2.1 Mechanism of Shrinkage Control by LPA

High polymerization shrinkage, about 7-10% is created by free radical copolymerization of unsaturated polyester resin and styrene. This causes warpage, wavy surfaces, and internal voids and cracks especially in fiber reinforced products, and a post-mold processing may be needed to get the desired surface finish. Some thermoplastic polymers such as polyvinyl acetate (3-5%) may be used to reduce the shrinkage [Cheremisinoff 1998, Dong et al 2005].

2.1.1 Low Profile Additives

Thermoplastic materials as low profile additives (LPAs) are compatible thermoplastic particles that become incompatible with the resin molecules during cure. They are used to compensate for curing shrinkage and therefore cause to produce the parts with a better dimensional accuracy and surface finish. They are called low profile additives because they decrease surface roughness and improve surface smoothness or “profile” by reducing the shrinkage of the thermosetting resin as a part is cured during molding. LPAs have been found to be highly effective in controlling the curing shrinkage of UPE resins in high-temperature moulding processes such as
compression moulding of sheet moulding compounds (SMCs) and injection moulding of bulk moulding compounds (BMCs) [Li et al., 1998].

When significant cure shrinkage occurs, a cross section of the surface appears rough under high magnification showing large peaks and valleys. When cure shrinkage is reduced, the surface is smoother, and its cross section appears smoother, having lower peaks and shallower valleys. The objective of an effective low profile additive is to reduce the difference between the highest peaks and shallowest valleys to a minimum. Even the best low profile additives however, do not achieve a mirror-like surface [Dennis Fisher, 1996].

Using dilatometric measurements Bartkus et al [1970] showed that the volumetric profile of the unsaturated polyester styrene reacting system in high temperature molding process exhibits three stages of volume change. The result is shown in Figure 2.1 (a). During the initial heating, the mixture first goes through a thermal expansion and after that shrinks due to polymerization and thermal contraction. As the sample was demolded and cooled to room temperature the final volume shrinkage was about 7.1%.

Figure 2.1 (b) shows the volumetric profile of the resin using acrylic thermoplastic as LPA [Barkus et al, 1970]. The result shows that the resin with LPA expanded at the initial setup followed by a second increase, which was due to presence of LPA in resin. The volume shrinkage due to polymerization and cooling was not as large as in the pure resin and finally it resulted in to a volume expansion of 2.8%. Also excellent surface smoothness and dimensional stability was reported in this resin system.

A typical picture in Figure 2.2 shows two cured unsymmetric composite laminates made of glass-fiber bundles in two perpendicular directions (cross-ply laminate). The two bundle layers are stitched together with a very thin fiber bundle. The asymmetric laminate without LPA shows a significant curvature due to curing stresses. The asymmetric plate containing 25% LPA in the resin does not show a significant curvature [Liu et al, 1999].
Several thermoplastic compatible with UP resins used as a low shrinkage or low profile additives (LPAs) to control the polymerization shrinkage of unsaturated polyester resins and improve the surface smoothness include polyvinyl acetate, thermoplastic polyester, acrylics, polymethyl methacrylate, styrene copolymers, polyvinyl chloride and its copolymers, cellulose acetate butyrate, polycaprolactones, and polyethylene powder [Cheremisinoff, 1998 and Dong et al, 2005].

Figure 2.1: Volume change profile of (a) conventional resin and (b) low profile resin [Barkus et al, 1970]
The effectiveness of volume shrinkage control generally increases with increasing polarity in LPA, i.e., PS < PMMA < PVAc, since the UP molecule is reasonably polar as the dipole moment data of LPAs were reported by researcher (uncured UP = 2.0-2.5, PVAc = 1.6, PMMA = 1.3, and PS = 0.3) [Huang et al, 1996]. This can be explained by polarity of thermoplastics. High polar thermoplastics tend to phase out and thermally expand during curing because unsaturated polyester resin which is polar before reaction (dipole moment of 2.0-2.5) became less polar (dipole moment of less than 1.0) as the reaction goes on.

