Effect of Nanoclay on the Curing and Thermal Conductivity of Unsaturated Polyester Resin

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Abstract -- This study was aimed at understanding the effect of nanoclay on the heat transfer mechanism in a nanoclay-filled amorphous polymer-matrix composite. Nanocomposites of 1 to 15% by volume filler content were fabricated using the solution intercalation method. Dispersion of the nanoclay was done via ultrasonication. Differential Scanning Calorimetry (DSC) scans were done on the pristine polymer and those combined with nanoclay using both isothermal and dynamic modes of heating to determine the curing kinetics. Thermal conductivity measurements were performed at 50°C, 75°C, and 100°C, with the data fitted into existing mathematical models to define the conduction mechanism that could have transpired in the material. Thermal conductivity of the nanocomposites increased from 1.24±0.07 W/mK to 7.40±0.07 W/mK at 50°C with increasing nanoclay content with an apparent percolation threshold at 13% filler content. Fitting the experimental data with existing models for thermal conduction in composites revealed that the best fit is that with the Hasselman and Johnson model. Using this model, the effective thermal conductivity of the nanoclay was calculated to be around 15.78 W/m which is within the theoretical range of values of the bulk thermal conductivities of the nanoclay component compounds. Fitting the measured thermal conductivities to the scaling law revealed that the percolation threshold is around 12.49% filler content. Results from the DSC scans revealed that the extent of cross-linking generally decreases with increasing nanoclay content. Given the above considerations, it can therefore be said that the mechanism of conduction in the composite material involved the improved conduction in the matrix that is in series with the conduction along the nanoclay fillers, which have higher conductivities at their nanometer dimensions.

Keywords: Unsaturated Polyester, MMT, Cure Kinetics, Thermal Conductivity, Percolation

I. INTRODUCTION

Nanocomposites with matrix based on organic polymers and Montmorillonite (MMT) filler have attracted great attention due to interesting properties such as reduced gas permeability [12], improved solvent resistance, superior mechanical [13] and enhanced flame-retardant properties [11] that have potential applications in automobile,
construction, electronics and electrical, food packaging, and aviation industries [1]. MMT is naturally occurring nanoclay with considerable deposits throughout the Philippines. MMT is conventionally called nanoclay because it is made up of layers of magnesium and aluminum silicate platelets, which are 1 nm thick and several tens to several hundreds of nanometers across [6].

An area where MMT-based nanocomposites have not been fully explored is in heat transfer applications. In the semiconductor industry, Thermal Interface Materials (TIM) are polymer composites used to enhance the heat transfer between a silicon die and the heat sink in a microelectronic device. Most commercial TIMs use silicone rubber as matrix and an array of particles as fillers, i.e. silver particles and alumina particles. These particles as well as silicone rubber are relatively expensive and difficult to process. Thus, the idea of fabricating a TIM from less expensive and more readily available materials is an attractive proposition.

Unsaturated Polyester (UP) is one of the most widely used polymer matrix, especially for structural composites, due to its relatively low cost, ease of processing, and commercial availability. When fully cured, UP has an amorphous structure. It has not been used for heat transfer applications because of its low thermal conductivity brought about by its amorphous structure which promotes phonon scattering.

II. OBJECTIVES

The aim of this study is to understand the heat transfer mechanism in a nanocomposite composed of an amorphous polymer (UP) matrix and MMT filler for the purpose of considering UP-MMT nanocomposite as a TIM. Specifically, the objective of this study is to determine the effect of MMT on the structure and thermal conductivity of UP.

III. METHODOLOGY

Nanocomposites of UP and MMT (1%-15% by weight) were prepared using Solution Intercalation. The MMT used was the commercially available, organically modified type (Cloisite 20A, average platelet thickness of 1nm). Cross-linking was induced by the addition of Methyl Ethyl Ketone Peroxide (MEKP) catalyst. To fully describe the cure kinetics of UP and UP-MMT nanocomposite, isothermal (40 minutes at 90°C) as well as dynamic (10°C/min, 15°C/min, and 20°C/min) DSC scans were performed immediately after the addition of MEKP. Thermal conductivity measurements were done on 5mm thick circular samples cured for 7 days at room temperature. Data from cure kinetics were fitted into accepted kinetic models using the Levenberg-Marquardt (LM) method. Measured thermal conductivity values were also fitted into existing mathematical models for thermal conduction in composites also using the LM method.

IV. RESULTS AND DISCUSSION

Isothermal DSC scans were done to initially assess the effect of MMT on the extent of curing of UP.

