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Modification of bifunctional epoxy resin using CO_2 fixation process and nanoclay

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HIGHLIGHTS

- A new epoxy resin was synthesized using CO_2 fixation reaction.
- The synthesized epoxy resin was modified by an organo nano-clay.
- CO_2 fixation noticeably changed the curing mechanism.
- CO_2 fixation reaction consumes CO_2 which is a harmful greenhouse gas.

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ABSTRACT

A bifunctional epoxy resin was modified by using a CO_2 fixation solution process in the presence of tetra n-butyl ammonium bromide (TBAB) as catalyst and the modified treated resin was treated by cloisite 30B as nano additive. The Unmodified epoxy resin (UME), CO_2 fixated modified epoxy resin (CFME), and CFME/clay nano composite (CFMEN), were cured by diethylenetriamine (DETA). A cycloaliphatic compound as a reactive diluent was used to control the viscosity of high viscose CFME. The exfoliation of organoclay in UME and CFME was investigated by X-ray diffraction and activation energy was computed using the advanced integral isoconversional method. The activation energy dependency demonstrated that the mechanism of UME curing did not change in the presence of nanoclay. In contrast, the CO_2 fixation results showed a significant change in the activation energy dependency. The Thermal stability parameters include the initial degradation temperature (IDT), the temperature at the maximum rate of weight loss (T_{max}), and the decomposition activation energy (E_d) were determined by thermal gravimetry analysis. Dynamic mechanical thermal analysis measurements showed that the presence of organoclay in CFME increases the T_g of nano composite in contrast to UME. The fracture roughness of UME, CFME and CFNE were determined by scanning electron microscope. The exfoliated UME/1%clay nanocomposite was confirmed by TEM image.

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1. Introduction

Epoxy resins are an important class of thermoset resins where synthesized and crosslinked by mixing with suitable catalysis show brittle behavior after curing. The application of epoxy resins is widespread, including adhesives, foams, coatings, laminates and composites. Epoxy resins as adhesives have ability to form a strong bond with various surfaces. Epoxy based- foams, composites and laminates are used in air- and spacecraft industries [1].

Epoxy modification methods are reported by many researchers [2–6]. In some methods, organo- montmorillonite (O-MMT) has been dispersed in epoxy resins to form nano composite [7,8]. Epoxy/nanoclay composites have superior properties such as flame retardancy, enhanced barrier properties and anti corrosive properties [9]. The properties of epoxy based nanocomposites such as thermal stability depend on the dispersion of organo montmorillonite into the matrix [10,11]. The toughness of epoxy resins has been modified by elastomeric modifiers such as poly siloxanes and fluroelastomers [12]. The thermal stability, mechanical properties, fracture toughness, morphology of epoxy/Al_2O_3 nanocomposites and the catalytic effect of alumina nano-particles on the curing of epoxy resins has been investigated [13–17].

Due to the increase in the amount of greenhouse gases such as Carbon dioxide, it is increasing to find ways to consume these gases. Carbon dioxide may be used as a profound resource for

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manufacturing commercially viable products through carbonation reaction. The fixation of carbon dioxide is one of the important processes which consumes CO_2 as primary material [18]. Carbon dioxide fixation is carried out in the presence of various catalysts such as, Alkaly ammonium halides [19], halide salts [20], ionic liquid salts [21–24], polymeric ion liquid [25], quaternary phosphonium salts [26,27], transition-metal complexes [28,29], and ion-exchange resins [30].This reaction may be carried out by a class of materials having epoxy group such as, epoxy resin [31], GMA based polymer [24,32,33], natural rubber [34], Vernonia Oil [35], and epoxidized Soybean Oil [36].

Cyclic carbonate, a result of reaction between CO_2 and epoxy group, is an important and attractive reaction in the variety of chemical systems. Because of high solubility, high boiling and flash point, low toxicity, and biodegradability, the cyclic carbonate is a useful aprotic solvent for paint stripping and cleaning [22]. The cyclic carbonates may react with various compounds such as, aromatic amines, alcohols, carboxylic acids and aliphatic alcohols, to synthesis polycarbonates and aliphatic amines to form urethane group [37].

CO_2 fixation reaction has been carried out on a bifunctional epoxy resin and the gel time, deflection temperature, impact resistant, dynamic viscosity, and mechanical properties have been investigated [31,38]. It is shown that, the gel time of the modified epoxy resin depends on the epoxy content and is less than that of unmodified epoxy resin. The reason is that, the activation energy of epoxy resin curing is higher than that of cyclic carbonate curing. The deflection temperature and the impact resistant of modified epoxy resin are higher than those of unmodified epoxy resin. The dynamic viscosity of the modified epoxy resin is also higher than that of unmodified epoxy resin due to the strong interactions between epoxy chains in modified epoxy resins. In the modified epoxy resin, the tensile strength and elongation at break are less than those of unmodified epoxy but the compressive strength and plastic strain are higher than those of unmodified epoxy resin.

In this work, an epoxy resin was modified using the carbon dioxide and bifunctional epoxy resin in the presence of methyl ethyl ketone as solvent and TBAB as catalysis, and characterized using FT-IR technique. Both unmodified epoxy resin (UME) and CO_2 fixation modified epoxy resin (CFME) were treated by organically modified clay (Cloisite® 30B). The effect of CFME polarity on the dispersion of organoclay for this new CFME/clay nano composite (CFMEN) was investigated. The curing behavior, dynamic mechanical properties, thermal stability and surface morphology of prepared resins were studied.

2. Experimental

2.1. Material

Chemical structures of technical-grade epoxy, curing agent and catalyst are shown in Table 1. A commercial grade epoxy resin mainly based on diglycidyl ether bisphenol A (DGEBA) with 185-192 EEW was cured with diethylene triamine in the presence of tetra-n-butyl ammonium bromide as catalyst. Organo-montmorillonite (Cloisite 30B) from Southern Clay Products was used as nanoclay. Reactive diluent (3,4 epoxy cyclo hexyl methyl -3,4 epoxy-cyclo hexane carboxylate) (ECC) was used to reduce the viscosity of system. Methyl ethyl ketone (MEK) was used as solvent provided by DAE Jung.

