

Studies of Cure Kinetics and Chemical Resistance of the Cured Products of DGEBA with Aromatic Diamines

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ABSTRACT

An investigation is conducted into the non-isothermal kinetics of the curing reaction of diglycidyl ether of bisphenol A (DGEBA) epoxy resin with two novel aromatic diamines, 4,4'-diaminostilbene (DAS) and 4,4'-diaminoazobenzene (DAAB), as curing agents. Kinetics analysis of the curing reaction of DGEBA with two different concentrations (29 wt% = 0.13 mol% and 19 wt% = 0.09 mol%) of the curing agents was studied using non-isothermal differential scanning calorimetry (DSC) technique. Two methods (Ozawa and Kissinger) for analysis of the scanning DSC data were applied to calculate the kinetic parameters and compared with kinetic parameters obtained from isothermal DSC tests using Kamal method. Activation energies in the range of 52.5-59.5 kJ/mol were obtained for both DGEBA/curing agent systems. The water absorption and resistance of the cured products against solutions of H₂SO₄ and NaOH were also studied. Water uptake curves for both systems are similar. Weight loss for the cured products of DGEBA/DAS and DGEBA/DAAB systems in 50% solution of NaOH reached the equilibrium values of 0.2% and 0.5%, respectively after about 80 h and weight gain of the cured products of both systems in 30% solution of sulphuric acid reached the equilibrium value of about 0.3% after about 40 h. The cured products from DGEBA/DAS system showed less weight loss during thermal degradation at 250°C but their water uptake was much higher.

Key Words:

resins;
DSC;
kinetics;
curing of polymers;
properties.

INTRODUCTION

Epoxy resins are used as adhesives, barrier film in food packing, matrix resins in fibre reinforced compositions and in a host of other applications. Linear epoxy resins are converted into a three-dimensional cross-linked thermoset network

during cure. Similar to the aliphatic amines, aromatic amines produce high exotherms during cure. Curing kinetics models are generally developed by analyzing experimental results obtained by differential thermal analysis technique.

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Differential scanning calorimetry both in the isothermal and dynamic modes has been used extensively, assuming a cure and extent of reaction [1-14]. Different non-isothermal kinetic methods such as Kissinger [15,16] and Ozawa-Flyn-Wall [17,18] methods were applied to DSC data to test their applicability in the epoxy-hardener systems. The advantages most apparent of aromatic amines over aliphatic amines for curing epoxy resins are the development of higher heat distortion temperatures in the cured products, longer pot lives of mixtures and greater chemical resistance after cure. Aromatic amines generally impart some of the best chemical resistance properties to epoxy resins. Acetic acid resistance is greatly improved over aliphatic amines and resistance is developed to oxidizing mineral acid [19].

Polymeric systems may be exposed to various environmental conditions during their service life. The performance of these systems may deteriorate to a certain extent upon exposure to harsh environments for a certain period of time. Moisture/water is the most commonly encountered service environment, and must be considered a critical factor in determining the long-term durability of polymers especially adhesively bonded joints. The cross-linked network structure of epoxy resin with highly polar nature of the specific functional groups such as hydroxyl and amines, are expected to have water uptake as bound water and as free water which becomes crucial when long-term properties of the material needed. The absorbed moisture may act as plasticizer for epoxies with resultant depression in the glass transition temperature (by as much as 20°C) and reduce the strength and the elastic modulus E' [20]. In several research studies [21,22] the equations based on the free volume concept [22] or classical thermodynamics [23] have been employed to predict the extend of plasticization of neat and reinforced epoxy resins. However, it has been pointed out that these predictions are questionable [24] or only qualitatively applicable with the condition that the higher the cross-link density, the more accurate the equation. Many studies have also shown that the water causes permanent chemical and physical changes. Antoon and Koeing [25] investigated the effects of moisture and demonstrated that hydrolytic attack of water takes place on anhydride-cross-linked epoxy resin films. It has been shown that moisture can

also cause structural damage by including microcavities or crazes in polymeric materials [26,27] which can further accelerate the moisture diffusion. Studies conducted by another worker [28] showed that absorbed water cannot be totally removed by thermal annealing and the residual water in the adhesive is believed to be the one which is strongly bonded to polar sites.

The main objective of the present work was to study the kinetics of the curing reaction of DGEBA with two aromatic diamines (DAS and DAAB), which according to our literature survey they have not been used as curing agents for epoxy resins before. The further objective of this work was to study the water uptake, chemical resistance and thermal degradation properties of the cured products. The effect of thermal degradation on the water uptake properties of the cured products was also studied.

