



Polymerisation kinetics of clay filled epoxy resin surface coatings

O G Igbum^a, L Leke^{b,*}, M U Okoronkwo^b and A Galadima^b

^aMaterial Science Centre, University of Manchester, Institute of Science and Technology, Manchester, UK.

^bDepartment of Chemistry, University of Aberdeen, AB24 3UE, Aberdeen, UK.

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ABSTRACT

Coating formulations were developed with diluent or modifiers that remained incorporated as a minority discontinuous phase. Epoxy resins were formed from a DGEBA (diglycidyl ether of bisphenol A), prepolymer (Epikote 828) and MXDA, (m-Xylylenediamine). Butyl laurate (BL) and clay (montmorillonite) were used as the modifier and the filler, respectively. The epoxy network forming systems were prepared by mixing the DGEBA with BL and/or clay and degassed, followed by addition of the MXDA and further degassing. Polymerisation kinetics during epoxy network formations were obtained using Differential Scanning Calorimetry (DSC) on samples of quenched reaction mixtures pre-reacted isothermally at 60 °C at 5 min intervals up to 1 h. The results showed a step-wise increase in T_g and conversion with time. The exothermic process in the clay-filled resins was controlled by the catalytic activity of the clay surface with the resin system.

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Introduction

The broad interest in epoxy resins originates from the extremely wide variety of chemical reactions that can be used for the curing and the many different properties that result. These include excellent adhesion, chemical and heat resistance, good-to-excellent mechanical properties and very good electrical insulating properties. The chemistry is unique among the thermosetting resins. In contrast to the conventional formaldehyde resins, no volatiles are given off during curing implying that minimum pressures are required for the various fabrication techniques. The shrinkage is less than that encountered in the vinyl polymerization used to cure unsaturated polyester resins. This means reduced stresses in the cured product. Furthermore, knowledge of the chemistry involved permits the user to cure the resins over a wide range of temperature and control the degree of cross linking, (Clayton and Yoshio, 1973).

Epoxy resins are toughened with inorganic fillers. Polymer Layered Silicate (PLS) nanocomposite have attracted great interest, both in industries and in the academia because they often exhibit remarkable improvement in materials properties when compared with virgin polymers or conventional micro and macro – composites, (Okada *et al.*, 1990). They are known to possess a high reinforcement efficiency even at low loading (1–5%) due to their high surface area and aspect ratio, as compared to conventional composites with loadings as high as (30 – 50%). (Ariadne and Graham, 2006). Their incorporation optimizes the mechanical, optical, gas barrier and, heat distortion temperature properties (Gilman, 2004; Wang *et al.*, 2006). They are also comparatively cheaper.

Min *et al.* (1990) followed the development of the glass transition temperature of a DGEBA/DDS system using DSC. They derived a model on the basis that the heat of reaction and the glass transition temperature had a relationship with the

degree of conversion and the reaction mechanism observed in the reacting system. They calculated the overall conversion from the measured heat of reaction according to equation 3 below.

$$p = \frac{\Delta H_t - \Delta H_0}{\Delta H_0} \quad (3)$$

Where ΔH_0 is the total heat of reaction for the unreacted samples and ΔH_t is the residual heat of the reaction for the sample at time, t and p is the conversion.

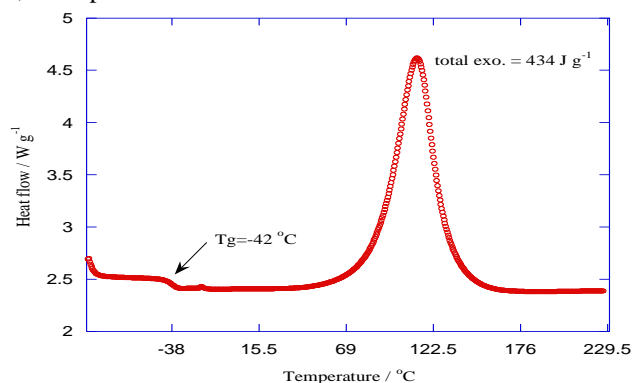


Figure 1: Total exotherm plot for DM reacted at room temperature showing a single T_g and an exotherm.

The total exotherm differs for the different reacting systems. Table 3 below shows the total exotherm for the epoxy resins formulation reaction. The total exotherm of the reaction in DM5u exceeds others with that of DM5B5u been lowest. The catalytic activity of montmorillonite is known to contribute to the exothermic process.