2.2. Preparation of CO_2 fixation modified epoxy resin (CFME)

65 g of epoxy resin, 3gr TBAB and 65 g MEK were poured into a flask and mixed at 78 °C for 1 h, and then CO_2 was purged into the vessel. CO_2 fixation reaction was conducted in two successive steps, after 160 min and 225 min respectively, 25% (25%CFME) and 39% (39%CFME) cyclic carbonate were formed. Then 39 g reactive diluent was added to 25%CFME and 39% CFME.

2.3. Preparation of CO_2 fixation nano composite modified epoxy resin (CFMEN) by solution method

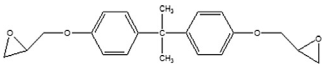
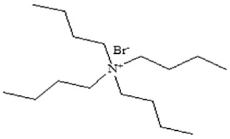
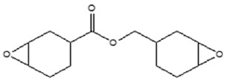
1%wt and 3%wt of cloisite 30B were added to MEK and sonicated for 10 min with a Bandelin HD3200 ultrasonic. The solution was added to CFME and vigorously mixed at 1700 rpm for 4 h. CFME was placed in a vacuum oven to remove the solvent, and then curing agent (DETA) was added by the weight ratio of 100:12 (DGEBA/hardener). The slurry mixtures were poured into aluminum molds and cured at 25 °C for 2 days and followed by post curing at 120 °C for two hours.

2.4. Characterization techniques

The curing behaviors of organoclay modified epoxy resin were studied using a differential scanning calorimeter (200-F3Maia) at heating rates of 8, 10, 12 and 15 °C min^{-1} and at temperature range of 30–300 °C.

The dynamic mechanical properties and the glass transition temperature were determined using a dynamic mechanical analyzer (TRITEC 2000 DMA) in a bending mode with

Table 1
Technical-grade epoxy, curing agent, catalyst and reactive diluents used in this study.

Material	Chemical structure	Chemical name	Commercial name
Epoxy resin		Diglycidyl ether bisphenol A (DGEBA)	EPON 828
catalyst		Tetra n-butyl ammonium bromide	TBAB
Reactive diluent		3,4 epoxy cyclo hexyl methyl -3,4 epoxy-cyclo hexane carboxylate(ECC)	Cyclo aliphatic reactive diluent
Curing agent	$_2\mathbf{HNCH_2CH_2NHCH_2CH_2NH_2}$	Diethylenetriamine	DETA

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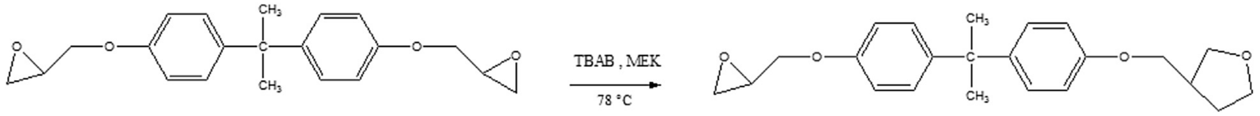

Scheme 1. CO_2 fixation reaction on epoxy resin.

0.01displacement at a frequency of 1 Hz, and temperature range of 30–250 °C with a scan rate of 5 °C min^{-1}. The sample size was $1.17 \times 5.15 \times 10.9$ mm^3.

The cyclic carbonate group and its content were determined by FT-IR. The uncured and cured samples in liquid and powder forms were analyzed with an EQUINOX 55 spectrometer using KBr pellets.

The thermal stability of cured samples was investigated with a TGA-PL 1500 analyzer at temperature range of 25–800 °C and at heating rate of 15 °C min^{-1} in a nitrogen atmosphere.

X-ray diffraction (XRD) were performed using X'pert MPD Philips Holand with Co Ka radiation, ($\lambda = 1.788$ Å) operating at 40 kV and 40 mA. The diffraction pattern was adjusted between angles (2Θ) of 1–10° at a step size of 0.02°. A powder samples and epoxy plates with size of $20 \times 10 \times 1$ mm^3 were used.

The morphology of modified epoxy resin nanocomposite was examined with a WEGA TESCAN scanning electron microscope.

TEM image were performed by CM200 Philips Holand operating at 200 kV. The Sample preparation was performed by ultramicrotom instrument (commercial name Leica-EM UC7 American) with 20 nm thickness at −80 °C.

3. Results and discussion

3.1. FT-IR

The reaction of epoxy resin with CO_2 in the presence of TBAB and MEK at 78 °C is illustrated in Scheme 1.

The reaction of CO_2 fixation was characterized by IR spectra. Fig. 1 shows the UME and CFME spectra with absorption bands at 914 cm^{-1} and 1185 cm^{-1} corresponding to the stretching vibration of epoxy group, and absorption bands at 1800 cm^{-1} and 1070 cm^{-1} corresponding to the C═O stretching vibrations in the 1,3-dioxolan-2-one ring (cyclic carbonate) and vibrations of the ring [38]. As shown in Fig. 1, the intensity of epoxy peak (914 cm^{-1}) is decreased during the CO_2 fixation reaction.

The conversion of the CO_2 fixation reaction was calculated by Eq. (1) [39].

$$\%\text{cyclic carbonate} = 1 - \frac{(S_e/S_b)_{\text{modified epoxy}}}{(S_e/S_b)_{\text{UME}}} \quad (1)$$

Where, S_e and S_b are the area of the epoxide group peak and benzene group peak (reference peak) respectively. The cyclic carbonate % development in the CO_2 fixation reaction is showed in Fig. 2.

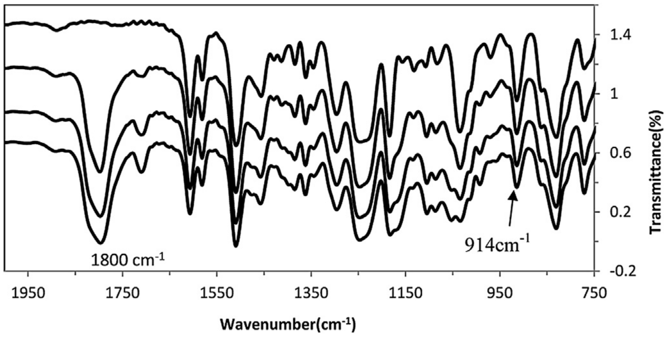

Fig. 1. IR spectra of UME and CFME, A:UME, B:16%CFME, C:25%CFME, D:39%CFME.