EXPERIMENTAL

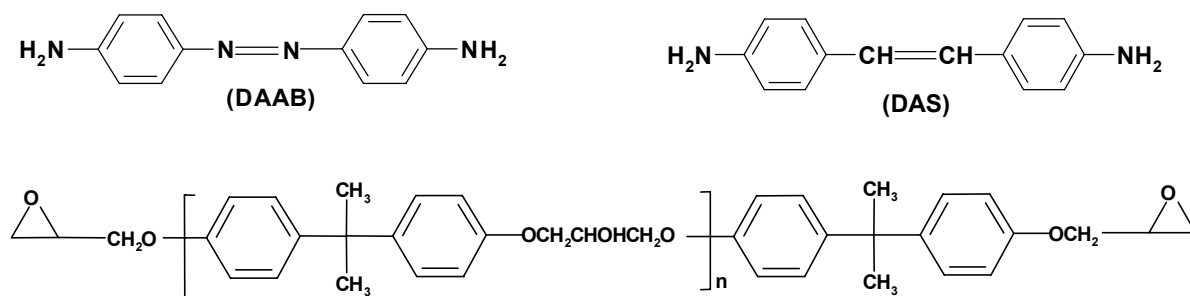
Sample Preparation

The epoxy compound used in this study was a diglycidyl ether of a bisphenol A-based epoxy (DGEBA) provided from Shell Chemical Co., Epon 828, with an epoxy equivalent weight (Epoxy.Eq.w) of 185. Other compounds such as: *p*-nitrotoluene, hydrazinehydrate 85%, diethylene glycol, *p*-aminoacetanilide, sodium perborate tetrahydrate, boric acid and methanol were obtained from Fluka and used without further purification.

The curing agents such as 4,4'-diaminostilbene (DAS) and 4,4'-diaminoazobenzene (DAAB) were synthesized according to the procedures given in the literature [29,30] (Scheme I). DAS was a brown solid (30% yield) with a melting range of 225-228°C and DAAB with a yield of 56% had a melting range of 236-239°C. Both of the curing agents were soluble in DGEBA during stirring at 50°C.

Experimental Technique

DSC Thermograms were recorded using a Perkins-Elmer instrument (DSC 4) over the temperature range of 50-350°C at different heating rates (10, 15 and 18°C/min). The instrument was first calibrated with pure indium for thermal response with the heat of



Scheme 1. DGEBA (composed principally of two homologs $n=0$ and $n=1$).

fusion and the temperature with the melting point. The stoichiometric amounts of the curing agents were calculated through the number of active amino hydrogens. Stoichiometric equivalent of 52.5 g of DAS or DAAB was used for 185 g of DGEBA (~29 wt%). A 5 mg well-mixed and uniform viscous liquid was put into a DSC sample pan and covered with an aluminium lid and closed tightly under pressure. The sample pan was placed in the DSC sample cell at ambient temperature and an empty pan was also placed in the DSC reference cell.

The samples for water absorption and chemical resistance tests were prepared by mixing DGEBA thoroughly with the stoichiometric amount of DAS or DAAB at room temperature and then cured in the vacuum oven at 50°C for 24 h. We selected this temperature preferentially to study the effect of low temperature curing on the water absorption process. Very hard brown colour cured products were obtained which could be cut into pieces for the resistance tests. Water absorption tests were conducted in distilled water and in 10% solution of NaCl. The chemical resistance tests were carried out in 50 and 30% solutions of sodium hydroxide and sulphuric acid, respectively.

Table 1. Sample preparation procedures for thermal oxidation tests.

Temperature		50°C	100°C	200°C
Sample				
DGEBA/DAS,	A	120 min	60 min	30 min
DGEBA/DAS,	B	30 min	60 min	120 min
Temperature		70°C	140°C	250°C
Sample				
DGEBA/DAAB,	C	120 min	60 min	30 min
DGEBA/DAAB,	D	30 min	60 min	120 min

Samples of almost the same sizes and the average of three readings were used for chemical resistance tests. All the measurements were made at room temperature and the surface of the samples was dried by a clean tissue before being weighed.

The cured samples for thermal degradation tests were prepared by using mixture of DGEBA with 29 wt% of curing agent and the procedures given in Table 1. The thermal stability was measured by weighing the sample during 6 days of heating in the air oven at 250°C.