Major contribution to the exothermic process includes the polymerization of DGEBA with the aid of the catalytic activity of the montmorillonite surface and the fact that only 40 % of the total ΔH available for the mixture was consumed in forming an exfoliated nanocomposite means that some 60 % of the total ΔH can still be exploited for further reaction. Consequently,

exfoliated structures can be realized with the completion of the reaction and a reaction may not be necessary to complete exfoliation. A simple calculation based on the constant diffusion coefficient of DGEBA confirmed that DGEBA can diffuse into the gallery between neighboring clay plates in a relatively short time (well within 1 h). Polymerisation kinetics of unmodified (DM) and modified unfilled Coatings was extensively studied in a previous publication and the Tg/conversion plot for DM will Epoxy Resin Surface thus be compared with clay filled epoxy resins for variation in the rate of reactions, (Ugalahi *et al*, 2006).

This research proposes to employ a type of epoxy resin pre-polymer (Epikote 828) and a diamine-curing agent (m-xylenediamine) for curing while varying amounts of the diluent (dibutyl dilaurate), which are miscible with the epoxy formulation comprising DGEBA and also with variable amounts of clay fillers with the different amounts of the epoxy formulation system in the polymerization process.

Experimental

Reagents used in resin network formulation

Epoxy prepolymer

The epoxide pre-polymer used in this study was Epikote 828 (Shell chemical, Belgium) - a diglycidyl ether of bisphenol A (DGEBA). Epikote 828 is a clear colourless highly viscous liquid with a nominal equivalent weight of 170 g mol^{-1} . The resin crystallizes over a long period of time at room temperature and has a melting point of $40 \text{ }^\circ\text{C}$. The chemical structure of DGEBA is shown in figure 2.

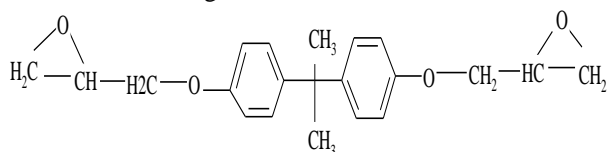


Figure 2: Structure of DGEBA.

Curing Agent

The curing agent used was an amine, m-xylenediamine (MXDA) (ex. Sigma-Aldrich). MXDA is a pale yellow liquid with a density of 1.032 g cm^{-3} . The structure is shown in figure 3.

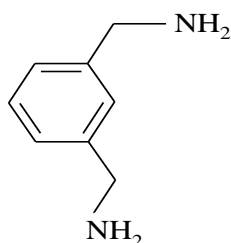


Figure 3: Structure of m-xylenediamine (MXDA)

Modifier

The modifier used was butyl laurate or dodecanoic acid butyl ester (ex. Sigma-Aldrich) which is a low viscosity clear liquid with a molar mass of 256 gmol^{-1} and a density of 0.858 gcm^{-3} . The structure is shown in figure 4.

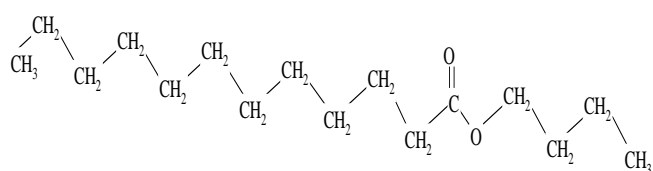


Figure 4: Structure of butyl laurate.

Clay filler

The clay used was montmorillonite (Nanacor) with a chemical exchange capacity of $145 \text{ meq} / 100 \text{ g}$ and contains $12 \text{ w/w} \%$ of moisture.

Unmodified montmorillonite clay and modified montmorillonite clay were used. The clay was modified with 6-amino caproic acid.

Characterisation of reagents

Epikote 828, MXDA and butyl laurate were initially characterized by (Munshi, 2003) as shown in table 2.

(a) viscosity of the reactants at $60 \text{ }^\circ\text{C}$

(b) Solubility Parameters calculated using Van Krevlin's group contribution method, (Van Krevelen, 1976).

(c) butyl laurate Tg not detected due to being masked by melting temperature at $-8 \text{ }^\circ\text{C}$.

