# A Study of the Effect of Al<sub>2</sub>O<sub>3</sub> Nanoparticles on the Cure behavior of Bisphenol A Epoxy Resin

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# ABSTRACT

A resin mix with 30% dispersed alumina nanoparticle (nano-Al<sub>2</sub>O<sub>3</sub>) was added to hot curing epoxy system (based 2,2-bis(4-hydroxyphenyl) propane-epichlorohydrin on resin/ an anhydride hardener/ an imidazole accelerator) such that the nano-Al<sub>2</sub>O<sub>3</sub> concentrations are 0, 2, 5, 10 % by weight. The influence of nano-Al<sub>2</sub>O<sub>3</sub> concentration on the zero shear viscosity  $(\eta_0)$  and curing of the epoxy systems was investigated using temperature-modulated differential scanning calorimetry (TMDSC) and parallel plates rheometer. Two modes of isothermal cure, at 70, 80 and 90°C, were conducted by rheometer for all samples, unidirectional shear and oscillatory shear. The  $\eta_0$  of the filled resins showed the same trend as unfilled systems. The gel time (T<sub>gel</sub>) decreases by increasing the cure temperature. The nano-Al<sub>2</sub>O<sub>3</sub> particles give rise to fast curing systems. Resin/nano-Al<sub>2</sub>O<sub>3</sub> mixes showed a decrease in the glass transition temperature  $(T_g)$  and enthalpy; while the degree of cure for all prepared mixes are nearly the same.

*Keywords*: epoxy resin, nano-alumina, gel time, glass transition temperature, zero shear viscosity.

# **1 INTRODUCTION**

Epoxy resins based composites are used as laminates for printed circuits boards, aerospace, ballistic and engineering hardware components, automotive parts, electrical components and rehabilitation products. However, some of its interior characteristics such as thermal stability, weather resistance and impact strength restrict their use in high performance applications. [1,2] Inorganic nanoparticles are excellent toughening and reinforcing materials to develop new nanoparticles. It has been reported that dispersion of rigid inorganic filler into epoxy resin is important for the improvement in strength, modulus and fracture toughness. [3,4] Alumina nanoparticles, which are cheap and can be easily functionalized have been used as fillers with a broad choice of polymer matrices such as epoxy [5], polymethyl methacrylate [6,7] polystyrene and poly(vinyl ester).[8] The nano-Al<sub>2</sub>O<sub>3</sub> increased the viscosity of the epoxy/alumina suspension, besides the concurrent catalytic effect on the cure of the resin. Moreover, the storage modulus increases

and the glass transition temperature decreases with increasing the nano-Al<sub>2</sub>O<sub>3</sub> content. Scanctuary et al. [9] studied the influence of untreated nano-Al<sub>2</sub>O<sub>3</sub> on the curing of an epoxy thermoset based on diglycidyl ether of bisphenol A. The nano-Al<sub>2</sub>O<sub>3</sub> fillers are shown to accelerate the growth of macromolecules upon isothermal curing. As a result of the faster network growth chemical vitrification occurs at earlier times in the filled resin and the specific reaction heat decreases with increasing nanoparticle concentration. Rheological measurements of the zero-shear viscosity confirm the faster growth of the macromolecules in the presence of the nanoparticles.

Rheology experiments are important for predicting the behavior of polymer melts in manufacturing processes and part design. The purpose of the rheology experiments is to study the rheological properties, thus gain more understanding of material behavior at different practical process conditions and ultimately to develop a better product.[10] Ratna et al. [11] investigated the gelation and vitrification of various epoxy systems by a rheological method. From his point of view, the different chemical structures of resins, namely the functionality of resin and corresponding branching of the thermosetting network would determine how a system gels and vitrifies. Haddadi et al. [12] studied the effect of reaction temperature on gelation time ranging from temperatures below and above the gelation temperature. They showed that a noticeable increase in the activation energy of the gelation process occurred at the gelation temperature.

## 2 METHODOLOGY

#### 2.1 Preparation of the Nano-alumina/Epoxy System

Hot curing epoxy system based on: an epoxy resin (Araldite LY 556) / an anhydride hardener (Aradur 917)/ an imidazole accelerator (DY 070) was supplied by Huntsman International LLC. A resin containing 30% dispersed alumina nanoparticles (type 090615-LY-30AluC-DW7D-150N) was supplied by Virtuelles Institute.

The hot curing epoxy system were mixed in a fixed ratio (Araldite LY 556) : (Aradur 917): (DY 070) 100: 90: 1 respectively. The procedure of preparing was done as the manufacturer's suggestion.