![Figure 2.2: A photograph of two asymmetric composite laminates, the transparent one wwu and the white one with 25% LPA.](image)

Also it is reported in comparison with PVAc that PMMA does not have a good performance at low temperature cure. The cause of this effect relates to the lower coefficient of thermal expansion of PMMA in comparison with PVAc [Beheshty et al, 2006].
2.1.2 Effective Factors of LPA

Different factors of LPA such as type, thermal expansion coefficient, concentration, molecular weight, glass transition temperature \( (T_g) \) and polarity are generally considered important [Atkins et al 1976, 1993] and the effect of them on resin shrinkage, surface quality and dimensional control of molded polymer composites have been studied by many researchers [Li et al, 1998].

2.1.2.1 Effect of molecular weight of LPAs

The effect of molecular weight of LPAs on the volume shrinkage control was investigated by many researchers [Dong et al, 2005, Bucknall et al, 1985, Melby et al, 1989]. They found that molecular weight of the LPAs is important in volume shrinkage control. For the St/UP/LPA systems containing low molecular weight of LPA, the most compatible system showed a better volume shrinkage control after curing, whereas the addition of a higher molecular weight of LPA resulted in a greater volume shrinkage [Dong et al, 2005]. The St/UP/LPA systems containing low molecular weight have better storage miscibility and exhibit more homogeneous morphology which cause to better shrinkage control where higher molecular weight of LPA can be effective to reduced shrinkage control at high temperature process.

For the St/UP/LPA sample solution containing PMMA, the addition of a higher molecular weight LPA (i.e., the more incompatible St/UP/LPA ternary system) led to a later onset of the cure reaction. Also, a relatively lower peak reaction rate resulted, which was an indication of a less compatible ternary system. This may support the trend of the compatibility of the cured St/UP/LPA systems with lower molecular weight [Dong et al, 2005].

In [Montagne et al, 2005] it is reported that with high molecular weight PVAc the microgels are larger than those obtained with the low molecular weight PVAc when cured under identical conditions. The larger microgels obtained with high molecular
weight PVAc clearly indicate that the greater incompatibility (high molecular weight PVAc has a lower surface tension than low molecular weight PVAc) has caused a coarser reaction induced phase separation, while the more compatible, lower molecular weight PVAc, causes a finer de-mixing [Montagne et al, 2005].

The solutions of PVAc in styrene and polyester resin are initially transparent but become cloudy after a few minutes at 130°C, suggesting that the system begins as a single phase which separates into two or more phases as a result of the chemical changes taking place during cure.

This kind of effect has been observed in a number of other polymerizing solutions, and its causes are well understood. Essentially, the increase in molecular weight of the polymerizing species reduces the entropic contribution to the free energy of mixing, so that the enthalpic contribution becomes dominant. Since mixing between polymers are usually endothermic, phase separation results [Bucknall et al, 1985].

2.1.2.2 Effect of LPA concentration

The relative microcracks volume fraction is varied with different concentrations of LPA. As the LPA concentration increased, the volume fraction of microcrack also increased. Also, at a fixed LPA content, the volume fraction of microcrack was the highest for the PVAc system, followed by PMMA and PS systems. These results generally support the volume shrinkage mechanism of strain relief through stress cracking, and the greater micro crack formation would give less volume shrinkage [Huang et al, 1996].

The effectiveness of volume shrinkage control generally increases with increasing polarity in LPA, i.e., PS < PMMA < PVAc < PU, since the UP molecule is reasonably polar. The overall volume change after the cure would be determined not only by the volume compensation for shrinkage due to microvoid formation but also by the intrinsic polymerization shrinkage.
The volume fraction of microvoids depends on the sample morphology and the segregating effect of LPA on microgel particles generated during the cure, which could be enhanced either by increasing the LPA concentration or by employing a relatively polar LPA, such as PVAc [Huang et al, 1996]. Therefore increasing LPA concentration reduces the fractional volume shrinkage after the cure.

At a fixed initial molar ratio (MR) of 2/1, both the mechanical properties and $T_g$ in the major continuous phase would be lower with increasing LPA concentration for the cured samples (except impact properties, tensile strains and fracture properties for PU and PVAc systems). The former could be mainly due to a reduction of volume fraction and a decline in network tightness in the major continuous phase, while the latter due to an enhanced plasticization effect of LPA on the major continuous phase [Huang et al, 1998].

