized below.

Phase transition induced by thermal treatment

In some case, the transition occurs reversibly between two forms, which are thermodynamically favored below or above a given temperature [10]. For instance, polytetrafluoroethylene (PTFE) undergoes a reversible first-order transition at 19°C at atmospheric pressure [109]. In this transition, the molecular conformation changes slightly from a 13/6 to a 15/7 helix. The molecular packing changes from an ordered structure with a triclinic unit cell corresponding to a positioning of the chain axes nearly hexagonal towards a partially disordered structure which has a partial intermolecular rotational disorder and a hexagonal positioning of the chain axes. Also, polyethylene (PE) and alternated co-polymer ethylene-tetrafluoroe-thylene (ETFE) can have thermally induced reversible transition [102].

In other cases, the transitions induced by thermal treatments are usually from a less stable state to a stable state and therefore irreversible. One example is the transition from the γ -form of syndiotactic polystyrene (sPS) with helical conformation of the chain towards the α form with a *trans*-planar conformation of the chain, which occurs giving sufficient times, only above 180°C [12]. Irreversible transition can also be observed for PP [10].

Phase transition induced by deformation and stress

Very frequent are the cases of stress-induced crystallization. For example, a slightly vulcanized natural rubber is able to crystallize when there is sufficient chain orientation and a tensile deformation. The crystalline phase reverts to its original amorphous phase after relaxation [102]. Also, Nylon 6 and polybutylene terephthalate (PBT) may have stress induced solid to solid transition [10].

Polymorphism and comonomeric units

The presence of comonomeric units can alter the polymorphic behavior of a polymer, favoring the formation of a particular crystalline polymorph in certain conditions [102]. For example, small amounts of tetrafluorethylene can force PVDF to crystallize in a new crystal form [110].

As usual, this can be due both to thermodynamic and kinetic reason. In fact, the presence of comonomeric units increases, in general, the energy content of all the crystalline forms. However, the extent of energy increase may be different for different chain conformation or packing [10]. In addition, the influence of the comonomeric units on the polymorphic behavior of a polymer can be also due to a change in the crystallization rates of the various forms [102].

Polymorphism and polymer blends

For instance, blends of PVDF with polymethylmethacrylate [111] and blends of Nylon 6 with polypropylene-grafted-maleic anhydride (PP-g-MAH) [112-115] have been reported recently in the literature in which the polymorphic behavior of the polymers appears to be altered. However, the reason why polymer blends can influence the polymorphism is still not clear [10, 102].

2.2.4. Polymorphism and properties in polymers

The presence of polymorphism can be either detrimental or beneficial for the performance and/or the processing of a polymeric material. The properties of a polymeric material depend

on its polymorphic behavior. In other words, different polymorphs exhibit different properties even for the same polymer [10-12, 102].

Therefore, it is critical to have an in-depth understanding of the physical properties, including mechanical, thermal, electrical and chemical properties of different polymorphic forms for a polymer [10-12]. Polymorphs and transformations of polymer materials have always attracted both academic and commercial interests [10]. The phase transitions in polymer crystals induced by changing temperature, pressure, stress, reagents and electric field have been studied [11].

2.2.5. Thermodynamic and kinetic consideration

Among all available polymorphs in a certain polymer, there is only one polymorph that is thermodynamically stable. Other polymorphs can be considered as metastable states, which possess a local free energy minimum but it may not have the lowest energy from a global point of view [10, 14]. This can be seen clearly in Figure 2.8. Decomposition of the metastable state requires activation. Although a metastable state may transform to an equilibrium state eventually, its lifetime can sometimes be longer than the time scale of the experiment [105].

Figure 2.8 An illustration of a metastable state in a plot between free energy (F) and order parameter $\langle \Phi \rangle$. The ΔF is an activation barrier.

However, in the majority of cases of phase transitions, the limiting state is practically determined by kinetics [10]. In a classical metastable state, therefore, the system can be trapped into a local F minimum that is not the global minimum. A general explanation based on kinetics is that such a state is attainable at a faster rate. In terms of statistical mechanics, due to the limited average fluctuation amplitude, the atoms or molecules of the system have a large probability to choose a pathway which possesses a lower F barrier regardless of the thermodynamic stability. In other words, these atoms and molecules are “blind” and can not predict the thermodynamic outcome behind the energy barrier [14]. If most of the atoms and molecules are at a local minimum, a macroscopic metastable state would form which can be detected as long as the time and size scales of this state are compatible with those of the experimental observation [105]. It is possible that during a transformation process, a metastable state may exist due to its fast kinetic pathway even though this state is thermodynamically less stable than the equilibrium state [102, 105].

Considering liquid to crystal transition in a single component system, a smaller barrier for the metastable state implies that not only the transition possesses a faster kinetics pathway at equivalent undercoolings (ΔT_s), but also lower ΔT is required for a practicably fast rate to be achieved when compared to the stable state [14, 105, 106]. For making a comparison on temperature scale, it must be noted that the upper stability limit of the metastable state is at a lower T , i.e., the metastable state has a lower melting point $(T_m)_{\text{meta}}$ compared to that of the stable state $(T_m)_{\text{st}}$ [105]. Figure 2.9 illustrates the relationship between the overall phase transition rates and temperature [14, 105]. Since $(T_m)_{\text{meta}} < (T_m)_{\text{st}}$, in the T region between $(T_m)_{\text{st}}$ and $(T_m)_{\text{meta}}$ (region I), no metastable state can be obtained. However, when T is lowered beyond $(T_m)_{\text{meta}}$, the formation rate for the metastable phase (R_{meta}) increases faster with decreasing T than the rate of formation for the stable phase (R_{st}). This results in a crossover of the two rate curves at T^* as shown in Figure 2.9. This may lead to the situation that when a liquid system is being cooled, the stability regime of a metastable solid (or mesomorphic) state can be reached before the ultimately stable phase had time to form [105]. Therefore, the formation of metastable phase would dominate.

Figure 2.9 Curves for the phase transformation rates, R , as a function of T for both stable and metastable states [14]

Polymers in general are highly under-coolable. In other words, they often require high ΔT_s to induce crystal formation. Therefore, the behavior shown in Figure 2.9 is often seen for polymers. In fact, there can be more than one metastable phase or even a whole spectrum of such phases forming a hierarchy of metastabilities which can evolve successively or in competition with others according to the Ostwald stage rule [10, 11, 14].

2.2.6. Metastability theory in polymer phase transitions

In the classical concept, thermodynamic states are considered to be of infinite large size. However, polymers may have metastable states present due to small phase size [14, 15]. Thus, although ordered and disordered models have been used to explain the phase

transformations in metals and alloys [105], they are not applicable in polymers due to many limitations [10].

The role of metastability in polymer phase transitions has been thoroughly discussed and examined by Keller and Cheng [14, 116]. In addition to classical metastability that describes the phase transformation from one state to another according to the Ostwald stage rule, circumstantial metastabilities including morphological, compositional and other types of metastability, were proposed and believed to be important as far as the phase transitions of polymers is concerned. The existence of circumstantial metastabilities needs to be invoked based on the constraints of size, dimensionality and so on [14]. The morphological metastability of the restricted states is associated with phase size, i.e., lamellar thickness. It is believed that small phase size or lamellar thickness would impede the transition from morphological metastable state to the stable state [14].

As is well known, the basic crystal units in a flexible chain polymer are lamellae containing the chains in a folded conformation with the lamellar thickness (l) equal or related to the fold length. In an isothermal crystallization process, the primary crystal growth takes place along lateral directions with constant thickness (hence fold length), where the lamellar thickness is determined by the prevailing ΔT ($\Delta T = T_m - T_c$) [14, 102]. This thickness is in the 10-50 nm range [14]. The small thickness of the lamellae lowers the crystal stability, thereby depressing the melting (or dissolution in the case of a solution crystallization) temperature and thus, in this sense the crystals are “morphologically metastable”. The melting temperature depression associated with the crystal size can be expressed quantitatively through the Gibbs-Thomson relation [106] which, as applied to polymer crystals in the Hoffman-Weeks formulation [14, 16], is

$$T_m = T_m^0 (1 - 2\sigma_e / l\Delta H) \quad 2.2$$

where T_m is the melting point of the crystal of thickness l , T_m^0 is the melting T of the ultimately stable crystal, ΔH is the heat of fusion, and σ_e is the surface free energy of the basal or fold-containing plane of the lamella. In this case, the effect of other side surfaces being considered negligible. It has been proved that this equation is usually closely obeyed for polymer crystallization [14].

One important issue is the causes for the formation of small phase size, which may include mutual impingement of domains, external constraints, interruption of phase formation, e.g., by vitrification of the melt, or inherent slow phase growth rate. In the case of chain-folded lamellar crystals in polymers, the presence of an explicit kinetic barrier at a particular ΔT , leads to the formation of certain lamellar thickness corresponding to a given ΔT . In other words, each thickness could be considered as a distinct metastable structure, i.e., a morphological “polymorph”.

Figure 2.10 Schematic plots of temperature versus reciprocal size ($1/l$), showing stability inversion of metastable and stable phases with decreasing size at the point Q (see also in reference 116)

The above discussion implies that each crystallographic polymorph, as associated with the lattice symmetry, can be in the form of small crystals. Therefore, each polymorph has its own size dependence according to Hoffman-Weeks equation, as determined by the parameters σ_e and ΔH , which describes a linear relationship between T_m and $1/l$ (see Figure 2.10) with T_m^o as an intercept along the abscissa, and a slope of $T_m^o(\sigma_e/\Delta H)$. If two different polymorphs are possible (one stable and the other metastable), then in view of the fact that $(T_m^o)_m < (T_m^o)_s$, the T_m versus $1/l$ lines can cross over under a condition that $(\sigma_e/\Delta H)_m < (\sigma_e/\Delta H)_s$, which is a frequently obeyed inequality [14]. Keller and Cheng [14] believe that a metastable phase defined by the classical metastable state may become the stable one and a conventionally

known stable phase may become metastable when the phase size is sufficiently small. In other words, the stability of polymorphs may invert with lamellar size.

Figure 2.10 may provide further information about the connection between stability and kinetics. The T_m versus $1/l$ lines in Figure 2.10 represents the minimum phase size that is stable at each T . This implies that the polymorph which is stable down to the smallest size at a specific T will appear first in the course of isothermal crystal growth at that T . From the viewpoint of kinetics [14, 16], the smallest stable size is referred to its critical nucleus that represents the energy barrier for crystal nucleation. The smaller the critical nucleus, the faster the crystallization rate of crystalline phase.

Metastability theory was a major step forward toward understanding the mechanism of polymer phase transition. However, due to the experimental limitations [15], there is very few attempts [16, 17] to apply this theory to explore phase transitions in polymers. For example, Ho et al [16] investigated syndiotactic polystyrene (sPS) annealed at 290°C and then crystallized at different temperatures. Three melt peaks are observed. The authors identified the highest melting as the melt of reorganized metastable α crystals and the intermediate melting should correspond to the melting of stable β crystals. They believed the evidence of lower melting of stable β phase as compared to metastable α phase provided the evidence that a structural stable phase became metastable if the lamellar size is small enough. However, in most other annealing studies on sPS, there is no report on assigning a higher temperature melting peak to the metastable α phase [10, 13, 96-98].

2.2.7 Characterization techniques

The wide angle X-ray diffraction (WAXD) [10, 102] technique is unique in providing detailed information on the structure organization at the molecular level in different crystalline polymers. Fourier transform infrared (FTIR) spectroscopy [10, 12] and solid-state nuclear magnetic resonance (NMR) [10, 102] can also be used advantageously in some case in the recognition and quantification of the different polymorphs in polymeric materials.

Differential scanning calorimetry (DSC) can be used to investigate polymorphism and phase transition in polymers. However, quantitative analysis of DSC results is considered less reliable and less discernable [9, 10, 15, 92] because polymers can easily shift from one metastable state to another with thicker lamellar crystal during heating [15].

2.3. Polymorphism and Phase Transition in Nylon 6

2.3.1 Polymorphism and phase transition in pure Nylon 6

Nylon 6 or polyamide 6 has found wide applications in the forms of fibers and engineering plastics. The polymorphism and crystalline transition or Brill transition of Nylon 6 have been extensively studied [117-122]. Nylon 6 exhibits two crystalline phases, namely α phase and γ phase [122].

The α phase has monoclinic structure and consists of fully extended planar zigzag chains, in which adjacent anti-parallel chains are joined by the hydrogen bonds. Therefore, it is thermodynamically more stable and can be obtained by slow cooling from the melt or crystallizing at higher temperature.

The γ phase also has a monoclinic structure, but the twisted chains allow hydrogen bonds to be formed between parallel chains. The γ phase is less stable and can only be obtained by fiber spinning at a high speed or by fast cooling from the melt or crystallizing at lower temperature. The behavior of the γ phase with temperature has been reported by Ramesh et al [117].

Figure 2.11 shows the crystal structure of α phase and γ phase in Nylon 6 [123].

Figure 2.11 The crystal structure of α phase and γ phase in Nylon 6 (a) α phase

(b) γ phase [123]

Comparison of α phase and γ phase in Nylon 6 are listed in Table 2.4.

Table 2.4 Comparison of α phase and γ phase in Nylon 6

	α phase [10, 118]	γ phase [10, 122]
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/a$
Lattice parameters of unit cell	$a=9.56\text{\AA}$	$a=9.33\text{\AA}$
	$b=17.2\text{\AA}$	$b=16.88\text{\AA}$
	$c=8.01\text{\AA}$	$c=4.78\text{\AA}$
	$\beta=112.5^\circ$	$\beta=121^\circ$
Number of monomeric units in an unit cell	8	4
Density (g/cm^3)	1.23	1.17

The α phase can be transformed into the γ phase by treatment in aqueous potassium iodide-iodine solution [117]. The γ phase can be transformed into α phase on heating. The phase transition in Nylon 6 has been well documented and is known as Brill transition. WAXD, NMR and FTIR have been used to study this phase transition. Because there is little energy difference between the two polymorphs, this transformation is seldom investigated by DSC [122]. In general, the Brill transition temperature in Nylon 6 is about 160°C [117].

In WAXD patterns, the α form crystal of Nylon 6 exhibits characteristic peaks at 2θ of 20.5° and 24° (α_1 and α_2) which are indexed as 200 and 002/202 reflections respectively.

Meanwhile, the characteristic peak of γ form is indexed as 001 and appears at 2θ of about 21.5° (see Figure 2.12).

Figure 2.12 X-ray diffraction patterns of α phase and γ phase in Nylon 6

Furthermore, Gurato et al [120] investigated the effect of crystallization temperature on polymorphism and phase transition in Nylon 6. Their results showed that high crystallization temperatures favored α crystal, while low crystallization temperatures favored γ crystal. At the same time, α_1 shifts to lower angle and α_2 shifts to higher angle with increasing crystallization temperature. The d -spacing corresponding to γ form crystal hardly has any change with increasing crystallization temperature [120]. The increase in the d -spacing of the α_1 at high temperature was attributed to the thermal expansion of the lattice, while the decrease in the d -spacing of the α_2 to the respective lattice distortion [120].

Understanding the changes in the physical properties of the semi-crystalline polymers during the phase transition is of practical importance [11]. Ito et al [29] has described the effects of crystalline forms on the deformation behavior of Nylon 6 and found the γ phase of Nylon 6 was more ductile than the α phase. The effect of crystal form on the ductility is explained based on the difference in the interchain interactions due to hydrogen bonding in the crystalline regions. The distance between adjacent amide groups, where hydrogen bondings are formed, is longer for the γ phase than for α phase. These results suggest that interchain interaction in γ phase is smaller than α phase [29].

2.3.2 Polymorphism and phase transition in Nylon 6/clay nano-composites

The polymorphism and phase transition in Nylon 6/clay nano-composites is closely related to their properties. One of the interesting results is that the γ phase crystals of Nylon 6/clay nano-composites tend to be more ductile than the α phase [29]. Meanwhile, Vaia et al [9] suggests that the stabilization of γ crystalline phase throughout the temperature range may be the reason why Nylon 6/clay nano-composites have much higher HDT. Therefore, since the initial studies by Toyota research group [3-7], the polymorphism and crystalline transition of Nylon 6 nano-composites have received considerable attention [9, 23, 30, 55, 92, 124].