The composition details of the nanocomposites prepared are given in the Table (1).

Nano-Al <sub>2</sub> O <sub>3</sub>	LY 556 <sup>*</sup>	LY-30AluC*	Aradur 917 <sup>*</sup>	DY 070 <sup>*</sup>
0%	50.00	0.00	45.00	0.50
1%	49.50	3.33	46.65	0.52
5%	38.08	16.66	44.77	0.50
10%	23.81	33.31	42.41	0.47

part by weight

Table 1: The composition of the control sample (0% Alumina) and nanocomposites prepared.

# 2.2 Calorimeteric Meaurements

Temperature modulated differential scanning calorimetery (TMDSC) not only allows for a systematic study of the kinetics of cure but simultaneously gives access to the evolution of the specific heat capacities of the thermosets. The technique thus provides insight into the glass transition behavior of the nanocomposites and hence makes it possible to shed some light on the interaction between the nanoparticles and the polymer matrix. The TMDSC experiments were done on a TA Instrument O2000 calorimeter nitrogen atmosphere. The samples were cooled isothermally at -70°C for 15 minutes then heated to 190°C at heating rate 2 K/min to follow the heat evolution due to the chemical reaction occurring in this temperature range. The cured sample was then cooled to  $-70^{\circ}$ C to minimize the enthalpy relaxation in the second heating scan. Finally, the sample was reheated to 190°C in order to determine the glass transition temperature (Tg). The experiments were alsocarried outat heating rate 5 K/min for all nanocomposites.Degree of cure was calculated from the DSC curve. [13]

# 2.3 Rheometer

The rheological properties for the samples were measured using a TA instrument AR2000ex with parallel plates of 25-mm diameter and 0.5 mm gap. Two types of rheological experiments were conducted for all samples:

*i) Temperature sweep:* these experiments were carried out to inspect the variation of rheological properties via changing the temperature. A unidirectional shear was applied to all samples along with temperature change from  $25^{\circ}$ C to  $150^{\circ}$ C at a heating rate  $2^{\circ}$ C /min and shear rate 10 s<sup>-1</sup>. *ii) Multiwave frequency* (MWF) *sweep: a* multiwave oscillatory strain is applied at 1 to 10 Hz (3 points per decades) at isotherms 70, 80 and 90 °C on all samples. The gel point is determined by taking several MWF sweeps to measure tan $\delta$  in the time scale of gelation.

# **3 RESULTS & DISCUSION**

## 3.1 **Results from DSC experiments**

Differential scanning calorimetry (DSC) analysis measures the heat flow during the curing of the resin system. In the case of a modulated (MDSC) analysis, the heat flow can be separated into reversible and nonreversible parts. The reversible part is caloric, which correlates to the change of specific thermal capacity of the sample; while the non-reversible part corresponds to the heat released by the chemical reaction. DSC experiments can either be isothermal or dynamic. Dynamic measurements are more reliable since instability effects (which appear in isothermal measurements) do not occur.[14]

Figure 1 shows the DSC signals for each of the initially uncured samples. It appears that the Al<sub>2</sub>O<sub>3</sub> nanoparticles have an influence on the total reaction heat released by the samples. The start of the network formation is visualized by the onsets of the peaks corresponding to the exothermic At the beginning of the dynamic cure reaction. predominantly linear experiments, the generation of molecules is not significantly hindered by the presence of nanoparticles. At intermediate stage of the cure process, the reaction heat depends on the concentration of alumina. At temperatures higher than 145°C, higher concentration of alumina (5 and 10%) show a trend which indicates further exothermal events. This additional heat may be due to the catalytic effect of alumina on the reactions taking place in the diffusion controlled regime. [15]



Figure 1: DSC signals obtained from dynamic scan of unfilled resin system (0%) and nano-Al<sub>2</sub>O<sub>3</sub>.

The enthalpy (total reaction heat) has been determined for each of the investigated nanocomposites from the DSC curves, as Figure 1. The enthalpy values were determined by drawing a straight line connecting the baseline before and after the reaction peak and integrating the peak area limited by the baseline, results are shown in Figure 2. Figure 2 showed a pronounced decrease in the reaction heat by increasing the filler loading that can be referred to the catalytic action of the  $Al_2O_3$  nanoparticles.



