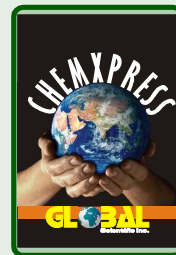




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Preparation and characterisation of short segment modifiers: Effect of modifiers and nanoclay on epoxy resins

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Abstract: The preparation and characterization of 10 tailored epoxides of 1, 4-, 1,5- and 1,6- methylene diols, bisphenol and hydroquinone with terephthalate or isophthalate backbones were reported. The solventless reaction of epoxides that have been tailor made with flexible and rigid segments systematically to enhance the properties of DGEBA epoxy resins were carried out systematically. The effect of these

newly synthesized epoxides and the nanoclay in improving the properties of conventional DGEBA/DDS systems were described by the analysis of thermal behaviour, thermal stability, mechanical properties, LC behaviour, degradation kinetic studies and structure morphology characteristic studies.

Keywords: Resins; Cure; Thermomechanical; Thermal properties.

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INTRODUCTION

Epoxy and its formulations occupy an important place in the class of thermosetting polymeric materials^[1,2]. These materials are identified as one of the best thermosetting polymers because of their good strength, excellent adhesion to variety of surfaces and good thermal properties^[3-9]. They find applications in various fields such as adhesives, coatings, structural materials, and printed circuit boards. Though epoxy resins are available in plenty, most of them suffer from poor damage tolerance properties. These drawbacks restrict them from finding applications in the areas where high mechanical strength materials are required. This is due to the formation of high crosslinking density polymers during the curing reaction of epoxies with amines. Hence, these materials are widely modified during the processes prior to curing^[10,11]. Therefore, many studies have been conducted to improve the impact and toughness of the cured networks, while retaining better properties.

There are two methods that can be followed to improve the strength of the DGEBA epoxy polymeric materials.

Method 1

The modification of DGEBA was carried out using the epoxies that have been designed and synthesised with flexible and rigid segments. It was well known from the literature that the thermoplastic polymers such as poly (aromatic ether), poly (sulfoxes), poly (ether sulfone), poly (sulphides), poly (ether ketone), and poly (acrylates) were added as tougheners to epoxy systems to improve the damage tolerance and toughness properties^[12]. However, these polymers possess high melt temperature and they could not be processed by the melt mixing methodology. They have poor solubility in organic solvents due to high molecular weights that lead to difficulties in discharge of organic solvents while processing. When the material was cured, the solvent that would entrap gets volatilized and leaves voids and/or irregularities in the matrix, which has reflected in decreasing their mechanical properties. These problems could be surmounted by the solventless procedure adopted for the incorporation of tailor made epoxies with backbones having flexible/or rigid segments^[13]. Further-

more, the tailored epoxies would help to improve the toughness similar to that of a thermoplastic modified epoxy resin. The rigid backbone having controlled molecular weights increases the T_g values and thermal resistance properties. The flexible structures though detrimental to the thermal properties, the mechanical properties such as impact and fracture toughness were improved. Nevertheless, the tailor made epoxies having aromatic and aliphatic backbones shows no compromise in the thermal property upon adding to the DGEBA. The epoxides with a rigid rod and flexible segments with ester as linking groups may form high crystallinity domains under certain conditions. The presence of mesogenic groups in the main chain and epoxy groups at the crosslinking end makes the tailored epoxides to be good candidates for self-reinforcing composite materials^[14-16].

Method 2

The preparation of polymer/clay nanocomposites is one of the well established areas of research^[17]. Dispersion of nanoclays in the epoxy resins have exhibited good toughening property in the cured polymer networks due to the nanosized platelets dispersed in the intercalated and exfoliated states^[18-22]. These modifications tend to increase toughness and impact strength properties of the epoxy systems. The aim here is to blend the epoxy resins with nanoclays to obtain composites with low crosslinking density.

The main focus of this work is to synthesize and characterize new epoxides having rigid and flexible segments built by using aromatic and aliphatic moieties in order to use as a reactive modifiers to the DGEBA. The synthesized epoxides were added to DGEBA/DDS and DGEBA/DDS/nanoclay systems and cured. The optical microscopic investigations were carried out to find out the ability of the epoxides to form mesophase. The prerequisite to get mesomorphic materials, the diepoxides should be linear and possess stiff or rigid benzene moieties linked through ester and methylene spacers. The physical, thermal and mechanical properties of these epoxy composites were studied. The morphological studies on the effect of addition of nanoclays to the different epoxide/DGEBA/DDS composites were carried out by SEM to investigate the phase behaviour of blends. Thermogravimetric analysis was used to determine

the thermal stability, flame retardant properties and degradation kinetic mechanisms.

EXPERIMENTAL

Preparation of dihydroxy esters

The dihydroxy ester compounds were prepared by the reaction of 2 moles of diols with 1 mole of acid chloride. Rigid type dihydroxy esters were prepared by reacting aromatic diols like bisphenol A and or hydroquinone with either terephthaloyl chloride or isophthaloyl chloride. Similarly, flexible type dihydroxy esters were prepared by reacting aliphatic 1, 4-methylene, or 1, 5-methylene, or 1,6-methylene diols with either terephthaloyl chloride or isophthaloyl chloride.

(a) Typical procedure for the synthesis of a dihydroxy ester

To a three-necked flask fitted with a overhead stirrer, nitrogen inlet and a dropping funnel was charged 100mL of tetrahydrofuran and 90g (1 mol) of 1,4-butane diol and stirred. To the reaction mixture, a solution of terephthaloyl chloride 81.2g (0.4mol) in 50mL THF was added dropwise with stirring at 0°C. Further, 88.8g (0.88mol) of triethylamine was added dropwise by maintaining the temperature at 0°C. After the complete addition of triethylamine, the reaction was continued to stir for a period of 2h and the solution was poured into excess cold water. The precipitated solid product was filtered and dried in a hot air oven at 20°C. Recrystallization was carried out in a mixture of methanol and water (1/1 V/V). A white solid product 1, 4-[Di-(4-hydroxy butane)]-terephthalate (DHBT) was obtained and the yield was found to be 186g (H⁺ 60 %).

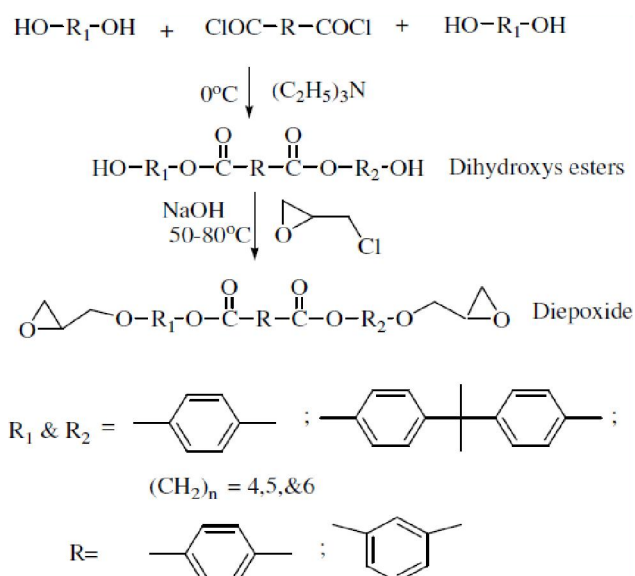
The other flexible dihydroxy esters namely 1,4-[Di-(5-hydroxy pentane)]-terephthalate (DHPT), 1,4-[Di-(6-hydroxy hexane)]-terephthalate (DHHT), 1,3-[Di-(4-hydroxy butane)]-isophthalate (DHBI), 1,3-[Di-(5-hydroxy pentane)]-isophthalate (DHPI) and 1,3-[Di-(6-hydroxy hexane)]-isophthalate (DHHI) were also prepared by employing the same procedure.

The rigid dihydroxy esters namely, 1,4-[Di-(4-hydroxy diphenyl-2,2'-propane)]-terephthalate

(DHDPT), 1,3-[Di-(4-hydroxy diphenyl-2,2'-propane)]- isophthalate(DHDPI), 1-1'-hydroxy bisphenyl-(4-hydroxy)-Phenyl terephthalate (HBPHPT), and 1-1'-hydroxy bisphenyl-(4-hydroxy)-Phenyl isophthalate (HBPHPI) were also prepared by employing the same procedure. The percent yield of all the compounds were found to be around 65%. All the dihydroxy esters were characterized by FT-IR, ¹H and ¹³C NMR spectroscopy. The presence of terminal hydroxyl groups in dihydroxy esters were analyzed using acetic anhydride titrimetric method^[23,24]. The average hydroxyl values for all the dihydroxy compounds were found were between 1.9 and 2.3.

Preparation of epoxides

The synthesis of diepoxides was shown in Scheme 1



Scheme 1 : Preparation of diepoxides.

(a) Typical procedure adopted for the synthesis of 1,4-[Di-(4-Glycidyloxy Butane)]-terephthalate (DGBT)

Into a flask fitted with a thermometer, condenser, nitrogen inlet and a dropping funnel 206.8g (2.23mol) of epichlorohydrin and 105g (0.34mol) of dihydroxy ester (DHBT) were taken. The reaction mixture was heated to 65°C and stirred for 3h. 40.65g (1.102mol) of NaOH (40% aqueous solution) was added, stirred at 70°C for 2h and cooled. The reaction mixture was washed several times with water to remove the re-

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sidial sodium chloride and excess reagents. The product was extracted with benzene and dried in vacuum at room temperature to evaporate the benzene. The product obtained was 57.2g ($\approx 40\%$).

Similarly, synthesis of other flexible epoxides, such as 1,4-[Di-(5- glycidyloxy pentane)]-terephthalate (DGPT), 1,4-[Di-(6- glycidyloxy hexane)]-terephthalate (DGHT), 1,3-[Di-(4- glycidyloxy butane)]-isophthalate (DGBI), 1,3-[Di-(5- glycidyloxy pentane)]-isophthalate (DGPI) and 1,3-[Di-(6- glycidyloxy hexane)]-isophthalate (DGHI)] were prepared.

The rigid epoxides namely, [1,4-[Di-(4- glycidyloxy diphenyl-2,20-propane)]-terephthalate (DGDPT), 1,3-[Di-(4- glycidyloxy diphenyl-2,20-propane)]- isophthalate(DGDPI), 1-1'- glycidyloxy bisphenyl-(4-hydroxy)-phenyl terephthalate (GBPGPT), and 1-1'- glycidyloxy bisphenyl-(4- glycidyloxy)-phenyl isophthalate (GBPGPI)] were prepared using the respective dihydroxy esters by employing the same procedure. All the products were characterized by FT-IR, ^1H and ^{13}C - NMR spectroscopic techniques. The epoxy equivalent weight (EEW) estimated by the titrimetric analysis were found to be 214 (theoretical: 211) for DGBT, 227(theo.: 223) for DGPT, 298(theo.: 297) for DGHT, 215(theo.: 211) for DGBI, 224(theo.: 223) for DGPI, 302(theo.: 297) for DGHI, 236(theo.: 235) for DGDPT, 216(theo.: 235) for DGDPI, 236(theo.: 234) for GBPGPT and 238(theo.: 234) for GBPGPI.

