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Blends of a New Thermoplastic in a Thermoset Epoxy Matrix

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Summary: Properties of thermoplastic modified epoxy network have been studied. The particularity of this work is the use of new thermoplastic epoxies whose structure is close to the final matrix. Blends of thermoset epoxy (Diglycidyl Ether of Bisphenol A/4-4' methylenebis [3-chloro 2,6-diethylaniline]) with a thermoplastic content from 5 to 40%w have been realised. Initial miscibility in the thermoset precursors shows an UCST behaviour with a maximal value near 130°C for a thermoplastic content of 10%. Due to the presence of tertiary amine and pendant hydroxyl groups on the thermoplastic backbone, epoxy amine reactions are faster than for the neat system but the thermoplastic seems not to have reacted with the thermoset network. The final blends are transparent but toughening increase is rather low.

Keywords: blends, kinetic, miscibility, thermoplastic epoxy, toughness

Introduction

The improving of the toughness of a thermoset epoxy network has been intensively studied with many thermoplastic modifiers such as high Tg polymers (poly(ether sulfone) PES or poly(ether imide) PEI).[1] The main issue is to avoid a dramatic decrease of the glass transition temperature of the reinforced thermoset epoxy. Generally the thermoplastic is dissolved in the initial reactive epoxy system. As the reaction goes on, epoxy molar mass increases and phase separation appears[2] at a relatively low conversion leading to a thermoplastic rich phase in an epoxy rich matrix. The size of the minor phase and the adhesion between phases determine the final properties such as mechanical ones.

A fully miscible system, i.e. with no phase separation but a miscible additive in the final network is an unusual behaviour. The homogeneity of polycarbonate based epoxy blends[3]

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was attributed to extensive trans-reactions between carbonate group of polycarbonate and the hydroxyl groups of the epoxy.

For our study, the thermoplastic was a poly(hydroxy-amino)-ether, from a new family of polymers.[4] These thermoplastic polymers, named BLOX* (* Trademark of the Dow chemical company) thermoplastic resins, are synthesized by reaction between epoxy monomer(s) and ethanolamine. In appropriate conditions, a linear chain is obtained.[5-6] These amorphous materials exhibit exceptional gas barrier protection properties, excellent adhesion on a variety of substrates, good mechanical toughness and stiffness.

BLOX present a similar chemical structure to Phenoxy. Phenoxy are epoxy homopolymers that have already been studied as a modifier of thermoset epoxies. Phenoxy are miscible over the entire composition range with Diglycidyl Ether of Bisphenol A (DGEBA) monomer. Miscibility and phase behaviour, morphology and then properties, are dependent on the choice of the curing agent.[7] The apparition of phase separation is controlled by both thermodynamic and kinetic factors.[7-8] The influence of the hydroxyl pendant groups during curing have been discussed.[9]

Our purpose was to investigate the initial miscibility of these new BLOX thermoplastics in an epoxy monomer with a close chemical structure and to appreciate its behaviour during the reaction leading to the epoxy network. Miscibility, kinetic and mechanical properties are presented and discussed.

Experimental

The epoxy monomer used in this study was Diglycidyl Ether of Bisphenol A (D.E.R. 330* liquid epoxy resin) with a polydispersity of $\bar{n}$= 0,15. The hardener, a bifunctionnal aromatic amine, was 4-4' methylenebis [3-chloro 2,6-diethylaniline] (LONZA). They were used without further purification.

Table 1. Characteristics of the BLOX.

Name	Resorcinol Content (%w)	Molar Mass (g/mol)	M_w/M_n	Glass Transition Temperature (°C)
BLOX00	0	~ 40,000	~ 3	~ 75
BLOX40	40	~ 60,000	~ 4	~ 55

Two amorphous BLOX thermoplastics have been used. The first one is a copolymer (BLOX00) obtained by reaction of DGEBA with ethanolamine. The second is a copolymer

(BLOX40) synthesised from the same monoamine but with two epoxy monomers, DGEBA and Diglycidyl Ether of Resorcinol. The characteristics and chemical structure of these products are described in Table 1 and Figure 1.