Compared with traditional neat resin (Nylon 6), there is more interesting result about the polymorphism in Nylon 6/clay nano-composites [3, 7, 9, 30, 92, 124]. That is: for Nylon 6/clay nano-composites, the addition of nano-clay could favor the formation of γ phase crystal. The results of Vaia et al [9] indicate that the γ form crystal forms near the surface of

the silicate layers and the α form crystal forms remote from the layers, where the influence of the silicate surface on chain conformation and the ability for the chains to fold is not substantial. However, the reason why the addition of nano-clay could favor the formation of γ phase crystal is still under discussion [9, 92].

2.3.3 Polymorphism and phase transition in Nylon 6 and functionalized polyolefin blends

The blends of polyamide and polyolefin, especially functionalized polyolefin, have been studied systematically mainly due to the technological application of these materials [112-114]. It has been shown that the presence of functional reactive groups, e.g., maleic anhydride on the polyolefin chains has a strong effect on the phase morphology, physical and mechanical properties of the blends. For Nylon 6 and non-functionalized polyolefin blends, just as neat Nylon 6, there is only α phase obtained. However, for Nylon 6 and functionalized polyolefin blends, γ crystalline phase is the major phase present [112]. The researchers believed this was just caused by the change in nucleation mechanism due to the reaction between the functional groups of polyolefin and the polar groups in polyamide chain [112].

2.3.4 Polymorphism and phase transition in Nylon 6/clay nano-composites and functionalized polyolefin blends

In recent years, the Nylon 6/clay nano-composites and functionalized polyolefin blends have also generated much academic and commercial interest [37, 91]. However, most of their work has focused on mechanical property enhancements. Up to now, there is no article published on the polymorphism and phase transition of the Nylon 6/clay nano-composites and functionalized polyolefin blends.

2.4 Polymorphism and Phase Transition in Syndiotactic Polystyrene

2.4.1 Polymorphism and phase transition in syndiotactic polystyrene

Syndiotactic polystyrene has four types of crystalline form (α , β , γ and δ) and two mesomorphic forms depending on the crystallization condition from melt or solution [13, 16, 125-129]. It has been shown that both the α and β forms have an all-trans planar zigzag (ttt)_n backbone conformation, whereas the γ and δ forms have a helical (trans, trans, gauche, gauche, (ttg⁺g⁺)_n) backbone conformation. The α form with a hexagonal unit cell and the β form with an orthorhombic unit cell, both with an identical $c = 5.1\text{\AA}$, can be obtained from the melt or the glassy state of sPS under different thermal conditions [13, 125]. The γ and δ forms, both with an identical $c = 7.8\text{\AA}$, can only be formed from solvent swelling of glassy sPS and have been shown to have the same monoclinic crystal structure. Among these four crystalline forms, the α form with $a = 26.26\text{\AA}$ and the β form with $a = 8.81\text{\AA}$, $b = 28.82\text{\AA}$ are the primary crystalline polymorphs and result from different thermal and pressure treatments above the glass transition temperature (T_g). The melting temperature for both forms is close to 270°C and the transformation from α form to the β form is hardly implemented even at temperatures close to the melt point [10, 13]. Furthermore, each of them can be further divided into two types by different degrees of structural order [126, 127]. The two limited disordered modifications are respectively known as α' and β' , and two limited ordered modifications are referred to as α'' and β'' . This means that **α form** is a general designation of α' and α'' , and **β form** has the same meaning. In general, being crystallized from the melt, sPS forms the β' form crystal or α'' form crystal because of different crystallization conditions [16].

In WAXD patterns, the α form crystal of sPS exhibits characteristic peaks at $2\theta = 6.7$ (110), 11.6° (300), while the β form at $2\theta = 6.1$ (020), 12.2 (040), and 18.6° (060) (Figure 2.13).

Figure 2.13 X-ray diffraction patterns of α phase and β phase in sPS

A number of studies [10, 12, 13, 125-130] have been carried out on polymorphs of sPS. X-ray diffraction, electron diffraction, Fourier-transformed infrared (FTIR) spectroscopy and solid-state nuclear magnetic resonance (NMR) have been used in the determination and quantification of the different polymorphs in polymeric materials. Guerra and his coworkers [13, 127] first gave the nomenclature of α crystal and β crystal and studied their formation from melt and glass phase of sPS in detail. Their results showed that the cooling rate from the melt and the thermal history of the melt are the major factors influencing the formation of these forms. The formation of α crystal is a kinetically controlled process, meanwhile β

crystal structure is more stable thermodynamically. If the memory effect of nuclei is eliminated by heating to high enough temperature, cooling sPS down at a moderate cooling rate (say less than 20°C /min) from the melt, will lead to the formation of its β form, otherwise, the formation of α form. The α form can also be obtained by quenching from the melt or by annealing from the amorphous phase. The intensities and Bragg distance observed in the powder patterns for the α and β modifications have been given by Guerra *et al.* [13]. Ho *et al.* [16] also discussed the effects of maximum annealing temperature, the cooling rate to the crystallization temperature, crystallization temperature and crystallization time on the polymorphism of melt-crystallized syndiotactic polystyrene, using the metastability theory given by Keller and Cheng [14].

2.4.2 Polymorphism and phase transition in sPS/clay nano-composites

The polymorphs of sPS/clay nano-composites have also been studied [96, 97, 100, 101]. The formation of α crystal and β crystal and their relative fractions in sPS/clay nano-composites are also strongly dependent on the cooling rate from the melt and the thermal history of the melt. However, a significant change in polymorphism of sPS was observed by the inclusion of different clays [96, 97]. The temperature regime of the α crystal formation in sPS was found to expand considerably by the presence of the organoclay. In other words, the organoclay was observed to favor the formation of α crystal [97].

2.5 Polymorphism and Phase Transition in Super-critical Fluid

Figure 2.14 Schematic plots of supercritical fluid

With increasing pressure and temperature over a certain critical temperature and critical pressure, a pure component will reach its supercritical fluid (SCF) region (Figure 2.14). All kinds of the supercritical fluid have some interesting properties [18-20, 130-132]. In the supercritical region, a substance that is a gas at normal condition exhibits a liquid-like density and a more increased solvent capacity that is pressure-dependent. SCFs begin to exhibit significant solvent strength when they are compressed to liquid-like densities. A supercritical fluid has its viscosity similar to a gas and its fluidity much better than a liquid, and its surface tension is substantially less than that of a liquid so that the fluid can diffuse much more readily into a solute material, as in the nature of a gas. Consequently, a reaction which is diffusion-controlled in the liquid phase can be enhanced by conducting it at supercritical conditions, due to higher diffusivity and elimination of gas/fluid and fluid/fluid

interphases. The unique property of an SCF is its pressure-dependent density, which can be continuously adjusted from that of a vapor to that of a liquid.

Therefore, SCFs exhibit interesting behavior by combining the properties of conventional liquids and gases. Specifically, their liquid-like densities allow for solvent power in orders of magnitude higher than gases, while gas-like viscosities lead to high rates of diffusion [18, 130].

SCFs offer a series of technical advantages. Their characteristics have been exploited in chromatography and chemical engineering, particularly in a variety of extraction and separation processes [132]. Also, SCFs can be used as reaction media. They form a single-phase mixture with gaseous reactants, sometimes avoiding a rate-limiting mass-transfer step and thus enhancing reaction rates [130]. Currently, large-scale chemical manufacture is facing a serious solvent problem due to environmental concerns. Regulation of the use of hazardous organic solvents such as chlorinated hydrocarbons is becoming increasingly stringent [130].

Supercritical carbon dioxide (SCCO₂), readily accessible with a critical temperature of 31.1 °C and a critical pressure of 73.8 atm, has excellent potential for achieving this goal. It is abundant, inexpensive, nonflammable, nontoxic, and environmentally benign. It has a high solubility for nonpolar organic compounds. Although its ability to dissolve polar, ionic, or polymeric compounds is exceedingly limited, small amounts of a polar entrainer or an appropriate surfactant dramatically change the microenvironment to greatly increase the solubility of such substances [18, 130].

The applications of SCFs are in the area of polymer processing, which includes polymerization process, polymer purification and fractionation, ultrafine powder formation and environmentally preferable solvents for solution coatings [130, 131]. In making microcellular polymers, supercritical CO₂ is chosen as the foaming agent due to its easily attainable critical parameters as well as nontoxicity, nonflammability and commercial availability in high purity [132].

The principles of molecular thermodynamics provide the vehicle for connecting classical thermodynamics with the physicochemical properties of the components in polymer/SCF solution. To form a stable polymer-SCF solvent solution at a given temperature and pressure, the Gibbs free energy must be negative and at a minimum. The Gibbs free energy of mixing is

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad 2.3$$

where ΔH_{mix} and ΔS_{mix} are the change of enthalpy and entropy, respectively, on mixing. Enthalpic interactions depend predominately on solution density and on polymer segment-segment, solvent-solvent and polymer segment-solvent interaction energies. ΔS_{mix} depends on both the combinatorial entropy of mixing and the noncombinatorial contribution associated with the volume change on mixing, a so-called equation of state effect. It is reasonable to assume that the combinatorial entropy of mixing a polymer with an SCF solvent should not vary significantly with temperature and pressure near the conditions where the polymer dissolves in solution as long as the solvent density does not change dramatically [130]. The combinatorial entropy always promotes the mixing of a polymer with a solvent. However, the parameters that govern solubility of polymers in CO₂ are not fully understood.

SCCO₂ is not expected to be a good solvent for polymers [18, 130]. However, supercritical CO₂ has significant solvent capacity, fluidity and diffusion ability. It can infuses into solid polymer, increases the degree of polymer swelling, increases chain mobility, accelerates the relaxation of the macromolecules, increases the free volume and depresses the glass transition temperature [18, 130].

In supercritical CO₂, the conditions of phase transformation must be different from those not in supercritical CO₂. For example, normally only amorphous polycarbonate (PC) can be obtained. But in supercritical fluid, crystalline PC was presented because of the change in crystalline kinetics [20]. Further, phase transformation from α crystals to β crystals of sPS, which can not occur at normal condition, can occur in supercritical CO₂ [19]. Both thermodynamics [19] and kinetics [20] of phase transformation are different from those not in supercritical CO₂. So investigation of polymorphism and phase transition in supercritical fluid, may help us to have a deeper understanding of the thermodynamics and kinetics of phase transformation in polymer. However, up to now, there is no theory to explain the molecular mechanism for phase transition of polymer crystals in SCF.

Chapter 3 Polymorphism in Nylon 6/Nano-Clay/Functionalized Polyolefin Blends

In this chapter, X-ray diffraction and Fourier transform infrared spectroscopy (FTIR) have been used to analyze the crystallization behavior and the interaction of the Nylon 6/clay nano-composites and functionalized polyolefin blends.

3.1 Experimental Section

3.1.1 Materials

Commercial grade Nylon 6, UBE SF 1018A, was chosen as the matrix of polymer/clay nano-composites. Different amounts of montmorillonite mineral modified by Nanomer® I.30TC were mixed into Nylon 6 by using a twin screw extruder. Commercial grade polypropylene-grafted-maleic anhydride (PP-g-MAH), CXA 50E561 Dupont, was used to manufacture Nylon 6/clay nano-composites and functionalized polyolefin blends. Polypropylene (PP) used in this study was H101E supplied by Polyolefin Company.

3.1.2 Melt processing

Before blending, all components were dried under vacuum at 110°C for Nylon 6 and at 70°C for PP-g-MAH and montmorillonite mineral, for 24h. A twin screw extruder was used for the preparation of Nylon 6/clay nano-composites and functionalized polyolefin blends. The temperature of the extruder was 250°C, and the screw speed was maintained at 30 rpm. Each sample was extruded twice.

The Nylon 6/nano-clay/functionalized polyolefin blends prepared in this work are summarized in Table 3.1.

Table 3.1 Nylon 6/nano-clay/functionalized polyolefin blends prepared in this work

	Nylon 6	Nano clay	PP-g-MAH
Percentage (wt %)	100	0	0
	97.5	0	2.5
	95	0	5
	92.5	0	7.5
	90	0	10
	97.5	2.5	0
	95	2.5	2.5
	92.5	2.5	5
	90	2.5	7.5
	87.5	2.5	10
	95	5	0
	92.5	5	2.5
	90	5	5
	87.5	5	7.5
	85	5	10
	92.5	7.5	0
	90	7.5	2.5
	87.5	7.5	5
	85	7.5	7.5

	82.5	7.5	10
	90	10	0
	87.5	10	2.5
	85	10	5
	82.5	10	7.5
	80	10	10

3.1.3 Wide-Angle X-ray diffraction (WAXD)

The X-ray diffraction experiments were performed using a Rigaku RINT 2200 diffractometer with nickel-filtered Cu K α radiation. The generator was operated at 40 kV and 30 mA, and the scan rate is 3°/min. The films for wide-angle X-ray diffraction measurement were all prepared with a thickness about 0.05mm in the following way. For the crystallization from the melt, Nylon 6/clay nano-composites and functionalized polyolefin blends particles were sandwiched between two cover glasses of 0.16mm thick and heated on a hot stage at 300°C, prior being pressed into film and kept for 10 minutes. This process was able to eliminate any thermal history of Nylon 6. Finally, the samples were air cooled to room temperature.

It has been shown that the α form crystal of Nylon 6 exhibits characteristic peaks at around $2\theta = 20.5$ (α_1), 24° (α_2) which are indexed as 200 and 002/202 reflections respectively. Meanwhile, the characteristic peak of γ form is indexed as 001 and appear at about $2\theta = 21.5^\circ$. Deconvolution analysis was carried as described in 3.1.4.

3.1.4 Deconvolution analysis

The method of separation of overlapping X-ray diffraction peaks is based on a least square minimization procedure for a sum of several Gaussian and Lorentzian curves, corrected for absorption, polarization and background. To start the calculations, a set of initial parameters including postulated positions, widths and heights of peaks corresponding to reflections from various crystallographic planes, as well as those of amorphous halo, are usually required. The program, for each variable (position height and width of every peak), performs a search of surrounding n-dimensional grid of points (where n is the number of variable), to find points which can completely tally with the Gaussian-Lorentzian profiles. When no such a point is found, the search increment factor is decreased and the procedure is repeated, until the best fitting is achieved.

Deconvolution of the superposition of crystalline peaks and broad amorphous halo observed in the WAXS data was carried out using GRAMS/32 Spectral NotebaseTM with Gaussian peak shape. The apparent degree of crystallinity, ϕ_{mc} , is proportional to the ration of the total intensity of crystalline reflections to the total observed intensity (crystalline + amorphous) [9, 114]. Figure 3.1 shows an example of deconvolution of the WAXD data.

Figure 3.1 An example of deconvolution of the WAXD data

The apparent degree of crystallinity of α form, $\phi_{mc\alpha}$, is calculated as follows:

$$\phi_{mc\alpha} = \frac{A_{\alpha 1} + A_{\alpha 2}}{A_a + A_\gamma + A_{\alpha 1} + A_{\alpha 2}} \quad 3.1$$

and γ form, $\phi_{mc\gamma}$, is calculated as follows

$$\phi_{mc\gamma} = \frac{A_\gamma}{A_a + A_\gamma + A_{\alpha 1} + A_{\alpha 2}} \quad 3.2$$

where $A_{\alpha 1}$ is the area of α_1 peak, $A_{\alpha 2}$ is the area of α_2 peak, A_γ is the area of γ peak and A_a is the area of amorphous peak [9, 114].

3.1.5 Transmission electron microscopy (TEM)

TEM specimens were cut from nano-composite blocks using a Leica Ultracut UCT Ultramicrotome equipped with a diamond knife. Thin specimens, 80-100 nm, were cut from a mesa of about $0.5 \times 0.5 \text{ mm}^2$. They were collected in a water-filled trough and placed on 200 mesh copper grids. Transmission electron micrographs were taken with a Jeol JEM 2010 microscope at an acceleration voltage of 200 kV.