RESULTS AND DISCUSSION

Kinetics

Typical dynamic DSC thermograms of the curing reaction of DGEBA with the curing agents are shown in Figure 1. The exothermic peak is due to the polymerization and etherification reactions of the epoxide groups with the amine groups of the curing agents and the hydroxyl groups present and also subsequently

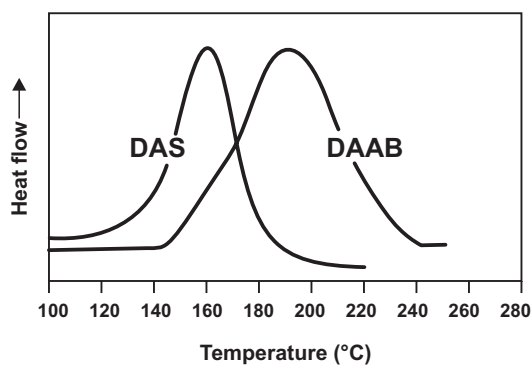


Figure 1. DSC Thermograms of DGEBA cured with 29 wt% of DAS and DAAB at the heating rate of 10°C/min.

formed along the polymer main chains during polymerization. Kinetic analysis of DSC data for the epoxy/hardener systems was performed using two methods: Kissinger and Ozawa [15,16]. These methods were used because it is not necessary to have a prior knowledge of the reaction mechanism to quantify kinetic parameters. It must be noted that multi-heating rate methods are iso-conversional methods, with the assumption that the conversion value, α_p , is constant at the peak exotherm temperature and is independent of the heating rate [31,32].

This makes it equally effective for both the n^{th} order and autocatalytic reactions. If one assumes that the extent of reaction, α , is proportional to the heat generated during reaction, the reaction rate ($d\alpha/dt$) can be expressed by means of the general law:

$$d\alpha/dt = K(T) f(\alpha) \quad (1)$$

where $f(\alpha)$ is a conversion-dependence function. An integrated form of the conversion-dependence function $g(\alpha)$ often appears as:

$$g(\alpha) = \int d\alpha/f(\alpha) = K(T) t \quad (2)$$

According to the method of Kissinger, the activation energy is obtained from the maximum reaction rate where $d(d\alpha/dt)/dt$ is zero under a constant heating rate condition. The resulting relation, for the analysis of DSC data, can be expressed as:

$$d[\ln(\beta/T_p^2)] = -E_a/R d(1/T_p) \quad (3)$$

Table 2. DSC Data for DGEBA cured at different concentrations and heating rates.

Hardener	Conc. (phr)	β , (°C/min)	T_c , (°C)	T_p , (°C)
DAS	19	10	100	160
DAS	19	15	106	170
DAS	19	18	113	175
DAS	29	10	95	157
DAS	29	15	102	167
DAS	29	18	108	172
DAAB	19	10	150	200
DAAB	19	15	154	212
DAAB	19	18	160	219
DAAB	29	10	144	191
DAAB	29	15	150	203
DAAB	29	18	155	209

T_c = cure onset temperature, T_p = maximum exotherm temperature.

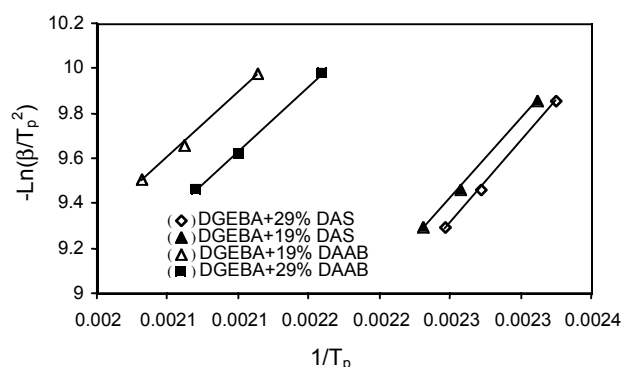


Figure 2. Plots for determination of E_a using Kissinger method.

