THE EFFECT OF MULTIWALLED CARBON NANO TUBES ON CURE KINETICS OF EPOXY RESIN

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ABSTRACT

The effects of incorporation of multiwall carbon nano tubes (MWNTs) on the cure reaction of a diglycidyl ether of bisphenol-A (DGEBA) and triethylene tetramine (TETA) as a curing agent have been studied with an isothermal differential scanning calorimetry (DSC) technique.

Kinetic analysis was performed with the phenomenological model of Kamal and Sourour. Isothermal kinetic parameters were determined and the results show that the kinetically controlled parts of reaction could be expressed well with Kamal and Sourour model while end of curing reaction is diffusionally controlled.

Activation energies and kinetic parameters are determined by fitting experimental data for MWNTs/epoxy Nano composites, the initial reaction rate increases and the time required for the maximum rate decreases with increase in MWNTs contents, because of the acceleration effect of MWNTs.

The initial rates of MWNTs/Epoxy Nano composites were found to be comparatively higher than that of neat Epoxy at all curing temperatures, whereas the time required to the maximum reaction rate of the Nano composites decreased with increasing MWNTs content, suggesting that MWNTs have an acceleration effect on the Epoxy cure reaction.

Compared with the neat DGEBA/TETA Epoxy, the MWNTs/Epoxy Nano composites exhibited lower activation energies for k_1 , and E_1 and decreased with increasing MWNTs. E_2 for The MWNTs/Epoxy Nano composites remained the same as that of the neat Epoxy.

The further reaction kinetic analysis indicates that the Kamal model can well fit the reaction rate at the kinetic controlled stage which is about 60 % conversion and rest of the reaction is diffusion ally controlled.

KEYWORDS: MWNT, DGEBA, TETA, DSC, CNT, SWNT

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1. INTRODUCTION

Figure 1 shows Carbon nano tube (CNT) is a fullerene related structure which consist of graphene cylinders closed at either end with caps containing pentagonal rings

Figure 2 shows CNTs have a unique atomic structure, very high aspect ratio, and extraordinary mechanical properties (strength and flexibility) makes them ideal reinforcing fibers in Nano composites.

Carbon nano tubes are of two types 1) Single walled carbon nano tube 2) Multi walled carbon nano tube

Figure 1: Rolled Graphene Sheet.

**Figure 2: a) Multi Walled Carbon Nano Tube.
b) Single Walled Carbon Nano Tube.**

2. PROPERTIES OF CNT

Elastic modulus: ~ 1 Tpa ; Tensile strength: ~ 50 Gpa ;

Thermal conductivity: $> 1,500$ W/m K, much higher than Cu – 400 W/m K; Electrical conductivity: Better than Cu;

Elongation: $> 30\%$;

Density: < 1.2 g / cm³ for single-wall CNTs, 2.0 g/cm³ for multi-wall CNTs.

Epoxy is also known as poly epoxide, is a thermosetting polymer formed from a reaction of an epoxide resin with polyamine hardener. Epoxy resins are the most important thermo sets, widely used as adhesives, coatings, and composite materials. To enhance or provide physical properties, such as modulus, thermal expansion, thermal and electrical conductivity, and magnetic recording properties, reinforced fillers, such as carbon black, carbon fibers and glass fibers are incorporated in the resins. In recent years, the use of carbon nano tubes (CNTs) in epoxy resin /carbon nano tube composites has attracted a great deal of attention. CNTs

Have a unique atomic structure, very high aspect ratio, and extraordinary mechanical properties (strength and flexibility) making them ideal reinforcing fibers in Nano composites.

3. EXPERIMENTAL

3.1. Aim of the Present Work

The aim of the present work is to study the cure kinetics of Epoxy resin (diglycidyl ether of bisphenol A-based-DGEBA) polymerized with an amine (triethylene tetramine-TETA) and DGEBA/TETA-MWNTS. Determination of experimental data

for both the neat DGEBA/TETA system and for epoxy/MWNTs Nano composites Kinetic analysis will be performed with the phenomenological model of Kamal and Sourour. Determination of activation energies and kinetic parameters by fitting experimental data.

4. MATERIALS

- **Resin:** Diglycidyl ether of bisphenol-A (DGEBA)
- **Hardener:** Tri ethylene tetramine (TETA)
- **MWNTs (Master batch):** EPOCYL

4.1. Specimen Preparation

A 2 wt % of master batch was added to 88 % of Epoxy resin (DGEBA) and 10% of TETA was slowly added with continuous hand mixing until a homogeneous mixture was observed, which took about 10 min. Several DSC aluminum pans were filled with the reaction mixture. The samples (20mg) were then cooled and stored in a freezer until required.

Figure 3: Differential Scanning Calorimeter.

Figure 4: DSC System for a Polymer Sample.