Adding LPA could delay the induction time and the time to reach the maximum reaction rate. Also, with LPA, a lower maximum reaction rate resulted and the final degree of cure was lower than neat UP resin [Huang et al, 1995, Lem et al, 1983].

The maximum exotherm temperature and the rate of cure decrease with increasing the concentration of LPA, but the gel time increases. Also the mechanical properties of cured resin decreases with increasing PVAc concentration. This may be regarded to the micro-void formation [Hayaty et al, 2004].

### 2.1.2.3 Some Other Factors of LPA

Effects of reactive low-profile additive are investigated in [Dong et al, 2006]. Besides microvoid formation, the intrinsic polymerization shrinkage is also important in determining the volume shrinkage control during the cure of St/UP/LPA system. The intrinsic polymerization shrinkage may be reduced by employing reactive PVAc-$b$-PS types of LPA with peroxide groups in their backbone, which could lead to expansion effects on microgel structures during cure. This is ascribed to the reduction in
cyclization of UP resin during the cure, caused by the intermolecular reaction between UP and reactive LPA, as well as the repulsive forces between chain segments of UP and LPA within the microgel structures.

The effect of pressure and thickener on LPA performance was investigated in [Kinkelaar et al, 1994]. Pressure and thickening were found to have a negative effect on LPA performance. In investigating the LPA mechanism, it was found that the UP morphology did not change significantly once established during cure; however, sample appearance was found to change markedly, turning opaque during the plateau region.

The residual styrene, volume shrinkage, and mechanical properties of unsaturated polyester resin with a low profile additive cured with a comonomer MMA were investigated in [Cao et al, 2003]. In the study of reaction kinetics, both DSC and FTIR were employed to obtain the overall and individual reaction rate and conversion profiles. It was found that the final conversion and residual styrene could be improved greatly by introducing the comonomer MMA into the resin system. The relative reaction profiles of styrene, MMA and UP C==C bonds suggests that a higher consumption rate of St occurs compared to the system without MMA, indicating a favorite copolymerization of St and MMA. The study on shrinkage shows that MMA has a negative effect on shrinkage control of UP/St/LPA system because the system becomes more compatible with the addition of MMA, indicated by a uniform and flat-like morphology. Consequently, phase separation becomes more difficult, leading to poor shrinkage control. The surface quality and the flexural property of unsaturated polyester resin depend strongly on the volume shrinkage and final conversion of the resin system.
2.1.3 Mechanism of LPAs


Although the detailed LPA mechanism for controlling polymerization shrinkage is still not well understood, a general explanation based on information available in the literature can be summarized as follows [Suspene et al 1991, Kinkelaar et al 1994, Li et al 1998 and 2000, Zeng et al 2001] which is shown in Figure 2.3:

In step 1, the system starts as a homogeneous mixture consisting of UPE, LPA, styrene and initiator.

In step 2, the reaction starts, where the UPE molecules are linked by either an inter or an intramolecular reaction. Because of the increase of UPE molecular weight and change of polarity, the compatibility of reacting UPE with both LPA and styrene decreases. Localized phase separation occurs. According to the mass balance, the microgel must be surrounded by an LPA-rich layer.

Further reaction in steps 3, 4 and 5, which includes inter- and intraparticle reactions, results in gelation and phase inversion between the LPA rich and the UPE-rich phases. In these steps, the reaction mixture turns cloudy and translucent. The viscosity starts to increase, and the system keeps shrinking.

In step 6, stress may build up internally because of the possible difference of the two phases in reaction rate and modulus. At a certain point, a local crack may be initiated and propagate along the interface or inside the weaker phase (LPA-rich phase). Microvoids are formed and stress is released; consequently, the polymerization
shrinkage is compensated. Here, the reaction mixture turns opaque and expansion starts.