Preparation of unmodified systems (UM)

100 parts of DGEBA and DDS were taken in a stoichiometric ratio. To that 10 weight percent of tailor made epoxide, either DGBT or DGPT or DGHT or DGBI or DGPI or DGHI or DGDPT or DGDPI or GBPGPT or GBPGPI was blended thoroughly by stirring with glass rod. All the blends were cured at 140°C for 3h, 160°C for 2 h and followed by a post curing at 180°C for 4h and 200°C for 2h. These blends were denoted as unmodified (UM) systems because they are not blended with the nanoclay.

Preparation of modified nanocomposite systems (M)

The DGEBA and DDS blend was taken in a stoichiometric ratio (i.e., 1:1 equivalent weight ratio) and

10Wt % of epoxide namely either DGPT or DGHT or DGBI or DGPI or DGHI or DGDPT or DGDPI or GBPGPT or GBPGPI) was added. Then 5Wt % of nanoclay (Nanomer 1.30E) was taken separately in a 100ml beaker and was dispersed with required amount of acetone (10 to 100ml). The clay dispersion was sonicated for 4 hours, then transferred to 100ml RB flask and continued stirring for 30min. The obtained nanoclay dispersion was added to the DGEBA/DDS/epoxide mixture and stirred for 5 h continuously. After the homogenization, the solvent was removed by using rotavapour. The blend was kept in an oil bath which was preheated at 90°C and stirred slowly until it became transparent. The obtained prepolymer was poured into a stainless steel mold that was preheated at 140°C . All the blends were cured at 140°C for 3h, 160°C for 2 h and followed by a post curing at 180°C for 4h and 200°C for 2h. The cured casts were cut into suitable dimensions required for testing physical, chemical, thermal and mechanical properties. These blends were denoted here as modified systems since these modified with nanoclay. Thus, all the epoxide resin formulations were incorporated with 5 weight % nanoclay (Nanomer 1.30E) of the total weight (DGEBA/DDS/ Epoxide) as shown in TABLE 1.

TABLE 1 : The blend composition details of unmodified (UM), and modified (M) systems.

Components	Quantity of blends Ratio (w/w/w)	
	UM system	M system
DGEBA*/Epoxide**/Clay	100/10/0	100/10/5

*Diaminodiphenyl sulfone (DDS) curing agent was added at the stoichiometric ratio to DGEBA and epoxide respectively; **Epoxides namely DGPT or DGHT or DGBI or DGPI or DGHI or DGDPT or DGDPI or GBPGPT or GBPGPI was added as 10 wt % to the 100 wt % of DGEBA/DDS blends.

RESULTS AND DISCUSSIONS

Characterization of dihydroxy esters

(a) FT-IR spectral analysis of dihydroxy esters

The DGBT, DHPT, DHHT, DHBI, DHPI and DHHI dihydroxy ester formations were confirmed by IR spectra were reported^[25]. Similarly the absorption peaks for rigid dihydroxy esters DHDPT, DHDPI, HGPHT and HGPPI observed around 2965 cm^{-1}

¹were attributed to the aromatic CH stretching. Aromatic C-C ring stretching was observed between 1575 cm⁻¹ - 1428 cm⁻¹. The C=O and C-O stretches for esters in conjugation with phenyl group were showed at 1738 cm⁻¹ and 1070 cm⁻¹ respectively. The sharp peak around 727 cm⁻¹ was due to the -OH out of plane bending in aromatic -OH group. The wide peak at 3354 cm⁻¹ was due to ortho aromatic OH group. The peak around 1362 cm⁻¹ was attributed to isopropyl group. The m- and p-substitutions in the benzene ring indicated around 721 cm⁻¹ and 831 cm⁻¹ respectively.

(b) NMR spectral analysis of dihydroxy esters

(A) ¹H and ¹³C NMR of flexible dihydroxy esters

The chemical shift for OH protons was observed at 4 ppm. The methylene protons attached to the OH groups was observed around 3 ppm. The DHHT having 6 methylene groups showed the shift at 1.1 ppm. The resonance signal between 7 to 8 ppm was attributed to the aromatic protons. The shift values observed between 3.6 to 3.7 ppm was due to CO-CH₂ group.

The resonance signal in ¹³C NMR between 62 to 62.3 ppm was due to H₂C-OH carbon. The shift at 25-26 ppm was due to CH₂ group of second methylene carbon and third methylene carbon occurs at 26-27 ppm. The ester carbon appeared at 165 ppm. The aromatic carbons showed chemical shifts at 129-134 ppm.

(B) ¹H and ¹³C NMR of rigid dihydroxy esters

The ¹H-NMR spectra of DHDPT/ DHDPI/ HBPHPT/ HBPHPI showed a sharp shift at 1.5 ppm was due to the OH protons. The signals around 1.6 ppm was attributed to the methyl proton of isopropyl group. The shift for terephthalate linked protons occurred at 2.1 ppm. The signals for isophthalate linked protons were occurred around 2.5 ppm. The shifts for aromatic protons appeared around 6.7-8.1 ppm.

The ¹³C NMR spectra of DHDPT/ DHDPI/ HBPHPT/ HBPHPI have showed a chemical shift at 163 ppm was due to the carbonyl carbon of the ester group. The chemical signal at 30 ppm was attributed to carbon of the isopropyl group. The aromatic car-

bon signal attached to the ester group occurred at 147 ppm. The shift at 155 ppm was due to the aromatic carbons attached to the OH group. The signals for other aromatic carbons occurred at 126, 130 and 114 ppm.

Characterisation of epoxides

(a) FT-IR spectral analysis of epoxides

From the FT-IR spectra of the flexible epoxides (terephthalate and isophthalate based) and rigid epoxides the conversion of OH group into the corresponding epoxy group was observed by the appearance of peak at 915 cm⁻¹. The ester carbonyls were noted at 1715-1730 cm⁻¹. The appearance of aromatic -CH and aliphatic -CH groups around 3400 and 2900 cm⁻¹ was clearly seen.

(b) ¹H and ¹³C NMR spectral analysis of epoxides

The ¹H and ¹³C NMR spectra of terephthalate and isophthalate based flexible epoxides were shown in Figure 1(A) and 1(B). From the ¹H NMR spectra, a singlet shift at 1.6 ppm for the isopropylidene protons and the epoxy propyl protons of O-CH₂, CH and CH₂ were seen at 3.3, 4.3, 6.7 ppm and aromatic protons were observed around 7.3 ppm.

The ¹³C and ¹H -NMR and spectra of the rigid epoxides were given Figure 1(C). From the ¹³C NMR spectra, the aliphatic carbons representing the epoxy group were observed in the region of 41-70 ppm. The ester carbonyl present in both the systems was seen at 165 ppm. The aromatic carbons were mostly observed around 113-156 ppm. The characteristic shifts for the carbon atoms of the isopropyl group were observed at 30 and 45 ppm.

XRD characterization of modified systems

The WAXD patterns of the modified nanocomposite after curing were shown in Figure 2. The basal reflections, characteristics of the nanomer 1.30E clay appeared at 2θ = 3.58°, 8.12° in the lower angle regions^[26]. But, the reflection peaks for lower angle d (001) plane clay layer arrangement was not speculated in the nanocomposites, except DGDPT-M, GBPGPI-M, DGBT-M and DGBI-M. This observation suggested that a homogeneous and complete intercalation has been achieved. Some of the systems have showed a small swelling around 5°. This swelling

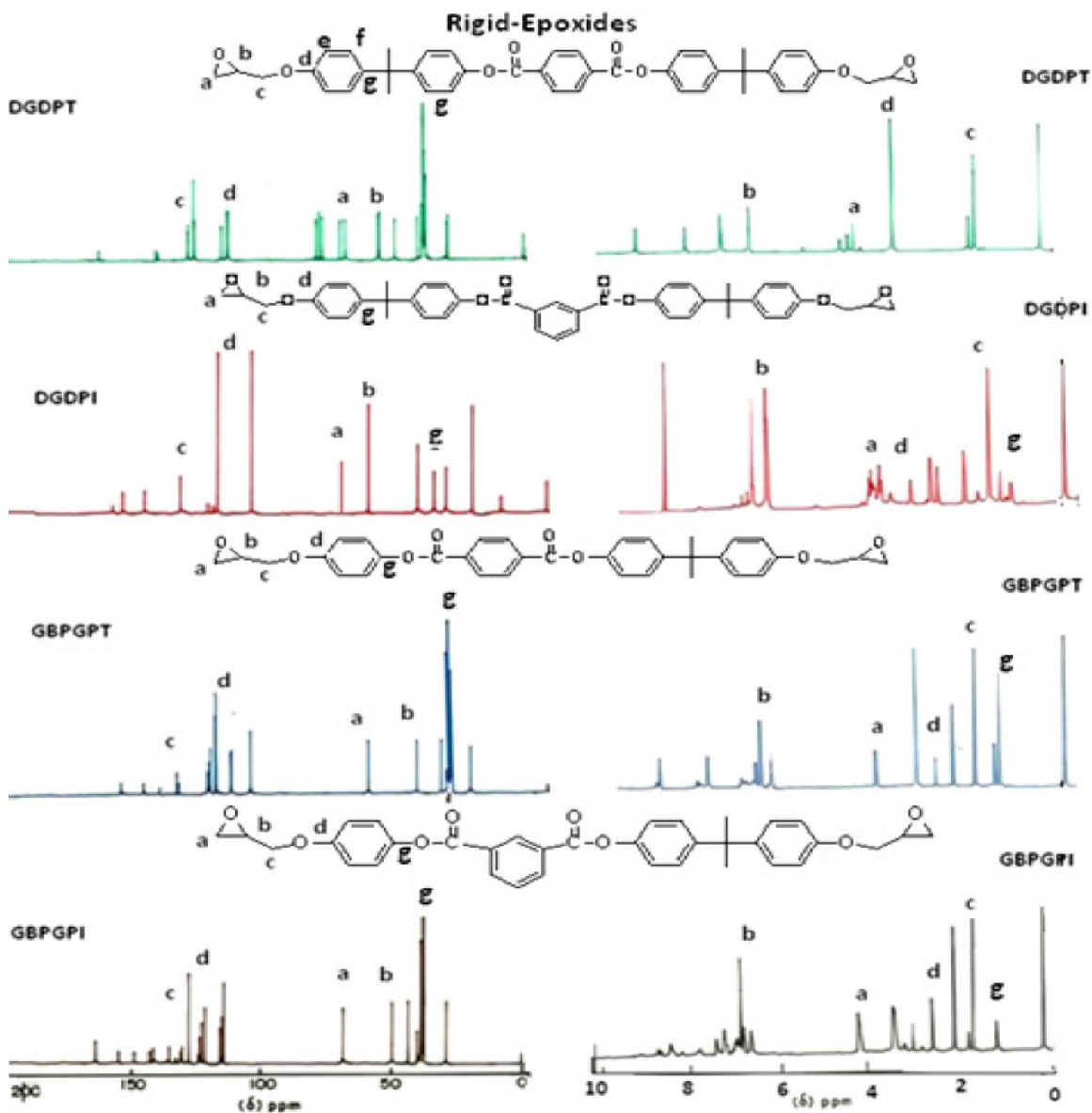


Figure 1(C) : ^{13}C and ^1H NMR and spectra of the rigid epoxides.