5. EXPERIMENTAL PROCEDURE

A differential scanning calorimeter (DSC Q20 TA instruments) was used for the dynamic and isothermal cure experiments and for data analysis under a nitrogen flow of 50ml/min. In dynamic scan 20mg of samples were heated from room temperature to 300⁰c at a heating rate of

10⁰c / min. In an isothermal scan each sample was ramped from room temperature to the desired isothermal temperature and then held isothermally. The isothermal experiments were conducted at three temperatures (80, 85 and 90⁰c).

The reaction was considered complete when the signal leveled off to baseline. The total area under the exotherm curve, based on extra polated base line at the end of the reaction was used to calculate the isothermal heat of reaction H_t (J/g), at a given temperature.

6. RESULTS AND DISCUSSIONS

The reaction rate, $d\alpha/dt$ as a function of time, t , was calculated from the measured heat flow dH/dt in isothermal DSC experiments by:

$$=$$

Where α is the extent of reaction (conversion) and H_t is the total heat of reaction obtained from isothermal scan. Assuming proportionality between the extent of the reaction and the heat evolved up to a time t , a general expression for the extent of the reaction, α , can be written as:

$$\alpha =$$

Where H_p is the heat evolved up to a certain time in an isothermal experiment.

Epoxy resin curing can be divided into two general categories: n^{th} order and autocatalytic. The nature is typically autocatalytic in all cases, with the maximum reaction rate after the start of the cure reaction.

The phenomenological model developed by Sourour and Kamal was used. The reaction rate, $d\alpha/dt$, and the extent of the reaction, α , are related to one another as follows:

Where m and n are the kinetic exponents of the cure reaction and $m+n$ represents the overall reaction order. The rate constants are k_1 and k_2 with two different activation energies and two pre-exponential factors.

The constant k_1 in this equation can be calculated from the initial reaction rate at $\alpha=0$. The rate constants k_1 and k_2 are assumed to be constant at a given temperature and follow an Arrhenius temperature dependence:

$$k = A \exp (-E/RT)$$

Where A is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature

Curve fit is conducted by the help of nonlinear least squares fitting (NLSF) method to compute the four parameters k_1 , k_2 , m and n from the experimental data. The results are shown in the Table 1.

Table 2 shows a plot of the rate constants, k_1 and k_2 with corresponding temperature ($1/RT$) gave a straight line. From the slope of the straight line, the associated activation energies E_1 and E_2 were calculated. According to Arrhenius equation, A_1 and A_2 can be obtained.

Figure 8 shows that according to the Kamal model, the calculated data from the model are in good agreement with the experimental results at range of 060 % conversions. At end of curing reaction ($\alpha > 60\%$), Kamal model are not in proper agreement with experimental data which indicates that the curing mechanism started to change from chemical kinetics control to control by diffusion. This is because of the phenomena of gelification, vitrification, and high viscosity exist in the reaction medium at the end of curing process [43].

Figure 5: Heat Flow Versus Time for DGEBA / TETA Epoxy and Its Nano Composites.

Figure 6: Reaction Rate Versus Time for DGEBA / TETA Epoxy and Its Nano Composites.

Figure 7: Conversion Versus Time of DGEBA / TETA Epoxy and its Nano Composites.

Figure 8: Comparison of Experimental Data with the Kamal Model in DGEBA / TETA + MWNTs.

Table 1: Kinetic Parameters K1, K2, M, N and M + N for Each MWNTs / Epoxy Nano Composite

MWNTs	Temp	k1 X	k2X10 ⁴	m	n	m+n
(wt %)	(°C)	10 ⁶	(min-1)			
		(min-1)				
0	80	4.552	22.44	0.086	1.679	1.765
		4		2	4	6
	85	1.518	36.246	0.204	1.851	2.055
		2		1	5	6
	90	0.6949	54.9118	0.2989	2.0495	2.3484
2	80	7.2832	23.642	0.0912	1.6245	1.7157
	85	2.366	36.943	0.2132	1.7428	1.956
	90	0.7814	56.432	0.3276	2.2468	2.5744

Figure 9: Curves of $\ln k_1$ Against $1/RT$ for Neat DGEBA / TETA Epoxy and 2 % MWNTs Nano Composites.

Table 2: Activation Energies and Pre-exponential Factors for Each MWNTs/Epoxy Nano Composite

MWNTs (wt%)	E ₁ (kJ/mol)	E ₂ (kJ/mol)	$\ln A_1$	$\ln A_2$
0	247.062	96.363	95.797	26.705
2	210.3	99.231	83.830	27.634

7. CONCLUSIONS

The initial rates of MWNTS / Epoxy Nano composites were found to be comparatively higher than that of neat Epoxy at all curing temperatures, whereas the time required to the maximum reaction rate of the Nano composites decreased with increasing MWNTs content, suggesting that MWNTs have an acceleration effect on the Epoxy cure reaction.

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