CHAPTER 4

Effect of Nanoclay on Morphology, Reaction Kinetics and Mechanical Properties of Cured Low Profile Unsaturated Polyester (UP) Resin

4.1 Introduction

The unsaturated polyesters contain approximately ten unsaturations per chain and are usually transformed into a crosslinked polymer network by free radical copolymerization with a vinyl monomer, i.e., styrene, which allows one polymer chain to connect with other polymer chains, and to create a three dimensional network, which cause to convert resin to a hard thermoset solid.

The curing of unsaturated polyester resin is an exothermic reaction. During isothermal cure, the generated exothermic heat depends on the number of reacted double bonds in the compound, so the degree of curing reaction can be determined by measuring the heat evolved at any time [Kamal et al 1973, Sourour et al 1975, Yang et al 1988and 1989, Ramis et al 1992].

The LPAs are thermoplastic materials which are widely used to reduce shrinkage in unsaturated polyester resin mixture. They are compatible, or partially compatible, with styrene and UP resin mixture before cure and become incompatible during cure. Although the detailed mechanism of shrinkage control in unsaturated polyester resin mixture by low-profile additives is still not well understood, but regarding to many researchers studies [Pattison et al 1974 and 1975, Lem et al 1983, Bucknall et al

In this study, the effect of LPA additives and nanoclay on reaction kinetics, conversion, morphology and mechanical properties of cured samples of low profile unsaturated polyester (UP) resin is investigated.

4.2 Experimental

4.2.1 Materials

The unsaturated polyester (UP) resin used in this study was procured from Satyen Polymers(espol™ 41.00). It was Npg-ISO based unsaturated polyester resin with high average molecular weight of 2700g/mol and contains 37 wt% Styrene. Whereas the molar ratio of ST to polyester C=C bonds was fixed at (MR) 2.2:1. The crosslinking monomer used was styrene (St).

The LPA used in this study was poly methyl methacrylate (PMMA) with number average molecular weight ($\bar{M}_n = 55800$ g/mol). The nanoclay, Cloisite 20A (20A) from Southern Clay, is a natural MMT modified with a quaternary ammonium chloride having two hydrogenated tallow (w65% C18; w30% C16; w5% C14). For curing in high temperature, the initiator used was t-butyl perbenzoate (TBPB). The amount of TBPB added into the resin was 1 wt%. The resin mixture used in this study was containing of 3% nanoclay20A and 5% poly methyl methacrylate
(PMMA). The resin mixture was prepared by mechanical stirring followed by ultrasonication using in-situ polymerization method.

4.2.2 Instrument and Procedure

4.2.2.1 Differential Scanning Calorimetry (DSC)

The curing of unsaturated polyester resin is an exothermic reaction. The reaction rate profiles were measured by using differential scanning calorimeter (DSC-60A, Shimadzu). For the cure kinetic study, 10 mg of sample solution was placed in a hermetic aluminum sample pan. Isothermal runs were conducted at 115°C for one hour. To verify whether the sample had completely cured during the isothermal experiment, a post-cure is done on the sample. The post-cure of samples can be carried out by a second isothermal run. The samples were then reheated from room temperature to 300°C with heating rate of 10°C /min to determine the residual reactivity left in the isothermally cured samples. The total heat of reaction was calculated from the area under the scanning DSC curve. The following equations are used to convert the exothermal data measured by DSC during cure to reaction rate and conversion as a function of time [Kamal et al 1973, Sourour et al 1975, Yang et al 1988 and 1989, Huang et al 1995]:

\[
\frac{d\alpha}{dt} = \frac{1}{\Delta H_T} \frac{d\Delta H_t}{dt} \tag{4.1}
\]

And

\[
\alpha = \frac{1}{\Delta H_T} \int_0^t \frac{d\Delta H_t}{dt} \, dt = \frac{\Delta H_t}{\Delta H_T} \tag{4.2}
\]
Where \( \frac{\text{d} \alpha}{\text{d} t} \) and \( \alpha \) are the overall reaction rate and total conversion at a given time, \( \Delta H_t \) is the heat release before the time \( t \), and \( \Delta H_T \) is the total heat release, which may be the summation of isothermal and residual scanning heat releases or the heat release from direct scanning DSC run.

### 4.2.2.2 X-ray Diffraction (XRD)

Generally, X-ray diffraction (XRD) analysis is widely used for the characterization of crystallographic structure, dispersion and exfoliation of nanoparticle. To determine the interlayer spacing of the silicate layers in the nanoclay and nanocomposites, the XRD was 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 4.3.