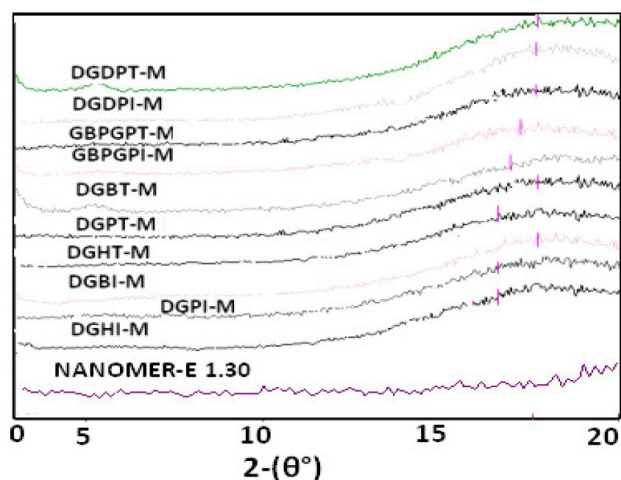


Figure 2 : The WAXD patterns of the nanocomposites (modified systems).

Thermal behaviour

(a) Differential scanning calorimetry (DSC)

In the present work, the segmented epoxides consist of alternating methylene groups denoted as flexible segments and aromatic units denoted as rigid segments because they are relatively stiff and hard. A comparative study of the different systems revealed that the rigid epoxide blend systems have high T_g compared to the flexible epoxide blend systems. Differential scanning calorimetric curves of unmodified systems and modified systems were given in Figure 3(A) and (B).

The studies among the flexible systems, terephthalate epoxide blends showed higher T_g values when

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compared to the isophthalate epoxide blends^[31,32]. The addition of new epoxides to the DGEBA provided the combined effect of backbone flexibility and crosslinking on the thermal behaviour of the cured polymer. The effect of T_g dependency upon varying the number of methylene units attached to the terephthalate or isophthalate was observed to be significant. Thus, decreasing methylene carbon numbers have decreased the T_g values. Vallo *et al.*^[33] concluded that the T_g of an epoxy based rigid network depends on concentration of elastic chains whereas, for a flexible network, the T_g depends on backbone flexibility. The difference was attributed to the greater facility of flexible chains to undergo relaxation within the chain structure. Increase in the length of methylene bridging unit improved backbone flexibility but lowered the density of hydroxyl groups along the backbone. The presence of ester groups linked to the rigid mesogenic segments could increase the intermolecular interactions due to the hydrogen bonding with the epoxy hydroxyls and they have the propensity to increase the T_g by augmenting the bond energy required to attain chain mobility.

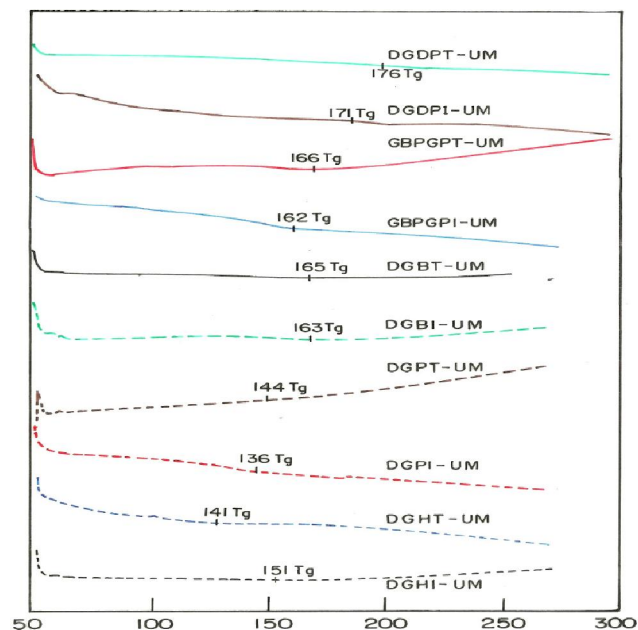


Figure 3(A) : Differential scanning calorimetric curves of unmodified systems.

Further, the comparative study of UM- systems with M-system have exhibited variations in the T_g values. The T_g values of the UM systems were found to be between 130 to 170°C, whereas the T_g of the

M systems were between 135°C and 180°C respectively. All the systems have showed increased T_g values except DGBT-M, DGPT-M and DGBI-M. Addition of nanoclays usually reduces the T_g with flexible spacers like methylene groups, The increase in the T_g values of the M-systems especially in the rigid systems could be due to the synergistic reinforcing effect of rigid rod segments in the epoxides and the addition of nanoclays. In addition to the clay layers, the long rigid structures itself could have acted as a barrier to the movement of the polymer segments because they need high activation energy for the translation and rotational motions.

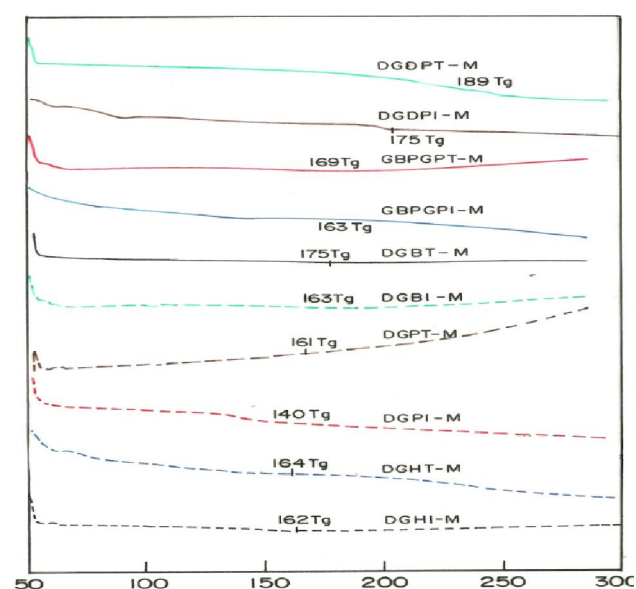


Figure 3(B) : Differential scanning calorimetric curves of modified systems.

(b) Estimation of M_c

The average molecular weight between crosslinks (M_c), is an important parameter governing the physical properties like crosslink density of cured thermoset resins. The polymer with a long spacer will have low degree of crosslinking and vice versa. Thus, when the spacer length increased, the M_c values increased because the degree of crosslinking decreased. At lower degree of crosslinking, and the presence of crosslinks effectively raises the molecular weight of the polymer. At higher degree of crosslinking, the increase in T_g becomes nonlinear as the rotational freedom of the average chain length between the crosslinks decreased with increased crosslink density^[34].

The correlation plot between T_g and M_c was given

Figure 5 (A) and (B). In all the systems, the Tg values inversely proportional to the Mc values as shown in TABLE 2. From the UM systems, the rigid systems also showed similar Mc Vs Tg relationship. The Mc values of the flexible segments were found to be higher than rigid segments. The Mc values increases with increase in the degree of crosslinking. The decrease in the Tg values conversely decreased Mc. In the flexible systems, the terephthalate epoxide based blends have shown their Mc values in the following order: (348) DGBT-UM < (419) DGPT-UM < (469) DGHT-UM. Mc decreases with increase in the spacer length. The highest Mc value was observed in the case of DGPI-UM due to the lowest Tg values obtained by the flexibilising effect of the pendant linkages. The odd numbers of methylene segments possess higher flexibility when compared to the even number methylene segments.

All the M systems showed lower Mc values when compared to the UM systems. The addition of nanoclay to the UM systems does affect the Tg due to imposition of steric effect on the M systems and thereby decreasing MC values.

Dynamic mechanical analysis (DMA)

DMA is a technique used to characterize polymeric materials^[35-37]. The dynamic mechanical properties refer to the response of a material when subjected to a periodic force. These properties may be expressed in terms of a dynamic modulus and a mechanical damping factor. From the dynamic mechanical analysis, the storage modulus (E') that deals with the ability of the materials to store the energy and the α -transition ($\tan \delta$) which is dependent on temperature could be investigated. The α -transition ($\tan \delta$) is related to the Brownian motion of the main chain at the transition from polymer going through one of the relaxations. It was observed that the storage modulus (E') and damping property ($\tan \delta$) were higher in the case of M systems when compared to the UM systems. The M systems showing the increase in the storage modulus was due to the dispersed clay in exfoliated state to the resin which has increased the stiffness by hindering the mobility of chain molecules. Further, the flexible systems have exhibited improved viscoelastic properties when compared to the rigid systems.

The Tg ($^{\circ}\text{C}$), storage modulus and $\tan \delta$ proper-

ties of unmodified and modified systems were given in TABLE 3.

TABLE 2 : Correlation studies of Tg and Mc values of flexible and rigid systems.

Rigid Systems	Mc	Tg($^{\circ}\text{C}$)	Rigid Systems	Mc	Tg ($^{\circ}\text{C}$)
DGBT-UM	348.21	163	DGDPT-UM	325.00	171
DGPT-UM	419.35	144	GBPGPT-UM	342.11	165
DGHT-UM	469.88	134	DGDPI-UM	351.35	162
DGBI-UM	382.35	153	GBPGPI-UM	351.35	162
DGPI-UM	493.67	130	DGDPT-M	302.33	180
DGHIUM	428.57	142	GBPGPT-M	328.84	169
DGBT-M	319.67	163	DGDPI-M	325.00	171
DGPT-M	386.14	144	GBPGPI-M	357.79	160
DGHT-M	375.00	155	DGPI-M	448.28	138
DGBI-M	378.64	153	DGHI-M	397.96	149

TABLE 3 : The Tg ($^{\circ}\text{C}$), storage modulus, and $\tan \delta$ properties of unmodified and modified systems.

