Polymer composites are an important class of engineering materials and unsaturated polyester resin is a premium resin in composite industry. Their properties such as low viscosity, fast cure, excellent chemical resistance, their simple processing and mainly their application in glass fiber reinforced plastics and ability to cure at room temperature and atmospheric conditions with low cost have resulted in rapid increase in their usage up to 85% in the plastics market comparing to other thermosetting resin. However their major disadvantage is high volumetric shrinkage which cause surface defects and in turn cause to limit of growth of many high-volume applications.

In this work, the effect of poly methyl methacrylate (PMMA) and nanoclay on shrinkage control, reaction kinetics, morphology and mechanical properties of cured unsaturated polyester (UP) resin was studied using density measurement method and different experimental techniques such as differential scanning calorimetry (DSC), scanning electron microscopy (SEM), X-ray diffraction (XRD), universal testing machine and impact tester.

The effects of poly (methyl methacrylate) (PMMA) and nanoclay on volume shrinkage of cured UP resins were investigated by using density measurements. It was found that the addition of low Molecular weight of poly (methyl methacrylate) (PMMA) as LPA results in further homogeneous morphology. This makes nanoclay more effective on phase separation in resin compound which lead to
better shrinkage control. The difference in dipole moment would act as a driving force to exhibit phase separation.

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.

During the phase separation the surface of microgel particles can be covered by a layer of PMMA as a segregating agent which cause to reduce merging of microgel particles and increase volume fraction of microvoids and microcracks in cured samples. The effect of segregating is increased with larger content of PMMA which in turn elevate microvoids and microcracks and exhibits better shrinkage control.

Comparing Cloisite 20A with gallery spacing about 2.4(nm) and Cloisite 30B with gallery spacing about 1.9 (nm), it was supposed that because of the bigger gallery spacing of Cloisite 20A 2.4(nm) comparing to Cloisite 30B 1.9 (nm), nanoclay 20A can intercalate more polymer and results in larger domain of separated phase in cured samples, which can affect on volume shrinkage control more than Cloisite 30B which was demonstrated by shrinkage data.

The organic treatment modifies the clay surface from hydrophilic to hydrophobic which can make it compatible to the resin system to assist inter-gallery absorption.

The MMT clay surface is polar and hydrophilic in nature. The organic treatment modifies the clay surface from hydrophilic to hydrophobic which can make it compatible to the resin system to assist inter-gallery absorption.

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. Also it is believed that filler can be attributed to an assisting effect on the nucleation of
phase separation which provide sites for formation of the separated phase using nanoclay 20A because it can act as a nucleation agent which in turn cause to earlier phase separation during curing.

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 a shorter induction time and higher peak reaction rate.

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.

Increasing curing temperature results in earlier stop of phase separation and smaller one which result in more micro-voids inside or interface of two phases and also exhibit a thermal expansion of LPA cause to further improvement of final volume shrinkage comparing curing at low temperature.

We found that using small amount of nanoclay in ST/UP/PMMA resin systems caused to a higher reaction rate and exhibit further effect like high temperature’s effect to further earlier stop phase separation. Above effects of nanoclay followed by its nucleation agent property leads to create smaller and larger number of separated phase with larger domain of LPA phase caused by collection of nanoclay in LPA phase.

Finally, the larger number and domain of LPA-rich dispersed phase can make more microvoids compared to the system without 20A and lead to much 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 is reported by volume shrinkage data in chapter 3.

It was found that addition of 3wt% 20A reduce impact strength which we conclude microvoids and less interfacial adhesion in ST/UP/PMMA/20A resin mixture cause to easily debonding of the crosslinked UP resin rich phase from the surface of nanoclay.
20A which in turn reduce impact strength. On the other hand addition of 3wt% 20A decrease flexural strength in ST/UP/PMMA/20A resin mixtures. We conclude addition of 3wt% 20A in resin system increase further volume fraction of microvoid which decrease flexural strength of cured samples comparing to system without nanoclay 20A.

Using the data values of UP shrinkage for different content value of PMMA additive and nanoclay Cloisite 20A in the resin, we obtained correlation equations which can be used to predict the shrinkage value for cure at room temperature or in high temperature with an acceptable absolute error, which is:

\[
z = a + bx + cy + dx^2 + ey^2 + fxy
\]

Where

\[
\begin{align*}
z & \text{ is the percentage of volume shrinkage,} \\
x & \text{ is the percentage of PMMA additive in resin,} \\
y & \text{ is the percentage of nanoclay Cloisite 20A in resin.}
\end{align*}
\]

The coefficient values are as the following:

The values for the coefficients for cure at 115 °C with the absolute error of 1.08311547013 are:

- \( a = 8.0857516153891833E+00 \)
- \( b = -1.7033510680340028E-01 \)
- \( c = -1.0327767140250663E+00 \)
- \( d = -2.1541926018140287E-02 \)
- \( e = -1.4299394681894043E-01 \)
- \( f = -1.5369825320608579E-01 \)

And the values for the coefficients for cure at room temperature with the absolute error of 0.562915387693 are:
• $a = 7.7681629023652858 \times 10^0$
• $b = 2.6638434406315043 \times 10^{-2}$
• $c = 1.6677954630782635 \times 10^{-1}$
• $d = -1.8822025609106056 \times 10^{-2}$
• $e = -1.3171577054556560 \times 10^{-1}$
• $f = -9.1700604659442145 \times 10^{-2}$

Experimental results showed that using nanoclay 20A exhibit better volume shrinkage control with negative effect in mechanical properties because of increasing volume fraction of microvoid. More investigation to reduce negative effects of using nanoclay 20A on mechanical properties of ST/UP/PMMA/20A resin systems and effect of nanoclay on reaction rate can be great interest to further works.