Unmodified and modified clay

Clay used in this study was montmorillonite. The unmodified clay was dried in a vacuum oven at $120 \text{ }^\circ\text{C}$ for 4 h to dry up any volatiles or moisture present. The dried clay was further modified by 6-amino caproic acid. The dried clay was grinded and sieved to fine powder using a sieve of mesh size 38. Preparation of unfilled and clay-filled epoxy resins

Unmodified/unfilled Epoxy resin was prepared by weighing the sample into a 250 ml sample bottle and degassed at room temperature in a vacuum oven for 30 min. The stoichiometric amount of MXDA was then weighed and added and stirred vigorously to get a homogenous mixture. The mixture was further degassed for 15 min and cast into preheated moulds and place in a preheated oven. The sample was then cured for 1 h at $60 \text{ }^\circ\text{C}$ and post cured at $140 \text{ }^\circ\text{C}$ for 1 h.

Clay filled Epoxy resin was prepared by weighing Epikote 828 (DGEBA) into a 250 ml sample bottle and the required amount of clay was weighed and added and stirred. 5% w/w butyl laurate (modifier) was weighed and added at room temperature. The mixtures were thoroughly stirred and degassed in a vacuum oven at room temperature for 30 min to remove air trapped during stirring. A stoichiometric amount of MXDA was then added and mixed thoroughly. The homogenous mixture was further degassed at room temperature in a vacuum oven for 15 min. The mixture was then hand cast into a PTFE mould and placed in a pre-heated oven to pre-react at $60 \text{ }^\circ\text{C}$ for 1 h, after which the sample was post-cured at $140 \text{ }^\circ\text{C}$ for 2 h.

From table 1, the formulations were based on the mass of DGEBA (Epikote828). DGEBA was weighed out and the required amount of MXDA was calculated using equation 1 below.

$$A_m = \left(\frac{E_m}{E_{n \text{ epoxy}}} \right) \left(\frac{E_{n \text{ amine}}}{2} \right) \quad (1)$$

Where E_m and A_m are the masses (in grams) of the DGEBA and MXDA respectively and $E_{n \text{ epoxy}}$ and $E_{n \text{ amine}}$ are the equivalent weights (g mol^{-1}) of DGEBA and MXDA, respectively.

The mass of modifier, M_m (butyl laurate) was calculated according to equation 2

$$M_m = x \frac{(E_m + A_m)}{(1-x)} \quad (2)$$

where E_m and A_m are the masses (g) of DGEBA and MXDA, respectively, and x is the mass fraction of modifier. Hunt and James, (1993).

Mass of unmodified clay was also calculated using equation 2 where M_m in this case is mass of clay, and x mass fraction of unmodified clay.

Modified clay is calculated by multiplying the mass of DGEBA weighed, by a factor 0.059 for 5 %wt of modified clay.

In the filled Epoxy resins, mass fraction of clay were 5 %w/w for unmodified clay and while the mass of modified clay was 5 %wt of the clay.

Network sample coding

Modifier used was butyl laurate (liquid) and clay (powder) was used as the filler. The samples were therefore coded according to the amount of modifier and filler used. Each sample was formulated from DGEBA (D), MXDA (M) and %w/w butyl laurate (%B) or clay (unmodified clay (u) and modified clay (m)). For butyl laurate systems, a total of 6 samples were prepared and are represented in the table 2 below. For the clay/DGEBA (filled epoxy resin) system, a total of 4 samples were prepared with two being unmodified epoxy resin and two being modified epoxy resin.

Polymerization kinetics

In order to understand the kinetics of epoxy reaction, it would be necessary to identify the chemical species in the reaction; these are primary, secondary and tertiary amines as well as the epoxy. Initially there is a reaction between epoxy and hardener reactive groups so that somewhat larger molecules are formed. As the reaction proceeds, larger and larger molecules are formed but it should be noted that the average molecular size is still small even when half the reactive groups have reacted. Molecular size increases as the reaction progresses. Some very highly branched molecules are formed and then more and more highly branched structures develop.

Experimental methods for quenched epoxy samples were used to study the polymerization kinetics of the curing reaction. Differential Scanning Calorimetry technique was used to monitor the rate of conversion of the system with time and the change in glass transition temperature as the reaction proceeded. Samples of freshly mixed epoxy network forming system (approx 10 – 15 mg) were carefully added to pre-weighed aluminum DSC pans. These were then placed on an accurately temperature controlled hot plate (60 ± 1 °C). Samples were sequentially removed from the hot plate at various times, quenched and stored in liquid nitrogen prior to use.

Quenched samples were subsequently scanned from -100 °C to 250 °C at 10 °C.min⁻¹ in nitrogen atmosphere against an empty reference DSC pan. The exothermic peak of the heat flow versus temperature plots was integrated to get the heat of the reaction. Conversion data for a particular reaction time was then calculated from the heat of reaction.