SYSTEMS	Tg($^{\circ}\text{C}$) by DMA		Tan δ		E' (MPa)	
	UM	M	UM	M	UM	M
DGDPT	171	180	0.415	0.536	1620	1700
GBPGPT	165	169	0.576	0.642	2625	2900
DGBT	163	173	0.633	0.823	3250	2875
DGPT	144	152	0.300	0.420	2750	2925
DGHT	134	155	0.411	0.445	3100	3175
DGDPI	162	171	0.401	0.425	2380	2460
GBPGPI	162	160	0.479	0.535	2675	3225
DGBI	153	154	0.648	0.441	2620	3000
DGPI	130	138	0.399	0.347	2850	2800
DGHI	142	149	0.413	0.611	3250	3255

The increase in the Tg values observed in the case of M systems was due to the incorporation of organoclay. The nanoclay layers dispersed in the epoxy resins hindered the benzene ring mobility and at the same time facilitated the aliphatic segmental mobility because of its high exfoliation that was reflected in high storage modulus and high damping ($\tan \delta$) properties in the flexible systems. Thus, the polymer relaxation motions will be not constrained fully because of the presence of clay fillers. Therefore, we could be able to conclude that the clay layer has acted as a typical toughener.

Thermogravimetric analysis (TGA)

(a) Thermal properties

The thermograms of the DGEBA blended with

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epoxides [unmodified (UM systems)] and with nanoclay [modified (M systems)] were shown in Figures 4(A, B) and 5(A, B).

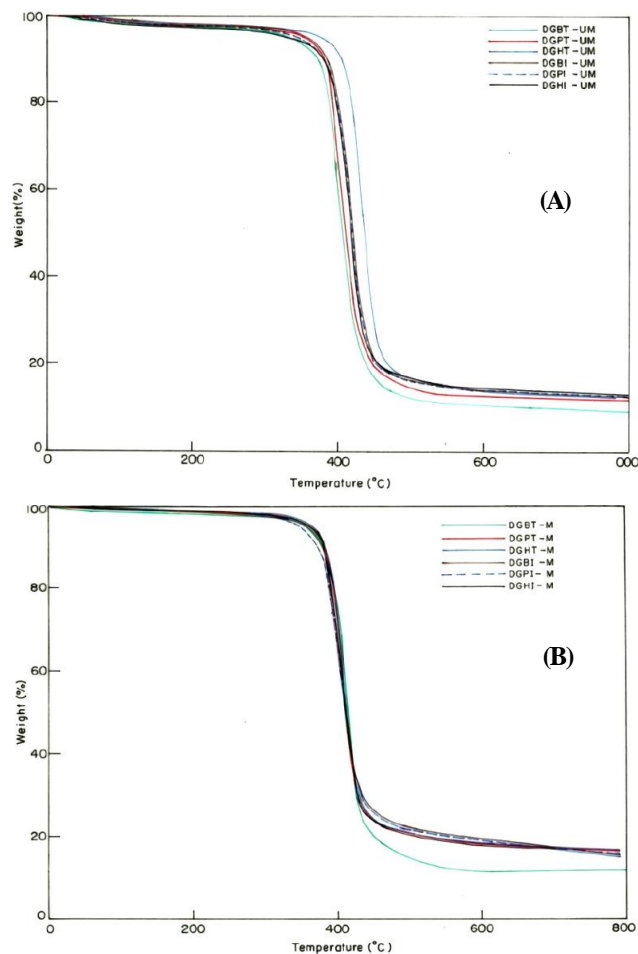


Figure 4 : Thermogravimetric curves of flexible epoxides blend: (A) Unmodified and (B) Modified systems.

TABLE 4 : Thermal properties of flexible epoxide (unmodified and modified) systems.

Flexible system	Onset Temp. (°C)	% Weight loss			MDT (°C)	Char Yield %	OI
		25%	50%	80%			
DGBT-UM	388	396	421	456	412	8.39	20.85
DGPT-UM	403	414	421	450	421	12.15	22.36
DGHT-UM	405	421	435	450	438	12.37	22.44
DGBI-UM	407	414	432	523	420	12.00	22.43
DGPI-UM	395	409	431	521	413	12.42	22.47
DGHI-UM	395	411	430	519	421	12.54	22.52
DGBT-M	392	411	421	450	416	12.29	22.42
DGPT-M	394	409	417	505	411	16.39	24.06
DGHT-M	395	413	419	505	415	16.92	24.27
DGBI-M	390	404	422	450	409	15.52	23.71
DGPI-M	394	407	424	450	412	15.63	23.75
DGHI-M	390	411.2	417	505	410	16.88	24.25

The thermal decomposition temperatures at different weight loss percentages and the char yields were listed in TABLES 4 and 5.

TABLE 5 : Thermal properties of rigid epoxide (unmodified and modified) systems.

Rigid system	Onset	% Weight loss			% Char yield	OI
		25%	50%	MDT		
DGDPT-UM	403	404	421	421	22.76	26.60
GBPGPT-UM	405	428	435	438	12.37	22.44
DGDPI-UM	392	392	424	411	22.71	26.58
GBPGPI-UM	403	414	421	414	12.15	22.36
DGDPT-M	381	407	417	410	54.64	39.35
GBPGPT-M	388	407	417	406	38.65	32.96
DGDPI-M	364	396	432	404	45.98	35.89
GBPGPI-M	424	428	442	398	24.03	27.11

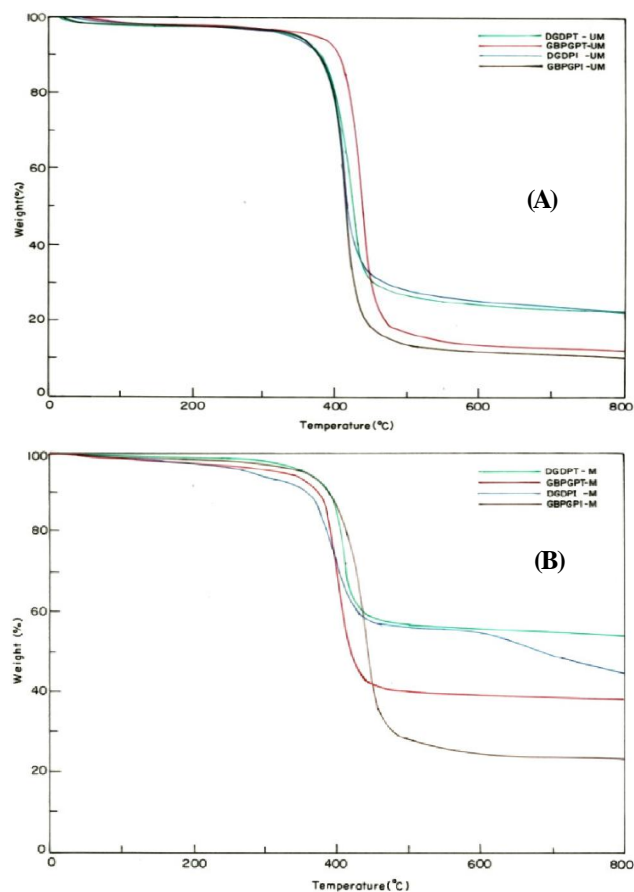


Figure 5 : Thermogravimetric curves of rigid epoxides blend: (A) unmodified and (B) modified systems.

The thermal stability of the DGEBA/epoxides cured polymers has improved the thermal stability of the blend systems. Single step decomposition was observed in the case of UM and M systems due to the possibility of the components which were reactive and

can react with each other. It was also observed that the shape of the thermograms was linear during the degradation process in all the systems. The onset thermal temperatures were observed between 388 and 407°C for UM flexible systems. The UM rigid systems have exhibited the onset temperatures between 381 and 425°C showing the excellent thermal stability of the composites. The terephthalate based epoxide blends have shown higher thermal stability (IDT) upto 407°C compared to the isophthalate based epoxide blends (upto 395°C). The low thermal stability of the isophthalate epoxide blends was due to the greater possibilities of bond scissions at lower temperatures. The entire M systems have showed lower IDT values of 395°C except GBPGPI-M and maximum decomposition temperature (MDT = 406°C). On the other hand, the UM systems onset and MDT values were values 407°C and 438 °C.

The DGEBA modified with the epoxides have exhibited enhanced char yield values. The char yields obtained seems to be higher for all the UM and M systems. The rigid systems have showed higher char residues of 12.15-54.64% decomposition compared to the flexible systems 8.39-16.88%. The char yields increased with the increasing in the methylene groups.

DGHT-UM (12.4%) > DGPT-UM (12.2%) >

DGBT-UM (8.4%)

DGHI-UM (12.5%) > DGPI-UM (12.4%) >

DGBI-UM (12.00%)

Among the rigid systems, high molecular weight epoxides have showed highest char percent values for example, DGDPT-UM (26.6%) and DGDPI-UM (35.9%). This could be due to the presence of higher molecular mass of aromatic carbons in the cured system when compared to the other systems^[38,39]. The lowest char yield observed in DGBT-UM (8.4%) could be attributed to the improper mixing of the epoxide with the DGEBA.

All the M systems have exhibited higher char yields. The terephthalate based epoxide blends have showed increased char yield residues. The flexible groups in the modified systems showed upto 16.9% and rigid groups showed 39.4% when compared to the isophthalate epoxide blends of flexible-M: 16.9 and rigid-M: 35.9%. The 1,4-substituted terephthalate were stiff which hindered the free rotation of the mol-

ecules thereby leading to higher char yield.

(b) Flame retardant properties

From the obtained char yields, it could be possible to correlate with the flame retardant properties of the systems. Thus, the char yield values were directly proportional to the oxygen index values from the empirical formulae proposed by Krevelen et al.^[40].

$$OI = 17.5 + 0.4 CR \quad (1)$$

Where OI = Oxygen index, and CR = Char residue in weight. The limiting oxygen index (LOI) values obtained were increasing with increase in the char yields. The addition of nanoclay increases the flame retardant properties was confirmed from the increase of the oxygen index values in M systems compared to the UM systems.

The LOI values obtained followed linear relationship with the char yield. The DGEBA modified with the 10Wt% epoxide in the case of the UM systems have shown LOI values of 20-24. The M systems added with 10% epoxide and 5% nanoclay have exhibited the LOI around 22-39.