**Figure 2.3:** Illustration of LPA mechanism [Kinkelaar et al, 1994]
It is believed that when part cooling occurs. Above the $T_g$ of the UP resin phase, the bulk coefficient of thermal expansions of the LPA phase and the UP phase are about the same. Below the $T_g$ of the UP phase, the UP phase will shrink much less on cooling than the LPA phase. This difference in cooling shrinkage will cause more microvoids to occur in the LPA phase as more stress is applied over the LPA phase, and this will continue until the $T_g$ of the LPA phase has been reached.

Since the resin thermal histories in the high-temperature processes such as SMC compression moulding and in the low-temperature processes such as SCRIMP are totally different, the performance of LPAs may vary from process to process. In a typical SMC processing, the compound is first heated from room temperature to the mould temperature, which is typically 150°C. Then, there is a strong reaction exotherm, which will further increase the compound temperature to possibly 200°C. The temperature decreases after the exothermic peak. Finally, the moulded part is cooled down during demoulding. Therefore, there is a large temperature variation during moulding. Correspondingly, the volume change of the moulded material during moulding can be divided into three stages: thermal expansion during heating, polymerization shrinkage and thermal expansion/contraction during curing, and further thermal contraction during demoulding and cooling. To achieve the maximum shrinkage control in SMC processing, a large thermal expansion of the LPA during heating and reaction and microvoid formation during cooling are essential. In contrast, SCRIMP is conducted at room temperature. There is little temperature variation during curing and the curing cycle is usually long. Obviously, thermal expansion of LPA can no longer be counted for in this low-temperature moulding process [Li et al, 1998 and 2000].

In high temperature cure (>80°C) several mechanisms have been proposed for shrinkage control of LPA [Barkus et al 1970, Kinkelaar et al 1994, Li et al 1998 and 2000, Beheshty et al 2006]. They have reported that thermal expansion of the resin and LPA during heating cause to control the resin shrinkage. Also during curing phase separation and inversion between the LPA-rich and resin-rich phase, and
creating the micro-voids at the inside or interface the LPA-rich phase cause to control the resin shrinkage during curing and cooling.

The low-temperature LPA mechanism is quite similar to the high-temperature LPA mechanism, except for the effect of thermal history. For higher curing temperatures (>80°C), the thermal expansion/contraction resulting from the large temperature gradient during moulding plays the most important role in compensating shrinkage. Therefore, LPAs with high thermal expansion coefficient and low glass transition temperature (i.e. lower molecular weight) are preferred [Li et al, 1998 and 2000].

It is believed that after phase separation when the network is gradually constructed by the separated microparticles, near the maximum reaction rate the reaction takes place very fast and creates a strong shrinkage force or stress. The shrinkage stress then passes through the interfacial area into the LPA phase. Because the LPA is a weak thermoplastic, the shrinkage stress tears off the LPA phase and forms microvoids in the LPA phase [Suspenne et al, 1991].

Also it is reported that for a fast reaction, such as SMC moulding of pure resin without LPA, the shrinkage stress tears off the UP macronetwork and forms microcracks in the final products. The microcracks break the macronetwork and lead to a broken moulded part. Moulding with LPA, the microcracks are only located in the LPA phase and do not destroy the UP network. The LPA phase acts as a channel or a buffer area for microcrack propagation. Shrinkage stress cannot penetrate into fillers and fiber glasses. It finally forms microcracks around the fillers and fiber glasses, which also partly compensates for volume shrinkage [Suspenne et al, 1991].

It is believed that when styrene is absorbed on a low-profile additive, it polymerizes at slower rate than the bulk, and boils in the late stages due to increase of the temperature, and it thus creates an internal pressure and compensates for the shrinkage [Cheremisinoff, 1998].

However the real morphology formation during reaction is dependent on the reaction kinetics and phase separation. This will be greatly influenced by the process involved
and the processing conditions, such as temperature and pressure. In addition, although the microvoids are observed for volume compensation, the correlation of microvoid formation to volume control and surface quality of a moulded resin is still to be further investigated [Suspene et al, 1991].

### 2.2 Polymer Layered Silicates Nanocomposites

#### 2.2.1 Introduction

A nanocomposite material can be defined as one that consists of two or more different material components, at least one of which has a dimension (i.e., length, width, or thickness) below 100 nm. There are many types of nanocomposites presently under research and development including polymer/inorganic particle, polymer/polymer, metal/ceramic, and inorganic-based nanocomposites [Chanda and Roy 2009].