3.2. X-ray diffraction (XRD)

Fig. 3 shows the XRD pattern of cloisite 30B, UME, and CFMEN with various content of CO_2 fixation. The XRD pattern of Cloisite 30B shows diffraction peak corresponding to the (001) plane at 18.47 Å. The XRD pattern of UME/1%clay does not show the same peak, this is due to the exfoliation of organoclay in the matrix [5,7,8]. On the other hand, the EDAX pattern shows a good distribution of organoclay into the matrix (Fig. 4). The XRD pattern of 39%CFMEN/1%clay shows a diffraction peak at 17.38 Å. This confirmed that the organoclay is not exfoliated. It is suggested that CO_2 fixation reaction increases the polarity of epoxy resin due to the high polarity of cyclic carbonates. These polar groups raise strong interactions among epoxy chains. Because of presence of long aliphatic chain in the chemical structure of Cloisite 30B, (T in Scheme 2) the epoxy chains with high polar cyclic carbonates cannot penetrate into the galleries of nanoclay.

3.3. Kinetics of curing

Because the epoxy curing is a complex and multi-step process, its apparent activation energy varies with the curing temperature

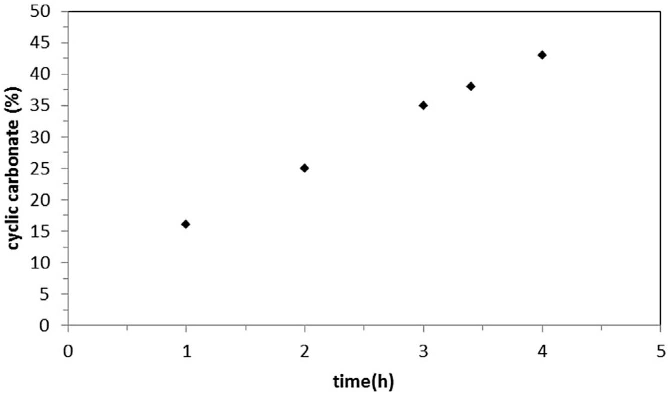

Fig. 2. Cyclic carbonate % vs. time of reaction.

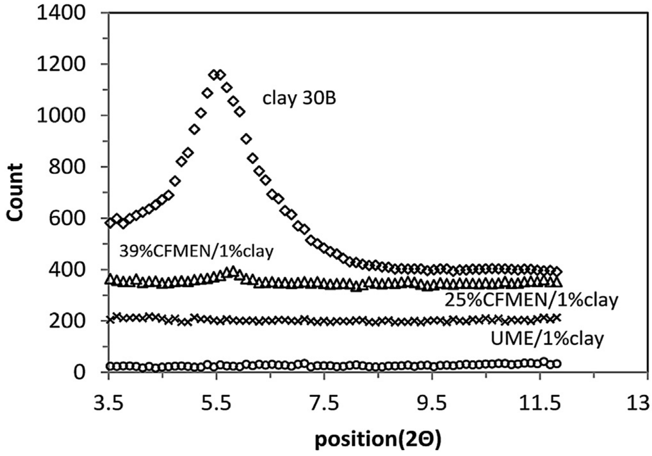

Fig. 3. XRD pattern of UME and CFMEN.

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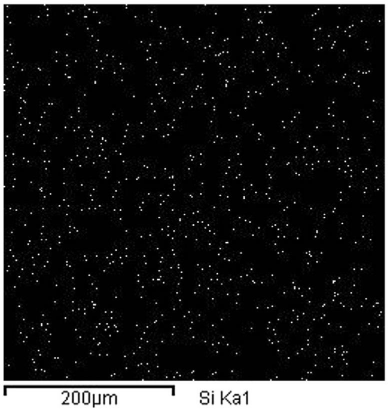


Fig. 4. EDAX. distribution of 1%clay in UME.

program. The curing process involves several steps but, at each temperature region, only one of them determines the overall kinetics. In fact, the activation energy is changed due to the variation of rate-determining step of reaction. The use of isoconversional methods allow determining the activation energy dependence without making any assumption about the reaction model [40–42]. For this reason, these methods are frequently reffered to as model-free methods. In other words, isoconversional methods describe the kinetics of curing by using multiple single-step kinetic equations, each of them is associated with a certain extent of conversion. Therefore, these methods allow complex (i.e., multi-step) process to be detected via a variation of E_α with α. Conversely, independence of E_α on α is a sign of a single-step process [43].

The rate of a single-step reaction can be expressed as a function of the temperature, *T*, and the extent of conversion, α, as follows:

$$\mathrm{d}\alpha/\mathrm{d}t = k(T)f(\alpha) \tag{2}$$

Where $k(T)$ is the rate constant, $f(\alpha)$ is the reaction model and *t* is the time. The rate constant is commonly described by Arrhenius equation:

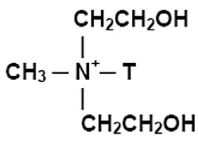
$$K(T) = A\exp\left(-\frac{E}{RT}\right) \tag{3}$$

Where *A* and *E* are the intrinsic pre-exponential factor and the intrinsic activation energy respectively, and *R* is the universal gas constant.

The fundamental assumption of the iso-conversional methods is that the reaction model $f(\alpha)$, as defined in Eq. (2), does not depend on the temperature or heating rate. Therefore, the reaction rate, $d\alpha/dt$, at a given extent of conversion is only a function of temperature as [44];

$$\left[\frac{\partial Ln(d\alpha/dt)}{\partial T^{-1}}\right]_\alpha = -E_\alpha/R \tag{4}$$

Where the subscript α indicates iso-conversional values.



$$CH_3-\overset{\displaystyle CH_2CH_2OH}{\underset{\displaystyle CH_2CH_2OH}{N^+}}-T$$

Scheme 2. The chemical structure of Cloisite 30B organic modifier.

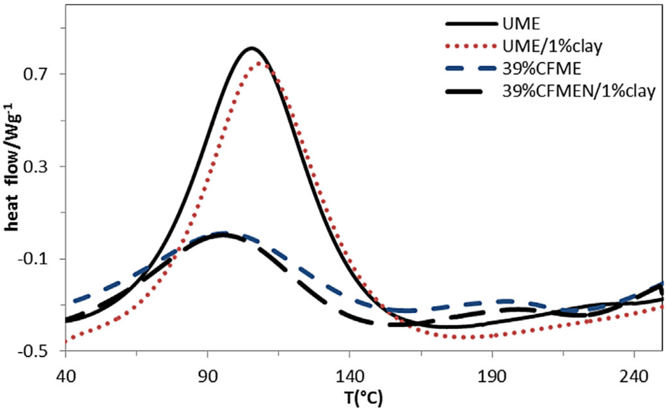


Fig. 5. DSC thermograms for epoxy and modified epoxy materials at heating rate of 10 °C min^{-1}.