3.1.6 Fourier transform infrared spectroscopy (FTIR)

FTIR analyses were carried out in transmission mode using a Perkin Elmer 2000 spectrometer. Total of 200 scans were used for signal averaging. About 10 μm thick films of Nylon 6 and Nylon 6/clay nano-composites were prepared. Granules of Nylon 6 or Nylon 6/clay nano-composites were placed between two glass slides and heated on a hot stage at 300°C. This was followed by pressing the granules into film and kept for 10 minutes. Finally, the film was cooled down at ambient temperature.

KBr pellets of nano-clay were used for FTIR. About 50 μm thick films of PP, PP-g-MAH and their blends with nano-clay, were obtained by pressing 0.1-0.2g sample under about 1MPa pressure at 190°C for 30s [133]. After pressing, the films were dried under vacuum at 120°C for 20h.

3.1.7 Differential scanning calorimeter (DSC)

The crystallization behavior was also investigated by using a TA Instruments MDSC 2920 differential scanning calorimeter. Before the data gathering, all samples were heated to 300°C and held in the molten state for 10 min to eliminate the influence of thermal history. Temperature scans were carried out at 2°C/min. All operations were carried out under a nitrogen environment. Samples weights were between 5~10 mg.

3.2 Polymorphism of Nylon 6/clay nano-composites

The X-ray diffraction patterns of the Nylon 6/clay nano-composites with different contents of clay (0, 2.5, 5, 7.5, 10 wt%) are reported in Figure 3.2. For all samples, there is no peak existing at $2\theta < 5^\circ$. This indicates that most of clay is exfoliated or intercalated [7, 28].

Figure 3.2 The X-ray diffraction patterns (Cu Kα) of the Nylon 6/clay nano-composites with different contents of clay

In order to elucidate visually the extent of clay dispersion in the polymer matrix, the microstructures of the samples were further analyzed using TEM. TEM micrographs of Nylon 6/clay nano-composites with different contents of clay are shown in Figure 3.3, where the dark lines seen are silicate layers. It can be seen that for melt intercalation method, clay was partially exfoliated in the polymer matrix. For Nylon 6/clay nano-composites with clay 2.5%-7.5% (Figure 3.3 (a)-(c)), mixed morphology of highly intercalated and exfoliated structure were observed. On the other hand, Nylon 6/clay nano-composite with 10% clay (Figure 3.3 (d)), has a mostly intercalated structure with some degree of exfoliation.

Figure 3.3 TEM micrographs of Nylon 6/clay nano-composites with different contents of clay (a) 2.5 wt% (b) 5 wt% (c) 7.5 wt% (d) 10 wt%

Figure 3.4 shows FTIR spectra of Nylon 6/clay nano-composites with different contents of clay. The characteristic absorption peaks of the α phase are 930, 959 and 1030 cm^{-1} in FTIR spectrum [8, 121, 122]. The band at 1030 cm^{-1} has been identified as “fold band” arising from wagging and twisting modes of CH_2 groups coupled with CONH groups. The band at 930 is recognized as CO-NH in plane vibration. The band at 959 cm^{-1} is also assigned to CO-

NH in-plane vibration in α phase. However, in γ phase, this band moves to 976 cm^{-1} . This is because the hydrogen bonding is between anti-parallel chains in α phase and it is between parallel chains in γ phase [123, 134].

Figure 3.4 FTIR spectrum of Nylon 6/clay nano-composites with different contents of clay:

(a) 0 wt% (b) 2.5 wt% (c) 5 wt% (d) 7.5 wt% (e) 10 wt%

The reflections at 20.5° and 24° (α_1 and α_2) in WAXD patterns (Figure 3.2), and the characteristic absorption peaks at 930 , 959 and 1030 cm^{-1} in FTIR spectrum (Figure 3.4), clearly indicate that the α form crystal is predominant in neat Nylon (0 wt% clay). The α form crystal is comprised of an extended, anti-parallel arrangement of chains [123]. In contrast, the Nylon 6/clay nano-composites exhibit an additional reflection at about 21.5° in

WAXD patterns (Figure 3.2) and an additional absorption at 976 cm^{-1} in FTIR spectrum (Figure 3.4) [8], which is due to the γ form crystal. The γ form crystal is comprised of a twisted, parallel chain arrangement [123]. There is an increasing trend of γ form crystal with increasing clay content. Thus, it can be concluded that the addition of nano-clay could favor the formation of γ phase crystal.

Figure 3.5 DSC of Nylon 6/clay nano-composites with different contents of clay at $2^{\circ}\text{C}/\text{min}$:

(a) 0 wt% (b) 2.5 wt% (c) 5 wt% (d) 7.5 wt% (e) 10 wt%

Figure 3.5 shows the DSC curves of Nylon 6/clay nano-composites with different contents of clay. It is clearly seen that neat Nylon 6 has only one melting peak at about 220°C . This peak corresponds to the melting of α crystal [9]. However, Nylon 6/clay nano-composites show double peaks at 220°C and 210°C , attributable to the melting of α and γ crystal respectively

[9]. DSC results are consistent with the observations from WAXD and FTIR experiments, which also confirm that the addition of nano-clay could favor the formation of γ phase crystal.

The apparent degree of crystallinity (Φ_{mc}) for both alpha and gamma crystals is shown in Figure 3.6. Φ_{mc} was determined as the ratio of the area of the crystalline reflections to the total area of crystalline and amorphous phases from the WAXD results given in Figure 3.2. With increasing clay content in the composites, γ form crystal becomes the major phase present in Nylon 6/clay nano-composites. Especially, when the content of clay is 10 wt%, there is almost only γ form crystal present. These results are similar to the results reported by other researchers [7, 9, 30, 92, 124]. The results of Vaia et al [9] indicate that the γ form crystal forms near the surface of the silicate layers and the α form crystal forms away from the surface. However, the exact reason why the addition of nano-clay favors the formation of γ phase crystal is still under discussion [9, 92].

Figure 3.6 Apparent degree of crystallinity (Φ_{mc}) of the Nylon 6/clay nano-composites with different contents of clay

3.3 Polymorphism of Nylon 6/PP-g-MAH Blends

Figure 3.7 The X-ray diffraction pattern (Cu $K\alpha$) of PP-g-MAH

The X-ray diffraction pattern of PP-g-MAH is shown in Figure 3.7. At normal condition, the α form of PP-g-MAH is obtained. There are seven peaks between 10° and 30° . Peak at 2θ of 14° is indexed as 110, 17° is indexed as 040, 18.5° is indexed as 130, 21° is indexed as 111, 22° is indexed as 041 and -131 , 25.5° is indexed as 060, and 28.5° is indexed as 220 [114, 115].

Figure 3.8 The X-ray diffraction patterns (Cu K α) of PP-g-MAH, Nylon 6/PP-g-MAH blend and Nylon 6/nano-clay/PP-g-MAH blend

Figure 3.8 shows the X-ray diffraction patterns of PP-g-MAH, Nylon 6/PP-g-MAH blend and Nylon 6/nano-clay/PP-g-MAH blend (10 wt% of PP-g-MAH). Because the content of PP-g-MAH in this study is lower than 10 wt%, the contribution of the crystallization of PP-g-MAH to the X-ray diffraction patterns is very difficult to be observed. Before deconvolution of the WAXD data, the effect of PP-g-MAH in Nylon 6/nano-clay/PP-g-MAH blends was eliminated [9, 114].

Figure 3.9 X-ray diffraction patterns of Nylon 6 and PP-g-MAH blends with different contents of PP-g-MAH

Figure 3.9 shows the X-ray diffraction patterns of pure Nylon 6 and PP-g-MAH blends with different contents of PP-g-MAH (2.5, 5, 7.5, 10 wt%). Because the content of PP-g-MAH in this study is lower than 10 wt%, the contribution of the crystallization of PP-g-MAH to the X-ray diffraction patterns is difficult to be observed. It can also be seen that as the percentage of PP-g-MAH in the blends increases, the strength of the reflection peak of γ form crystal ($2\theta = 21.5^\circ$) increases. The apparent degrees of crystallinity of α and γ crystals in these blends are reported in Figure 3.10. With the increasing of PP-g-MAH content in the blends, the percentage of γ form crystal increases while that of the α form crystal decreases. This means that the addition of PP-g-MAH in Nylon 6 also favors the formation of γ phase crystal. The same trend was observed by Galeski et al [114]. A chemical interaction between Nylon 6 and

functionalized polyolefin was believed to be responsible in this case. The maleic anhydride groups of PP-g-MAH may react with the amino end groups of Nylon 6 [114, 115].

Figure 3.10 Apparent degree of crystallinity (Φ_{mc}) of Nylon 6 and PP-g-MAH blends with different contents of PP-g-MAH

Figure 3.11 shows the X-ray diffraction patterns of Nylon 6 and Nylon 6 blended with 10 wt% PP without functional groups. It can be seen that the addition of PP without functional groups dose not influence the polymorphism of Nylon 6. The same results were also obtained by other researchers [114, 115].

Figure 3.11 X-ray diffraction patterns of Nylon 6 and Nylon 6 blended with 10 wt % PP without functional groups

3.4 Polymorphism of Nylon 6/nano-clay/PP-g-MAH blends

Figure 3.12 shows the TEM images of Nylon 6/clay nano-composites (5 wt% clay) with different contents of PP-g-MAH. There is almost no change for Nylon 6/clay nano-composites with different contents of PP-g-MAH 0 wt% and 10 wt% (Figure 3.12 (a) and (b)). This indicates PP-g-MAH have almost no influence on the dispersion or exfoliation of nano-clay in this study.

Figure 3.12 TEM micrographs of Nylon 6/clay nano-composites (5 wt% clay) with different contents of PP-g-MAH (a) 0 wt% PP-g-MAH (b) 10 wt% PP-g-MAH

Figures 3.13 to 3.16 show the X-ray diffraction patterns of Nylon 6/clay nano-composites, containing 2.5, 5, 7.5 and 10 wt% of clay respectively, each blended with different contents of PP-g-MAH (0, 2.5, 5, 7.5, 10 wt%). For Nylon 6/nano-clay/PP-g-MAH blends with 2.5 (Figure 3.13) and 5 wt% (Figure 3.14) of clay, the reflections of γ form crystal decrease first and then increase with increasing PP-g-MAH content. For those blends with 7.5 (Figure 3.15) and 10 wt% (Figure 3.16) of clay, although it is difficult to discern the trend by visual observation of the WAXD patterns, the trend becomes clear after quantitative analysis as discussed below (in Figures 3.17 (c) and (d)).

Figure 3.13 X-ray diffraction patterns of Nylon 6/clay nano-composites (with 2.5 wt% clay) and PP-g-MAH blends with different contents of PP-g-MAH

Figure 3.14 X-ray diffraction patterns of Nylon 6/clay nano-composites (with 5 wt% clay)

and PP-g-MAH blends with different contents of PP-g-MAH

Figure 3.15 X-ray diffraction patterns of Nylon 6/clay nano-composites (with 7.5 wt% clay)

and PP-g-MAH blends with different contents of PP-g-MAH

Figure 3.16 X-ray diffraction patterns of Nylon 6/clay nano-composites (with 10 wt% clay) and PP-g-MAH blends with different contents of PP-g-MAH

The above observation is more clearly seen in Figure 3.17 where the apparent degrees of crystallinity of these blends are presented. From Figure 3.17, it can be seen that for Nylon 6/nano-clay/PP-g-MAH blends with 2.5 (Figure 3.17 (a)) and 5 wt% (Figure 3.17 (b)) of clay, γ form crystal decreases upon the addition of PP-g-MAH initially and then increases when PP-g-MAH content exceeds certain level. Further, the minimum of the apparent degree of crystallinity of γ form crystal in these blends shifts to higher content of PP-g-MAH in samples with higher clay content. For Nylon 6/nano-clay/PP-g-MAH blends with 2.5 and 5 wt% of clay, the minimum of γ form crystal appears at about 2.5 and 5 wt% contents of PP-g-MAH respectively. For those blends with 7.5 (Figure 3.17 (c)) and 10 wt% (Figure 3.17 (d)) of clay, the addition of PP-g-MAH, up to 10 wt%, causes a monotonous decrease of γ form crystal, which indicates that the minimum has not been reached even after adding 10 wt% PP-g-MAH. This peculiar phenomenon was observed for the first time. Meanwhile, it is worth mentioning that the α form crystal in each blend shows an opposite trend of that of the γ crystal.

Figure 3.17 Apparent degree of crystallinity (Φ_{mc}) of Nylon 6/nano-clay/PP-g-MAH blends with different contents of PP-g-MAH: (a) 2.5 wt% clay; (b) 5 wt% clay; (c) 7.5 wt% clay; (d) 10 wt% clay

As we know, both nano-clay and functionalized polyolefin would favor the formation of γ phase crystal of Nylon 6. However, why does the co-interaction or co-existence of nano-clay and functionalized polyolefin exercise such a peculiar influence on polymorphism of Nylon 6 as described above in these ternary systems? One possible reason is the interaction between the nano-clay and PP-g-MAH.

As it is known, natural montmorillonite is hydrophilic and not compatible with polymers. In order to produce polymer/clay nano-composites, ω -amino surfactants or similar chemicals were chosen as intercalation additives [3, 7, 90]. Thus, there may be reaction between the

treated nano-clay and functionalized polyolefin to form succinimide groups, as shown in scheme 3.1.

Scheme 3.1 The formation of succinimide groups

An experiment was carried out to further prove this hypothesis. Figure 3.18 shows FTIR spectra of nano-clay and polypropylene blends with and without functional groups. As it can be seen, for nano-clay, polypropylene without functional groups and their blend, there is no absorption band between 1800 and 1700 cm^{-1} . The FTIR spectrum of PP-g-MAH shows an absorption band at about 1780 cm^{-1} , which corresponds to the anhydride $\text{C}=\text{O}$ stretching vibration [135, 136]. It is important to note, for the nano-clay and PP-g-MAH blend, an

absorption band is seen at about 1720 cm^{-1} , which can be assigned to the succinimide groups [135, 136]. Hence the FTIR results confirm the reaction shown in scheme 3.1 between nano-clay and functionalized polyolefin.

Figure 3.18 FTIR spectra of nano-clay and polypropylene blends with and without functional groups

Therefore, for Nylon 6/nano-clay/PP-g-MAH blends, upon the addition of PP-g-MAH, a part of nano-clay in the blends may react with the functional groups of PP-g-MAH. This also means that certain proportion of clay surface would be covered by PP-g-MAH. Since the γ crystal of Nylon 6 forms only near the surface of the silicate layers [9], it is easy to understand that less γ crystal would be formed when the nano-clay is covered by another polymer, i. e., PP-g-MAH in this case. At the same time, the PP-g-MAH, after reacting with

nano-clay, would have fewer functional groups. Consequently the PP-g-MAH would have reduced effect to promote γ crystal formation in Nylon 6/nano-clay/PP-g-MAH blends according the known mechanism discussed earlier in Chapter 2 [112-115].

Figure 3.19 X-ray diffraction patterns (Cu K α) of Nylon 6/clay nano-composites (with 5 wt% clay) blend with different contents of PP

Figure 3.19 shows the X-ray diffraction patterns of Nylon 6/clay nano-composite and Nylon 6/clay nano-composite blended with 10 wt% PP without functional groups. It can also be seen that because there is no reaction between PP and nano-clay, the addition of PP without functional groups will have almost no influence on the polymorphism of Nylon 6.

Our observation clearly shows that the interaction or reaction between nano-clay and PP-g-MAH causes an antagonistic effect on the formation of γ crystal of Nylon 6. In other words,

both nano-clay and PP-g-MAH promote γ crystal formation in Nylon 6 when each acts individually in Nylon 6/nano-clay and Nylon 6/PP-g-MAH binary blends. However, the co-existence of both nano-clay and PP-g-MAH in the Nylon 6/nano-clay/PP-g-MAH ternary blends antagonizes each other's promotional effect on γ crystal formation in Nylon 6. Results suggest that this may be due to the reaction between nano-clay and PP-g-MAH.