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

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

### 4.2.2.3 Morphological Examination (SEM)

For the morphological study, the fracture surfaces of the samples were observed by SEM with 10 kV power and magnification of 10000 X on the cured samples. All samples were cured at 115°C for 1 hour followed by a post cure at 150°C for another 1 hour in the thermostated oven.
4.2.2.4 Izod Impact and Flexural Strength Tests

The flexural strength tests on the composite samples were carried out according with ASTM D790 by using Universal Tensile Testing Machine. The Izod impact test of the composites was carried out accordance to ASTM D256 by using Zwick Impact Tester. For both mechanical tests, all samples were prepared by using a aluminum mold with dimensions of (127mm x 12.7 mm x 3.2 mm) but for impact test we cut each samples to two equal part (63.5mm x 12.7 mm x 3.2 mm) which is related to ASTM D256. The cure of all samples was followed by a post cure at 150°C for one hour in the thermostated oven.

4.3 Results and Discussion

4.3.1 Effect of LPA and Nanoclay on Reaction Kinetics and Conversion

The effect of LPA and nanoclay on reaction kinetics and final conversion of total C==C bonds of unsaturated polyester (UP) resin was investigated using differential scanning calorimeter (DSC-60A, shimadzu). All experiments were carried out isothermally at 115°C with 3 % nanoclay 20A and 5% PMMA (LPA) with number average molecular weight of ($M_n = 55800$ g/mol) and 1% TBPB as initiator.

For the St/UP sample mixture, the isothermal DSC rate profiles at 115°C in Fig.4.1 shows that the addition of 5% PMMA leads to longer induction time and a relatively lower peak reaction rate comparing with the neat UP resin.
Figure 4.1: Effect of LPA (5%) and nanoclay 20A (3%) on reaction rate of UP resin with 1% TBPB at 115°C isothermally cured by DSC.

Figure 4.2 shows that the addition of LPA cause to reduce the final conversion of the total C=≡C bonds comparing with the final conversion of the neat UP resin. On the other hand in Fig.4.1, the St/UP/PMMA sample mixture with 3% Cloisite 20A shows a shorter induction time and too higher peak reaction rate comparing with both St/UP and St/UP/PMMA cured sample mixtures. As already mentioned in chapter 2, 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. Here also it is demonstrated by DSC result which by adding 3% Cloisite 20A it shows a shorter induction time and too higher peak reaction rate comparing with both St/UP and St/UP/PMMA cured sample mixtures. As this will be shown and demonstrated by SEM results in figure 4.4, the higher reaction rate caused by addition of 3% Cloisite 20A result in smaller size and larger number of LPA-rich dispersed phase on St/UP/PMMA/3% 20A resin system.
Figure 4.2: Effect of LPA (5%) and nanoclay 20A (3%) on conversion profiles of UP resin with 1% TBPB at 115°C isothermally cured by DSC.

Also Fig.4.2 exhibits that the addition of small amount of Cloisite 20A (3%) to St/UP/PMMA sample mixture cause to increase the final conversion of the total C==C bonds comparing with the final conversion of the St/UP/PMMA sample mixture without nanoclay.

4.3.2 Clay Partition

X-ray diffraction (XRD) was employed to verify the X-ray diffraction patterns for the modified nanoclay, Cloisite 20A and the nanocomposites of UP/LPA/20A mixture. X-ray diffraction (XRD) patterns were recorded by a diffractometer.
equipped with Cu Kα radiation at 40 KV ($\lambda = 1.5418$ Å). The experiments were performed in a scan range $(2\theta)$ from 2° to 15° at a scanning rate of 1°/min.

In figure 4.3, the XRD pattern for the clay 20A powder exhibits a strong X-ray diffraction peak, with a silicate gallery spacing of about 2.5 nm, while The XRD pattern for the nanocomposites of UP/LPA/20A exhibits a broadened peak with less intensity which is a characteristic of a exfoliated structures. As already mentioned in chapter 2, in an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix results in a featureless diffraction pattern.

![Figure 4.3: XRD patterns for clay 20A powder and nanocomposites of UP/LPA/20A](image)

Figure 4.3: XRD patterns for clay 20A powder and nanocomposites of UP/LPA/20A
4.3.3 Morphology of Nanocomposite Samples

During resin mixture curing, unsaturated polyesters (UP) resin molecules rearrange themselves to change from liquid phase to solid phase and density increases, which lead to create volume shrinkage about 7-10% during curing.