An advanced nonlinear integral iso-conversional method has been developed by Vyazovkin [45,46]. According to this method, for two experiments carried out at two constant heating rates of β_1 and β_2 the E_α value is determined as a value that minimizes the function $\Phi\,(E_\alpha)$:

$$\phi(E_\alpha) = \frac{I(E_\alpha, T_{\alpha,1})\beta_2}{I(E_\alpha, T_{\alpha,2})\beta_1} + \frac{I(E_\alpha, T_{\alpha,2})\beta_1}{I(E_\alpha, T_{\alpha,1})\beta_2} \tag{5}$$

Where

$$I(E_\alpha, T_{\alpha,i}) = \int_{T_{\alpha-\Delta\alpha,i}}^{T_{\alpha,i}} \exp[-E_\alpha/RT]\mathrm{d}T \quad i = 1,2 \tag{6}$$

$T_{\alpha,1}$ and $T_{\alpha,2}$ are the experimental temperatures at given extent of conversion α for two typical experiments #1 and #2 respectively, and $I(E,T)$ is the temperature integral which may be solved numerically. A computer code was developed based on the genetic algorithm to minimize $\Phi(E_\alpha)$, as defined in Eq. (5), for α values between 0.01 and 0.99 with a step size of $\Delta\alpha = 0.01$

The dynamic DSC experiments were conducted for UME, UME/clay, CFME and CFMEN at four heating rates of 8, 10, 12 and 15 °C min^{-1}. The DSC thermograms for samples run at 10 °C min^{-1} are shown in Fig. 5. It is clearly observed that the shape of the UME thermogram is noticeably changed due to the CO_2 fixation process.

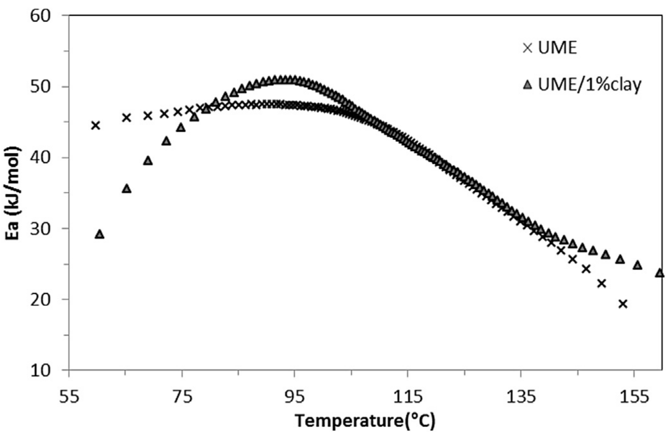


Fig. 6. E_α vs temperature for UME and UME/1%clay.

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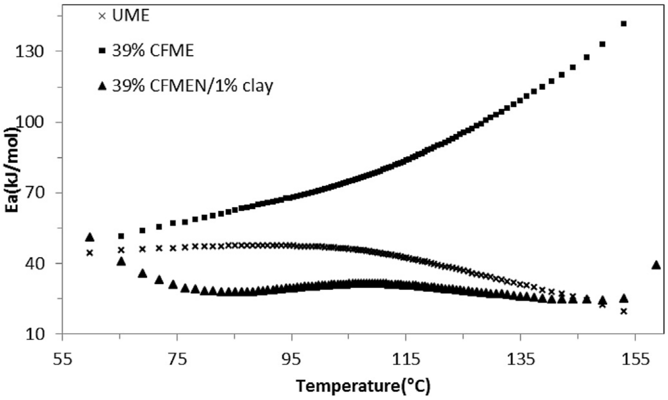

Fig. 7. E_α vs temperature dependences for UME, 39%CFME and 39%CFMEN/1%clay.

This suggests a possible modification of the cure mechanism and so of the activation energy due to the presence of cyclic carbonate groups. On the other hand, the shape of the thermograms is slightly changed due to the modification with nanoclay.

Fig. 6 shows the E_α dependences evaluated using the advanced nonlinear integral iso-conversional method of Eqs. (5) and (6) for DSC data of UME and UME/1%clay systems. The value of E_α obtained at the beginning of curing for UME ($\sim$46 kJ mol^{-1}) consists with the value obtained for primary amine/epoxy system [47]. We may note that the two systems have relatively the same E_α dependency. This indicates that the curing mechanisms have probably not been changed due to the presence of nanoclay. According to Scheme 2, cloisite 30B does not have the primary or secondary ammonium cations (RNH_2^+ or NH_3^+) so it could not act as epoxy ring-opening initiator to produce primary or secondary amine which entering in competition with DETA curing agent. As Fig. 6 shows, the E_α values at low temperatures ($50 < T < 80$ °C) for UME/1%clay is lower than that of UME. This is due to the fact that the DETA molecules penetrate into the intercalated interlayer space of 30B first, then reacts with epoxy molecules. Therefore, at early stages, the curing process is diffusion controled and the activation energy may be assigned to the diffusion which is about 20 kJ mol^{-1}.

Fig. 7 shows the E_α dependences for UME, 39%CFME and 39% CFMEN/1%clay. The illustrated results clearly show that the mechanisms of curing are dramatically changed due to CO_2 fixation. Both UME and 39%CFME at the beginning of the curing have the same E_α value ($\sim$46 kJ mol^{-1}). But with proceeding of the cure reaction the E_α value for 39%CFME increases to a high value ($\sim$140 kJ mol^{-1}) which is not similar to that of the epoxy resins. This high value may be due to the presence of cyclic carbonate group. According to Fig. 7, the E_α dependency for 39%CFMEN/1% clay is significantly changed compared with 39%CFME. In this case, the mechanism of the cure reactions has considerably changed due to the presence of 30B. The E_α for this system is about 30 kJ mol^{-1} and practically independent of temperature (or extent of conversion), which indicates that the rate of curing is controlled by a single step.