The weight advantage of using PNCs in automotive manufacturing could have significant impact on environmental concerns besides many other potential benefits. Thus, it has been reported that wide and large scale use of PNCs by U.S. vehicle manufacturers could save 1.5 billion liters of gasoline over the life of one year’s production of vehicles and the corresponding reduction in carbon dioxide emissions would be more than 10 billion pounds [Chanda and Roy 2009]. The use of nanocomposites is also expected to improve manufacturing speed and promote recycling.

In recent years, polymer/layered silicate (PLS) nanocomposites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in materials properties when compared with virgin polymer or conventional micro and macro-composites. Compared to their micro and macro
counterparts and the pristine polymer matrix, polymer-clay nanocomposites (PCNs) exhibit higher tensile strength and moduli, lower thermal expansion coefficients, greater swelling resistance, enhanced ion conductivity, also increased heat resistance and biodegradability of biodegradable polymers, and decreased gas permeability and flammability [Ray et al 2003, Chanda and Roy 2009].

Nanoparticles added to thermoplastic polymers improve the mechanical properties, increase $T_g$ and enhance fire retardancy. Nanoparticles in UP resins bring similar effects [Penczek et al, 2005].

Various nano reinforcements currently being developed are nano-clay (layered silicates), cellulose nano-whiskers, ultra fine layered titanate, and carbon nanotubes. Carbon nanotubes, however, are the most promising of the new nanomaterials. Carbon nanotube-based polymer composites are poised to exhibit exceptional mechanical, thermal and electrical properties [Mai and Yu 2006].

When particle diameter, layer thickness or fibrous material diameter reduces from micrometer to nanometer, increase the surface area/volume ratio by three orders in magnitude which is shown in Figure 2.4[Thostenson et al, 2005].

### 2.2.2 Structure and Properties of Organically Modified Layered Silicate (OMLS)

One of the most promising PNC systems is the one based on organic polymers and inorganic clay minerals with layered structure, which belong to the general family of 2:1 layered silicates [Chanda and Roy 2009].
Of particular interest are polymer and organically modified layered silicate (OMLS) nanocomposites because of their demonstrated significant enhancement, relative to an unmodified polymer resin, of a large number of physical properties, including barrier, flammability resistance, thermal and environmental stability, solvent uptake, and rate of biodegradability. These improvements are generally attained at lower silicate content (5 wt.%) compared to that of conventional filled systems. For these reasons polymer/OMLS nanocomposites are far lighter in weight than conventional composites, and this makes them competitive with other materials for specific applications.

The main reason for these improved properties in nanocomposites is the nanometer scale of the dispersed fillers and the interfacial interaction between matrix and OMLS as opposed to conventional composites. Layered silicates have layer thickness in the order of 1 nm and very high aspect ratios (e.g. 10 - 1000). A few weight percent of OMLS that are properly dispersed throughout the matrix thus create a much higher
surface area for polymer filler interactions than do conventional composites. Layered silicates have two types of structure: tetrahedral-substituted and octahedral-substituted [Mai and Yu 2006]. The structure of 2:1 layered silicates is shown in figure 2.5 [Shipp et al, 2010].

In the case of tetrahedrally-substituted layered silicates the negative charge is located on the surface of silicate layers, and hence, the polymer matrices can interact more readily with these than with octahedrally-substituted material.

![Structure of 2:1 Layered Silicates](image)

**Figure 2.5**: The structure of 2:1 layered silicates [Shipp et al, 2010].
Two particular characteristics of layered silicates that are generally considered for PLS-nanocomposites are the ability of the silicate particles to disperse into individual layers, and the ability to fine-tune their surface chemistry through ion exchange reactions with organic and inorganic cations.