### Figure 2: The values of enthalpy, J/gm<sup>-1</sup>, as a function of nanoAl2O3 concentration at heating rate 2 and 5 K/min.

the DSC spectrum for the investigated From nanocomposites, the glass temperatures (T<sub>G</sub>) values were obtained and represented as shown in Figure 3. The T<sub>G</sub> decreases as the concentration of nanoparticles increases in the nanocomposites. This is assumed to be due the arising of interphases, due to interaction between the Al<sub>2</sub>O<sub>3</sub> or chelatesand the resin matrix, with a structure different to the one of the epoxy bulk. These interphases force chemical vitrification to occur at earlier curing time. Knowing that the chemical vitrification emerges when the curing temperature is lower than the glass transition temperature of the fully cured network; thus we can interpret the decrease in the measured T<sub>G</sub> values. Same behavior was also reported for PMMA/alumina nanocomposites, where the author suggested that the nanoparticles actually increase the polymer mobility in the composites.[16] However, it is noteworthy that the change in Tg for nano-sized filled composites has been controversial. Some authors have found that Tg of nanocomposites increase as a function of the filler loading, whereas others have observed an opposite trend. However, the Tg of an epoxy based composite may be changed due to network tacticity, molecular weight, crosslinking density and the amount of reaction residue, etc.



Figure 3: The effect of nano-Al<sub>2</sub>O<sub>3</sub> concentration on the  $T_G$  of nanocomposites.

The most commonly used method to determine material conditions during cure is monitoring the degree of cure

( $\alpha$ ).[13,17] Figure 4 reflects the relationship between cure degree and temperature, which was directly obtained by analyzing the dynamic DSC curves with origin software. It is clear that the presence of nano-Al<sub>2</sub>O<sub>3</sub> particles has no influence on the degree of curing of the epoxy system. This figure is important for estimating the suitable temperature range for cure completion to range between 145-150°C. Further increase of curing temperature may cause a reversion of the cure process as shown in Figure 4. Same results were obtaind at heating rate 5K/min.



Figure 4: Degree of cure for nanocomposites at heating rate 2 K/min

### **3.2 Results from Rheometer Experiments**

At low shear rates polymer melts show a Newtonian behavior with a constant viscosity. The viscosity in the Newtonian regime is called the zero shear viscosity  $\eta_0$ . The behavior of the viscosity curve, obtained from the rheometer temperature sweep at low shear rates, are in general very crucial for the characterization of polymer melts and of great importance for processing purposes. Moreover it throw shed on the polymer filler interaction. Figure (5) showed that the addition of nanoAl<sub>2</sub>O<sub>3</sub> leads to an increase in the  $\eta_0$  values at early stage of curing where the cure reaction is chemically controlled. This was suggested by Shung et al [15] to be due to the interaction between the alumina surface and resin. Yet at higher temperatures, when the cure reaction became diffusion controlled, the filled systems had nearly the  $\eta_0$  values as unfilled resin system.



Figure 5: Viscosity vs Temperature for unfilled and filled resin systems

The gel point in the rheological graph (Tan $\delta$  vs time) is usually defined as the point at which the storage modulus (*G*') is equal to the loss modulus (*G*"), knowing that Tan $\delta$ = *G*'/*G*".[18] Isothermal multiwave frequency (MWF) sweep at different curing temperatures were carried out. Figure 6 is an example of the curves from which T<sub>gel</sub> is estimated. The results ares illustrated in Figure 7, which shows clearly that the gel time decreases with the increase of isothermal temperature. This result is industrially important since by shortening cure time, a sustainable reduction of cycle time can be achieved through application of resin systems wiyh a shorter cure time,this resulting in higher productivity and lower costs.



Figure 6: Tano vs time for unfilled resin at isothermal temperature 80°C.



Figure 7:Effect nano-Al<sub>2</sub>O<sub>3</sub> on the the  $T_{gel}$  of nanocomposites at different isothermal temperature.

# 4 CONCLUSION

DSC and rheometer analysis of the commercial epoxy resin system Araldite LY 556 / an anhydride hardener (Aradur 917)/ an imidazole accelerator (DY 070) filled with nanoAl<sub>2</sub>O<sub>3</sub> particles suggest the following results:

1- The proper curing temperature to be range from 145 to  $150^{0}$ C; meanwhile the degree of cure is not affected by the presence of nanofiller.

2-The catalytic effect of  $nanoAl_2O_3$  on the curing reaction is evidenced by the DSC exthothermic peaks. The decrease

of enthalpy by adding nano- $Al_2O_3$  ensures the catalytic effect of the nanofiller.

3- The glass transition temperature of nano composites is lower than that of neat resin system.

4-The time of gelation dramtically decreasing by increasing the isothermal temperature.

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