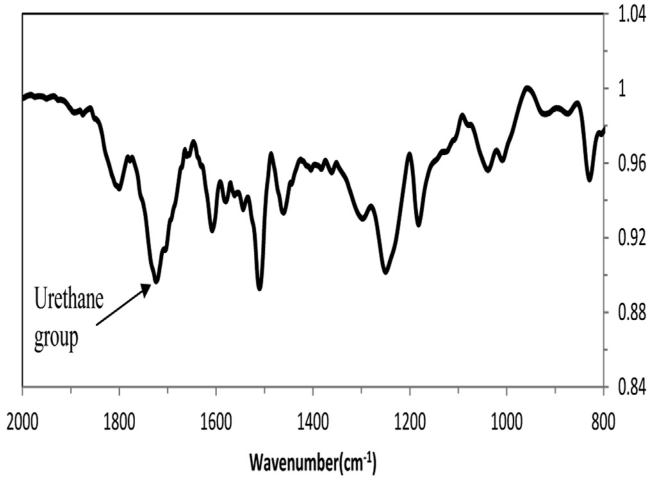

Fig. 9. IR spectrum of cured modified epoxy resin with DETA.

3.4. Curing of CFME

Cyclic carbonate groups can react with primary and secondary amines [34]. UME, CFME and CFMEN were cured with DETA. The reactive diluents (R.D) was also used because the viscosity of mixture was high. The EEW of epoxy/reactive diluent mixture was calculated by Eq. (7) [48].

$$E.E.W\ \text{of Mixture} = \frac{\text{Total Weight of Mixture}}{\text{Weight}\cdot 1/E.E.W(R.D)+\text{Weight}\cdot 2/E.E.W(\text{resin})} \tag{7}$$

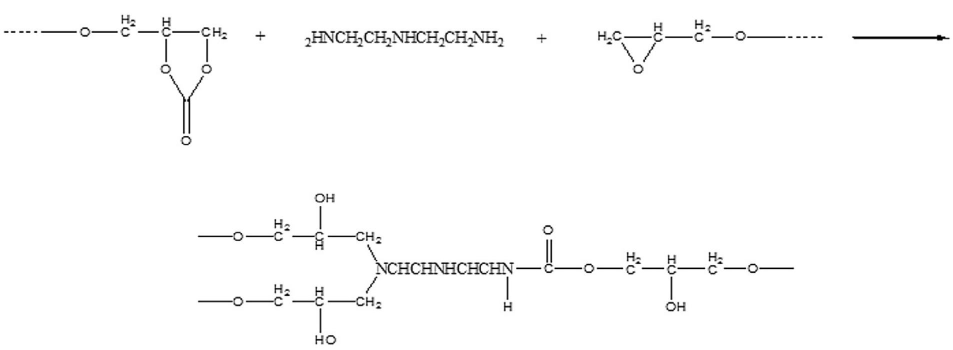

Fig. 8. reaction of DETA with epoxy and cyclic carbonate.

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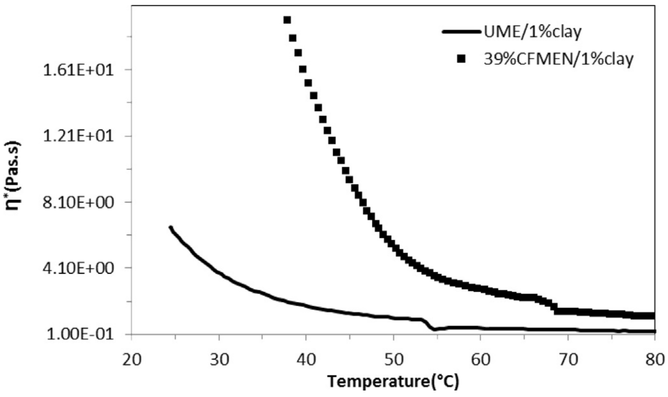

Fig. 10. reduction of viscosity of 39%CFMEN/1%clay and UME/1%clay.

Fig. 8 shows the reaction of DETA with cyclic carbonate and epoxy group that produce urethane group. The reaction of cyclic carbonate group with amine group of curing agent is faster than that of epoxy group with amine group of curing agent, so the gel time of modified epoxy resin is lower than that of UME [34].

Fig. 9 shows the IR spectrum of CFME after curing with DETA. The reaction of primary and secondary amine with cyclic carbonate produces urethane group and the peak of epoxy group is omitted [34]. In this spectrum, absorption band at 1724 cm^{-1} is corresponding to the stretching vibration of urethane group in cured CFME.

3.5. Rheometry

Fig. 10 shows the complex viscosity versus temperature curves for UME/1%clay and 39%CFMEN/1%clay. With increasing temperature, the hydrogen bonds are broken and the viscosity of resins is decreased. The rate of viscosity decreasing for 39% CFMEN/1% clay is higher than that for UME/1%clay. This clearly demonstrated that the number of hydrogen bonding sites in 39%CFMEN/1%clay is higher than that of UME/1% clay [42,49].

3.6. Dynamic mechanical properties

The dynamic mechanical properties were measured by DMA accomplished from 25 °C to 280 °C to investigate simultaneously the effect of organoclay and CO_2 fixation on T_g and the crosslink density of nano composite. Tan δ versus temperature for the epoxy resin/organoclay at various cyclic carbonate content is shown in Fig. 11.

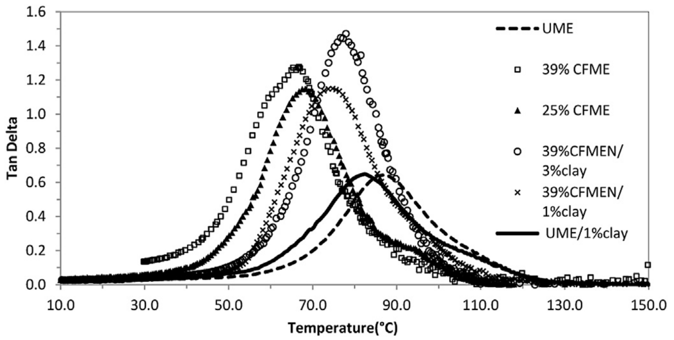

Fig. 11. Tan δ versus temperature of epoxy resin with various cyclic carbonate content and nano clay percentage.

Table 2
T_g, G' and ρ of UME and CFME with various cyclic carbonate content and nano clay percentage.