The physical mixture of a polymer and layered silicate may not form a nanocomposite. This situation is analogous to polymer blends, and in most cases separation into discrete phases takes place. In immiscible systems, which typically correspond to the more conventionally filled polymers, the poor physical interaction between the organic and the inorganic components leads to poor mechanical and thermal properties. In contrast, strong interactions between the polymer and the layered silicate in PLS nanocomposites lead to the organic and inorganic phases being dispersed at the nanometer level. As a result, nanocomposites exhibit unique properties not shared by their micro counterparts or conventionally filled polymers.

Pristine layered silicates usually contain hydrated Na or K ions. Obviously, in this pristine state, layered silicates are only miscible with hydrophilic polymers, such as poly ethylene oxide (PEO), or poly vinyl alcohol (PVA). To render layered silicates miscible with other polymer matrices, one must convert the normally hydrophilic silicate surface to an organophilic one, making the intercalation of many engineering polymers possible. Generally, this can be done by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations. Alkylammonium or alkylphosphonium cations in the organosilicates lower the surface energy of the inorganic host and improve the wetting characteristics of the polymer matrix, and result in a larger interlayer spacing. Additionally, the alkylammonium or alkylphosphonium cations can provide functional groups that can react with the polymer matrix, or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix [Ray et al, 2003].
During the ion exchange reaction, the hydrophilic nature decreases as the organic cations replace the original inorganic cations in MMT clay surface. However, a portion of the clay surface may not be covered by the organic cation which makes the MMT clay surface still remain polar and more compatible with polar molecules [Zeng et al, 2001].

### 2.2.3 Types of Nanocomposites

There are two idealized structures in Polymer-Layered Silicate Nanocomposites (PLSN) materials (excluding immiscible systems, which normally should not be regarded as nanocomposites), as depicted in Figure 2.6 [Shipp, 2010]. These are (1) intercalated materials, where the organic polymer is present within the inorganic silicate layers (i.e., a well ordered and structured arrangement exists), and (2) exfoliated materials, where the organic polymer host matrix contains delaminated silicate crystallites (i.e., disordered and well dispersed). Notice that in the exfoliated case the surface area between organic and inorganic is increased compared with the intercalated materials. This is speculated to lead to greater enhancement of physical properties of exfoliated composites when compared with similar intercalated materials. It should be pointed out, however, that many polymer–nanocomposite materials are not simply only exfoliated or just intercalated. They often tend to have mixtures of structures [Shipp, 2010].

![Diagram of nanocomposites](image)

**Figure 2.6:** Idealized accessible structures for PLSNs [Shipp, 2010].
2.2.4 Methods of Polymer Layered Silicates Nanocomposites Preparation

The preparative methods are divided into three main groups according to the starting materials and processing techniques: polymerization, solution intercalation, and melt processing (or melt blending). Each of the three main approaches may yield exfoliated, intercalated, or a mixed of exfoliated and intercalated structures. The degree of exfoliation versus intercalation depends on a host of experimental conditions, such as monomer type, solvents, temperatures, etc. [Shipp, 2010, Ray et al 2003]. Also, The mixing techniques include three main techniques: ultrasonication, mechanical or shear mixing and static mixing.

2.2.4.1 In Situ Polymerization

In this method, the layered silicate is swollen within the liquid monomer or a monomer solution so the polymer formation can occur between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator, or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step.

There are various approaches to in situ polymerization, with each one relying on the addition of monomer, either neat or in solution, to the silicate layers to swell or even exfoliate the silicate layers before polymerization occurs.

2.2.4.2 Solution Intercalation /Exfoliation

Layered silicates are well known to be dispersible in an appropriate solvent. By adding a polymer to the dispersed layered silicate and then removing the solvent one can make a PLSN that is in some cases exfoliated, but normally the silicate layers
reform a (semi)ordered stack, thus yielding an intercalated PLSN. A drawback of this approach being commercially useful is the use of large quantities of solvents, particularly if they are organic, although water has potential.

### 2.2.4.3 Melt Processing

This method involves annealing, statically or under shear, a mixture of the polymer and OMLS above the softening point of the polymer. This method has great advantages over either in situ intercalative polymerization or polymer solution intercalation. First, this method is environmentally benign due to the absence of organic solvents. Second, it is compatible with current industrial process, such as extrusion and injection molding. The melt intercalation method allows the use of polymers which were previously not suitable for in situ polymerization or solution intercalation.