It was classified that the materials possessed LOI <20.95, LOI <28.0 and LOI <100 were considered as 'flammable', 'slow-burning' and 'intrinsically non-flammable' respectively. In order to describe precisely, the polymers possessed with LOI ≥ 20.95, and ≥ 26.0 were considered as 'marginally stable' and 'self-extinguishable' respectively^[41-43]. According to this scale, the UM systems comes under the 'marginally stable' category and the M systems (except GBPGPT-UM and GBPGPI-UM) falls into the 'self-extinguishable' category.

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(c) The IPDT properties

The IPDT proposed by Doyle^[44] was calculated

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using

$$\text{IPDT } (^\circ\text{C}) = A^*K^*(T_f - T_i) T_i \quad (2)$$

Where, A^* represents the area ratio of total experimental curve divided by total TGA thermogram, K^* is the coefficient of A^* , T_i is the initial experimental temperature, and T_f is the final experimental temperature. All the systems have exhibited the IPDT values in the similar range of 736- 903 which confirmed the high thermal stability of the materials. IPDT values of all the UM systems showing in the similar range owes to the structural similarity lies between epoxide and DGEBA. The isophthalate based epoxide blends have shown higher IPDT could be due to the miscibility property enhanced by the isophthalate segment. In the rigid systems, DGDPT-UM and DGDPI-UM have showed higher IPDT, when compared to the GBPGPT-UM and GBPGPI-UM systems. This could be not only due to higher molecular mass but also due to the isopropyl functional groups in the bisphenyl moieties of the epoxide. These groups might have hindered the rotation of the polymer networks during the degradation which has reflected in high thermal property index.

(d) Degradation kinetics study

TGA is a useful method to investigate the thermal degradation kinetics mechanism of polymers. The degradation behaviour was studied by using integral models of Broido, Horowitz-Metzger and Coats-Redfern^[45-47] derived from the Arrhenius equation and the details were given under materials and methods.

A plot of $\ln(-\ln(1-y))$ in the case of Broido model, $\ln[-(1-y)/T^2]$ in the case of C-R method and $(1-y)$ in the case of H-M method versus $1000/T$ for major degradation follow linear relationship by obtaining straight line^[48-51]. The kinetic analyses were carried out considering the degradation loss from 2.5% till the end of maximum weight loss of a material. The graphs plotted for Broido, Horowitz-Metzger and Coats-Redfern models follow first order reaction and the results were shown in Figure 6(A) for flexible epoxide blend systems (UM and M) Figure 6(B) for rigid epoxide blend (UM and M) systems.

The activation energy (E_a) values calculated from the slope of plots were given in TABLE 6.

The results revealed that the degradation patterns

of the both the systems followed first order of reaction with correlation coefficient values of approximately at 0.9. The values of correlation coefficients, close to unity indicated to be the best fit. The activation energies obtained from these models were compared for flexible epoxide systems. The E_a values were in the following order:

H-M < C-R < Broido models for rigid epoxide systems.

The H-M model showing variations in the E_a values were in accordance with the variations in the T_{max} of the blends. The E_a values varied with respect to the structural types of blends in UM and M systems were also observed. In all the three kinetic models used, the M systems have exhibited higher activation energy when compared to the UM systems. The comparison of E_a values of M systems calculated according to the Broido model have shown in the range of 198-247 kJ/mol for flexible-M systems and 200-247 kJ/mol for rigid-M blend systems. The range of activation energies of 133-193 kJ/mol and 190-247 kJ/mol for flexible-UM systems and rigid-UM blend systems respectively. The increase in E_a values in the M systems was due to the presence of nanoclay as a thermal barrier which required higher energy for the decomposition. The flexible-UM systems have shown the E_a values in the range of 193-247 kJ/mol for terephthalate and 133-136 kJ/mol for isophthalate epoxide blends. The flexible-M systems have showed higher E_a values of 240-247 kJ/mol for isophthalate epoxide blends when compared to the 198-231 kJ/mol E_a values of terephthalate epoxide blends. This may be due to the better miscibility and chemical reaction of the isophthalate (1,3-position) epoxides with DGEBA/DDS. The flexible UM and M systems showing high activation energy values could be due to the crystallization of the methylene segments in the ordered state during the curing process. This is in agreement with the report by Mano et al.^[52] that greater the crystallinity nature would result in greater activation energy.

Mechanical properties

The mechanical properties of the DGEBA/DDS cured composites were generally known to give high strength materials. The DGEBA/DDS system was

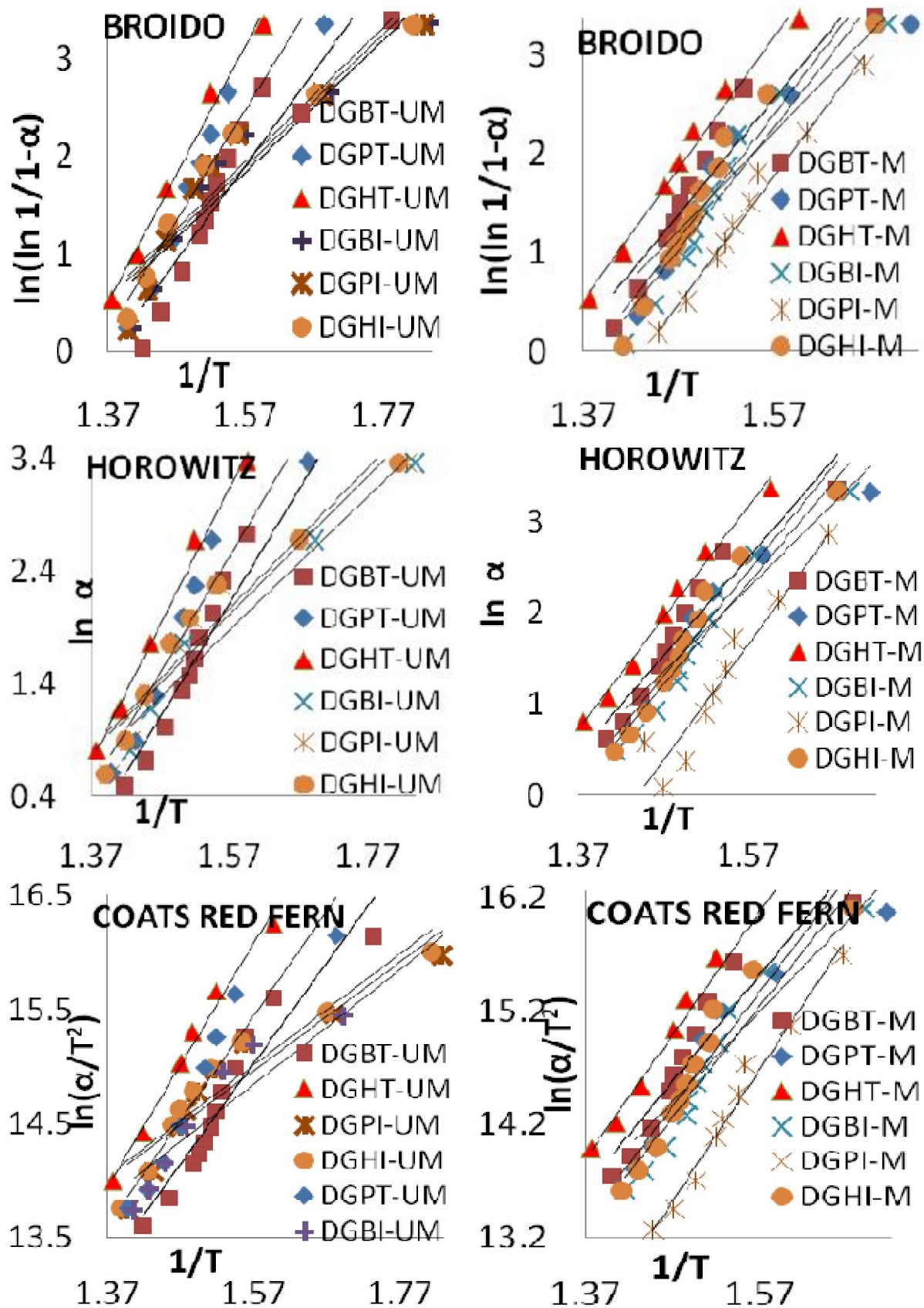


Figure 6(A) : The graphs for the calculations of activation energy unmodified and modified systems with flexible epoxides.

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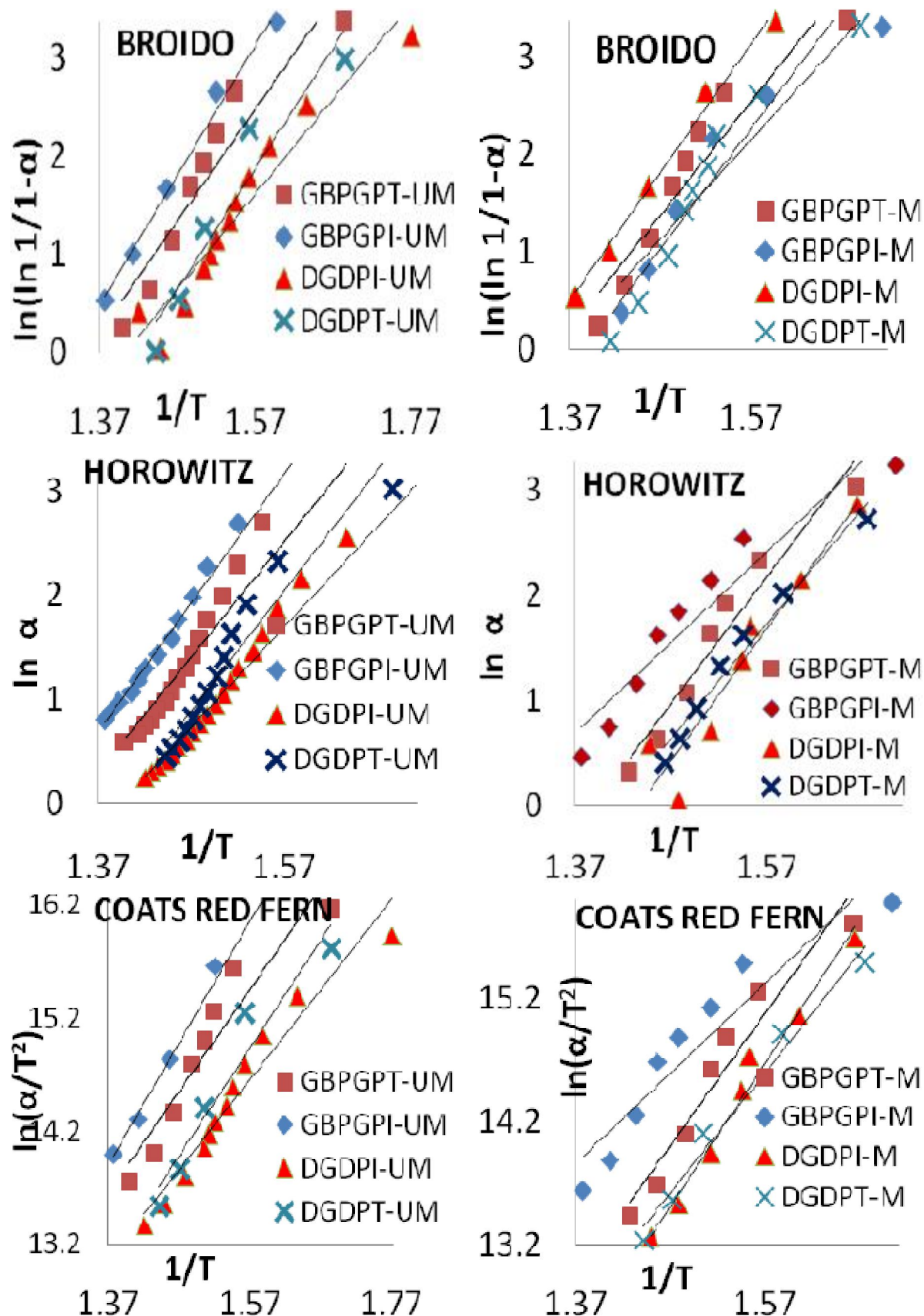