Modified epoxy resin	T_g(°C)	G'(MPa s)	ρ(mol cm^{-3})
UME	85.3	9.81	3E -3
39%CFME	64.9	3.51	1.07E -3
25%CFME	69.1	3.54	1.08E -3
39% CFMEN/3%clay	76.1	1.94	5.9E -4
39%CFMEN/1%clay	72.7	3.04	9.3E -4
UME/1%clay	79	10.1	3.09E -3

The glass transition temperature (T_g), storage modulus (G') and the crosslink density (ρ) were determined from the DMA curves as listed in Table 2.

The crosslink density is calculated by Eq. (8) [7];

$$\rho = G'/RT \tag{8}$$

Where ρ is the crosslink density expressed in mol cm^{-3}, G'; the shear storage modulus of resin at temperature above T_g, R is the universal gas constant (8.314472 J K^{-1} mol^{-1}), and T is the absolute temperature (K) at which the experimental modulus was determined.

As shown in Table 2, the ρ value was slightly decreased by increasing cyclic carbonate content because the N—H of urethane group was produced through the reaction of primary amine and cyclic carbonate does not continue the curing reaction. But in the reaction of primary amine and epoxy group, both N—H groups are reacted with each epoxy groups [27,34].

According to Table 2, the T_g of UME (85.3 °C) is higher than that of 39% CFME (64.9 °C). This is due to the CO_2 fixation that results in reduction of crosslink density. As shown in Fig. 6, the CO_2 fixation is caused to vanish the diffusion regime. This also demonstrates that the CO_2 fixation has reduced the crosslink density of cured samples [34]. As shown in Table 2, the presence of organoclay has reduced the T_g of UME. This may be attributed to the organoclay plates which act as physical barriers and do not allow to form a high density network [7]. But the presence of clay in CFME increases T_g due to the strong interaction between polar carbonyl groups in the matrix and OH groups in clay. As seen in Table 2, the T_g of 39%CFMEN/3% clay (76.1 °C) is higher than that of 39%CFMEN/1%clay because of more interactions between organoclay and carbonyl groups [49].

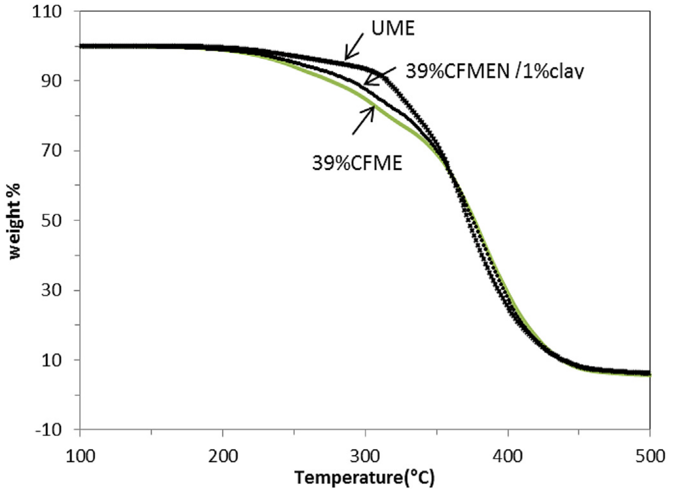

Fig. 12. TGA spectra of UME, CFME and CFMEN.

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Table 3
Thermal stability parameters of neat and modified epoxy resin.

Epoxy resin	IDT (95%)	T_{max} (°C)	E_d (kJ mol^{-1})	% char
UME	279	377	12.46	4.15
39% CFMEN/1%clay	251	393	11.01	3.52
39% CFME	243	389	8.87	5.11

3.7. Thermal stability

Fig. 12 shows TGA curves (the residual weight percentage versus temperature) of neat and modified epoxy resin at nitrogen atmosphere. These curves show the effect of CO_2 fixation and organoclay on thermal stability. Thermal stability parameters including the initial degradation temperature (IDT), the temperature at the maximum rate of weight loss (T_{max}), the decomposition activation energy (E_d) and % char for UME, CFME and CFMEN are shown in Table 3. The IDT of UME (279 °C) is higher than that of CFME (243 °C) because crosslink density of UME is higher than that of CFME [34]. Due to the formation of urethane polar groups in CFME and creation robust interactions between chains, the T_{max} of CFME is higher than that of UME [50]. The IDT and T_{max} of 39%CFMEN/1% clay are higher than those of 39%CFME, due to presence of carbonyl groups in 39%CFMEN/1%clay have interaction with nanoclay layers, so epoxy chains present between the clay layers undergo the restricted segmental motion which reflected in higher thermal stability properties than the UME [6,7].

The decomposition activation energy was calculated using the integral method of Coats and Redfern through calculating the slope of Ln(α/T^2)versus ($-1/T$). The equation of Coats and Redfern (Eq. (9)) is given as follows [6]:

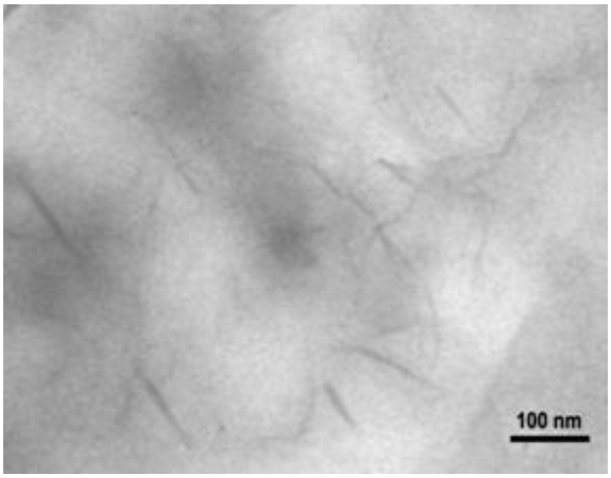

Fig. 14. TEM image of UME/1%clay nanocomposite.

$$\ln\alpha\Big/T^2 = \ln\frac{AR}{\beta E_d}\left(\frac{1-2RT}{E_d}\right) - E_d/RT \qquad (9)$$

Where α is the decomposed fraction, T the degradation temperature (K), A the pre exponential factor, β the heating rate (K min^{-1}),