### 2.2.5 Characterization of Layered Silicate Nanocomposite

To characterize of the crystallographic structure of the silicate layers in the nanoclay and nanocomposites, the X-ray diffraction (XRD) is widely used.

X-ray diffraction (XRD) data can be converted to $d$, layers distance of nanoclay and polymer/clay nanocomposite by using the Bragg equation, which is shown in Equation (2.1).

$$2d \sin \theta = n \lambda$$  \hspace{1cm} (2.1)

where $d$ is the distance between silicate layers, and $\theta$ the diffraction angle, $n$ is the order of diffraction and $\lambda$ the wavelength of the X-ray.

Figure 2.7 shows typical data from different idealized PLSN structures collected from X-ray diffraction (XRD). In particular, the XRD results show the intergallery spacing.
increases from the immiscible case to the exfoliated case. In an exfoliated nanocomposite, XRD spectra do not have a characteristic peak due to the regular stacking of the silicate layers [Shipp, 2010].

![Figure 2.7: Schematic of X-ray diffraction spectra for different types of polymer layered silicate nanocomposites [Shipp, 2010].](image)

The exfoliated state may maximize interfacial contact between the organic and inorganic phases leading to homogeneous dispersion, which results in obtaining the nanocomposites with optimum performance properties. Therefore, exfoliation is the most desirable morphological state for the polymer-clay nanocomposites (delamination) [Koo, 2006].

### 2.2.6 Crystallization Behavior and Morphology of Nanocomposites

Crystallization is one of the most effective processes used to control the extent of intercalation of polymer chains into silicate galleries, and hence to control the mechanical and various other properties of the nanocomposites. Okamoto et al. first studied the crystallization behavior and morphology of neat PP-MA and three different nanocomposites (PPCNs) in detail. They found that clay particles act as a nucleating agent for the crystallization of the matrix PA-MA, but that the linear growth rate and overall crystallization rate is not influenced significantly by the presence of clay. XRD analyses reveal that the intergallery spacing increases with
crystallization temperature $T_c$ for any amount of clay content in nanocomposites. Furthermore, at constant $T_c$ the extent of intercalation increases with decreasing clay content. The nucleation and growth processes of N6 in N6CN are presented in Figure 2.8. A unique mechanism can explain the higher crystallization rate along with the morphology and developed internal structure of N6CNs. This sandwiched structure, with each silicate layer strongly covered by polymer crystals, makes the system very rigid [Ray et al, 2003].

![Diagram of nucleation and growth mechanism in N6CN](image)

**Figure 2.8**: Schematic view of the nucleation and growth mechanism in nylon-6 nanocomposite [Ray et al, 2003].

The factors can affect the properties of polymer nanocomposites include [Koo, 2006]:

- Type of nanoparticles and their surface properties;
- Polymer properties, such as molecular weight and polymer chemistry;
- Synthesis methods, such as melt compounding and in-situ polymerization.
- Morphology of polymer nanocomposite.
2.3 Scope of Study:

In this chapter, literature concerning role of LPA and nanoclay in reducing volume shrinkage was reviewed. Several studies of different LPA’s have proven that PVAc and PMMA are two most promising thermoplastics for reducing volume shrinkage. Several studies have been carried out on UP/LPA nano-composites using organically modified clay [Xu et al 2004, Schubel et al 2005, Beheshty et al 2009]. Beheshty et al [2009] has been studied properties of UP/PVAc/OMC nanocomposites at low temperature cure and found that the addition of OMC to the low-profile UP/St systems can affect the volume shrinkage control but did not noticeably change the shrinkage control. While Xu et al [2004] and Schubel et al [2005] reported using organically modified clay with UP/PVAc at low temperature cure can control shrinkage. To our knowledge no work has been reported on the shrinkage control of UP/PMMA/OMC nanocomposites at different temperature cure (low temperature cure and high temperature cure).

The objective of this study is an integrated analysis of effect of nanoclay on the volume shrinkage control, reaction kinetics, morphology and mechanical properties of cured UP/PMMA/OMC nanocomposites.