Figure 6(B) : The graphs for calculating activation energy for unmodified and modified systems with rigid epoxides.

modified with a low functionality linear epoxide and nanoclay to get a less crosslinked material with improved toughness. The tensile strength, flexural strength, impact strength and fracture toughness properties of the UM and M systems were given in Figure 7 (A, B) and 8(A, B). The addition of epoxide and nanoclay has resulted in the increase of the properties. The spacer groups of the epoxides had effect on enhancing the properties of the cured resins, was attributed to the chemical structure of the spacers.

TABLE 6 : The activation energy (Ea) and regression coefficient (R²) values from the plots of Flexible-UM & M systems, and rigid-UM & M systems.

Flexible UM systems	Briodo's model		Horowitz-Metzger model		Coats-Redfern model	
	Ea (KJ/mol)	R ²	Ea (KJ/mol)	R ²	Ea (KJ/mol)	R ²
DGBT-UM	193.93	0.896	193.56	0.952	170.3	0.941
DGBT-M	231.95	0.915	207.03	0.930	183.19	0.914
DGHT-UM	247.41	0.987	194.49	0.989	199.91	0.987
DGHT-M	198.04	0.906	178.87	0.926	155.55	0.906
DGBI-UM	133.07	0.901	119.34	0.926	96.60	0.896
DGBI-M	240.32	0.938	210.85	0.951	187.2	0.940
DGPI-UM	134.44	0.895	120.61	0.920	97.87	0.888
DGPI-M	243.05	0.940	240.86	0.953	189.56	0.943
DGHI-UM	136.08	0.902	122.07	0.926	99.14	0.896
DGHI-M	247.96	0.934	217.40	0.951	193.56	0.940
Flexible-M systems						
DGBT-M	231.95	0.915	207.03	0.930	183.19	0.914
DGPT-M	198.04	0.906	178.87	0.926	155.55	0.906
DGHT-M	198.29	0.914	178.94	0.933	155.36	0.915
DGBI-M	240.32	0.938	210.85	0.951	187.2	0.940
DGPI-M	243.05	0.940	240.86	0.953	189.56	0.943
DGHI-M	247.96	0.934	217.40	0.951	193.56	0.940
Rigid-UM and M systems						
DGDPT-UM	190.47	0.914	172.44	0.939	149.13	0.923
DGDPT-M	205.93	0.890	211.39	0.974	188.09	0.968
DGDPI-UM	196.47	0.945	174.56	0.968	151.41	0.959
DGDPI-M	240.86	0.901	240.86	0.986	217.41	0.983
GBPGPT-UM	226.67	0.919	202.11	0.933	178.5	0.917
GBPGPT-M	236.7	0.910	231.22	0.958	207.63	0.950
GBPHPI-UM	247.41	0.987	224.49	0.989	199.93	0.987
GBPHPI-M	194.15	0.899	167.5	0.921	146.02	0.904

(a) Tensile and flexural strength properties

The UM and M rigid systems have demonstrated higher strength properties when compared to the UM and M of the flexible systems. Among the M systems, the DGDPT-M and the DGBT-M have showed highest tensile strength values of 25.57 Mpa and 25.11 Mpa respectively. This was due to the orientation of clay platelets and polymer chains with respect to the

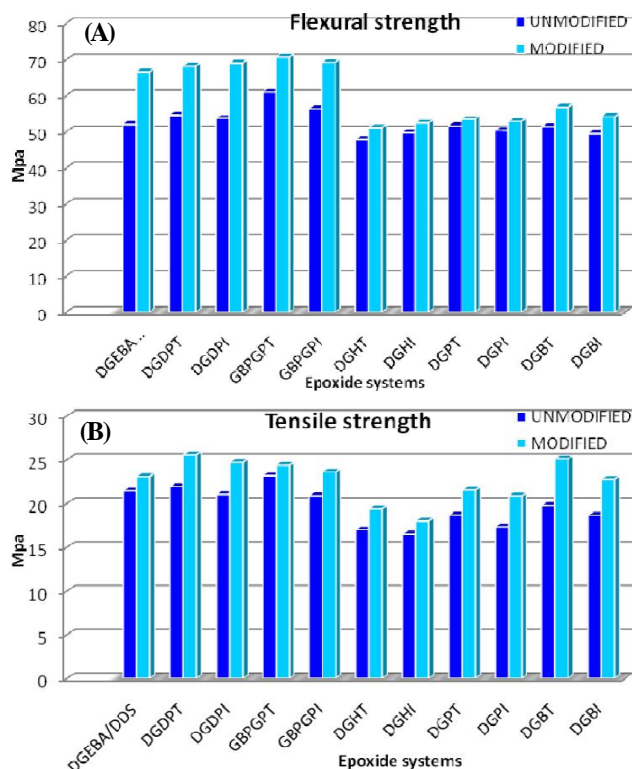


Figure 7 : The mechanical properties of the unmodified and modified systems: (A) tensile strength and (B) flexural strength properties.

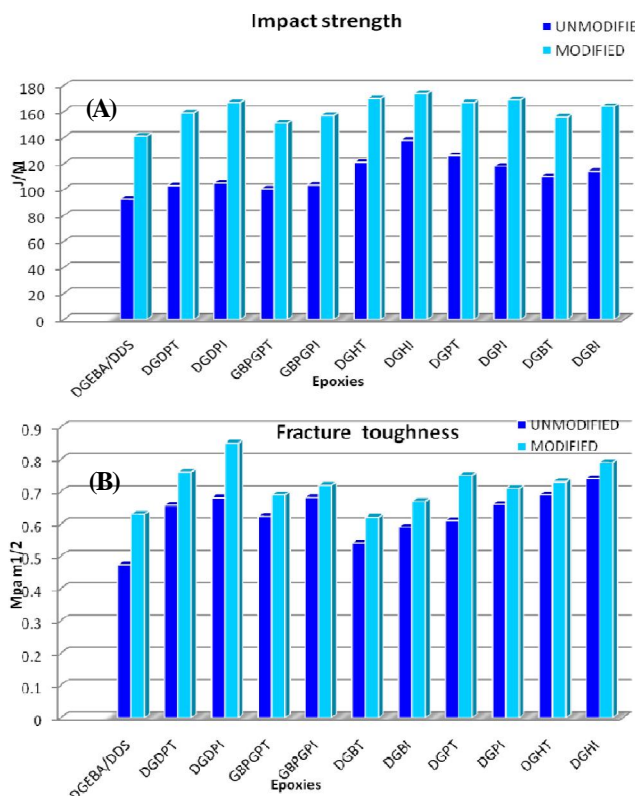


Figure 8 : The mechanical properties of the unmodified and modified systems: Impact strength and (B) Fracture toughness properties.

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loading direction that have contributed to the reinforcement effect. In the M systems, the GBPGPI-M and DGBT-M have showed highest flexural strength values of 70.8 Mpa and 56.8Mpa respectively. The enhanced flexural strength property exhibited was due to the effective stress transfer capacity of the blends on counting the shearing ability of the nanoclay layers.

(b) Impact strength properties

The M systems have exhibited improved impact strength properties around 147-167J/m for Flexible-M and 156-174J/m for rigid-M systems compared to the UM systems, i.e., 100.6-104.9 J/m flexible-UM and 110-138 J/m for rigid-UM systems. It is not worthy that, the entire UM and M systems have shown superior impact strength properties when compared to the conventional DGEBA/DDS system, i.e., 92.6 J/m for UM and 141 J/m for M systems. The system that contained longer methylene spacer groups showed improved toughness, which might be attributed to the free movement of the long molecules in coherence with the possibility of the formation of less dense cured structures. The packing prevention of the methylene containing polymer resulted in the increased free volume fraction. This is responsible for the increase in impact strength when compared to unmodified system.

(c) Fracture toughness properties

The fracture toughness of the flexible and rigid systems was found to be in the same range except the DGBT and DGBI which possess shortest methylene linkages. The toughness of the cured polymers based on methylene spacers containing epoxy was found to be in the following order: DGHT>DGPT>DGBT.

Thus, the increase in the number of methylene spacer units have increased the fracture toughness of the materials. The repetitive availability of epoxy hydroxyl groups have decreased by the increase in the number of methylene groups. Therefore, the density of the hydroxyl groups along the backbone of the cured polymer decreases in epoxies which tend to produce less crosslinked structures. This increases the fracture toughness. The entire M systems have shown increased fracture toughness properties. The improved toughness property obtained by reinforcing

such hard nanophase particles was due to some energy absorption mechanisms like crack pinning, crack arresting and good polymer-surface bonding. The increased toughness could be also be due to the shear yielding, crazing, or cavitations mechanisms^[53]. The analysis indicates that nano clay platelets provides superior fracture toughness is a direct consequence of ductility or the maximum shear strain of the organic matrix in terms of repeated nano dispersion of clay layers. The higher fracture strength observed was a result of its ordered intercalated regions of the clay layers with significant overlap of the platelets and high shear strength of the epoxies.

Morphological studies

The nanoclay dispersion in the M system was examined by using scanning electron microscope. The surface morphology of M systems was carried out from the tensile fractured specimens. The SEM pictures of all the M systems were shown in Figure 9 and all showed similar structure morphologies.