The low profile additives (LPAs) are 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.

As already mentioned in chapter 2, the phase separation and micro-voids formation is however the most favored concept for curing shrinkage control. It is generally believed that thermal expansion of the resin and LPA during heating cause to control the resin shrinkage. Also during curing, phase separation between the LPA-rich and UP resin-rich phase and creating the micro-voids at the inside the LPA-rich phase or interface of two phase cause to control the resin shrinkage during curing and cooling.

Morphology studies with a scanning electronic microscope (SEM) were carried out with 10 kV power and magnification of 10000 X on the cured samples. Figure 4.4 shows SEM micrographs of the fractured surface for the resin systems cured isothermally at 115°C and initiated by 1% TBPB. Figures 4.4 a, b and c are the SEM micrographs of the fractured surface for the UP/St/ 0% LPA/ 0% clay, UP/St/ 5% LPA/ 0% clay and UP/St/ 5% LPA/ 3% 20A, respectively.

As mentioned in chapter 2, In the UP/St/ PMMA system, unreacted UP resin (dipole moment of 2.0-2.5) becomes less polar (dipole moment of less than 1.0) during curing which cause that the polar thermoplastic PMMA (dipole moment of 1.3) tends to phase out during curing because the more polar. Therefore the low profile additives (PMMA) are become incompatible with the resin molecules during cure and create two phases in system, the LPA-rich phase and UP resin-rich phase, which in turn create the micro-voids at the inside the LPA-rich phase or interface of two phases, as it was demonstrated by Figures 4.4 which by addition of 5% PMMA, the sample
appearance changed from one phase to two phases, LPA-rich disperse phase and UP-rich continuous phases.
Figure 4.4: SEM micrographs of the fractured surface for the UP/St/LPA/clay systems cured isothermally at 115°C and initiated by 1% TBPB.
(a) UP/St/ 0%LPA/ 0% clay
(b) UP/St/ 5%LPA/ 0%clay
(c) UP/St/ 5%LPA/ 3% 20A

As already discussed, the phase separation shown in figure 4.4 (b) can lead to create the micro-voids at the inside the LPA-rich phase and interface of two phases which cause to better control of resin shrinkage during curing and cooling which is already reported by volume shrinkage data in chapter 3 and here it is demonstrated by SEM morphology of the sample (figure 4.4 (b)). As already discussed, 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. Here also less polarity of cured UP resin (dipole moment of less than 1.0) results to collect polar nanoclay 20A in PMMA (dipole moment of 1.3) phase as LPA phase which in turn create larger domain of LPA phase.
It is generally known that a higher reaction rate and shorter induction time of cure limits collection of unreacted styrene monomers and UP resin in the LPA-rich phase which leads to smaller size and larger number of LPA-rich dispersed phase. This is conformed with our experimental results that higher cure reaction rate and shorter induction time caused by addition of 3% Cloisite 20A to St/UP/PMMA resin system (shown in figure 4.1) result in smaller size and larger number of LPA-rich dispersed phase (shown in figure 4.4 c).

The larger number and domain of LPA-rich dispersed phase in St/UP/PMMA/20A resin system makes more microvoids compared to the system without 20A and lead to a better shrinkage control. As it was reported by volume shrinkage data in chapter 3, using 5%LPA and 3%nanoclay 20A in resin system could reduce volume shrinkage data from 8.4% to 0.15%.

### 4.3.4 Mechanical Properties

#### 4.3.4.1 Effect of LPA and Nanoclay on Impact Strength

Figure 4.5 shows the influence of PMMA and nanoclay 20A on the impact strength of cured samples. The addition of 5wt% PMMA exhibits a decrease in impact strength and decreases more by adding 3wt%20A in the resin mixture. It is known that the weak interfacial adhesion between the crosslinked UP resin-rich phase and the LPA-rich dispersed phase can affect on impact strength results.

As already mentioned, the UP resin system containing nanoclay 20A exhibits a larger number and domain of LPA-rich dispersed phase during the cure, which in turn leads to the worse interfacial adhesion for the resin mixture. On the other hand the easy debonding of the crosslinked UP resin-rich phase from the nanoclay 20A surface gives an explanation of the more weakness of these structures which leads to more decrease of impact strength.
4.3.4.2 Effect of LPA and Nanoclay on Flexural Strength

The effect of PMM and nanoclay 20A on the flexural strength of cured samples in Figures 4.6 shows that the addition of 5wt% PMMA and 3wt%20A both result to decrease flexural strength in the resin mixture.