Therefore, the observations in Figure 3.17 can be explained by the above discussion. It may be worth mentioning that, for Nylon 6/nano-clay/PP-g-MAH blends with lower clay contents, e.g., 2.5 wt% and 5 wt%, increasing PP-g-MAH content initially reduces the percentage of γ crystal. But then after furthering addition of PP-g-MAH, the amount of γ crystal still increases. This is easily understood because the initial addition of PP-g-MAH would react with the nano-clay to lead to the reduction in γ crystal due to the antagonistic effect discussed above. However after sufficient PP-g-MAH is added to react with the available clay surfaces, further addition of PP-g-MAH would again make available the anhydride functional groups to the blends. These functional groups would then be able to enhance the γ crystal formation.

3.5 Summary

The crystallization behavior of Nylon 6/clay nano-composites and functionalized polyolefin blends has been investigated. The results indicate, in Nylon 6/nano-clay and Nylon 6/PP-g-MAH binary blends, both nano-clay and functionalized polyolefin would favor the formation of γ crystal of Nylon 6. However, the interactions among them are more complicated when they co-exist in Nylon 6/nano-clay/PP-g-MAH ternary blends. The co-existence of both nano-clay and PP-g-MAH in the Nylon 6/nano-clay/PP-g-MAH ternary blends antagonizes each other's promotional effect on γ crystal formation in Nylon 6. This finding is important

for in-depth understanding of the physical and chemical interactions between constituents and their effects on polymorphism in multi-component systems, such as Nylon 6/clay nanocomposites/PP-g-MAH blends.

Chapter 4 Polymorphism in Syndiotactic Polystyrene (sPS) and sPS/Clay Nano-composites

In this chapter, the influence of crystallization temperature on the formation of α and β crystals of syndiotactic polystyrene (sPS) was investigated by X-ray diffraction and nonisothermal DSC analysis. Moreover, the polymorphism in sPS/clay nano-composites has also been studied by X-ray diffraction.

4.1 Effects of Crystallization Temperature on the Polymorphism in Syndiotactic Polystyrene

4.1.1 Introduction

A number of studies [10, 12, 13, 125-130] have been carried out on polymorphs of sPS. X-ray diffraction, electron diffraction, Fourier-transformed infrared (FTIR) spectroscopy and solid-state nuclear magnetic resonance (NMR) have been used in the identification and quantification of the different polymorphs in polymeric materials. Guerra and his coworkers [13, 127] first gave the nomenclature of α and β crystals and studied their formation from melt and glass phase of sPS in detail. Their results showed that the cooling rate from the melt and the thermal history of the melt are the major factors influencing the formation of these forms. The formation of the α form is a kinetically controlled process; meanwhile the β form crystal structure is more stable thermodynamically. If the memory effect of nuclei is eliminated by heating to high enough temperature, cooling sPS down at a moderate cooling rate (less than 20°C /min) from the melt, will lead to the formation of its β form, otherwise,

the formation of α form. The α form can also be obtained by quenching from the melt or by annealing from the amorphous phase. The intensities and Bragg distance observed in the powder patterns for α and β crystals have been given by Guerra *et al.* [13].

However, other researchers [12] scrutinized the effect of crystallization temperature on the formation of α crystal and β crystal of syndiotactic polystyrene without any thermal history by using infrared spectroscopy and X-ray diffraction. The results clearly indicate that the crystallization temperature is the intrinsic factor controlling the formation of α crystal and β crystal. The pure β form is only produced at higher temperatures. The pure α form is obtained at lower temperatures.

At the same time, there is a considerable interest in understanding the crystallization of syndiotactic polystyrene. Cimminno *et al.* [137] and Lawrence *et al.* [138] all have described the kinetics of isothermal crystallization of sPS using differential scanning calorimetry (DSC). The crystallization kinetics of sPS under non-isothermal conditions have also been analyzed by Wesson [139]. Though the formation of α crystal or β crystal is closely related to the crystallization kinetics of each kind of crystal (especially nonisothermal crystallization kinetics), up to now, no report involves both polymorphism and non-isothermal crystallization kinetics at the same time to study the polymorphic behavior of sPS.

In this study, X-ray diffraction and nonisothermal DSC analysis have been combined to answer the question: which one is the more significant factor controlling the formation of α and β crystals for sPS samples without any thermal history, the crystallization temperature or the cooling rate from the melt?

4.1.2 Experimental section

Materials

The sPS was provided by Prof. Hu Youliang (Institute of Chemistry, Chinese Academy of Science) [12]. The polymer has its M_w of 630000 and M_w/M_n of 4.5, as determined by GPC and a syndiotacticity of 97%, as determined by high resolution NMR. Its T_m is 272°C.

Wide angle X-ray diffraction (WAXD)

The X-ray diffraction experiments were performed using a Rigaku RINT 2200 diffractometer system consisting of a rotating anode generator and wide angle powder goniometer fitted with a high-temperature attachment. The generator was operated at 40KV and 30mA. The sample holder was an aluminium block, and a thin film of the sample was formed on that block by melt pressing the sample. The effects of the background have been eliminated by computer program. Each sample was used only once in order to avoid the influence of other factors, e.g. thermal degradation.

The samples were initially heated in a hot stage at 340°C and kept for 5 minutes. This process was proved enough to eliminate any thermal history and the memory effects of the α form in the melt [12, 137, 138]. Then samples were cooled at different cooling rates (2°C, 5°C, 10°C, 20°C, 40°C and 80°C/min) to certain temperatures (230°C and 120°C, respectively). Wide-angle X-ray diffraction (WAXD) was used to determinate the crystalline forms at 230°C and 120°C, respectively. The scanning 2θ angle ranged between 5° and 40° with a scanning rate of 5°/min. Other samples were quenched to 230°C at a rate of 120°C/min by a programmed procedure (during this course, there was no crystallization at all, see Figure 4.5), and then

cooled at different cooling rates (2°C, 5°C, 10°C, 20°C, 40°C and 80°C/min) to 120°C, Wide-angle X-ray diffraction (WAXD) scanning was carried at 120°C. The preparation of X-ray diffraction samples is shown schematically in Figure 4.1.

Figure 4.1 Schematic representation of the preparation of X-ray diffraction samples

The determination of the sPS crystalline forms was conducted by wide-angle X-ray diffraction, and diffraction patterns were obtained with nickel-filtered Cu K α radiation. It has shown that the α form crystal exhibits characteristic peaks at $2\theta = 6.7$ (110), 11.6° (300), while the β form at $2\theta = 6.1$ (020), 12.2 (040), and 18.6° (060). The measurement of the content of α crystal and β crystal was carried out according to the method described in reference 13.

The 2θ region 10° - 15° was considered, and a base line between the two intensity minimal located at $2\theta = 10.8^\circ$ and $2\theta = 14.8^\circ$ is drawn. The areas (A) of the two peaks located at 2θ

$=11.6^\circ$ and $2\theta =12.2^\circ$ were measured, and the percentage of the α form in the crystalline fraction was evaluated by the approximate relation [13]:

$$P_{\alpha} = \frac{1.8A(11.6)/A(12.2)}{1+1.8A(11.6)/A(12.2)} \times 100 \quad 4.1$$

where 1.8 was the ratio between the intensities (measured under the same experimental conditions) of the peaks at 11.6° and 12.2° for samples of equal thickness and crystallinity in the pure α and β forms respectively.

Nonisothermal DSC analysis

The nonisothermal crystallization behaviors of sPS samples were investigated by using a PERKIN-ELMER DSC-7 differential scanning calorimeter. Before the data gathering, all samples were heated to 340°C and held in the molten state for 5 min to eliminate the influence of thermal history. All operations were carried out under a nitrogen environment. Samples weights were between 4~7 mg.

Nonisothermal crystallization experiments were carried out by cooling samples from 340°C to ambient temperature using different cooling rates. The exotherms as a function of temperature were recorded with the cooling rates 2, 5, 10, 20, 40 and $80^\circ\text{C}/\text{min}$, respectively.

Nakamura *et al.* [140] suggest the relative crystallinity, $X(t)$, in semicrystalline polymers may be expressed as

$$X(t) = 1 - \exp\left\{-\left[\int_0^t K(T) dt\right]^n\right\} \quad 4.2$$

Where $K(T) = k(T)^{1/n}$, and n is related to the crystal growth dimension. This equation assumes as a first approximation that the system is isokinetic, i.e., the crystal growth rate divided by the probability to form new nuclei is constant and is not a function of temperature. The equation may be expressed as a function of temperature by incorporating the cooling rate transformation $\Phi = dT/dt$, giving rise to

$$X(T) = 1 - \exp\left\{-\left[\frac{1}{\Phi} \int_{T(0)}^{T(t)} [k(T)]^{1/n} dT\right]^n\right\} \tag{4.3}$$

4.1.3 Crystallization at different cooling rates

Figure 4.2 X-ray diffraction patterns (Cu Kα) of sPS samples melted at 340°C and then cooled at different cooling rates to 120°C

The X-ray diffraction patterns of the sPS samples, melted at 340°C and then cooled at different cooling rates (2°C, 5°C, 10°C, 20°C, 40°C and 80°C/min) to 120°C, are reported in Figure 4.2. For low cooling rates up to 10°C/min, the β form samples (characteristic peaks at $2\theta = 6.1, 12.2, 18.6^\circ$) are always present. For cooling rate higher than 80°C/min, only typical α form peaks (at $2\theta = 6.7, 11.6^\circ$) are obtained. For cooling rates between 10°C/min and 80°C/min, both α and β crystals coexist, and the amount of the α form in the samples increasing with the cooling rate. The above observation is more clearly seen in Figure 4.3.

(a)

(b)

Figure 4.3 Percentage in the crystalline fraction of sPS cooled at different cooling rates to 120°C (a) α crystal (b) β crystal

The percentage of α crystal and β crystals in the crystalline fraction of sPS are plotted against the cooling rate as shown in Figures 4.3(a) and 4.3(b). From Figure 4.3, it can be seen that the percentages of the α form in the crystalline phase, calculated from WAXD patterns for the samples cooled at 10°C, 20°C, 40°C and 80°C/min, are about 0%, 20%, 75% and 100% respectively. All these results are almost the same as the observation of Guerra *et al.* [13, 127].

4.1.4 Crystallization at different temperatures

Figure 4.4 X-ray diffraction patterns (Cu Kα) , recorded at 230°C, of sPS samples melted at 340°C and then cooled at different cooling rates to 230°C

The X-ray diffraction patterns of the sPS samples, recorded at 230°C and reported in Figure 4.4, are obtained from the samples which were cooled from 340°C at different cooling rates (2°C, 5°C, 10°C, 20°C, 40°C and 80°C/min) to 230°C. It is seen that for all samples (cooled down to 230°C at different cooling rates), there are only β form peaks (at 2θ = 6.1, 12.2, 18.6°) appear, though some of the β form crystals may be obtained just during the X-ray diffraction experiments at 230°C. These do not conflict with the earlier results that pure β form is only produced at higher temperatures. Above about 230°C, even though the cooling rate from the melt is high up to 80°C/min, α form crystals are still not able to form. This result clearly indicates that the cooling rate from the melt should not be the major factor

influencing the formation of α and β crystals at least when the crystallization temperature is higher than 230°C.

Figure 4.5 X-ray diffraction patterns (Cu K α) of sPS samples quenched from 340°C to 230°C and then cooled at different cooling rates to 120°C

Figure 4.5 shows the X-ray diffraction patterns of the samples quenched from the melt to 230°C and then immediately cooled at different cooling rates (2°C, 5°C, 10°C, 20°C, 40°C and 80°C/min) to 120°C. It can be observed that for all samples (cooled down from 230°C to 120°C at different cooling rates), there are only α crystal characteristic peaks (at $2\theta = 6.7, 11.6^\circ$) exist. During this course, there is not any β crystal peaks obtained, viz., no matter how slow the cooling rate is, only α form can be obtained when crystallization temperature is lower than 230°C. This exhibits the similar results as Figure 4.4, i.e. the cooling rate should

not be the major factor influencing the formation of α and β forms when the crystallization temperature is lower than 230°C.

Both Figure 4.4 and Figure 4.5 definitely exhibit the similar results, i.e. for both crystallization temperature ranges, above 230°C or below 230°C, the cooling rate is not the intrinsic factor controlling the formation of α crystal and β crystal. And the crystallization temperature seems certain to be the more important influence. The α form can only be obtained when the crystallization temperature is lower than about 230°C, whereas the β form can only be presented while the crystallization temperature higher than about 230°C.

In theory, there must be a temperature region in which both α crystal and β crystal can be obtained [14]. However, for the samples in this study, this temperature region is very narrow. So when the temperature is higher than the on set temperature above which the β crystal can be obtained, the β crystal rapidly becomes predominant.

4.1.5 Nonisothermal crystallization.

The above conclusion looks as if it were quite different with the observation of Figure 4.2 and Guerra *et al.* [13]. In fact, nonisothermal DSC analysis could supply a deep explanation of this difference in appearance.

Because there is almost no energy difference between the two polymorphs, the transformation from α crystal to β crystal is hardly implemented at the normal condition [10, 19]. From a technological point of view, non-isothermal crystallization conditions are almost the same as that of X-ray diffraction experiments, so that the study of crystallization of sPS

under non-isothermal conditions is of great importance. Because the non-isothermal crystallization is a temperature-changing process, the relative crystallinity increases with the temperature decreasing (or crystallization time prolonging).

The plots of relative crystallinity with temperature are shown in Figure 4.6. The relative crystallinity as a function of temperature, was determined by fractionating the exothermic crystallization peak. Running integrals, which relate the total peak area to the area at a specified temperature, were used.

Figure 4.6 Plots of relative crystallinity *versus* temperature for sPS samples cooled from 340°C at different cooling rates to 120°C, determined by DSC

Figure 4.6 shows that with the increasing of cooling rate, the onset crystallization temperature decreases evidently and the relative crystallinity of sPS at higher temperature

drops rapidly. From Wesson's observation [139], similar conclusion has been obtained. For low cooling rates up to $10^{\circ}\text{C}/\text{min}$, the relative crystallinities have almost reached the maximum of the sample by cooling to 230°C . For cooling rate higher than $80^{\circ}\text{C}/\text{min}$, there is almost no crystallization when the temperature cooled down to 230°C . For cooling rates at $20^{\circ}\text{C}/\text{min}$ and $40^{\circ}\text{C}/\text{min}$, the relative crystallinity of each sample when the temperature cooled down to 230°C , is 80% and 25% approximately.

From Figures 4.4 and 4.5, it can be seen that β form is produced at high temperatures above about 230°C [12]. The relative crystallinities above 230°C , which were obtained from Figure 4.6, are in agreement with the percentage of the β crystals estimated by X-ray diffraction. It can supply another evidence to prove the conclusions that, for sPS, α form can only be obtained when the crystallization temperature is lower than about 230°C , whereas the β form can only be presented at the crystallization temperature higher than about 230°C . In other words, when crystallization temperature is lower than about 230°C , the crystallization rate of α crystal is much faster than that of β crystal. However, when the temperature is higher than about 230°C , the crystallization rate of α crystal is too slow to be examined.

Using the results of Figure 4.6, the difference among Figure 4.4, Figure 4.5 and Figure 4.2 can be explained as follows:

For sPS samples without any thermal history, since the β form crystallizes at high temperature from the melt, it will crystallize first during cooling until the temperature cooled down to about 230°C , and then the α will have a chance to crystallize. At low cooling rates up to $10^{\circ}\text{C}/\text{min}$, the relative crystallinities have almost reached the maximum by cooling to

230°C (Figure 4.6). During this course, only β form crystals can be present. So even the temperature for the α form formation is reached (below about 230°C), there is no more crystallizable sPS portion for the α form formation. The observed β form in the sample cooled to room temperature is already formed before the sample is cooled to 230°C. This is the reason why only β form can be obtained when sPS is cooled down at a slow or moderate cooling rate from the melt.

For cooling rate higher than 80°C/min, there is almost no crystallization when the temperature cooled down to 230°C (Figure 4.6). This means β form has almost no time to crystallize at high temperature, only α form can crystallize as the temperature keeps on decreasing. That is the reason why only α form crystal is obtained under quenching conditions.