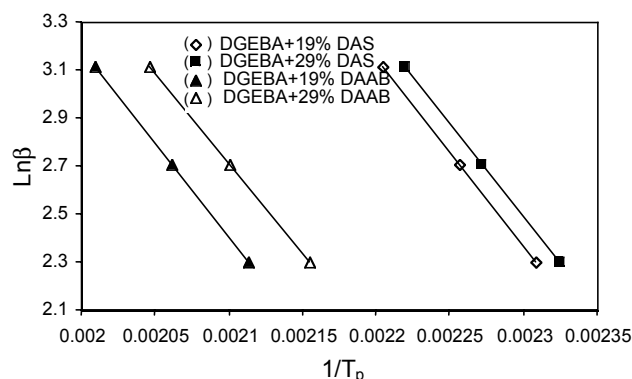


Figure 3. Plots for determination of E_a using Ozawa method.

where T_p is the maximum rate temperature and β is constant heating rate, which are given in Table 2 for both systems at different concentrations of curing agents. The activation energy (E_a) can be calculated from the slope of the linear plot of $-\ln(\beta/T_p^2)$ against $(1/T_p)$, as shown in Figure 2. The obtained values of activation energies are given in Table 3. We have used T_p of the first maximum which is related to the initial curing reaction taking place between the epoxy oligomers and the hardener.

Ozawa-Flynn-Wall Method based on Doyle's approximation [33] is an alternative method for the calculation of activation energy and is expressed as follows:

$$\log \beta = 1/2.303 \ln \beta = -0.4567E_a/RT_p + (\log A E_a/R - \log f(\alpha) - 2.315) \quad (4)$$

Plot of $\ln(\beta)$ versus $(1/T_p)$ should give a straight line with a slope of $1.052E_a/R$, as shown in Figure 3. This can provide activation energy for different levels of conversion, but at the present study it was only

Table 3. Values of activation energies of DGEBA cured on different heating rates.

Curing agent	Conc. (phr)	E _a (kJ/mol) (a)	E _a (kJ/mol) (b)	E _a (kJ/mol) (c)
DAS	19	56.13	60.02	72.31
DAS	29	55.30	59.18	70.22
DAAB	19	52.37	57.43	70.64
DAAB	29	53.08	57.93	71.47

(a)=Kissinger method (b)=Ozawa method (c)=isothermal method [13].

applied to the maximum rate where the peak appears and it was assumed that when the exotherm of peak is reached the degree of conversion is independent of the heating rate. The calculated activation energies based on Ozawa method are given in Table 3. The activation energies obtained by Kissinger and Ozawa methods were very close and are higher than those reported for the same resin cured with aliphatic and aromatic diamantes [33,34]. The activation energies for the same systems and at the same concentrations obtained by isothermal DSC experiments [13] are also given in Table 3 for comparison.

Chemical Resistance

The water absorbed in the polymer is generally divided into free and bound water. Water molecules that are dispersed in the polymer matrix and attached to the polar groups of the polymer are designated as bound water. Moy and Karasz [24], reported that at low temperatures, absorbed water in epoxy resins initially interacts with binding sites of the polymer and then exists in the liquid-like state of water. At high temperatures, they proposed that the water sorption mode is associated with simple solution sorption. Antoon et al. [35], found that water absorbed in an epoxy resin usually interacts with the polar groups by hydrogen bonding and the epoxy-water interactions are completely reversible. The major factors affecting water absorption are the presence or absence of hydrophilic groups in the cross-linked network. However, there are other relevant factors to consider notably free volume which generally increases with cross-link density because of the development of a rigid macromolecular framework. Water molecules which are contained in the free volume of the polymer and are relatively free to travel through the microvoids and holes are identified as free water. The primary goal of this part

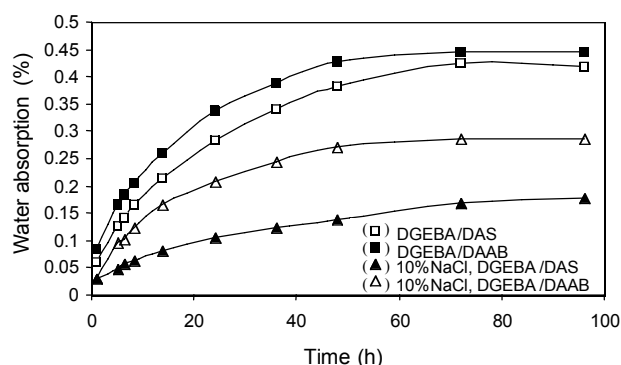


Figure 4. Water absorption of the products cured at 50°C for 24 h.