As already discussed, with addition of 5% PMMA, the sample appearance changes from one phase to two phases, LPA-rich disperse phase and UP-rich continuous phases (shown in figure 4.4 (b)).

It is known that the phase separation lead to create the micro-voids and micro cracks at the inside the LPA-rich phase or interface of two phases in cured UP resin samples which in turn help to create more cracks in samples within flexural test and decrease flexural strength.

On the other hand, with addition of 3wt% 20A, the low profile UP resin system exhibits a larger number and domain of LPA-rich dispersed phase during the cure...
which in turn increases volume fraction of microvoid in the cured samples, and decreases flexural strength further.

![Figure 4.6: The effect of 5% PMM and 3% nanoclay 20A on the flexural strength of cured samples](image)

4.4 Effect of Different Curing Agent on Morphology and Reaction Kinetic

4.4.1 Effect of Different Curing Agent on Reaction Kinetic and Conversion

The effect of two different curing agent a) 1% TBPB and b) 1.5 wt% methyl ethyl ketone peroxide (MEKP) and 0.5 wt% cobalt octoate on reaction kinetics and final conversion of total C==C bonds of unsaturated polyester (UP) resin in UP/St/ LPA
/nanoclay resin mixture was investigated using differential scanning calorimeter (DSC-60A, Shimadzu).

All experiments were carried out isothermally at 115°C with 3% nanoclay 20A and 5% PMMA as LPA with number average molecular weight ($M_n = 55800 \text{ g/mol}$). The samples were then reheated from room temperature to 300°C with heating rate of 10°C/min to determine the residual reactivity left in the isothermally cured samples. Fig.4.7 shows that the addition of 1.5 wt% MEKP, 0.5 wt% cobalt octoate exhibits higher peak reaction rate and shorter induction time for all resin mixtures, UP/St, UP/St/LPA and UP/St/LPA/20A, comparing to samples with TBPB as initiator (Fig.4.1). Also, it is shown that the addition of Cloisite 20A exhibit same effect on the reaction rate and induction time in resin mixtures with using any of curing agents, either MEKP and cobalt octoate or TBPB.

![Graph showing reaction rate vs. time for different resin mixtures](image)

**Figure 4.7:** Effect of LPA (5%) and nanoclay 20A (3%) on reaction rate of UP resin with 1.5 wt% MEKP and 0.5 wt% cobalt octoate, at 115°C isothermally cured by DSC.
As already discussed in chapter 2, the alkylammonium or alkylphosphonium cations can provide functional groups. We conclude that the alkylammonium or alkylphosphonium cations act as accelerator to decompose the initiator and start the polymerization of polymers and monomers which cause to shows a shorter induction time and higher peak reaction rate. Here also it is demonstrated by DSC result which by adding 3% Cloisite 20A it shows a shorter induction time and too higher peak reaction rate comparing with both St/UP and St/UP/PMMA cured sample mixtures by using any of curing agents, either MEKP and cobalt octoate or TBPB.

**Figure 4.8:** Effect of LPA (5%) and nanoclay 20A (3%) on conversion profiles of UP resin with 1.5 wt% MEKP and 0.5 wt% cobalt octoate, at 115°C isothermally cured by DSC.
In Fig.4.8, UP resins system using MEKP exhibits that all samples, UP/St, UP/St/LPA and UP/St/LPA/20A result in the same final conversion \( a = 1 \) of the total 
\( C=C \) bonds, while with using TBPB as initiator (Fig. 4.2), resin mixtures, UP/St , UP/St/LPA and UP/St/LPA/20A, showed final conversion \( a = 79\% \), \( a = 74\% \) and \( a = 77\% \) respectively. We found that in the resin systems using both curing agents, MEKP and TBPB, addition of LPA to UP resin decreases reaction rate and final conversion while addition of 20A to UP/LPA mixture can accelerate polymerization and increases reaction rate and final conversion.

### 4.4.2 Effect of Different Curing Agent on Morphology

Morphology studies with a scanning electronic microscope (SEM) (Philips SEM-515), were carried out with 20 KV power and magnification of 600 X on the cured samples UP/St, UP/St/LPA and UP/St/LPA/20A resin systems with using 1.5 wt% methyl ethyl ketone peroxide (MEKP) and 0.5 wt% cobalt octoate as curing agent. All samples were cured at 115°C for 1 hour followed by a post cure at 150°C for another 1 hour in the thermostated oven.