Fig. 1 shows a decrease in the heat flow with the addition of nanoclay relative to the pure unsaturated polyester matrix. Cross-linking is generally exothermic, thus less exothermic heat flow could be interpreted as decrease in the extent of curing. For the pristine UP, the heat flow is exothermic until around 1300 seconds. This could mean that curing was completed at around that time at
90°C. For the case of the nanocomposites, exothermic heat flow stopped at around 600 seconds for 3% and 5% filler loading, and around 1100 seconds for the 13% filler loading. The absence of exothermic heat flow means that curing has ceased for the nanocomposite sample. The relatively higher heat flow for the 13% filler content could mean increase in the extent of cross-linking relative to the lower filler content composites, but this has to be verified by dynamic DSC scans. Another possible reason for the increased heat flow for the 13% filler content sample could be the relatively large amount of nanoclay in relation to the amount of polymer. The total exothermic heat flow was calculated from the area under the curve using the Origin Pro™ software. The values are 26.37 J/g for UP, 9.44 J/g for 3% filler content, 2.85 J/g for 5% filler content, and 24.09 J/g for 13% filler content.

Fig. 2 show that in general, there are three peaks for each dynamic scan for the neat resin and the nanocomposites, specifically those containing 3% and 5% nanoclay. For these three samples, the first peak is attributed to the decomposition of MEKP during initiation reaction [5]. The two subsequent peaks correspond to the two reactions happening after initiation which are cross-linking (1st peak) and homopolymerization of polyester molecules and styrene molecules (2nd peak) [7]. Unlike the two other nanocomposite samples, the 13% filler content exhibited an endothermic peak. With this, a similar scan for nanoclay was performed to determine the possible cause of the peculiar behavior of the 13% filler content. Fig. 2 shows that the scan for both 13% filler content and the nanoclay were almost identical. Thus, the endothermic peak for the 13% filler content is attributed to the presence of a relatively large amount of nanoclay. The endothermic peak is attributed to the evaporation of water trapped within the nanoclay structure [4].

Figure 1. Isothermal DSC scans taken at 90°C for the matrix material, and upon addition of 3, 5, and 13% by volume nanoclay.

Figure 2. Dynamic DSC scans at 10°C/min at varying nanoclay contents (Heat flow values were normalized to better reveal varying peak temperatures)

The dynamic scans also allow for the determination of the activation energies for the two reactions mentioned. A higher heating rate would result to a shift of the peak position of the reactions to a higher temperature. These different temperatures and corresponding heating rates were analyzed using the Kissinger equation.
This equation allows the calculation of the activation energy \((E_a)\) of a reaction (i.e. curing) from the plotted values of heating rate \((\beta)\) and the corresponding maximum temperature \((T_p)\) of the exothermic DSC peak of that reaction. \(A\) is a pre-exponential constant and \(R\) is the gas constant. Fig. 3 shows a comparison of the average calculated values of the \(E_a\) for the neat resin and the nanocomposites with different filler loadings. The calculated \(E_a\) and \(A\) for the neat resin were used to calculate for the reaction rate constants \((k)\) for the cross-linking and homopolymerization reactions using the equation shown below.

\[
-k = A \exp \left( -\frac{E_a}{RT} \right) \tag{2}
\]

The DSC scans allowed for the calculation of the extent of cure of UP and the UP-MMT nanocomposite samples. Fig. 4 shows that the extent of cure for unsaturated polyester increases with time and reached full curing at around 1280 seconds (≈21 minutes) at 90°C isotherm. The same method was used to calculate for the extent of cure of 3%, and 5% by volume MMT nanocomposites. For the same length of time as that of the pure polymer (1278 seconds), the extent of cure was calculated to be 25% and 10.3% for the 3% and 5% filler content samples, respectively. These values mean that while the pure polymer is fully cured after about 20 minutes at 90°C, the extent of curing for the nanocomposites is only around 26% or less under the same conditions and the same length of time. This can be used to explain why physical inspection of the nanocomposites revealed that they are less rigid (softer) than the pure polymer samples.

Having calculated the reaction rate constants, \(k_1\) and \(k_2\), the values of the order of reactions, \(m\) and \(n\) can then be calculated. The values of \(k_1\) and \(k_2\) at 27°C (300 K) were calculated at 0.0792 \((s^{-1})\) and 0.0053 \((s^{-1})\), respectively. These were substituted in the Kamal Model to come up with:

\[
\frac{d\alpha}{dt} = [0.0792 + 0.0053 \alpha^m] [1-\alpha]^n \tag{3}
\]

The calculated values of \(d\alpha/dt\) and \(\alpha\) for the pure polymer were fitted into the equation above to determine values of \(m\) and \(n\). Data fitting was done using the Levenberg-Marquardt (LM) method of non-linear curve fit. The initial estimates for the values of \(m\) and \(n\) were determined from initial fitting using MS Excel. After employing the method described above, the values were determined to be \(m=2.14\) and \(n=1.47\). With these, the equation now becomes:

\[
\frac{d\alpha}{dt} = [0.0792 + 0.0053 \alpha^{2.14}] [1-\alpha]^{1.47} \tag{4}
\]

This equation represents the rate of cure of unsaturated polyester as a function of temperature and further suggests that the cross-linking reaction is more of a 2\(^{nd}\) order reaction while the homopolymerization reaction is more of a first order reaction.