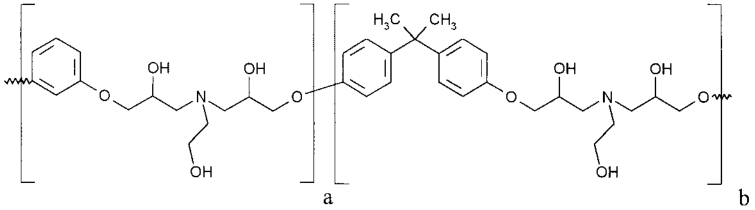
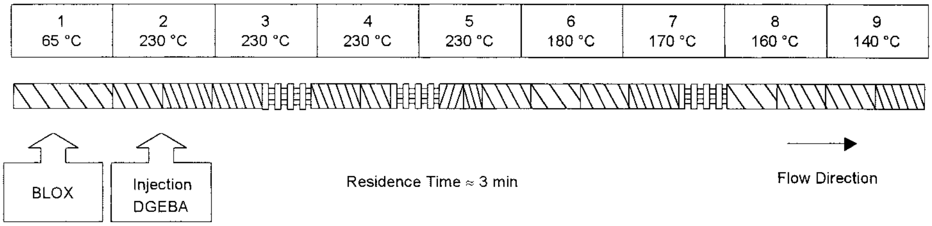


Fig. 1. Chemical Structure of BLOX, a and b corresponding respectively to resorcinol and bisphenol A unit.

During BLOX synthesis, the ethanolamine is used in a small excess to control chain ends (no epoxy groups) and molar masses. This means that a secondary amino group is on both BLOX chain ends: BLOX-NH-C_2H_4OH.

BLOX thermoplastic was ground into fine powder to increase contact surface with DGEBA. Initial epoxy monomer/BLOX blends have been prepared in a twin-screw extruder (CLEXTRAL BC21). 30/70 and 50/50 blends (DGEBA/BLOX weight content) have been prepared with a classical thermoplastic/liquid monomer screw profile as shown in Figure 2. Extrudates were quenched in water and dried two days at room temperature.



1	2	3	4	5	6	7	8	9
65 °C	230 °C	230 °C	230 °C	230 °C	180 °C	170 °C	160 °C	140 °C

Fig. 2. Temperature and screw profile for BLOX/DGEBA blends preparation.

For the determination of the cloud point curve, samples were prepared at 135°C during 5 min from extrudates.

For the kinetic study, DGEBA/BLOX blends were heated during 4 min at 135°C, the hardener was then stoechiometrically added and mixed 1 min more.

For the mechanical tests, 100g samples were blended at 135°C for 15 min in a glass reactor and then poured into a mould. The concentration of BLOX was varied between 5% to 40%w/w.

Cloud-point setup was home-made and used visible incident light and a photo transistor.[10]

Steric exclusion chromatography in tetrahydrofuran (THF) was carried out to follow the kinetic of curing. Every 15 min, samples were removed from the regulated oven and quenched in ice. THF was then added to reach a concentration around 3 g/mol. The solution is introduced in the apparatus (2 columns WATERS, pores diameter ~500nm and ~100nm). Evolution of the DGEBA main peak (peak n=0) may be expressed by: $X = 1-(A_t / A_0)$ with A_0 and A_t respectively the peak area for time=0 and t, X the conversion in molecules. As we suppose that the epoxy groups exhibit the same reactivity,[10] conversion can be calculated by the following expression: $x = 1-(A_t / A_0)^{½}$ with x the conversion in functions. Kinetic of the neat DGEBA-MCDEA system has been previously published.[11]

Rheological measurements have been performed in order to estimate the gel time. The sample was introduced between two parallel plates of 25 mm diameter, heated at 135°C and a constant strain is applied. A frequency sweep was used between 1 and 100Hz. The moduli G' and G'' and their ratio (tan δ) were registered as a function of time.

The critical stress intensity factor, K_{IC} was obtained from three-point bending tests performed on single-edge notched specimens (SEN). The procedure proposed by Williams and Cawood[12] was strictly followed with a crosshead speed of 10 $mm\cdot min^{-1}$. K_{IC} were calculated as the mean values of 7 tests.

Results

Initial Miscibility

The cloud point curve (CPC) of the initial thermoplastic/DGEBA system is shown in Figure 3. The vitrification curve (FOX equation [13]) has been plotted on the same graph. The curves obtained are typical of Upper Critical Solution Temperature (UCST) behaviour. For a temperature higher than the cloud point curve (CPC), the system is transparent for a fixed BLOX content. Characteristic points of such CPC are the threshold point, the maximum of the CPC and the intersection of the CPC curve with the vitrification curve. The threshold is around (5%, 110°C) for BLOX00 and higher for BLOX40 (10%, 135°C). Despite the similarity of their chemical structure and the eventual development of hydrogen bonds, the affinity between DGEBA monomer and BLOX thermoplastic is poor. Blends with a BLOX content higher than 45% are miscible and transparent over the whole temperature range.

The miscibility window in DGEBA for the copolymer BLOX00 is wider than that for the copolymer BLOX40. As there is no noticeable difference between the two BLOX molar masses, the difference in miscibility essentially results from the difference in the chemical structures. The presence of the resorcinol groups appears to decrease the miscibility of the thermoplastic.