At the cooling rate during 10°C/min and 80°C/min, there is some crystallization when the temperature cooled down to 230°C, but no time to crystallize to the maximum crystallinity of sPS (Figure 4.6). Under this condition, the α form has a chance to crystallize at low temperatures and both α and β crystals coexist. And what is more, as calculated from WAXD, the amount of the β form in the samples at different cooling rates: 2°C, 5°C, 10°C, 20°C, 40°C and 80°C/min, is 100%, 100%, 100%, 80%, 25% and 0% respectively. Meanwhile being obtained by nonisothermal crystallization, the amount of the β form in the samples at different cooling rates can support the same conclusion. This precisely proves β form can be obtained above about 230°C, whereas the α form can be presented while the crystallization temperature is lower than about 230°C.

According to the metastability theory (Figure 2.10 [116]), the stability of the phase is largely size dependent. The stability of stable phase and the stability of metastable phase both decrease with decreasing size of the phase. At the same time, the difference between the stability of stable phase and the stability of metastable phase also decreases with decreasing size of the phase. When the size of the phase is sufficiently small, the stability inversion occurs. This means that a metastable phase becomes the stable phase, and conversely, a conventionally stable phase becomes metastable when it is sufficiently small. When phase size is smaller than the crossover point, Q , shown in Figure 2.10, the stability of the stable phase is lower than that of the metastable phase. Furthermore, the stable phase should have a lower crystallization rate in this case [14]. Thus, under this condition, almost no stable phase can be formed. In other words, 230°C is the onset or minimum temperature above which the stable phase can be obtained in sPS in this study.

In fact, there are some early papers [16, 125, 127, 141, 142] that have noticed the influence of crystallization temperature on the formation of α crystal and β crystal of syndiotactic polystyrene. Their results indicate that at high enough crystallization temperature, only β form was observed. With the increasing cooling rate, the relative crystallinity of sPS reduces when the temperature cooled down to 230°C. This can explain the observation of De Rosa et al [127], where the amount of the α form increases with increasing cooling rate.

As the crystallization of syndiotactic polystyrene largely depends on their preparation method, syndiotacticity, molecular structures and so on, the crystallization of α and β crystals should change with the different sPS. So the onset or minimum temperature, above which the stable phase can be obtained in syndiotactic polystyrene (230°C in this study), must be shifted with

different sPS. But there must be a temperature, that β form can only be presented above this temperature.

4.2 Polymorphism in SPS/Clay Nano-composites

The polymorphism of sPS/clay nano-composites has also been studied [96, 97, 100, 101] by other researchers. They investigated the effect of the premelting temperature and crystallization temperatures on the polymorphic behavior of sPS/Clay Nano-composites. The polymorphic behavior of sPS/clay nano-composites is strongly dependent on their thermal history (just as neat sPS) and the weight ratio of clay. Quenching from the melt induces crystallization into the α crystal. Melt crystallization of sPS and sPS/clay nano-composites at higher temperatures favors the formation of the β crystal.

4.2.1 Experimental section

Materials

Syndiotactic polystyrene was kindly provided by Dow Chemical with its stereo regularity about 99%. The polymer has its M_w of 210000 and M_w/M_n of 2.2, as determined by GPC. Its T_m is about 271°C.

Organo-modified clay ‘Cloisite 10A’ (C10A) was obtained from Southern Clay Products Inc. (USA). Table 4.1 shows the typical properties of this clay.

Table 4.1 Typical properties of Cloisite 10A

Treatment/Properties:	Organic Modifier (1)	Modifier Concentration	% Moisture	% Weight Loss on Ignition
Cloisite® 10A	2MBHT	125 meq/100g clay	< 2%	39%

(1)2MBHT: dimethyl, benzyl, hydrogenated tallow, quaternary ammoniumsalt

Figure 4.7 shows the chemical structure of the modifier of Cloisite 10A, where HT is hydrogenated tallow (~65% C18; ~30% C16; ~,5% C14).

Figure 4.7 Chemical structure of the modifier of Cloisite 10A

Sample preparation

Solution intercalation technique was employed to prepare the sPS/clay nano-composites using 1, 1, 2, 2-tetrachloroethane (TCE) as the solvent [97]. About 2 wt% polymer solution was stirred for 4 h at 130°C to dissolve sPS. The solution was then cooled to 60°C and the organoclay was added into it. The clay suspension was stirred constantly at 60°C in an oil bath for 48 h. The resultant mixture was then cast as thin film at 60°C for 24 h on the aluminum pan. Temperature control was provided by placing the aluminum pan on a hot plate. The cast films so obtained were vacuum-dried at 110°C for 7 days and were grounded to fine powder manually after that. The powdered samples were further dried at 110°C for 7

days for complete removal of the solvent.

For better comparison, neat sPS was also dissolved in TCE just as the other nano-composite samples

Characterization

WAXD experiments were performed as described in 3.1.3. SPS nano-composites were sandwiched between two cover glasses of 0.16mm thick and heated on a hot stage at 340°C, followed by being pressed into film first and kept for 5 minutes. This process was proved enough to eliminate any thermal history of sPS [12, 137, 138]. Finally, the samples were slowly cooled to the room temperature.

TEM experiments were performed as described in 3.1.3.

FTIR analyses were carried out in transmission mode using a Perkin Elmer 2000 spectrometer. The wave number range scanned was 1000-850 cm^{-1} , with 200 scans collected. About 10 μm thick films of sPS and sPS/clay nano-composites were prepared. Granules of sPS or sPS/clay nano-composites were placed between two glass slides and heated on a hot stage at 340°C. This was followed by pressing the granules into film and kept for 5 minutes. Finally, the film was cooled down in the air at ambient temperature.

It has been shown [142] that the α form crystal exhibits a characteristic band at 902 cm^{-1} , while the β form 911 cm^{-1} .

The crystallization behavior was also investigated by using a TA Instruments MDSC 2920 differential scanning calorimeter. Temperature scans were carried out at 2°C/min. All operations were carried out under a nitrogen environment. Samples weights were between 5~10 mg.

4.2.2 Dispersibility of clay in sPS/clay nano-composites

The dispersion of clay in sPS can be examined by WAXD pattern and TEM micrograph. Figure 4.8 shows XRD patterns of sPS/clay nano-composites in this study. It is known that organo-modified clay (C10A) shows basal reflection around $2\theta = 4.6^\circ$ [97].

Neat sPS presents only one β form peak (at 2θ around 6.1°). For sPS/clay nano-composite with 2.5 wt% clay, both α crystal peak (at 2θ about 6.7°) and β crystal peak coexists. However, no significant XRD peak in the region of 2θ between 2.5 - 5° . This result indicates that sPS is successfully intercalated between the silicate layers and a minimum interlayer distance of several nanometers [97]. For sPS/clay nano-composite with 5 wt% clay, there are also two α crystal and β crystal peaks. However, there is still another peak around 4 - 6° which should be caused by organoclay. This result shows clay is difficult to be dispersed in sPS at higher loading.

Figure 4.8 Dispersion and intercalation of clay in sPS

The XRD result only reveals the relationship between the silicate layers, and it may be insufficient for the measurement of exfoliation of clay. In order to elucidate visually the extent of clay dispersion in the polymer matrix, the microstructures of the samples were further analyzed using TEM.

TEM micrographs of sPS/clay nano-composites with different contents of clay are shown in Figure 4.9, where the dark lines seen are silicate layers. For sPS/clay nano-composite with 2.5 wt% clay (Figure 4.9 (a)), mixed morphology of highly intercalated and exfoliated structure was observed. On the other hand, sPS/clay nano-composite with 5 wt% clay (Figure 4.9 (b)), has a mostly intercalated structure with some degree of exfoliation.

Figure 4.9 TEM micrographs of sPS/clay nano-composites with different contents of clay (a) 2.5 wt% (b) 5 wt%

4.2.3 Polymorphism in sPS/clay nano-composites

Figure 4.10 FTIR spectrum of sPS/clay nano-composites

Figure 4.10 shows FTIR spectra of sPS/clay nano-composites. It is seen that for neat sPS, there is only one absorption at 911 cm^{-1} which indicates only β crystal obtained. For sPS/clay nano-composites with 2.5 and 5 wt% clay, both bands at 902 cm^{-1} and 911 cm^{-1} indicate mixed (α + β) crystals can be obtained.

Figure 4.11 X-ray diffraction patterns (CuK α) of sPS/clay nano-composites

The X-ray diffraction patterns of the sPS/clay nano-composites are reported in Figure 4.11. For neat sPS, there are only typical β form peaks present at $2\theta = 6.1^\circ, 12.2^\circ, 18.6^\circ$. For sPS/clay nano-composites with 2.5 and 5 wt% clay, both α form (e.g. the peaks at $2\theta = 6.7^\circ, 11.6^\circ$) and β form are present. There is an increasing trend of α form crystal with increasing

clay content.

The percentages of the α form in the crystalline phase, calculated from WAXD patterns for the samples with different clay content 0, 2.5 and 5 wt%, are about 0%, 20% and 65% respectively. Thus, it can be concluded that the addition of nano-clay favors the formation of α phase crystal. This result is the same as the observation of Woo *et al* [97].

Figure 4.12 DSC trace of neat sPS and sPS/clay nano-composite with 5 wt% of clay

Figure 4.12 shows the DSC curves of sPS and sPS/clay nano-composite with 5 wt% clay. It is clearly seen that neat sPS 6 has a narrow melting peak at about 271°C. This peak should correspond to the melting of β crystal. However, sPS/clay nano-composite with 5 wt% clay shows one broad melting peaks also at about 271°C. This peak should correspond to the

melting of mixed α and β crystals. It is hard to separate the melting of α crystal from that of β crystal. Therefore, for this system, DSC is less useful to investigate the polymorphism in sPS/clay nano-composites.

4.3 Summary

The influence of crystallization temperature on the formation of α crystal and β crystal in syndiotactic polystyrene has been investigated. The results of X-ray diffraction and nonisothermal crystallization experiments indicate that the cooling rate should not be the intrinsic factor controlling the formation of α crystal and β crystal. And the crystallization temperature seems certainly to have a more important influence. The onset or minimum temperature above which the stable phase can be obtained was obtained in syndiotactic polystyrene (230°C for the material used in this study).

Furthermore, sPS/clay nano-composites were successfully prepared by solution intercalation technique using 1, 1, 2, 2-tetrachloroethane (TCE) as the solvent. The polymorphism in sPS/clay nano-composites has been investigated by WAXD and FTIR. The result shows that the addition of nano-clay could favor the formation of α crystal.

Chapter 5 Metastability in Polymer/Clay Nano-composites and Blends

For Nylon 6/clay nano-composites and sPS/clay nano-composites, the addition of nano-clay could all favor the formation of metastable phase. However, up to now, the reason is not very clear. In order to better understand the unique polymorphic behavior of polymer/clay nano-composites, metastability in polymer/clay nano-composites and blends was investigated in this chapter using X-ray diffraction and Differential scanning calorimetry.

5.1 Introduction

In the classical concept, thermodynamic states are considered to be of infinite large size. However, polymers may have metastability states present due to small phase size [14, 116]. Thus, although ordered and disordered models have been used to explain the phase transformations in metals and alloys [105], they are not applicable in polymers due to many limitations [10].

The theoretical basis of metastability in polymer phase transitions has been proposed and thoroughly discussed by Keller and Cheng about a decade ago [14, 116]. Keller and Cheng believed that, in addition to classical metastability that describes the phase transformation from one state to another according to the Ostwald stage rule, circumstantial metastabilities are also important in polymer phase transitions. These circumstantial metastabilities may be originated from morphological, compositional and other structural factors in a polymer system. In reality, an equilibrium stable state of a crystalline polymer with infinite crystal

size, i.e., extended chain crystals, is usually unattainable due to its unique long chain structure. Physical or structural constraints of size, composition variations, and dimensionality are the likely factors closely related to the circumstantial metastabilities [14, 116]. The morphological metastability of the restricted states is associated with the phase size, e.g., lamellar thickness. It is well-known that polymeric crystals are usually lamellae containing chains in a folded conformation with the lamellar thickness equal or related to the fold length. For example, during isothermal crystallization, the lamellar thickness is determined by the extent of under-cooling, ΔT , which is the difference between melting and isothermal crystallization temperature. Thus, the morphological metastability is expected to vary with crystallization temperature for a given polymer. Furthermore, the metastability theory predicts that a metastable phase (defined by the classical metastable state) may become the stable one and a conventionally stable phase may become metastable when the phase dimensions can be made sufficiently small [14]. In other words, the stable and metastable polymorphs may undergo a stability inversion at a very low dimension according to Keller and Cheng's theory.

Since the proposition of the polymer metastability theory, there is very few reported attempt in literature [16, 17] to apply this theory to explain phase transitions in polymers. For example, Ho et al [16] investigated syndiotactic polystyrene crystallized at different temperatures. In their DSC study, besides the two melting peaks usually observed for the metastable α crystal and stable β crystal of sPS, they reported the emergence of a third melting peak at a higher temperature. The authors speculated that this new higher temperature melting peak is originated from 'a reorganized metastable α crystals', and hence an evidence for the stability inversion of the metastable α crystal and stable β crystal in sPS.

The author further speculated that this inversion is also due to size effect, although no evidence was given on how and why the different sizes were attained. However, in most other annealing studies on sPS, there is no report on assigning a higher temperature melting peak to the metastable α phase [10, 13, 96-98]. Although the metastability theory is a major step forward towards understanding the mechanisms of polymorphic phase transitions in polymers, the lack of studies on polymer structures using this theory may be attributed to experimental limitations. Very recently, Cheng has reiterated this point [15] when commenting on a report of preparation of single crystal polyethylene nano-particles [144, 145]. Although these new nano-structures may have given hope for new insight into the metastability theory because of their very small sized crystals, deciphering the information coming out of the experimental data of such polymer nano-crystals is still expected to be a great challenge [15].

The increasing interest in polymer/clay nano-composites over the last decade is due to their demonstrated as well as anticipated potential property enhancements, relative to the neat resin. The polymorphism of polymer-clay nano-composites has also been studied in many systems [3, 7, 9, 30, 92, 96, 97, 100, 101].

In this study, metastability theory is used to understand phase transition phenomenon observed in polymer/clay nano-composites. Although polymorphism has been reported in nano-composites of clay with different polymers, and it is known that the polymorphic behavior of nano-composites is very different from the neat polymers [3, 7, 9, 30, 92, 96, 97, 100, 101], the aim of this study is to attempt to better understand the unique polymorphic behavior of polymer/clay nano-composites using the theory of metastability. In fact, it is

understood that the large surface area of nano-clay gives rise to constraining effect during crystallization of a polymer. Nano-clay should provide excellent confinement of polymer crystals, because the apparent crystallite size decreases with increasing nano-clay content [124, 146]. Therefore, it is believed that polymer/clay nano-composites should be a good model system to apply the metastability theory. In this study, annealing study on neat Nylon 6, Nylon 6/clay nano-composite and neat sPS, sPS/clay nano-composite is carried out. Through a set of intentionally designed experiments using WAXD and DSC analysis, the onset or minimum annealing temperature, above which the 'stable' phase starts to crystallize, is compared between the neat polymers and the nano-composites. Furthermore, the stability of the 'metastable' phase is assessed.

5.2 Experimental Section

5.2.1 Neat Nylon 6 and Nylon 6/clay nano-composite

The particles of Nylon 6 and Nylon 6/clay nano-composite with 5 wt% clay were sandwiched between two cover glasses of 0.16mm thick and heated on a hot stage at 300°C. The particles were then pressed into a film and kept for 10 minutes. This process proved to be able to eliminate any thermal history of Nylon 6. Then, for annealing at different temperatures, the samples were transferred quickly from the hot stage to a silicon oil bath and kept at seven desired temperatures for 120 minutes. Finally, the samples were quickly removed from oil bath and quenched in liquid nitrogen.

The samples were characterized by DSC and WAXD. Deconvolution analysis was carried just as described in 3.1.4.

The crystallization behaviors were investigated using a TA Instruments MDSC 2920 differential scanning calorimeter. Temperature scans were carried out at 2°C/min. All operations were carried out under a nitrogen environment. Samples weights were between 5~10 mg. The heat of crystallization for Nylon 6 is 190 J/g [9].