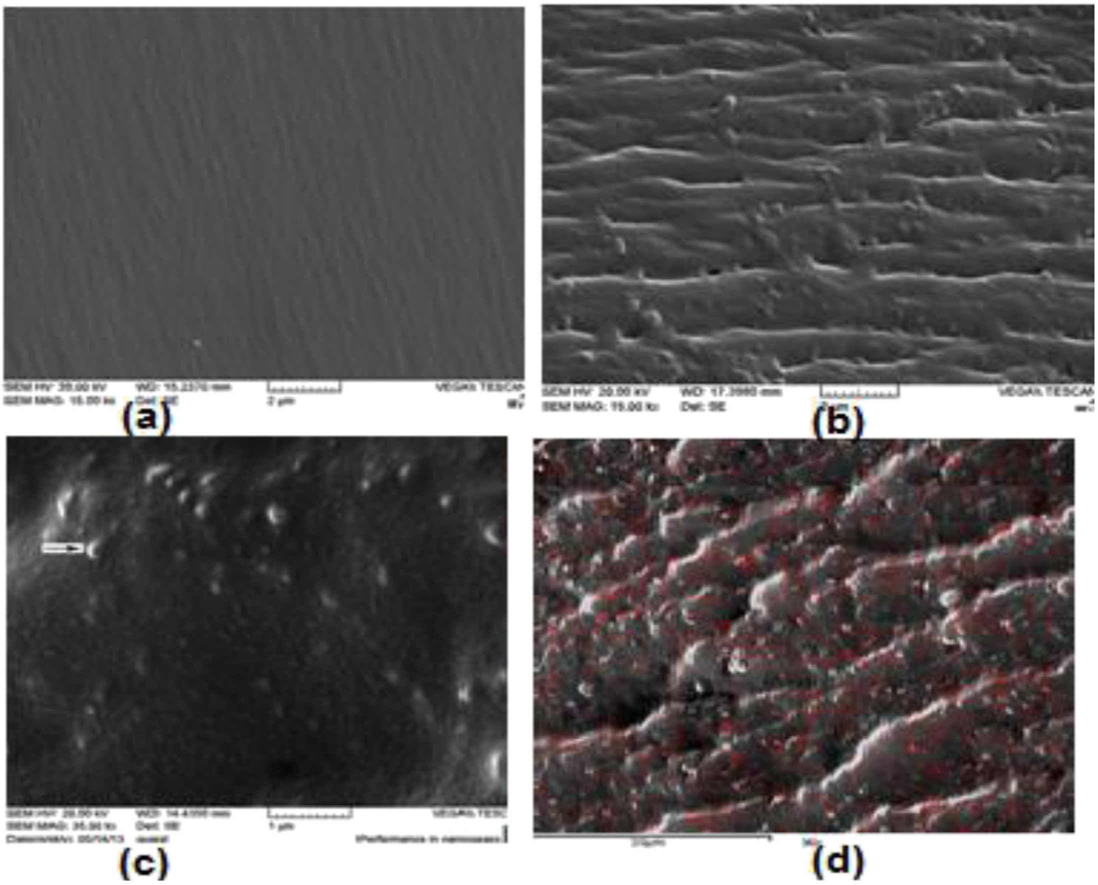

Fig. 13. fracture surface morphology (a)UME. (b):39% CFME. (c):39%CFMEN/1% clay.(d):EDAX of 39%CFMEN/1% clay.

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E_d the decomposition activation energy (kJ mol^{-1}), and R the gas constant [8.3146 J/(mol^{-1} K^{-1})].

The activation energy of UME (12.46 kJ mol^{-1}) is higher than those of CFME (8.87 kJ mol^{-1}) and CFMEN (11.01 kJ mol^{-1}) due to the crosslink density of CFME and CFMEN is lower than that of UME.

3.8. Scanning electron microscopy

Fig. 13 shows the surface morphology of UME, 39%CFME and 39%CFMEN/1%clay using electron microscope technique. UME shows a smooth and flat fracture surface morphology due to the brittle structure [7] (Fig. 13(a)). 39%CFME shows a non-smooth fracture surface morphology because its crosslink density is lower than that of UME (Fig. 13(b)). Fig. 13(c) show good dispersion of nano particle with size 58 nm in epoxy matrix. The EDAX image of fracture surface of 39%CFMEN/1% clay shown by Fig. 13(d) confirms a well dispersion of organoclay particles in epoxy matrix.

3.9. Transmission electron microscopy

Fig. 14 shows the cross-section of UME/1%clay which indicate that MMT is well exfoliated in epoxy matrix. The dark line in Fig. 14 are cross-section of single or multiple nano clay plates that reveal good distribution of silicate layer in matrix, which the average thickness of MMT plates are approximately 4 nm and the average length are 140 nm. Based on analysis of XRD and TEM, the exfoliated structure of UME was confirmed.

4. Conclusions

In this study, a bifunctional epoxy resin was modified using CO_2 fixation process and then Cloisite 30B as a nano additive was incorporated into the CO_2 fixation modified epoxy resin (CFME) to obtain CFME/clay nano composite (CFMEN). The FT-IR spectra showed that cyclic carbonate and urethane groups, were formed before and after curing. The XRD results showed that the organoclay was not exfoliated in the CFME matrix but it was exfoliated in the unmodified epoxy resin. The cure kinetic behavior was significantly influenced by CO_2 fixation and nanoclay. The viscosity variation demonstrated that the number of hydrogen bonds in CFMEN is higher than that in unmodified epoxy/nanoclay mixture. The dynamic mechanical analysis showed that the presence of nanoclay in CFMEN leads to an increase in T_g, while in unmodified epoxy leads to an decrease in T_g. The CO_2 fixation reaction and the presence of nano clay increased the temperature at the maximum rate of weight loss (T_{max}) and reduced the initial degradation temperature (IDT) of epoxy resin. CO_2 fixation reaction reduced decomposition activation energy of epoxy resin. Scanning electron microscopy showed a smooth and flat fracture surface morphology for unmodified epoxy and a non-smooth fracture surface morphology for CFME. TEM image is confirmed the exfoliated UME/1%clay nanocomposite.