It has to be noticed that when a sample containing 10%w of BLOX in DGEBA is heated at 135°C during 1 hour and then cooled at room temperature in the cloud point apparatus, the temperature obtained for the cloudy/transparent transition is lower than for sample without any pre-heating. As observed by SEC measurements, the DGEBA slowly homopolymerizes in presence of BLOX and miscibility is therefore increased. Apparently no DGEBA grafting on BLOX was detected. This surprising result will be further investigated and discussed in another paper.[14]

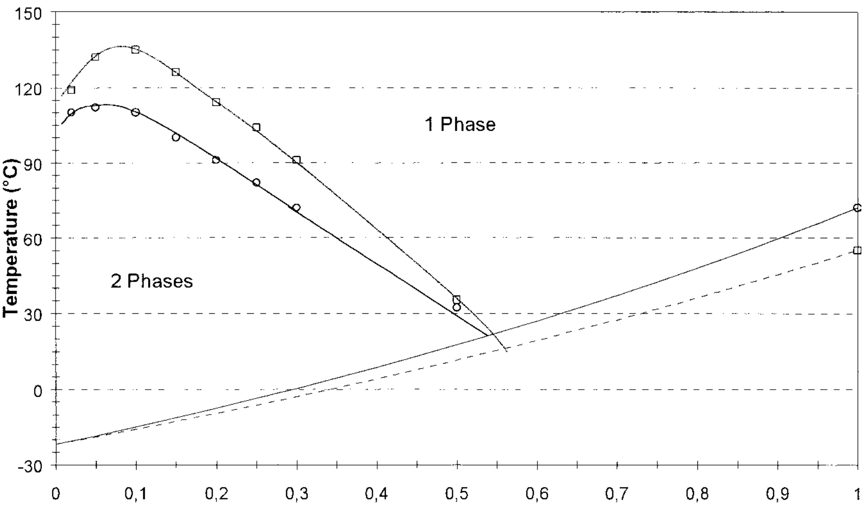


Fig. 3. Initial cloud point and vitrification curves for DGEBA/BLOX00 (○)(-) and DGEBA/BLOX40 (□)(---).

From DSC measurements, a single glass transition temperature near 30°C for a 50w/50w blend has been evidenced. These results are in agreement with the visual observations of the blends at the end of the extruder: 30/70 blends were cloudy whereas 50/50 were transparent at room temperature.

We have to notice that during blending (3min at 190°C in the extruder), the amine secondary end-groups of BLOX have probably reacted with the DGEBA in excess leading to epoxy end-groups without chain extension.

Kinetic

The epoxy/amine reactions have been carried out at 135°C for the neat system and for three blends containing 2, 10 and 20 BLOX00 (%w/w) respectively. The evolutions of epoxy conversion with time are presented in Figure 4.

Whatever the initial composition, the kinetic is faster in presence of BLOX compared to the neat system even if the epoxy and amino groups are diluted by the presence of the thermoplastic. The higher is the BLOX content, the faster is the kinetic. This behaviour can be explained by the presence of hydroxyl groups on the BLOX backbone and also by tertiary amines which catalyse the amine/epoxy reactions. Molecules containing tertiary amine are often used as accelerator for epoxy/amine reaction.

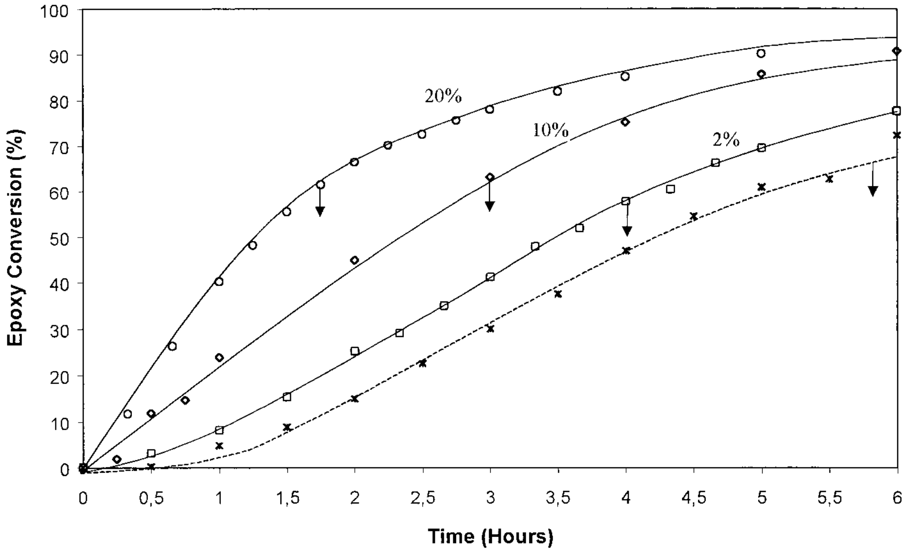


Fig. 4. Conversion versus time for different DGEBA/MCDEA/BLOX00 blends cured at 135°C: Neat (×), 2%TP (□), 10% TP (◇) and 20% (○). Arrows (↓) indicate gelation.