The annealing time is set as 120min. This is because, for both neat Nylon 6 and Nylon 6/clay nano-composite, there is almost no difference (see Figure 5.1 and 5.2) between the samples annealing for 120min and 48 hours even at 180°C (higher than normal phase transition temperature).

Figure 5.1 The X-ray diffraction patterns (Cu Kα) of Nylon 6 annealed at 180°C for 120min and 48h

Figure 5.2 The X-ray diffraction patterns (Cu K α) of Nylon 6/clay nano-composite with 5wt% clay annealed at 180°C for 120min and 48h

5.2.2 Neat sPS and sPS/clay nano-composite

The samples were initially heated on a hot stage at 340°C and kept for 5 minutes. This process was proved enough to eliminate any thermal history and the memory effects of the α form in the melt [12, 137, 138]. Then, for annealing at different temperatures, the samples were transferred quickly from the hot stage to a silicon oil bath and kept at six desired temperatures for 48h. Finally, the samples were quickly removed from oil bath and quenched in liquid nitrogen. The samples were characterized by WAXD. The percentage of the α form in the crystalline fraction was evaluated just as the description in 4.1.2.

5.3 Metastability in Neat Nylon 6 and Nylon 6/Clay Nano-composite

From 3.2, it can be concluded that the addition of nano-clay is able to enhance the formation of γ crystal of Nylon 6. Although several reports have come to the same conclusion [3, 7, 9, 30, 92], the explanation as to why the addition of nano-clay could enhance the formation of γ phase has been vague and still under debate and discussion [9, 92, 124]. Nevertheless, it is accepted that the interaction between nano-clay and Nylon 6 must have played an important role. We believe that this enhancement in formation of the 'metastable' γ phase crystal can be link to the theory of metastability proposed by Keller and Cheng [14, 116].

Nano-clay has enormous surface area, which constrains the crystallization of Nylon 6 [124]. At the same time, multiple nuclei can be easily formed on the surfaces of nano-fillers [105]. Both would result in substantial reduction in crystal sizes because the growth of a crystal stops when it impinges the clay surfaces or other crystals. In particular, the polymer intercalated between the galleries of clay platelets certainly has very limited space to crystallize, which is expected to be in several nanometers. As discussed earlier, the size effect is the essence of the metastability theory.

Thermodynamics of polymorphism

In the classical thermodynamic theory, the assumption is that the crystals are sufficiently large so that there is no need to consider the size or other kinetic effects [116]. In general, polymers are much more prone to form the metastable region than small molecules or metallic matters. Polymers may have metastable states due to small phase size, multiphase compositions and other kinetic reasons. Furthermore, according to the metastability theory [14], the stability, represented by the melting point, of a crystal is size dependent as shown schematically in Figure 2.10 (which was when the theory was first proposed by Keller and

Cheng [116]). The stability, or melting point, of both the ‘stable’ and the ‘metastable’ phases decreases with decreasing size, l . At the same time, the stability difference between the ‘stable’ and the ‘metastable’ phases diminishes with decreasing size of the crystals. The theory actually predicts a stability inversion when the size is sufficiently small. This means that a metastable phase becomes the stable phase, and conversely, a conventionally stable phase becomes metastable. This is reflected in the changes in melting temperatures before and after the ‘Q-point’ as shown in Figure 2.11. When the phase size is smaller than the crossover point, Q , the stability (reflected by the melting point) of the stable phase is lower than that of the metastable phase. Furthermore, the stable phase is expected to have a lower crystallization rate in this case [14, 116].

The metastability theory implies if suitable dimensional conditions were met, the metastable phase would be preferentially formed over the stable phase. Also, there is a minimum phase size for the stable phase to exist or to be formed, i.e., the minimum critical nucleus size of the stable phase. In other word, there can be a scenario when the ‘stable’ phase of the polymorphs cannot be formed when the size is sufficiently small. We believe such conditions could be possible in polymer clay nano-composites due to the unique confinement effect of clay.

Perhaps it is now relevant to consider from the viewpoint of classical thermodynamics. According to classical thermodynamics, crystallization begins by the formation of very small solid particles or nuclei [105, 106]. At a certain crystallization temperature, there is a corresponding critical nucleus size, which is the smallest stable particle size for that phase at that temperature. Further, the critical nucleus size is proportional to $1/\Delta G_v$, where ΔG_v is the difference between the free energies per unit volume of solid crystal and liquid melt [105,

106]. At a given crystallization temperature T , ΔG_v is expressed by the following equation [106]:

$$\Delta G_v = L_v(T_m - T)/T_m \quad 5.1$$

where L_v is the latent heat of fusion per unit volume and T_m is the melting temperature for that phase. Therefore, the critical nuclei size can be tuned by varying the crystallization or annealing temperature. To form large sized critical nuclei, higher crystallization temperature T is required, and vice versa. As it is known that the stable phase is always obtained at higher crystallization temperature and the metastable phase obtained at lower temperature. Based on the above discussion, it can be deduced that the lowest temperature (onset temperature), at which the stable phase can be obtained, should correspond to the minimum critical nucleus size of the stable phase. It may be further deduced that the crystallization of the stable phase is expected to be more difficult in polymer/clay nano-composites than in neat polymers. Also, the stability of the metastable phase in a polymer/clay nano-composite is higher than that in the neat polymer.

Annealing of Nylon 6 and Nylon 6/clay nano-composite

Based on the above understanding, isothermal crystallization behavior and polymorphic structures of neat Nylon 6 and the Nylon 6/clay nano-composite with 5 wt% clay were studied using samples annealed at different temperatures.

Figure 5.3 The X-ray diffraction patterns (Cu $K\alpha$) of Nylon 6 annealed at different temperatures

Figure 5.3 shows the X-ray diffraction patterns of neat Nylon 6 annealed at different temperatures. It can be seen that in samples annealed at 80°C and 100°C, there is only one peak present at about 21.5° corresponding to γ crystal. Two additional peaks or shoulders characteristic of α crystal begin to appear at around $2\theta = 20.5^\circ$ and 24° , corresponding to α_1 and α_2 , in samples annealed at 120°C. As the annealing temperature increases further, the peaks for α crystal increase. It can be seen that the α phase becomes the dominant one and the γ phase has almost disappeared in neat Nylon 6 annealed at 200°C. In contrast, the X-ray diffraction patterns of the Nylon 6/clay nano-composite with 5 wt% clay annealed at different temperatures are presented in Figure 5.4. It is seen that the γ phase dominates in the nano-composite up to the annealing temperature as high as 160°C and appreciable amount of α phase only appears at annealing temperature higher than 160°C. Even in samples annealed

at 200°C, α phase has not yet become dominant and there is still considerable presence of γ crystal in the nano-composite sample.

Figure 5.4 The X-ray diffraction patterns (Cu $K\alpha$) of Nylon 6/clay nano-composite with 5wt% clay annealed at different temperatures

Figures 5.5 and 5.6 show the DSC traces of the annealed neat Nylon 6 and the nano-composite. Their polymorphic behavior observed from the DSC traces is consistent with that seen from WAXD analysis. However quantitative analysis of DSC results is considered less reliable because of the possible structural changes during DSC heating scan [9, 10, 15].

Figure 5.5 DSC traces of Nylon 6 annealed at different temperatures

Figure 5.6 DSC traces of Nylon 6/clay nano-composite with 5wt% clay annealed at different temperatures

In our view, the observation clearly indicates that the metastable γ crystal is stabilized in the nano-composite in comparison to that in the neat Nylon 6. The questions are whether or not this is related to the metastability theory, and furthermore whether we can have experimental evidence indicating or inferring the ‘stability inversion’ between the metastable and stable phase as predicted by the metastability theory. In order to understand further, the apparent degrees of crystallinity of γ crystal, $\phi_{m\gamma}$, and α crystal, $\phi_{m\alpha}$, of neat Nylon 6 and Nylon 6/clay nano-composite are plotted against the annealing temperature as shown in Figures 5.7(a) and (b).

(a)

(b)

Figure 5.7 Apparent degree of crystallinity (ϕ_{mc}) of Nylon 6 and Nylon 6/clay nano-composite with 5 wt% clay annealed at different temperatures (a) γ crystal (b) α crystal

For both samples, $\phi_{mc\gamma}$ first gradually increases and then drops rather sharply with annealing temperature. The initially increase of $\phi_{mc\gamma}$ is related to higher rate of crystallization at higher annealing temperatures and the drop is due to γ to α , or metastable to stable phase transition. For neat Nylon 6, the sharp drop of $\phi_{mc\gamma}$ starts when annealing temperature reaches 140°C (Figure 5.7(a)), and $\phi_{mc\gamma}$ becomes barely detectable and $\phi_{mc\alpha}$ (33%) dominants in the sample annealed at 200°C. In the nano-composite, however, $\phi_{mc\gamma}$ is always higher than that in the neat Nylon 6 at all annealing temperatures. Also, the drop of $\phi_{mc\gamma}$ in the nano-composite starts at 160°C and γ phase still dominants even in sample annealed at 200°C when $\phi_{mc\gamma}$ (18%) is still higher than $\phi_{mc\alpha}$ (13%).

Further insight is revealed by examining the crystallization of the α crystal which is the 'stable' phase (γ crystal being the 'metastable' phase for Nylon 6). Figure 5.7(b) shows a general increasing trend of $\phi_{m\alpha}$ with annealing temperature for both neat Nylon 6 and the nano-composite. At the same time, $\phi_{m\alpha}$ in the nano-composite is always lower than that of the neat Nylon 6 throughout the wide range of annealing temperatures used in this study. This indicates that α crystal of Nylon 6 has become more difficult to form in the presence of nano-clay. Closer examination of Figure 5.7(b) has also revealed that the α phase first appears at above 100°C for neat Nylon 6, but α crystal in the clay nano-composite only begins to appear above 140°C during the annealing study. This means that the onset of formation of the 'stable' α phase is delayed for 40°C in Nylon 6 because of the presence of nano-clay.

Meanwhile, the crystallinity of γ crystal and α crystal, of neat Nylon 6 and Nylon 6/clay nano-composite calculated from Figure 5.5 and 5.6, are plotted against the annealing temperature as shown in Figures 5.8(a) and (b). The results from the DSC traces are almost the same as those from WAXD analysis.

(a)

(b)

Figure 5.8 Crystallinity of Nylon 6 and Nylon 6/clay nano-composite with 5 wt% clay annealed at different temperatures (a) γ crystal (b) α crystal

We believe that the higher transition temperature from γ to α phase and higher onset or minimum temperature above which stable α phase can be obtained in the nano-composite comparing to the neat Nylon 6 can be understood from the viewpoint of the metastability theory. According to the metastability theory, the stability of both α and γ phases is size dependent, and the stability difference between the stable α and metastable γ phase becomes less and less pronounced with decreasing size. The theory predicts an eventual, hypothetical ‘stability inversion’ of the stable and metastable phase when the size is sufficiently small. This changing or tuning of the size can be achieved by varying the annealing temperature as understood from Equation 5.1. However, when annealed at the same temperature, the phase size in the nano-composite is expected to be smaller than that in neat Nylon 6. In the nano-composite, there is an effective downward tuning of phase size by the presence of the unique structure of nano-clay. Therefore, in the presence of nano-clay, an higher annealing temperature is needed to attain the minimum critical nucleus size required for the growth of α form crystal.

Although it is difficult to conclude whether or not this clay-induced downward tuning of phase size is sufficient to cause the stability inversion under the conditions of this present study, it is clear that the presence of clay has narrowed the stability difference between the stable α and the metastable γ phase, because it has made the stable α phase less readily to form (requiring higher annealing temperature as shown in Figures 5.7(b) and 5.8(b)). Although there is no directly observation of the stability inversion of α and γ phase in the nano-composite (A direct proof means the observation of transition from α phase to γ phase.), there is strong evidence that the phase transition from the metastable γ phase to the stable α

phase, as expected from thermodynamics, has become more difficult in the nano-composite in comparison to the neat Nylon 6.

In fact, some previous works [9, 147] have found the special phase transformation from α to γ phase in Nylon 6/clay nano-composites. However, they do not relate to metastability theory. So they can not clearly explain the stability of polymorphism inverts with size.

The raw material used in our previous work [147], Nylon 6 and its layered-silicate nano-composites with approximately 4 wt % clay were originally from Unitika, Ltd. (Japan) in the form of granular samples. The detailed material compositions are proprietary, but both are described as reactor grade in-situ polymerized nano-composites derived from a synthetic phyllosilicate or mica nano-filler with octadecylamine treatment, or a similar long-chain aliphatic amine treatment. Nano-clay has a fully exfoliated morphology in these Nylon 6/clay nano-composites. For this Nylon 6/clay nano-composite, after annealing at 190 °C for different times, the relationships between enthalpies of transition and logarithmic annealing time ($\log t$) showed that ΔH_γ of the endothermic shoulder peak was found to increase with increasing annealing time and ΔH_α showed a slight decrease after annealing (Figure 6 in reference 147). This means during this course, there is a phase transition from α crystal to γ crystal. In other words, at this condition, the stability of polymorphism inverts with size.

Another example is Vaia's previous work [9]. They also used nylon 6/clay nano-composites made by in-situ polymerization. When the samples were heated at a rate of approximately 2°C /min from room temperature, the apparent degree of α crystal decreases and that of γ

crystal increases (Figure 6 and 7 in reference 9). This result also supports the evidence of phase transition from α crystals to γ crystal in Nylon 6/clay nano-composites.

5.4 Metastability in Neat SPS and SPS/Clay Nano-composite

In order to deeply understand metastability in polymer/clay nano-composites, metastability in neat sPS and sPS/clay nano-composite with 5 wt% clay has also been investigated.

Figure 5.9 The X-ray diffraction patterns (Cu Kα) of sPS annealed at different temperatures

The X-ray diffraction patterns of neat sPS annealed at different temperatures are reported in Figure 5.9. It can be seen that for samples annealed at 200°C to 210°C, there are only α form crystal characteristic peaks (at $2\theta = 6.7, 11.6^\circ$) exist. For annealing above 220°C, the β form

peaks (at $2\theta = 6.1, 12.2, 18.6^\circ$) are present. Also, as the annealing temperature increases further, the β crystal increases quickly and rapidly becomes the major phase in sPS. At 240 and 250°C , almost only β crystals can be obtained.

Figure 5.10 The X-ray diffraction patterns (Cu $K\alpha$) of sPS/clay nano-composite with 5 wt% clay annealed at different temperatures

In contrast to neat sPS, the X-ray diffraction patterns of sPS/clay nano-composite with 5 wt% clay annealed at different temperatures are presented in Figure 5.10. When the samples are annealed at below 240°C , there are only α crystals. The β form characteristic peaks appear at 250°C . Even at that temperature, α crystal is still predominant in the samples.

The percentage of α crystal and β crystals in the crystalline fraction of neat sPS and sPS/clay nano-composite are plotted against the annealing temperature as shown in Figures 5.11(a) and (b).

(a)

(b)

Figure 5.11 Percentage in the crystalline fraction of sPS and sPS/clay nano-composite with 5 wt% clay annealed at different temperatures (a) α crystal (b) β crystal

For both samples, the initially percentage of α crystal in the crystalline fraction is 100%. With increasing annealing temperature, the percentage of α crystal finally drops. However, in neat sPS, the sharp drop of percentage of α crystal starts when annealing temperature reaches 210°C (Figure 5.11(a)), and β crystal rapidly becomes dominant. There is only β crystal in the sample annealed above 240°C. In the nano-composite, however, the drop of percentage of α crystal starts at 240°C and α phase still dominants even in sample annealed at 250°C.

Figure 5.11(b) shows a general increasing trend of the percentage of β crystal with annealing temperature for both neat sPS and sPS/clay nano-composite. At the same time, the percentage of β crystal in the nano-composite is always lower than that of the neat sPS

throughout the wide range of annealing temperatures used in this study. This indicates that β crystal of sPS has become more difficult to form in the presence of nano-clay. Furthermore, it can be observed that the β phase first appears at above 210°C for neat sPS, but β crystal in the clay nano-composite only begins to appear above 240°C during the annealing study. This means that the onset of formation of the ‘stable’ β phase is delayed for 30°C in sPS because of the presence of nano-clay.