The results of DSC experiment suggested that there is a decrease in the extent of cross-linking with the addition of nanoclay. There could be several reasons for this and two of them could be intercalation [4] and/or inhibition of cross-linking by the organic component of the nanoclay [5].

It has been established that the extent of cross-linking of unsaturated polyester is decreased in the presence of nanoclay. This could lead to an increase in thermal conductivity of the UP-MMT nanocomposites in relation to that of the neat resin. In a study by Hansen, et al. [14], they concluded that for similar types of polymers that has linear and branched (or cross-linked form); the linear configuration will have the higher thermal conductivity. This projected increase in the
thermal conductivity as a result of lesser extent of cross-linking in the presence of nanoclay was validated by the thermal conductivity measurements on the nanocomposites shown in Fig. 5.

Figure 3. Relative change in calculated activation energy with varying nanoclay content

Figure 4. Plot of calculated extent of cure versus time for UP, 3% nanoclay content, and 5% nanoclay content

Figure 5. Thermal Conductivity of the nanocomposites as a function of MMT content at different temperatures.

Measurement of the thermal conductivity of UP-MMT nanocomposites paved the way for the estimation of the non-bulk thermal conductivity of nanoclay. The bulk conductivity of nanoclay was measured to be at 3.6 W/mK using a pelletized form of the nanoclay subjected to the thermal conductivity apparatus. This value, however, combined with that of the unsaturated polyester at 1 W/mK could not explain the measured thermal conductivity of the nanocomposites that were as high as 9 W/mK because typically, properties of composites can only be between those of the matrix and the filler. This suggests that the effective thermal conductivity of the nanoclay should be much higher than the measured bulk conductivity. The effective thermal conductivity of the nanoclay filler was calculated from the experimental data using existing mathematical models. The LM Method was employed to fit to the different models and determine the values of unknown variables.

Fitting the experimental data with the Maxwell’s and Rayleigh’s models show poor fit as shown in Fig. 6. The experimental data was also fitted into the Hasselman and Johnson model for plate-like fillers. The fitting gave a value for the nanoclay thermal conductivity of 15.78 W/mK with $R^2$ value of
0.92. Additionally, the factor $ah_c$ representing heat transfer at the interface of matrix and the filler was calculated to be 0.41 W/mK.

A sharp increase in the thermal conductivity at 13% filler loading can be observed after a steady, almost linear increase of the same property from 1% to 11% filler content (see Fig.5). This suggests that at 13% filler content, thermal transfer in the composite is apparently optimized and is speculated to be induced by the optimization of filler distribution and configuration leading to the formation of a continuous conducting path, which happen to be technically defined as the percolation threshold. From earlier discussions, intercalation led to less cross-linking in UP and therefore the structure became more linear. This more linear structure increased the thermal conductivity of the UP matrix since linear polymers have higher thermal conductivity than their cross-linked counterparts. If and when the intercalated structure of the nanoclay with the linear UP molecule in its intergalleries and the agglomerates form a link with each other at a certain temperature, then a continuous conducting path is created, leading to percolation as shown in Fig. 8.
conductivity data in the scaling equation as described by Mandal, et al [10]. Data fitting was done using the non-linear fitting method previously used in this study. The values were determined to be: C=0.33, f_p=0.1249 and t=0.07. The equation describing percolation in thermal conduction for the UP-MMT nanocomposites thus becomes:

\[ k = 0.33(f-0.1249)^{0.07} \] (5)

In summary, thermal conductivity of the nanocomposites can be described by the Hasselman and Johnson model at low filler loadings, i.e. <9% by volume, while it can be described by the percolation theory at higher filler loadings, i.e. between 9% and 15% by volume.

V. CONCLUSIONS

This study found that nanoclay increases the thermal conductivity of unsaturated polyester due to the following reasons: (1) Nanoclay has a much higher thermal conductivity than unsaturated polyester, thus mixing the two would result to a higher thermal conductivity for the mixture; (2) Intercalation of polymer chains into the nanoclay galleries led to lower cross-linking density, making the polymer more linear in structure resulting to a higher thermal conductivity. Given the above considerations, it can therefore be said that the mechanism of conduction in the composite material involved the improved conduction in the matrix that is in series with the conduction along the nanoclay fillers, which have higher conductivities at their nanometer dimensions.

REFERENCES


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