of study was to describe the interactions between the absorbed moisture involves cooperative motion of water molecules and the 3-dimensional resin network. We report the experimental results merely qualitatively because the quantitative predictions of kinetic parameters of water uptake are questionable as they depend on the conditions of the preparation of the cured products, size and the surface properties of the samples and the measurement conditions. The experimental average values of water uptake, $W_t(\%)$, were obtained from the water uptake of three samples after exposure to identical conditions. The relative weight increase in each sample was calculated as:

$$\Delta w_t = (w_{ti} - w_{0i}) / w_{0i} \times 100 \quad (5)$$

And the average weight increase as:

$$W_t(\%) = \sum_{i=1}^3 \Delta m_{ti} / 3 \quad (6)$$

The experimental curves were plotted up to the beginning of equilibrium plateau. The experimental data for the cured products from DGEBA/DAS and DGEBA/DAAB systems results in curves shown in Figure 4. The water uptake curves for both systems are similar, although the cured products from DGEBA/DAAB system showed higher water absorption which can be due to presence of the polar azo groups in the cross-linked structure. Shape of the curves suggests that water uptake processes are quasi-equilibrium stages. The equilibrium water uptake is almost 0.45% for both systems which has been reached after 80 h immersion at room temperature. The cured products, at 50°C for 24 h, were hard

brown solids and the percent of absorbed water shows that a relatively high density cross-link network was formed. A low density cross-link network can absorb large volume of water due to the presence of larger voids which may cause disintegration of the sample. The water absorption of an aliphatic diamine cured epoxy resin was reported approximately 5.4% while a polyamide /epoxy had an absorption of about 2% [19]. It was predicted by Moy et al. [24] and Jelinski et al. [36] that the water value around this is essentially bound water. The increase of excess water uptake which has been reported to be progressively more relevant as the temperature is increased is attributed to microvoiding. The presence of 10% NaCl in water has reduced the water uptake of the samples by more than 50%, the curves for this experimental data are also shown in Figure 4.

The importance of the curing of epoxy resins is also resistance to chemicals. The average weight loss for the cured products of DGEBA/DAS and DGEBA/DAAB systems in 50% solution of NaOH reached the equilibrium values of 0.2% and 0.5%, respectively, as shown in Figure 5. The average weight gain of the cured products of both systems in 30% solution of sulphuric acid reached an equilibrium value of about 0.3% (Figure 6). The wide spectrum of chemical resistance which is characteristic of aromatic amine cured compositions far exceeds the resistance properties of other fast setting adhesives based on accelerated aliphatic polyamine curing agents. DGEBA cured with Epi-Cure 874 at room temperature for a week showed 3.9% weight gain after immersion in 33% sulphuric acid at 65°C [19]. In terms of chemical linkages in the cured systems, ether links are

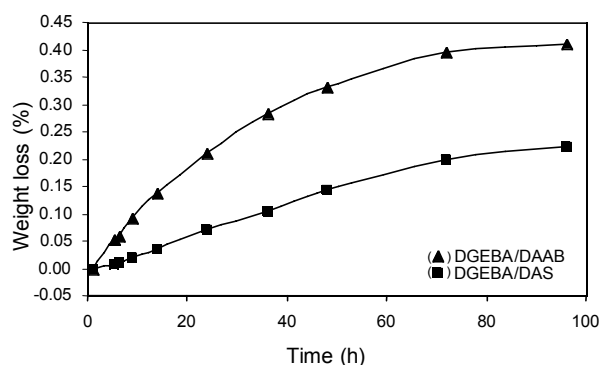


Figure 5. Effect of 50% NaOH solution on the products cured at 50°C for 24 h.

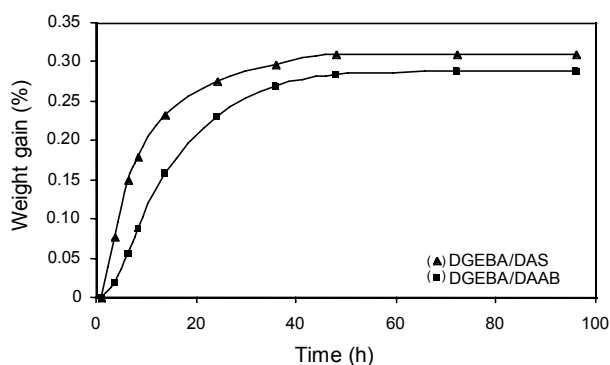


Figure 6. Effect of 30% solution of sulphuric acid on the products cured at 50°C for 24 h.

fairly stable against most inorganic and organic acids as well as against caustics. The carbon-amine nitrogen link is fairly stable in the presence of most inorganic acids, poor in organic acids, and good in caustics. It should be borne in mind that the structure of the cured system will often provide results different from what would be expected in terms of the nature of the chemical linkages alone.