The single phase morphologies observed in the case of M systems confirmed the complete dispersion of the clay particles. The nanoclay particles have been fully bonded with epoxy matrix to form a single phase structure was evident. The absence of clay agglomerations also indicated the downsizing of the clay particles, due to the effective method of sonication employed. The pure DGEBA/DDS resins showed a smooth and linear crack surface morphological characteristic attributed to brittle failure^[54]. Smooth line patterns were totally disappeared and irregular fracture surfaces were emerged upon the addition of organoclay. The sheared crack behaviour was seen in the case of M systems attributing the rubbery nature brought by the inclusion of the ester epoxy and nanoclay particles. The similar structural morphology existed between the DGEBA and epoxide. The uniform scattering of clay platelets was witnessed by the tortuous microcracks and especially in the flexible systems. The vertically aligned line patterns observed in the rigid systems could be due to the crystallization of the spacers to a very high order which has reflected in the increase of the T_g, E_a values, char yields and mechanical properties. The SEM results were very well correlated with the properties.

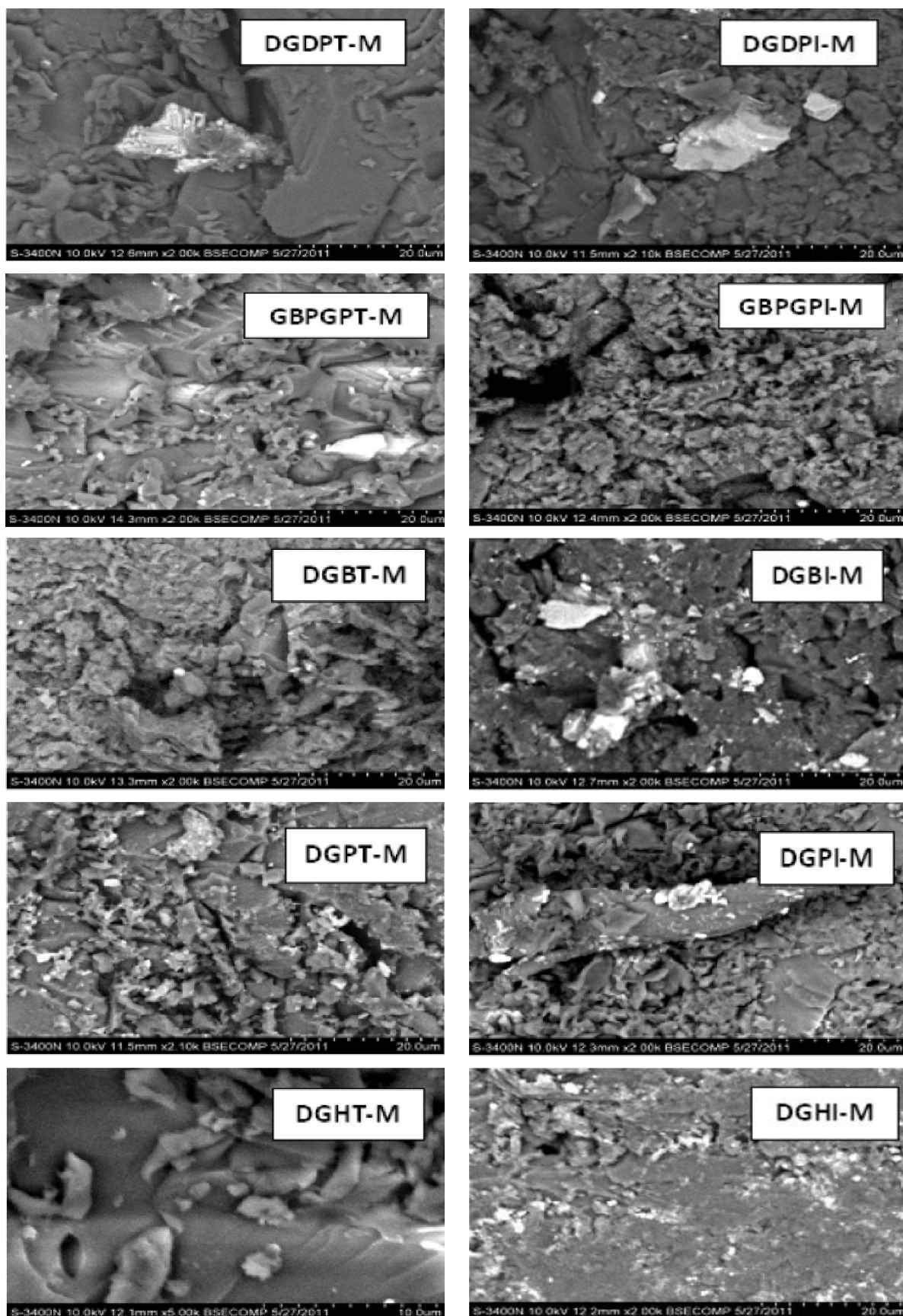


Figure 9 : The fractured surface morphology of nanocomposite (modified) systems.

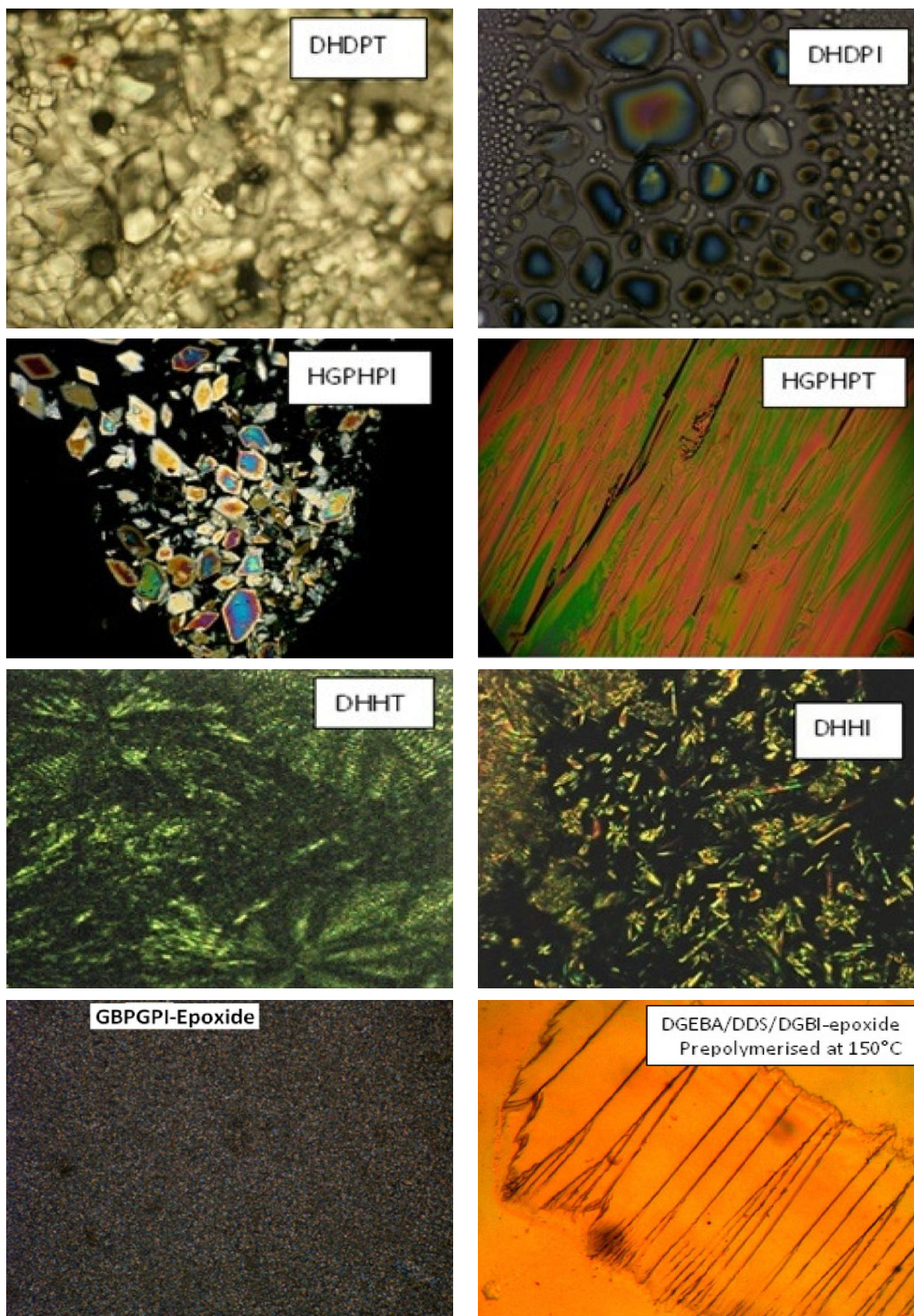
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Figure 10 : The optical micrograph pictures of dihydroxy esters and representative pictures of an epoxide and modified system showing ordered crystalline patterns.

Optical micrograph structural characteristics

Liquid crystalline epoxies are known to show mesophase behaviours by maintaining a certain degree of orientational order during melting or while cooling from the melt. Upon crystallization, the molecules of the epoxides have packaged closely and this may not be always be possible for more complicated structures. In the crystal state, the molecules were held together by strong intermolecular forces of attraction due to the presence of linear and rod-like structures^[55-57]. Here, the dihydroxy esters and their respective epoxides, and the M systems were showing ordered crystalline patterns because of mesogenic segments available in the epoxide molecules (Figure 10).

A slow curing process was adopted to obtain macroscopically aligned LC thermosets. The rate of curing is important as sufficient time is required to facilitate the orientation of the spacer molecules^[58]. The anisotropic orientations help the reactive functionalities like epoxy and amine molecules to be parallelly closer to each other. The parallelly aligned molecules cured at that positions will show higher mechanical properties especially like fracture toughness. We have observed better mechanical properties in our modified systems. The combination of excellent thermal properties and mechanical properties exhibited in a liquid-crystalline phase systems have been reported^[59]. The concentration of the mesogenic groups of each cured system was calculated by using^[60]:

Concentration of the mesogenic groups

$$= \frac{M_{\text{mesogen}}}{M_1 \text{ basic unit}}$$

Where M_1 basic unit is the molecular weight of the structure formed by the linking of two epoxy molecules with one curing agent molecule and M_{mesogen} is the molecular weight of the mesogenic moiety per basic unit. The percentage concentration of the mesogenic groups in the UM systems were shown in the increasing order:

(DGBT-UM and DGBI-UM) 0.74% < (DGPT-UM and DGPI-UM) 0.75%, < (DGDPT-UM and DGDPI-M) 0.78% < (DGHT-UM and DGHI-UM) 0.97%, < (GBPGPT and GBPGPI) 0.91.

The relationships of fracture toughness values with respect to mesogen concentrations though not seem to have influenced much in the rigid epoxide blends.