Results and Discussion

From the plot in figure 5, it can be seen that the T_g increases with increase in reaction time. The increase in T_g in the unmodified DGEBA shown in figures 6 and 8 (DM5B5u and DM5u denoted by the rectangular plot points) tend to occur in a stepwise manner, so is conversion as calculated from equation 3. The scan shows a single T_g and a single exotherm related to the total heat of reaction. DSC scans were obtained at intervals of 5 min. The extent of reaction was determined from equation 3 above. These data was used to construct conversion time plots for the unmodified systems and all the composite systems. There

is an increase in the rate of conversion and T_g with time. At higher time, the rate of conversion becomes slow as cross-linking progresses; the amount of reactive functionalities decreases resulting in the decreased rate. At higher conversion the reactive end-groups become incorporated into the network thus reducing the mobility of the reactive end groups. 100 % conversion is thus assumed to occur at final T_g of the sample. As the reaction progresses the rate of conversion could no longer be calculated at higher temperatures and reaction time, as the residual enthalpy peak reduces to the baseline therefore cannot be accurately measured. As the reaction occurs, gelation followed by vitrification occurs therefore the sample is post cured to its final T_g . The relationship between T_g and conversion is shown in the plots of T_g vs. conversion (figures 6, 7, 8 and 9). The T_g /conversion plot for DM is thus compared for variation in the rate of the reaction in the same figures.

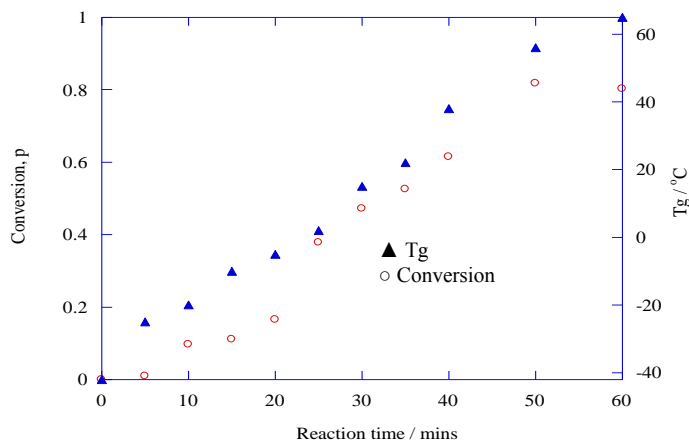


Figure 5: Tg-conversion time plots for DM reacted isothermally at 60°C

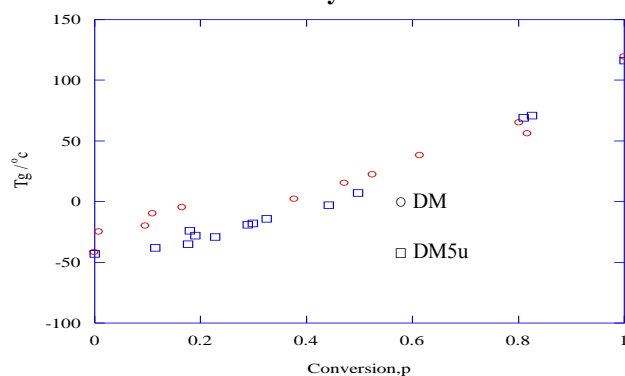


Figure 6: Comparative Tg-conversion plots for DM & DM5u reacted isothermally at 60°C

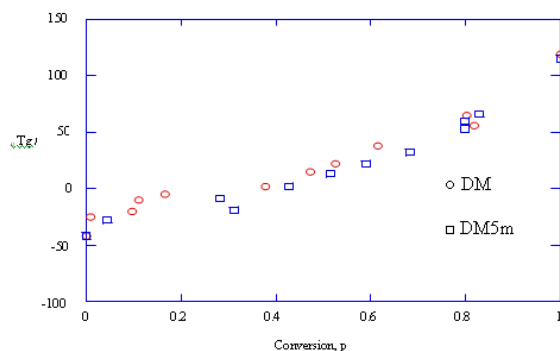


Figure 7: Comparative Tg-conversion plots for DM and DM5m reacted isothermally at 60°C.