Figures 4.9 shows SEM micrographs of UP resin mixture samples cured isothermally at 115°C by using 1.5 wt% MEKP and 0.5 wt% cobalt octoate. Figures 4.9 a, b and c are the SEM micrographs for cured samples of the UP/St/ 0%LPA/ 0% clay , UP/St/ 5%LPA/ 0%clay and UP/St/ 5%LPA/ 3% 20A respectively.

Figures 4.9 exhibits that with addition of 5% PMMA, the sample appearance changes from one phase (a) to two phases (b), LPA-rich and UP-rich co-continuous phases. Also The addition of 3% 20 A shows similar structure of the samples without nanoclay, except that the domain of the LPA-rich phase further increases as shown in Figure 4.9(c). As already mentioned, 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. On the other hand , unreacted UP resin (dipole moment of 2.0 - 2.5) becomes less polar (dipole moment of less than 1.0) during
curing which cause to collect polar nanoclay 20A in PMMA (dipole moment of 1.3) phase as LPA phase which in turn create larger domain of LPA phase.
Figure 4.9: SEM micrographs of isothermally cured samples of UP/St/LPA/clay systems at 115°C and initiated with using 1.5 wt% (MEKP) and 0.5 wt% cobalt octoate.
(a) UP/St/ 0%LPA/ 0% clay;
(b) UP/St/ 5%LPA/ 0%clay
(c) UP/St/ 5%LPA/ 3% 20A

Finally we found that addition of 3% nanoclay 20A in the resin systems using any of MEKP and TBPB as curing agents increase cure reaction rate, reduce induction time and increases domain of the LPA-rich phase, which is shown in SEM results of Fig.4.9 and Fig.4.4 for resin mixtures using MEKP and TBPB as curing agents respectively.

4.5 Conclusions

In this chapter, it was investigated that how the addition of low profile additives (LPAs) and small amount of nanoclay can affect in samples morphology, reaction kinetics, mechanical properties and shrinkage control of the unsaturated polyester UP resins.
The addition of 5% PMMA to unsaturated polyester UP resins lead to a later onset of the cure reaction and a long induction time. Also, it has shown a relatively lower peak reaction rate. While the St/UP/PMMA sample mixture with 3% Cloisite 20A shows a more earlier onset of the cure reaction and a short induction time and higher peak reaction rate comparing with both, St/UP and St/UP/PMMA sample mixtures by using any of curing agents, either MEKP and cobalt octoate or TBPB, the alkylammonium or alkylphosphonium cations can provide functional groups. We conclude that the alkylammonium or alkylphosphonium cations act as accelerator to decompose the initiator and start the polymerization of polymers and monomers which cause to shows a shorter induction time and higher peak reaction rate. The difference in dipole moment can act as a driving force to exhibit phase separation. During curing the unreacted UP resin (dipole moment of 2.0 - 2.5) becomes less polar (dipole moment of less than 1.0) which cause that the polar thermoplastic PMMA (dipole moment of 1.3) tends to phase out during curing because the more polar. Therefore the low profile additives (PMMA) are become incompatible with the resin molecules during cure and create two phases in system, the LPA-rich phase and UP resin-rich phase, which in turn create the micro-voids at the inside the LPA-rich phase or interface of two phases, as it was demonstrated by Figures 4.4 which by addition of 5% PMMA, the sample appearance changed from one phase to two phases, LPA-rich disperse phase and UP-rich continuous phases. On the other hand, as already reported (Figure 4.1), we found that by addition of 3% 20A to St/UP/PMMA resin systems lead to a higher reaction rate and short induction time of cure which cause to create smaller size and larger number of LPA-rich dispersed phase in cured samples, shown in Figure 4.4 (c). Finally, the larger number and domain of LPA-rich dispersed phase can make more microvoids compared to the system without 20A and lead to better shrinkage control. This can be a good explanation for effect of 20A to reduce volume shrinkage data from 8.4% to 0.15% which was reported by volume shrinkage data in chapter 3.

The addition of LPA and nanoclay could reduce the volume shrinkage by generating microvoids in the UP/St system. The formation of microvoids can definitely reduce
interfacial adhesion for the resin mixture and also exhibit easy debonding of the crosslinked UP resin-rich phase from the surface of nanoclay 20A which cause to reduce impact strength. On the other hand the formation of microvoids helps to create cracks in cured sample within flexural test and decrease flexural strength. Therefore by creating larger number and domain of LPA-rich dispersed phase with addition of 3wt% 20A , the UP resin system exhibits further volume fraction of microvoid in the cured samples and decrease flexural strength of cured samples further.