But, it was observed the effect in the case of flexible epoxide blends. As the mesogen concentration increased, the fracture toughness values were also increased both in the terephthalate and isophthalate epoxide blends. Thus, increasing mesogen content leads to increased intermolecular interactions between the polymer chains and thereby reduces the micro-Brownian motion as well as free volume. These properties were inturn manifested as increased elastic moduli and increased onset decomposition temperatures.

CONCLUSIONS

The effect of tailored epoxide and nanoclay loading to the DGEBA/DDS composites were studied. The blends prepared with epoxide (UM systems) and the blends prepared with epoxide and nanoclay (M systems) have showed that the blends were homogeneous with a single phase morphology structures. The DMA analysis provided single Tg and SEM analysis showing single phase morphology structure was also confirmed the single phase morphology. The storage modulus increased with the incorporation of epoxide and nanoclay due to the reinforcement imparted by the spacer back bone moieties in the epoxide and the nanoclay layers. The mechanical properties such as tensile strength, flexural strength, impact strength and fracture toughness were also improved by the modification of DGEBA/DDS system. The increase in the mechanical properties was due to the linear, long and flexible/rigid backbone moieties present in the epoxides. These functional groups have led to form liquid crystalline thermosets. The thermal stability of the systems was increased with the addition of epoxide and nanoclay which was clearly seen from the increase in the activation energy of the composites.

REFERENCES

- [1] F.N.Billmeyer; Textbook of polymer science, Chapter 16, 3rd Edition, Wiley, New York, (1984).
- [2] H.Lee, K.Neville; Handbook of epoxy resins, Mc Graw-Hill, New York, (1967).
- [3] M.Gaschke, B.Dreher; Journal of Coatings Technology, 48, 46–51 (1976).

ORIGINAL ARTICLE

- [4] R.G.Schmidt, J.P.Bell; *Advances in Polymer Science*, **75**, 33–71 (1986).
- [5] N.Kinjo, M.Ogata, K.Nishi, A.Kaneda; *Advances in Polymer Science*, **88**, 1–48 (1989).
- [6] L.S.Schadler, S.C.Giannaris, P.M.Ajayan; *Applied Physics Letters*, **73**, 3842–44 (1998).
- [7] C.Baley, P.Davies, Y.Grohens, G.Dolto; *Applied Composite Materials*, **11**, 99–126 (2004).
- [8] K.Fujihara, K.Teo, R.Gopal, P.L.Loh, V.K.Ganesh, S.Ramakrishna, K.W.C.Foong, C.L.Chew; *Composites Science and Technology*, **64**, 775–88 (2004).
- [9] M.H.Chen, C.R.Chen, S.H.Hsu, S.P.Sun, W.F.Su; *Dental Materials*, **22**, 138–45 (2006).
- [10] L.V.McAdams, J.A.Gannan; *Encycl of polym sci and engg*, 2nd Edition, Wiley, New York, (1986).
- [11] R.S.Bauer; *Chemical Technology*, **10**, 692 (1980).
- [12] R.B.Seymour, G.S.Krishanbaum; *High performance polymers: Their origin and development*, Elsevier, New York, (1989).
- [13] M.Suguna Lakshmi, B.S.R.Reddy; *European Polymer Journal*, **38**, 795–801 (2002).
- [14] W.F.A.Su, K.F.Schoch, J.D.B.Smith; *Journal of Applied Polymer Science*, **70**, 2163–67 (1998).
- [15] M.Ochi, D.Hori, Y.Watanabe, H.Takashima, M.Harada; *Journal of Applied Polymer Science*, **92**, 3721–29 (2004).
- [16] M.Harada, K.Sumitomo, Y.Nishimoto, M.Ochi; *Journal of Polymer Science Part B: Polymer Physics*, **47**, 156–65 (2009).
- [17] L.A.Utracki; *Clay-containing polymeric nanocomposites rapra technology: Shropshire, England*, **1**, (2004).
- [18] M.Kawasumi, N.Hasegawa, M.Kato, A.Usuki, A.Okada; *Macromolecules*, **30**, 6333 (1997).
- [19] Z.Wang, T.J.Pinnavaia; *Chemistry of Materials*, **10**, 1820 (1998).
- [20] J.K.Kim, C.G.Hu, R.S.C.Woo, M.L.Sham; *Composites Science and Technology*, **65**, 805 (2005).
- [21] K.Chrissooulou, I.Altintzi, S.H.Anastasiadis, E.P.Giannelis, M.Pitsikalis, N.Hadjichristidis, N.Theophilou; *Polymer*, **46**, 12440 (2005).
- [22] I.Altintzi, K.Chrissooulou, S.H.Anastasiadis, M.Pitsikalis, N.Hadjichristidis, N.Theophilou, E.P.Giannelis; *Abstracts of Papers of the American Chemical Society*, **229**, 1127 (2005).
- [23] E.J.Malec, R.A.Christman; *Methods for the rapid determination of hydroxyl numbers in polyesters* Mobay chemical Co., Unpublished.
- [24] G.M.Kline; *Analytical chemistry of polymer*, Interscience, New York, 127 (1959).
- [25] M.S.Lakshmi, M.Srividhya, B.S.R.Reddy; *Journal of Polyme Research*, **10**, 259 (2003).
- [26] N.Artzi, Y.Nir, D.Wang, M.Narkis; *J.Polym. Comp.*, **22(5)**, 710 (2001).
- [27] D.L.Lee, D.C.Wang, W.Y.Chiu; *Journal of Polymer Research*, **1(1)**, 1-6 (1994).
- [28] H.J.Sue, K.T.Gam, N.Bestaoui, A.Clearfield, M.Miyamoto, N.Miyatake; *Acta Materialia*, **52**, 2239 (2004).
- [29] H.J.Sue, K.T.Gam, N.Bestaoui, N.Spurr, A.Clearfield; *Chemistry of Materials*, **16**, 242 (2004).
- [30] W.J.Boo, L.Sun, J.Liu, A.Clearfield, H.J.Sue, M.J.Mullins, H.Pham, N.Verghese; *J.of Polym Sci: Part B: Polym.Phys.*, **45**, 1459–69 (2007).
- [31] Y.G.Wan, J.Galy, J.P.Pascault, J.Verdu; *Journal of Polymer Science Part B: Polym.Phys.*, **29**, 981 (1991).
- [32] M.Skrifvars; *Academic dissertation university of Helsinki, Finland, August 11* (2000).
- [33] C.I.Vallo, P.M.Frontini, R.J.J.Williams; *Jl.Polym. Sci.Part B: Polym.Phys.*, **29**, 1503 (1991).
- [34] *Characterization and failure analysis of plastics by ASM international, The materials information society, ISBN: 0-87170-789-6*, (2003).
- [35] A.V.Tobolsky; *Properties and structure of polymers*, John Wiley Intersciences, New York, (1960).
- [36] L.E.Nielson; *Mechanical Properties of Polymers*, Reinhold, New York, (1962).
- [37] J.D.Ferry; *Viscoelastic properties of polymers*, 2nd Edition, John Wiley Interscience, New York, (1970).
- [38] H.-Q.Yan, S.Chen, G.-R.Qi; *Polymer*, **44**, 7861 (2003).
- [39] M.L.Ramirez, R.Walters, R.E.Lyon, E.P.Savitski; *Polym Degrad and Stab.*, **78**, 73 (2002).
- [40] D.W.Van Krevelen; *Polymer*, **16**, 615–20 (1975).
- [41] M.I.A.Nelson; *Combustion Theory and Modeling*, **5**, 59–83 (2001).
- [42] A.R.Horrocks, M.Tunc, D.Price; *Textile Progress*, **18(1-3)**, 1–205 (1989).
- [43] C.P.Fenimore; *Candle-type test for flammability of polymers. In flame retardant polymeric materials*, M.Lewin, S.M.Atlas, E.M.Pearce (Eds); New York: Plenum, **1**, 371–397 (1975).
- [44] C.D.Doyle; *Analytical Chemistry*, **33**, 77–79 (1961).

- [45] Shah Ryar Pashaei, Siddaramaiah, Maziar Mansouji Avval, Akheel Ahmed Syed; *Chemical Industry & Chemical Engineering Quarterly*, **17(2)**, 141–151 (2011).
- [46] J.W.Holubka, J.E.Devries, R.A.Dickie; *Industrial and Engineering Chemistry Product Research and Development*, **23**, 63 (1984).
- [47] W.Raudenbush; *Epoxy resin chemistry*, In: R.S.Bauer (Ed); ACS symposium series no. 114, American Chemical Society, Washington, DC, (1979).
- [48] A.Al-Mulla, H.I.Shaban; *International Journal of Polymeric Materials*, **57(3)**, 275–287 (2008).
- [49] K.S.Muralidhara, S.Sreenivasan; *World Applied Sciences Journal*, **11(2)**, 184–89 (2010).
- [50] M.A.Ashok, B.N.Achar; *India Academy of Science Material Science*, **31(1)**, 29–35 (2008).
- [51] K.S.Muralidhara, S.Sreenivasan; *World Applied Sciences Journal*, **9(11)**, 1272–79 (2010).
- [52] J.F.Mano, D.Koniarova, R.L.Reis; *Jl.of Mater Sci.: Materials in Medicine*, **14(2)**, 127–35 (2003).
- [53] S.Wu, S.C.Tjong, S.P.Bao; *J.Polym.Sci.Part B: Polym.Phys.*, **43**, 585–95 (1985).
- [54] R.Velmurugan, T.P.Mohan; *Journal of Mater.Sci.*, **24**, 7333–9 (2004).
- [55] S.Jahromi, W.A.G.Kuipers, B.Norder, W.Mijs; *Journal of Macromolecules*, **28**, 2201–2211 (1995).
- [56] G.G.Barclay, S.G.McNamee, C.K.Ober, K.Papathomas, D.Wang; *Jl.of Polym.Sci.Part A: Polym.Chem.*, **30**, 1845 (1992).
- [57] C.Carfagna, E.Amendola, M.Giamberini; *Liquid Crystals*, **13**, 571 (1993).
- [58] Jun Yeob Lee; *Jl.Appl.Polym.Sci.*, **102**, 1712–16 (2006).
- [59] M.Harada, M.Ochi, M.Tobita, T.Kimura, T.Ishigaki, N.Shimoyama, H.Aoki; *Jl.Polym.Sci. Part B: Polym.Phys.*, **41**, 1739–43 (2004).
- [60] M.Harada, Y.Watanabe, Y.Tanaka, M.Ochi; *Jl.of Polym.Sci.: Part B: Polym.Phys.*, **44**, 2486–94 (2006).