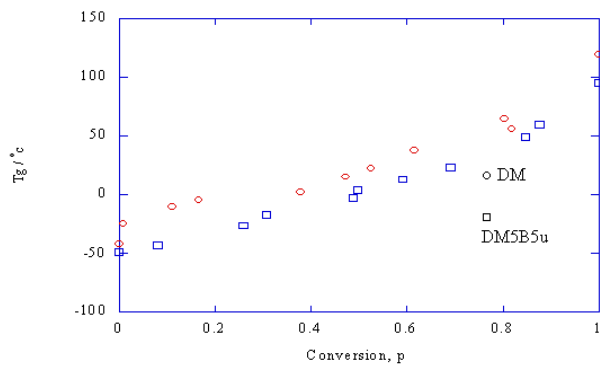


Figure 8: Comparative Tg-conversion plots for DM and DM5B5u reacted isothermally at 60 °C.

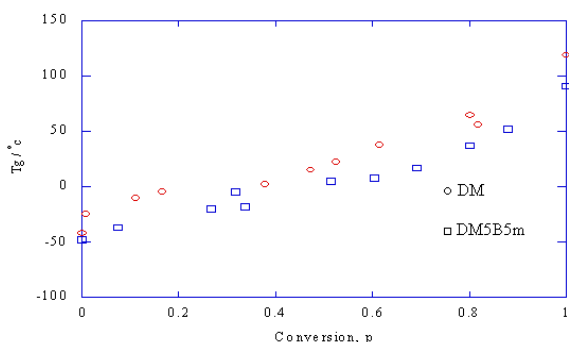


Figure 9: Comparative Tg-conversion plots for DM and DM5B5m reacted isothermally at 60 °C

In all cases, a considerable increase in Tg was observed with conversion. The rate of conversion in DM was observed to be higher than in the samples with modifiers, with the rate of conversion for DM5u system being slower than other system (figure 6). About 80 % conversion for DM5u was achieved at ~65 min of curing at 60 °C (figure 6). This can be explained as the clay been unmodified therefore less intercalation of the epoxy-amine with time.

In DM5B, DM5B5u, DM5B5m, phase separation was observed as the reaction progressed which led to a stepwise increase in Tg/conversion. DM5m shows rapid increase in Tg/conversion as much as in DM (figure 7). It has been reported that the addition of the org-MMT reduces the gelation time Tg, and increases the rate of curing reaction and the value of the kinetic constant K (Chen *et al*, 2003). The relationship between Tg and conversion for a network material is a central concept in analyzing structure development, this is because the process of a network forming coating must be performed above the Tg of the uncured material so that it can be applied in a state of low viscosity (Venditti, and Gillham, 1997).

Conclusion

Polymerization kinetics were carried out by DSC analysis of quenched samples reacted isothermally at 60 °C on a hot plate and conversion/Tg monitored at intervals of 5 min. The total exotherm at time, 0 mins, reacted at room temperature differs for all the reactions; the exothermic process includes the polymerisation of DGEBA with the aid of the catalytic activity of the montmorillonite surface, which differ for the reactions.

From the Tg/conversion/time plot for the unmodified DGEBA, a stepwise increase in Tg/conversion with increase in reaction time was observed until at higher time where conversion is slowed and Tg still increasing. 100 % conversion is thus assumed to occur at final Tg of the sample. In all cases, a considerable increase in Tg with conversion was observed, the rate of conversion in DM been higher than the other samples with modifiers. DM5m showed rapid increase in the rate of conversion as in DM as well as DM5B5u and DM5B5m.

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Table 1 Total exotherm of reactions at time, t = 0 for the unfilled and filled epoxy resin formulation.

Sample Name	Total Exotherm at t=0 /J g ⁻¹
DM	434
DM5B	434
DM5u	480
DM5m	463
DM5B5u	390
DM5B5m	408

Table 2: Summary of values of characterization of reagents, (Munshi, 2003)

Sample name	Mass/ g mol ⁻¹	ρ / g cm ⁻³	T _g / °C	η ^(a) / mPa s	E _a / kJ mol ⁻¹	δ ^(b) / J ^{1/2} cm ^{-3/2}
DGEBA	346.8	1.160	-22	132.0	74.85	18.57
MXDA	136.2	1.032	-92	3.2	15.28	21.22
Butyl laurate	256.0	0.858	(c)	3.2	8.25	16.66

Table 3: Sample code for clay-filled epoxy resin (modified and unmodified).

Modifier/filler	Sample code
5%w/w unmodified clay	DM5u
5%wt modified clay	DM5m
5%w/w unmodified clay/5%w/w Butyl laurate	DM5B5u
5%wt modified clay/5%w/w Butyl laurate	DM5B5m