This result is just the same as that of Nylon 6/clay nano-composite and can also be successfully explained using metastability theory.

Based on the above discussion, it is clear that the metastability theory is very useful in understanding the polymorphic behavior in Nylon 6/clay nano-composite and sPS/clay nano-composite. One of the practical limitations of clay nano-composites is their possible variation of clay dispersion, and hence the experimental observation reflects an average effect for a particular system, although the overall fundamentals are essentially the same. It is believed that the discussion in this study should be universally applicable to clay nano-composites of different semi-crystalline polymers. Therefore, it has been demonstrated that polymer/clay nano-composites may serve as a direct paragon to study the metastability phenomenon in semi-crystalline polymers, although Cheng has highlighted the potential challenges in a recent commentary article which appeared in Nature [15].

5.5 Metastability in Nylon 6/Nano-clay/PP-g-MAH Blends

Because there are chemical reactions in Nylon 6/nano-clay/PP-g-MAH blends, the chemical structures and the thermodynamic parameters of the materials must be changed. However, up to now, it is difficult to explain the influence of chemical reactions on the polymorphism of polymer, even using metastability theory. This may be one of the meaningful fields which will be worth further investigation. Therefore, only the main results for this study is listed here.

Figure 5.12 to 5.15 show the X-ray diffraction patterns of Nylon 6 and PP-g-MAH blends with different contents of PP-g-MAH (2.5, 5, 7.5, 10 wt%) respectively, each annealed at different temperatures. Meanwhile, the apparent degree of crystallinity of these blends is shown in Figure 5.16.

Figure 5.12 X-ray diffraction patterns (Cu $K\alpha$) of Nylon 6 and PP-g-MAH blends (with 2.5 wt% PP-g-MAH) annealed at different temperatures

Figure 5.13 X-ray diffraction patterns (Cu Kα) of Nylon 6 and PP-g-MAH blends (with 5 wt% PP-g-MAH) annealed at different temperatures

Figure 5.14 X-ray diffraction patterns (Cu Kα) of Nylon 6 and PP-g-MAH blends (with 7.5 wt% PP-g-MAH) annealed at different temperatures

Figure 5.15 X-ray diffraction patterns (Cu $K\alpha$) of Nylon 6 and PP-g-MAH blends (with 10 wt% PP-g-MAH) annealed at different temperatures

(a)

(b)

Figure 5.16 Apparent degree of crystallinity (ϕ_{mc}) of Nylon 6 and PP-g-MAH blends annealed at different temperatures. (a) α crystal, (b) γ crystal

Figures 5.17 to 5.20 show the X-ray diffraction patterns of Nylon 6/nano-clay/PP-g-MAH blends (containing 5wt% of clay) with different contents of PP-g-MAH (2.5, 5, 7.5, 10 wt%) respectively, which were annealed at different temperatures. Meanwhile, the apparent degree of crystallinity of these blends is shown in Figure 5.21.

Figure 5.17 X-ray diffraction patterns (Cu $K\alpha$) of Nylon 6/nano-clay/PP-g-MAH blends (5 wt% clay and 2.5 wt% PP-g-MAH) annealed at different temperatures

Figure 5.18 X-ray diffraction patterns (Cu $K\alpha$) of Nylon 6/nano-clay/PP-g-MAH blends (5 wt% clay and 5 wt% PP-g-MAH) annealed at different temperatures

Figure 5.19 X-ray diffraction patterns (Cu $K\alpha$) of Nylon 6/nano-clay/PP-g-MAH blends (5 wt% clay and 7.5 wt% PP-g-MAH) annealed at different temperatures

Figure 5.20 X-ray diffraction patterns (Cu $K\alpha$) of Nylon 6/nano-clay/PP-g-MAH blends (5 wt% clay and 10 wt% PP-g-MAH) annealed at different temperatures

Figure 5.21 Apparent degree of crystallinity (ϕ_{mc}) of Nylon 6/nano-clay/PP-g-MAH blends (5 wt% clay) annealed at different temperatures. (a) α crystal, (b) γ crystal

5.6 Summary

Polymer/clay nano-composites provide a good model system to study the metastability theory. From quantitative analysis of WAXD results, it can be noticed that the stability of metastable phase in polymer/clay nano-composites is higher than that in neat polymers. Furthermore, the onset or minimum temperature above which the stable phase can be obtained in polymer/clay nano-composites is much higher than that in pure polymers. The higher stability of metastable phase and higher onset or minimum temperature above which the stable phase can be obtained, provide a direct paragon to explore the metastability in polymer/clay nano-composites.

Chapter 6 Metastability in Polymer/Clay Nano-composites in Supercritical Fluid

The metastability and phase transitions of Nylon 6 and sPS with and without the presence of nano-clay in supercritical CO₂ were investigated by WAXD. The differences between polymers and polymer/clay nano-composites annealed at same temperatures at normal condition and in supercritical CO₂ have been compared

6.1 Introduction

Supercritical fluids (SCFs) have shown great advantages in promoting the crystallization of polymers over conventional organic solvents. The solvent strength of SCFs can be tuned over a wide range through small changes in the temperature, pressure, or both while in the vicinity of the critical point. Therefore, the degree of polymer swelling and partitioning of penetrants can be adjusted. The liquid like densities of SCFs allow for solvent powers orders of magnitude higher than those of gases, whereas gas like viscosities lead to high rates of diffusion. After experimentation, the fluid is easily removed from the polymer matrix by the simple depressurization of the system.

Carbon dioxide (CO₂) is nontoxic, nonflammable, naturally occurring, environmentally benign, and relatively inexpensive and has a moderate critical temperature and pressure (31.1°C and 7.38 MPa respectively). These properties make supercritical CO₂ convenient for many applications, such as the extraction of low-molecular-weight compounds from

polymers [131], polymerization [130, 148], the impregnation of polymers with chemical additives [149], the formation of small and uniform polymeric particles by rapid solvent expansion [150] and the creation of polymer foams [132, 151].

Although supercritical CO₂ is a weak solvent for polymers except for some fluoro-polymers and silicones [18], it can plasticize polymers by reducing the glass transition temperature (T_g). The absorbed CO₂ reduces the polymer T_g because of an increase in the free-volume fraction or the mobility of the chains. This can lead to considerable swelling for an amorphous polymer and to the induction of crystallinity or growth of the already nucleated crystalline phase for crystallizable or semi-crystalline polymers at lower temperatures. This indeed was found to be the case for a CO₂/poly(ether ether ketone) (PEEK) system [152] in which crystal was induced at temperatures as low as 100°C. Similar investigations of supercritical CO₂ used to induce and promote crystallization have been reported in other polymers [18-20, 130, 152]. In general, these studies show that supercritical CO₂ can reduce the crystallization temperature (T_c) of polymers and increase the crystallization rate with increasing temperature and pressure.

Bisphenol A polycarbonate (PC) is a semi-crystalline polymer characterized by a very low crystallization rate, because of its chain rigidity and the difficulty in transforming into a crystalline structure. The plasticization effect of SCCO₂ increases the mobility of polymer chains, reduces the energy-barrier for crystallization, and hence induces crystallization of PC under moderate conditions [19, 152-154]. The effects of supercritical CO₂ pressure and temperature on the crystallization characteristics of linear PC have been investigated in details by He et al [152-154].

Furthermore, polymers absorbed with CO₂ can undergo some solid-solid transitions that can not be induced under ambient pressure. Handa et al [19] studied the effect of compressed CO₂ on the phase transition and polymorphism in sPS. They found that sPS treated with compressed CO₂ underwent the planar mesophase to β , α to β , and γ to β transitions that only occurred in the presence of liquid solvents. They also found that the phase transitions of glassy sPS to the planar mesomorphic and to the α form, and γ to α transition occurred at lower temperature in compressed CO₂ than those under ambient pressure. Glassy sPS was directly transformed into the γ form when treated with 57 atm (5.8 MPa) of CO₂ at 90 and 175°C. However, the conditions of the previous experiments did not reach the supercritical condition of CO₂ [19]. He et al. [155] found the solid phase transition of the α crystal to the β crystal of sPS in supercritical CO₂. The other phase transitions in sPS in supercritical CO₂ have also been investigated by He et al [156-159].

However, there are few papers [160-162] published on polymer/clay nano-composites in supercritical CO₂. Nawaby et al [160] investigated the effect of nano-clay loading on the glass transition temperature behavior and the solubility and diffusivity of compressed CO₂ gas in PMMA/clay nano-composites relative to that of the neat PMMA. Turng et al [161] have also studied the effects of the addition of nano-clay and processing parameters on the cell development of microcellular injection-molded Nylon 6/clay nano-composites and neat resin in supercritical CO₂. Their results showed even in supercritical CO₂, the presence of nano-clay would also favor the formation of γ crystal in Nylon 6/clay nano-composites. Hu et al [162] found in the absence of SCCO₂, nano-clay does not change the crystallization behavior of PC under their experimental conditions. However, in the presence of SCCO₂, nano-clay enhances the crystallization of PC.

Up to now, there is no paper published on the metastability in supercritical CO₂. In this study, metastability and phase transitions of Nylon 6 and sPS with and without the presence of nano-clay in supercritical CO₂ were investigated by WAXD.

6.2 Experimental Section

6.2.1 Neat Nylon 6 and Nylon 6/clay nano-composite

The particles of Nylon 6 and Nylon 6/clay nano-composite with 5 wt% clay were sandwiched between two cover glasses of 0.16mm thick and heated on a hot stage at 300°C. The particles were then pressed into a film and kept for 10 minutes. This process proved to eliminate any thermal history of Nylon 6. Then, the samples were rapidly quenched in liquid nitrogen. X-ray analysis revealed the films to be completely amorphous [92, 124]. Finally, the samples were annealed in supercritical CO₂ (30 MPa and 48h) at different temperatures.

A high-pressure apparatus was used for SCCO₂ treatment. The original samples were enclosed in the autoclave. The autoclave was flushed with low-pressure CO₂ and then was heated up to the experimental temperatures. Finally, the autoclave was filled with more CO₂ and once the CO₂ pressure reached the desired value, the timing began.

The samples were characterized by WAXD. Deconvolution analysis was carried just as the description in 3.1.4.

6.2.2 Neat sPS and sPS/clay nano-composite

The samples were initially heated in a hot stage at 340°C and kept for 5 minutes. This process was proved enough to eliminate any thermal history and the memory of the α -form in the melt [12, 137, 138]. Then, the samples were rapidly quenched in an ice-water bath. X-ray analysis revealed the films to be completely amorphous [19, 156]. Finally, the samples were annealed in supercritical CO₂ (30 MPa and 48h) at different temperatures. The samples were characterized by WAXD. The percentage of the α form in the crystalline fraction was evaluated just as the description in 4.1.2.

6.3 Metastability in Neat Nylon 6 and Nylon 6/Clay Nano-composite in Supercritical CO₂

Figure 6.1 The X-ray diffraction patterns (Cu K α) of neat Nylon 6 annealed in supercritical CO₂ (30 MPa and 48h) at different temperatures

Figure 6.1 shows the X-ray diffraction patterns of neat Nylon 6 annealed in supercritical CO₂ (30 MPa and 48h) at different temperatures. It can be seen that in sample annealed 100°C, there is only one peak present at about 21.5° corresponding to γ crystal. Two additional peaks or shoulders characteristic of α crystal begin to appear at around $2\theta = 20.5^\circ$ and 24° , corresponding to α_1 and α_2 , in samples annealed at about 110°C. As the annealing temperature increases further, the peaks for α crystal increase. It can be seen that the α phase becomes the dominant one in neat Nylon 6 annealed at 160°C. In contrast, the X-ray diffraction patterns of the Nylon 6/clay nano-composite with 5 wt% clay annealed in supercritical CO₂ (30 MPa and 48h) at different temperatures are presented in Figure 6.2. It is seen that the γ phase dominates in the nano-composite up to the annealing temperature as high as 160°C and appreciable amount of α phase only appears at annealing temperature higher than 130°C.

Figure 6.2 The X-ray diffraction patterns (Cu $K\alpha$) of Nylon 6/clay nano-composite with 5 wt% clay annealed in supercritical CO_2 (30 MPa and 48h) at different temperatures

In order to understand further, the apparent degrees of crystallinity of γ crystal, $\phi_{m\gamma}$, α crystal, $\phi_{m\alpha}$, and total crystal ($\phi_{\text{total}} = \phi_{m\gamma} + \phi_{m\alpha}$) of neat Nylon 6 and Nylon 6/clay nano-composite are plotted against the annealing temperature as shown in Figures 6.3(a), (b) and (c).

(a)

(b)

(c)

Figure 6.3 Apparent degree of crystallinity (ϕ_{mc}) of Nylon 6 and Nylon 6/clay nano-composite with 5 wt% clay annealed in supercritical CO₂ (30 MPa and 48h) at different temperatures (a) γ crystal (b) α crystal (c) total crystal

For both samples, $\phi_{mc\gamma}$ drops rather with annealing temperature. For neat Nylon 6, the sharp drop of $\phi_{mc\gamma}$ starts when annealing temperature reaches 100°C (Figure 6.3(a)), and $\phi_{mc\gamma}$ becomes about 6% and $\phi_{mc\alpha}$ (26%) dominants in the sample annealed at 160°C. In the nano-composite, however, $\phi_{mc\gamma}$ is always higher than that in the neat Nylon 6 at all annealing temperatures. Also, the drop of $\phi_{mc\gamma}$ in the nano-composite starts at 120°C and γ phase still dominants even in sample annealed at 160°C when $\phi_{mc\gamma}$ (18%) is still higher than $\phi_{mc\alpha}$ (14%).

Further insight is revealed by examining the crystallization of the α crystal. Figure 6.3(b) shows a general increasing trend of $\phi_{mc\alpha}$ with annealing temperature for both neat Nylon 6 and the nano-composite. At the same time, $\phi_{mc\alpha}$ in the nano-composite is always lower than that of the neat Nylon 6 throughout the wide range of annealing temperatures used in this study. This indicates that α crystal of Nylon 6 has become more difficult to form in the presence of nano-clay even in supercritical CO₂ (30 MPa and 48h). Closer examination of Figure 6.3(b) has also revealed that the α phase first appears at above 100°C for neat Nylon 6, but α crystal in the clay nano-composite only begins to appear above 120°C during the annealing study. This means that the onset of formation of the ‘stable’ α phase is delayed for 20°C in Nylon 6 because of the presence of nano-clay in supercritical CO₂ (30 MPa and 48h).

The higher transition temperature from γ to α phase and higher onset or minimum temperature above which stable α phase can be obtained in the nano-composite comparing to the neat Nylon 6 in supercritical CO₂ (30 MPa and 48h) can also be explained from the viewpoint of the metastability theory. According to the metastability theory, the stability of both α and γ phase is size dependent, and the stability difference between the stable α and metastable γ phase becomes less and less pronounced with decreasing size. When annealed at the same temperature in supercritical CO₂ (30 MPa and 48h), the phase size in the nano-composite is also expected to be smaller than that in neat Nylon 6. In the nano-composite, there is an effective downward tuning of phase size by the presence of the unique structure of nano-clay. Therefore, in the presence of nano-clay, an higher annealing temperature is needed to attain the minimum critical nucleus size required for the growth of α form crystal.

From Figure 6.3 (c), it can be seen, for both neat Nylon 6 and Nylon 6/clay nano-composite, the total crystallinity is almost around 33% at any annealing temperature. This is because supercritical CO₂ can induce and promote crystallization at very lower temperature, the total crystallinity can reach the higher crystallinity even at 100°C. Also, the annealing time is sufficient (48h in this study), the Nylon 6 and Nylon 6/clay nano-composite tend to have similar total crystallinity.

Furthermore, compared with Figure 5.8, the effect of supercritical CO₂ (30 MPa and 48h) on the metastability and phase transition of neat Nylon 6 and Nylon 6/clay nano-composite can also be investigated.

From Figures 5.1 and 5.2, it can be seen that for both neat Nylon 6 and Nylon 6/clay nano-composite, there is almost no difference between the samples annealing for 120min and 48 hours even at 180°C. Therefore, when annealing temperature is lower than 180°C, the apparent degrees of crystallinity of α crystal which annealing for 48h must be the same as that annealing for 120min.