References

[1] M.S. Bhatnagar, The Polymeric Materials Encyclopedia, first ed., CRC Press, 1996.
[2] F.H. Gojny, M.H.G. Wichmann, U. Kopke, B. Fiedler, K. Schulte, Compos. Sci. Technol. 64 (2004) 2363–2371.
[3] A. Strauchs, A. Mashkin, A. Schnettler, IEEE Trans. Dielectr. Electr. Insul. 19 (2) (2012) 400–407.
[4] S. Qi Ma, W. Qu Liu, Ch. Hui Hu, Zh. Fang Wang, Iran. Polym. J. 19 (3) (2010) 185–196.
[5] S. Sinha Ray, M. Okamoto, Prog. Polym. Sci. 28 (2003) 1539–1641.
[6] J.Y. Lee, H.K. Lee, Mater. Chem. Phys. 85 (2004) 410–415.
[7] M. Jun, X. Jian, R. Jian-Hui, Y. Zhong-Zhen, M. Yiu-Wing, Polymer 44 (2003) 4619–4624.
[8] X. Kornmann, H. Lindberg, L.A. Berglund, Polymer 42 (2001) 1303–1310.
[9] Ali Olad, Polymer/Clay Nanocomposites, first ed., University of Tabriz,129–133, 2011.
[10] G. Baochun, J. Demin, C. Changgeng, Eur. Polym. J. 40 (2004) 1743–1748.
[11] M. Suguna Lakshmi, B. Narmadha, B.S.R. Reddy, Polym. Degrad. Stab. 93 (2008) 201–213.
[12] K.P. Unnikrishanan, Cochin University of Science and Technology, 34, 2006.
[13] S. Zunjarrao, R. Singh, Compos. Sci. Technol. 66 (2006) 2296–2305.
[14] B. Wetzel, P. Rosso, F. Haupert, K. Friedrich, Eng. Fract. Mech. 73 (2006) 2375–2398.
[15] A. Omrani, L.C. Simon, A.A. Rostami, Mater. Chem. Phys. 114 (2009) 145–150.
[16] S.H. Lim, K.Y. Zeng, C.B. He, Mater. Sci. Eng. A 527 (2010) 5670–5676.
[17] J. Baller, M. Thomassey, M. Ziehmer, R. Sanctuary, Thermochim. Acta 517 (2001) 34–39.
[18] M. Aresta, Carbon Dioxide as Chemical Feedstock, first ed., Wiley, Germany, 2010.
[19] V. Calo, A. Nacci, A. Monopoli, A. Fanizzi, Org. Lett. 4 (2002) 2561–2563.
[20] N. Kihara, N. Hara, T. Endo, J. Org. Chem. 58 (1993) 6198–6202.
[21] M. Yoshida, M. Ihara, Chem. Eur. J. 10 (2004) 2886–2893.
[22] T. Yu, G. Weiss, Green. Chem. 14 (2012) 209–216.
[23] Z. Anlian, J. Tao, H. Buxing, Z. Jicheng, X. Ye, M. Xiumin, Green. Chem. 9 (2006) 169–172.
[24] D. Won Park, N. Young Mun, H. Young Ju, Y. Choe, S. Wook Park, Stud. Surf. Sci. Catal. 159 (2006) 865–868.
[25] S. Ghazali-Esfahani, H. Liu, P.J. Dyson, Z. Fei, H. Song, G. Laurenczy, E. Paunescu, M. Bagherzadeh, F.D. Bobbink, N. Yan, Green. Chem. 15 (2013) 1584–1589.
[26] T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda, T. Sakakura, Chem. Commun. 15 (2006) 1664–1666.
[27] J.S. Tian, C.X. Miao, J.Q. Wang, et al., Green. Chem. 9 (2007) 566–571.
[28] T. Sakai, Y. Tsutsumi, T. Ema, Green. Chem. 10 (2008) 337–341.
[29] C.X. Miao, J.Q. Wang, Y. Wu, Y. Du, L.N. He, Chem.Sus.Chem 1 (3) (2008) 236–241.
[30] R.A. Watile, K.M. Deshmukh, K.P. Dhake, B.M. Bhanage, Catal. Sci. Technol. 2 (2012) 1051–1055.
[31] G. Rokicki, C. Wojciechowski, J. Appl. Polym. Sci. 41 (1990) 647–659.
[32] B. Ochiai, Y. Hatano, T. Endo, Macromolecules 41 (2008) 9937–9939.
[33] S. Yamamoto, K. Kawabata, O. Moriya, T. Endo, J. Polym. Sci. A Polym. Chem. 43 (2005) 4578–4585.
[34] S. Kawahara, T. Saito, J. Polym. Sci. A Polym. Chem. 44 (2006) 1561–1567.
[35] N. Mann, K. Mendon, W. Rawlins, F. Thames, J. Am. Oil Chem. Soc. 85 (2008) 791–796.
[36] P. Parzuchowski, M. Jurczyk-Kowalska, J. Ryszkowska, G. Rokicki, J. Appl. Polym. Sci. 102 (2006) 2904–2914.
[37] J.H. Clements, Am. Chem. Sci 20 (2003) 184–196.
[38] G. Rokicki, M. Lewandowski, Die Angew. Makromol. Chem. 148 (1987) 53–66.
[39] F. Long Jin, S. Jin Park, Bull. Korean. Chem. Soc. 30 (2) (2009) 334–338.
[40] H.L. Friedman, J. Polym. Sci. C 6 (1964) 183–195.
[41] T. Ozawa, Thermochim. Acta 203 (1992) 159–165.
[42] M.J. Starink, Thermochim. Acta 404 (2003) 163–176.
[43] S. Vyazovkin, N. Sbirrazzuoli, Macromol. Rapid Commun. 27 (2006) 1515–1532.
[44] S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Perez-Maqueda, C. Popescu, N. Sbirrazzuoli, Thermochim. Acta 520 (2011) 1–19.
[45] S. Vyazovkin, D. Dollimore, J. Chem. Inf. Comput. Sci. 36 (1996) 42–45.
[46] S. Vyazovkin, J. Comput. Chem. 18 (1997) 393–402.
[47] Y. Zhang, S. Vyazovkin, Macromol. Chem. Phys. 206 (2005) 1840–1846.
[48] Epoxy Chemicals Inc., www.epoxychemicals.com.
[49] S. Rock Lee, H. Man Park, H. Lim, T. Kang, X. Li, W. Jei Cho, C. Sik Ha, 43, 2002, 2495–2500.
[50] B. Ochiai, M. Matsuki, D. Nagal, T. Miyagawa, T. Endo, J. Polym. Sci. A Polym. Chem. 43 (2005) 584–592.

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