The results of thermal oxidative degradation at 250°C on the cured samples prepared under conditions stated in Table 1 are shown as the curves of weight loss against of time in Figure 7. Samples B and D showed higher weight loss than samples A and C. It is well known that density of the cross-linked network depends on the curing conditions including the rate of the curing reaction. A network with higher cross-link density is expected when the rate of the curing reaction is slow. Therefore, the higher weight loss of samples B and D during thermal degradation can be due to formation of imperfect cross-link network with less cross-link density. The average percent of weight loss

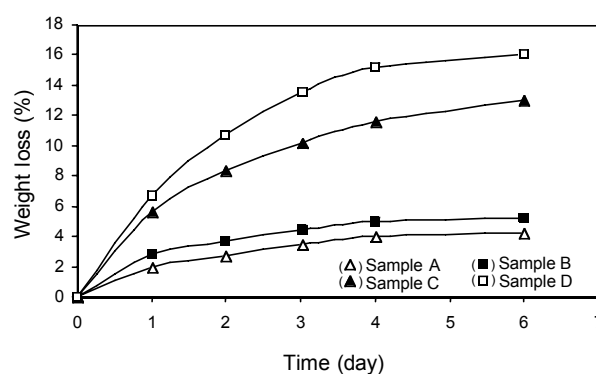


Figure 7. Weight loss of the cured products (samples A, B, C and D in Table 1) during thermal degradation at 250°C.

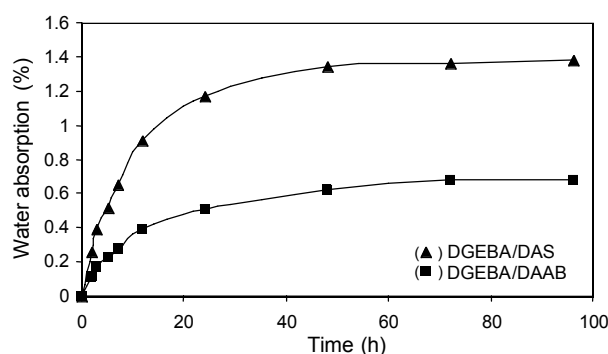


Figure 8. Water absorption of the cured products (samples B and D in Table 1) after thermal degradation.

for the samples C and D of DGEBA/DAAB system is much higher than the weight loss for the samples A and B of DGEBA/DAS system. The results of this study show that the epoxy network containing azo ($-N=N-$) groups is more susceptible to weight loss during heating at high temperature. The results of water absorption tests on thermally degraded samples of both systems are shown in Figure 8. Comparing the results shown in Figures 4 and 8, it can be seen that samples of DGEBA/DAS system cured and heated at high temperatures show higher water absorption than samples of the same system cured at low temperature, and also showed much higher water absorption than samples of DGEBA/DAAB system cured and heated at high temperatures. This can probably be due to sensitivity of carbon-carbon double bonds, present in the cross-linked network of the cured products of DGEBA/DAS system, to oxidative degradation which leads to the formation of more polar hydrophilic functional groups such as hydroxyl and carbonyl. The cured products of DGEBA/DAAB system will probably lose their polar functional azo groups (as N_2 molecules) during degradation at higher temperatures which is also evident from higher weight loss. However, the cured products of DGEBA/DAAB system showed considerably lower water absorption than the cured products of DGEBA/DAS system after degradation. More experiments to characterize the thermal degradation of the cured epoxy resin with the DAAB as the curing agent are underway.

CONCLUSION

Two different kinetic models based on multi-step

heating rate methods (Kissinger and Ozawa-Flynn-Wall) as well as single heating rate method were applied to DSC data to calculate kinetic parameters for the initial polymerization reaction. E_a Values obtained by Kissinger method are slightly smaller than those obtained by Ozawa method, and E_a of the curing reaction of DGEBA/DAS system is about 2 kJ/mol more than E_a of the DGEBA/DAAB system. E_a Values obtained by the dynamic DSC method are smaller than those obtained by the isothermal DSC method for the same system and at the same concentrations. The results show that water uptake process for the products cured at low temperature of both systems behaves similar, and reaches its equilibrium value of about 0.45% after almost 80 h immersion at room temperature. Both systems showed weight loss in NaOH solution and weight gain in sulphuric acid solution. The results of thermal oxidative degradation at 250°C showed that DGEBA/DAAB system is more susceptible to thermal decomposition as it is evident from its higher weight loss. The water uptake of thermally degraded samples of DGEBA/DAS system has increased almost three times which can be due to formation of more hydrophilic functional groups through the oxidation of carbon-carbon double bonds. The water absorption process of the cured samples of DGEBA/DAAB system did not show much change after thermal degradation.

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