The apparent degrees of crystallinity of α crystal, $\phi_{mc\alpha}$, of neat Nylon 6 and Nylon 6/clay nano-composite, at normal condition or in supercritical fluid, are plotted against the annealing temperature as shown in Figures 6.4(a) and (b).

(a)

(b)

Figure 6.4 Apparent degree of crystallinity ($\phi_{mc\alpha}$) of Nylon 6 and Nylon 6/clay nano-composite annealed at different temperatures at normal condition or in supercritical fluid

(a) neat Nylon 6 (b) Nylon 6/clay nano-composite

For neat Nylon 6, the onset or minimum temperature above which the stable phase can be obtained in supercritical CO₂ (30 MPa and 48h) is about 100°C, almost the same as that at normal condition. However, $\phi_{mc\alpha}$ in supercritical CO₂ is always higher than that at the normal condition throughout the wide range of annealing temperatures used in this study. This indicates that α crystal of Nylon 6 has become easier to form in supercritical CO₂. For Nylon 6/clay nano-composite, α crystal of Nylon 6 has also become easier to form in supercritical CO₂ than at normal condition. This can also be explained by metastability theory.

According to the metastability theory, the stability of both α and γ phase is size dependent, and the stability difference between the stable α and metastable γ phase becomes less and less pronounced with decreasing size. Meanwhile, supercritical CO₂ can plasticize polymers by reducing the glass transition temperature (T_g). The absorbed CO₂ reduces the polymer T_g because of an increase in the free-volume fraction or the mobility of the chains. This can lead to considerable swelling for an amorphous polymer and to the induction of crystallinity or growth of the already nucleated crystalline phase for crystallizable or semicrystalline polymers at lower temperatures. Therefore, when annealed at the same temperature, the phase size in supercritical CO₂ is expected to be larger than that at normal condition [152, 163]. Thus, in supercritical CO₂, for both neat Nylon 6 and nylon 6/clay nano-composite, α crystal is easier to form in supercritical CO₂.

For both in supercritical CO₂ and at normal condition, the onset or minimum temperature above which the stable phase can be obtained in polymer/clay nano-composites is much higher than that in pure polymers. However, this difference in supercritical CO₂ is about 20°C, much lower than that at normal condition (40°C). This may be explained as follows:

Supercritical CO₂ can gradually infuse into solid polymer, plasticizes the amorphous region by increasing the free volume of the amorphous regions in the crystallizable polymer, thereby increasing chain mobility with increasing the degree of polymer swelling. Supercritical CO₂ depresses the glass transition temperature of a polymer, accelerates the relaxation of the macromolecules. However, it is almost impossible to disperse clay completely in nano-size. It is believed that clay agglomeration will prevent the polymer chains from fully wetting and intercalating the clay particles, and therefore these sites may serve as low resistance gas transport pathways in the polymer/clay nano-composite [160]. So the corrected diffusion coefficient for CO₂ in Nylon 6/clay nano-composite may be higher than that in pure Nylon 6 for a particular pressure. The higher corrected diffusion coefficient for CO₂ makes α crystal in nylon 6/clay nano-composite is easier to form in supercritical CO₂.

The apparent degrees of crystallinity of γ crystal, ϕ_{mcy} , of neat Nylon 6 and Nylon 6/clay nano-composite, at normal condition or in supercritical fluid, are plotted against the annealing temperature as shown in Figures 6.5(a) and (b).

(a)

(b)

Figure 6.5 Apparent degree of crystallinity (ϕ_{mcy}) of Nylon 6 and Nylon 6/clay nano-composite annealed at different temperatures at normal condition or in supercritical fluid

(a) neat Nylon 6 (b) Nylon 6/clay nano-composite

For neat Nylon 6, the drop of ϕ_{mcy} starts when annealing temperature reaches 100°C in SCCO₂. However, at normal condition, this drop starts about 140°C. This indicates that γ crystal of Nylon 6 has become less stable in supercritical CO₂. For Nylon 6/clay nano-composite, the same result can be obtained.

For both Nylon 6 and Nylon 6/clay nano-composite at normal condition, ϕ_{mcy} gradually increases when annealing temperature is between 100 and 140°C. This increase of ϕ_{mcy} is related to higher rate of crystallization at higher annealing temperatures. It can be clearer to see for the total crystallinity shown in Figure 6.6.

(a)

(b)

Figure 6.6 Apparent degree of total crystallinity (ϕ_{total}) of Nylon 6 and Nylon 6/clay nano-composite annealed at different temperatures at normal condition or in supercritical fluid

(a) neat Nylon 6 (b) Nylon 6/clay nano-composite

At normal condition, for both Nylon 6 and Nylon 6/clay nano-composite, the total crystallinity gradually increases when annealing temperature is between 100 and 160 $^{\circ}\text{C}$. This increase is related to higher rate of crystallization at higher annealing temperatures. However, the total crystallinity of Nylon 6/clay nano-composite is always higher than that of neat nylon 6 at any annealing temperature (also see Figure 5.7(c)). This indicates that nano-clay will promote the crystallization of Nylon 6, especially at lower temperature.

In supercritical fluid, because SCCO_2 can induce and promote crystallization of polymer and the annealing time in this study is sufficient, the Nylon 6 and Nylon 6/clay nano-composite have almost the same total crystallinity at any temperature. It seemed that nano-clay may have no influence on the total crystallinity in SCCO_2 under our experimental condition.

6.4 Metastability in Neat SPS and SPS/Clay Nano-composite in Supercritical CO_2

Figure 6.7 The X-ray diffraction patterns ($\text{Cu K}\alpha$) of neat sPS annealed in supercritical CO_2 (30 MPa and 48h) at different temperatures

Figure 6.8 The X-ray diffraction patterns (Cu Kα) of sPS/clay nano-composite with 5 wt% clay annealed in supercritical CO₂ (30 MPa and 48h) at different temperatures

Figures 6.7 and 6.8 show the X-ray diffraction patterns of neat sPS and sPS/clay nano-composite with 5 wt% clay annealed in supercritical CO₂ (30 MPa and 48h) at different temperatures. For both neat sPS and sPS/clay nano-composite, as increasing annealing temperature, the reflections of β crystal increase. The trend becomes clearer after quantitative analysis as discussed below (in Figures 6.9(a) and (b)).

The percentage of α crystal and β crystal in the crystalline fraction of neat sPS and sPS/clay nano-composite are plotted against the annealing temperature as shown in Figures 6.9(a) and (b).

(a)

(b)

Figure 6.9 Percentage in the crystalline fraction of sPS and sPS/clay nano-composite with 5 wt% clay annealed in supercritical CO₂ (30 MPa and 48h) at different temperatures (a) α crystal (b) β crystal

For both samples, the initially percentage of α crystal in the crystalline fraction is 100%. With increasing annealing temperature in supercritical CO₂ (30 MPa and 48h), the percentage of α crystal finally drops. However, in neat sPS, the sharp drop of percentage of α crystal starts when annealing temperature reaches 180°C (Figure 6.9(a)), and β crystal rapidly becomes dominant when annealing temperature is above 200°C. There is only β crystal in the sample annealed above 230°C. In sPS/clay nano-composite, however, the drop of percentage of α crystal starts at 200°C and α phase still remains about 50% in sample even annealed at 240°C in supercritical CO₂ (30 MPa and 48h).

Figure 6.9(b) shows a general increasing trend of the percentage of β crystal with annealing temperature for both neat sPS and sPS/clay nano-composite. At the same time, the percentage of β crystal in the nano-composite is always lower than that of the neat sPS throughout the wide range of annealing temperatures used in this study. This indicates that β crystal of sPS is more difficult to form in the presence of nano-clay even in supercritical CO₂ (30 MPa and 48h). Furthermore, it can be observed that the β phase first appears at above 180°C for neat sPS, but β crystal in the clay nano-composite only begins to appear above 200°C during the annealing study. This means that the onset of formation of the ‘stable’ β phase is delayed for 20°C in sPS because of the presence of nano-clay even in supercritical CO₂ (30 MPa and 48h).

Compared with Figure 5.11, the effect of supercritical CO₂ (30 MPa and 48h) on the metastability and phase transition of neat sPS and sPS/clay nano-composite has also be investigated.

The percentage of β crystal in the crystalline fraction of sPS and sPS/clay nano-composite, at normal condition or in supercritical fluid, are plotted against the annealing temperature as shown in Figures 6.10(a) and (b).

(a)

(b)

Figure 6.10 Percentage of β crystal in the crystalline fraction of sPS and sPS/clay nano-composite annealed at different temperatures at normal condition or in supercritical CO_2

(a) neat sPS (b) sPS/clay nano-composite

For neat sPS, the onset or minimum temperature above which the stable phase can be obtained in supercritical CO_2 (30 MPa and 48h) is about 180°C , which 30°C lower than that at normal condition. At the same time, the percentage of β crystal in the crystalline fraction of sPS in supercritical CO_2 is always higher than that at the normal condition till 240°C which 100% percentage of β crystal is obtained. This indicates that β crystal of neat sPS has become easier to form in supercritical CO_2 . For sPS/clay nano-composite, the same result can be obtained.

Meanwhile, for both in supercritical CO₂ and at normal condition, the onset or minimum temperature above which the stable phase can be obtained in sPS/clay nano-composite is also much higher than that in neat sPS. Moreover, this difference in supercritical CO₂ is about 20°C, lower than that at normal condition (30°C).

The percentage of α crystal in the crystalline fraction of sPS and sPS/clay nano-composite, at normal condition or in supercritical fluid, are plotted against the annealing temperature as shown in Figures 6.11(a) and (b). Furthermore, it is worth mentioning that the α crystal in sPS and sPS/clay nano-composite shows an opposite trend of that of the β crystal.

(a)

(b)

Figure 6.11 Percentage of α crystal in the crystalline fraction of sPS and sPS/clay nano-composite annealed at different temperatures at normal condition or in supercritical CO₂

(a) neat sPS (b) sPS/clay nano-composite

All these results of neat sPS and sPS/clay nano-composite are just the same as those of neat Nylon 6 and Nylon 6/clay nano-composite. Of course, all these can also be explained by the same reasons just as those in 6.3.

The metastability and phase transitions of polymers with and without the presence of nano-clay in supercritical CO₂ are diffusion controlled processes [18, 131, 160, 164, 165]. So the results are controlled by annealing temperature, pressure and time. In general, higher temperature and pressure, longer annealing time will favor the formation of stable phase in

polymers [152]. Researchers [18, 132, 164] have given the thermodynamic explanations why temperature and pressure can influence the diffusion in supercritical CO₂. Egorow [165] also set up a model to explain the velocity time correlation function of diffusion in supercritical fluids.

6.5 Summary

The metastability and phase transitions of Nylon 6 and sPS with and without the presence of nano-clay in supercritical CO₂ were investigated by WAXD. Quantitative analysis of WAXD results, it can be obtained that the stability of metastable phase in polymer/clay nano-composites is higher than that in neat polymers even in supercritical CO₂. Furthermore, the onset or minimum temperature above which the stable phase can be obtained in polymer/clay nano-composites is also higher than that in pure polymers in supercritical CO₂. However, this difference between the two onset temperatures in supercritical CO₂ is lower than that at normal condition because of the higher diffusion coefficients for CO₂ in polymer/clay nano-composites.

Chapter 7 Conclusion and Recommendations for Further Work

7.1 Conclusion

Nylon 6/nano-clay nano-composites, Nylon 6/PP-g-MAH blends and Nylon 6/nano-clay/PP-g-MAH blends have been prepared by polymer melt intercalation technique. SPS/clay nano-composites have been successfully prepared by solution intercalation technique using 1, 1, 2, 2-tetrachloroethane (TCE) as the solvent.

The polymorphism and crystallization behavior of Nylon 6/clay nano-composites and functionalized polyolefin blends has been investigated by WAXD, FTIR and DSC. The peculiar results indicate that in Nylon 6/nano-clay and Nylon 6/PP-g-MAH binary blends, both nano-clay and functionalized polyolefin would favor the formation of γ crystal of Nylon 6. However, in Nylon 6/nano-clay/PP-g-MAH ternary blends, the interactions among them are more complicated. There is chemical reaction between nano-clay and PP-gMAH. Therefore, the co-existence of both nano-clay and PP-g-MAH in the Nylon 6/nano-clay/PP-g-MAH ternary blends antagonizes each other's promotional effect on γ crystal formation in Nylon 6.

The influence of crystallization temperature on the formation of α crystal and β crystal in syndiotactic polystyrene has been investigated. The results of X-ray diffraction and nonisothermal crystallization experiments indicate the crystallization temperature should be the intrinsic factor controlling the formation of α crystal and β crystal. The stable phase can only be obtained at higher crystallization temperature. The metastable phase will be observed

at lower crystallization temperature. The onset or minimum temperature above which the stable phase can be obtained was obtained in syndiotactic polystyrene. Furthermore, the polymorphism in sPS/clay nano-composites has been investigated by WAXD and FTIR. The result shows the addition of nano-clay could favor the formation of α crystal (metastable phase).

Metastability in Nylon 6/clay nano-composites and sPS/clay nano-composites has been investigated by WAXD and DSC. The results show polymer/clay nano-composites provide a good model system to study the metastability theory. Quantitative analysis indicates that the stability of metastable phase in polymer/clay nano-composites is higher than that in neat polymers. Furthermore, the onset or minimum temperature above which the stable phase can be obtained in polymer/clay nano-composites is much higher than that in pure polymers. The higher stability of metastable phase and higher onset or minimum temperature above which the stable phase can be obtained, provide a direct paragon to explore the metastability in polymer/clay nano-composites. Also, this is the thermodynamic reason why the addition of nano-clay would favor the formation of metastable phase.

The metastability and phase transition of Nylon 6 and sPS with and without the presence of nano-clay in supercritical CO₂ was investigated by WAXD. The differences between neat polymers and polymer/clay nano-composites annealed at same temperatures at normal condition and in supercritical CO₂ have been compared. The results show supercritical CO₂ will favor the phase transition from metastable phase to stable phase for both neat polymer and polymer/clay nano-composite. Meanwhile, the stability of metastable phase in polymer/clay nano-composites is also higher than that in neat polymers even in supercritical CO₂. The onset or minimum temperature above which the stable phase can be obtained in

polymer/clay nano-composites is also higher than that in pure polymers in supercritical CO₂. However, this difference between the two onset temperatures in supercritical CO₂ is lower than that at normal condition because of the higher diffusion coefficients for CO₂ in polymer/clay nano-composites.

7.2 Recommendations for Future Work

Although systematic studies on crystallization and phase transition of polymer nano-composites and blends were carried out in this work, there still have some meaningful fields worth further investigation. The following work is mostly suggested for the future:

- In the classical concept, thermodynamic states are considered to be of infinite large size. However, polymers may have metastable states present due to small phase size. Upon heating in a melting point experiment, polymers can easily shift from one metastable state to another that has thicker lamellar polymer crystals [14, 15]. Reorganization phenomena can be hindered by applying high heating rates. Therefore, high performance DSC (HPer DSC) was recently developed [166]. Although reorganization can not be avoided using current HPer DSC [167], as the development of equipment in future, it must be interested to study the polymorphism in polymers using HPer DSC.
- There is no evidence to show that the stability inverses with size in this study. This is because the size in this study is not sufficient small. At present, single crystal nano-particles made from polyethylene and polymer nano-fibers have been successfully prepared [144, 145]. This provides the possibility of studying the sufficient small crystals. If suitable testing methods or experiments can be designed to investigate the

metastability in polymer nano-crystals, this may cast light on fundamental studying of crystallization and phase transition in polymers.

- The influence of chemical reactions on the crystallization and phase transition in polymers is less investigated. It can be hoped that there will be more and more new and interested results in future on this topic.
- Supercritical fluids provide special conditions for polymorphism and phase transition in polymers. It is very easy to get different thermodynamics and kinetics conditions by simple adjusting the temperature and pressure. Therefore, systematic study on polymorphism and phase transition in supercritical fluids should help us to understand the influence of thermodynamics and kinetics conditions on the polymorphism and phase transition in polymers.

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