Gel times were then determined by two different measurements. Firstly the apparition of insolubles in THF and secondly the iso-frequency point on dynamical rheological measurement. The following Table 2 summarizes all the results.

Table 2. Gel time for DGEBA/MCDEA/BLOX00.

Thermoplastic content (%w)	Gel time		Conversion at the gel
	SEC	Rheology	
0 %	5 h ¾	6 h	~ 0.6
2 %	4 h	3 h 50	~ 0.6
10 %	3 h	3 h	~ 0.57
20 %	1 h ¾	1 h 40	~ 0.6

The initial composition of the blend is an epoxy-terminated BLOX in a stoechiometric epoxy monomer/hardener blend. During the epoxy/amine polyaddition, BLOX may react with its few epoxy terminal functions and/or the numerous hydroxyl groups of its backbone. Generally, the kinetic constant of epoxy/amine is greater than the one of epoxy/hydroxyl groups in the previous stage of curing when amino hydrogens are is still abundant.

Gelation appears for the same epoxy conversion ($x=0.6$) as the neat system. This result indicates that the growing thermoset is formed by polyaddition between a diepoxyde and tetrafunctional diamine. BLOX was supposed not to react with its pendant OH groups in our curing conditions; any reaction between hydroxyl groups of BLOX and DGEBA would have led to a decrease of the gel conversion. Similar result has been often obtained in thermosetting epoxy blends with phenoxy, a thermoplastic containing numerous hydroxyl pendant groups.[9] For a quite low curing temperature, no etherification appears in the previous stage of the reaction.

BLOX probably participate to the reaction with its epoxy chain ends. It may react as a diepoxyde with a higher molar mass than DER330. In this case, the functionality is not changed and the gel conversion is not affected as in our experiments.

An interesting point is that, in those conditions (curing reaction at 135°C and MCDEA as a hardener), no phase separation appears despite an initial UCST behaviour. It also means that the affinity and miscibility of BLOX is higher when the epoxy conversion increases. Two phenomena may explain this result.

i) The state of miscibility of any mixture may be described by the Flory-Huggins equation:[15]

$$\Delta G_m = RTV_r\,(\rho_1.\varphi_1.\ln\varphi_1/M_1 + \rho_2.\varphi_2.\ln\varphi_2/M_2) + RT\chi_{12}.\varphi_1.\varphi_2$$

with R: gas constant; T: temperature; V_r: reference molar volume; ρ_i: specific mass; φ_i: volume fraction; M_i: molar mass; χ_{12}: interaction parameter.

For thermoplastic/growing thermoset blends, the combinatorial first term decreases due to the increasing molar mass of thermoset precursors. The χ_{12} interaction parameter is usually rather constant and finally the Gibbs free energy of mixing increases leading to a lower miscibility of the thermoplastic in the growing thermoset and for a given conversion, a phase separation occurs. In our case the result is quite different. An explanation could be that the enthalpy may decrease as the conversion increases. Indeed, when the epoxyde react with the amino hydrogens, hydroxyl groups are formed. Numerous hydrogen bonds may appear between -OH groups of the growing thermoset and BLOX leading to specific interactions, to a possible decrease of χ_{12} up to negative value and an increasing solubility of the thermoplastic in the growing thermoset.

ii) Another explanation would be that a few amount of epoxy grafted BLOX or growing thermoset grafted BLOX may be generated due to the high concentration of BLOX hydroxyl pendant groups. Such grafted thermoplastic may increase the miscibility of BLOX in the final network.

Fracture Toughness

Samples with BLOX00 were cured at 135°C during 11h and post-cured 3h at 190°C (Cycle 1) to ensure a total conversion. As the maximum of the UCST curve for BLOX40/DGEBA is close to 140°C for 10%w, samples with BLOX40 were heated 11h at 150°C and also post-cured 3h at 190°C (Cycle 2) to avoid an initial immiscibility of the reactive blend.

The critical stress intensity factor is plotted as a function of the BLOX00 content in Figure 5. Only the values for BLOX00 are presented because results do not depend on the nature of BLOX. The K_{IC} can be seen to moderately increase with the thermoplastic concentration. This poor toughness increase may be explained by the miscibility of final blends. As no separation phase appears, no useful heterogeneous morphology in term of mechanical properties is produced during the cure. However, an interesting point is that final samples were transparent whatever the BLOX content and BLOX nature.

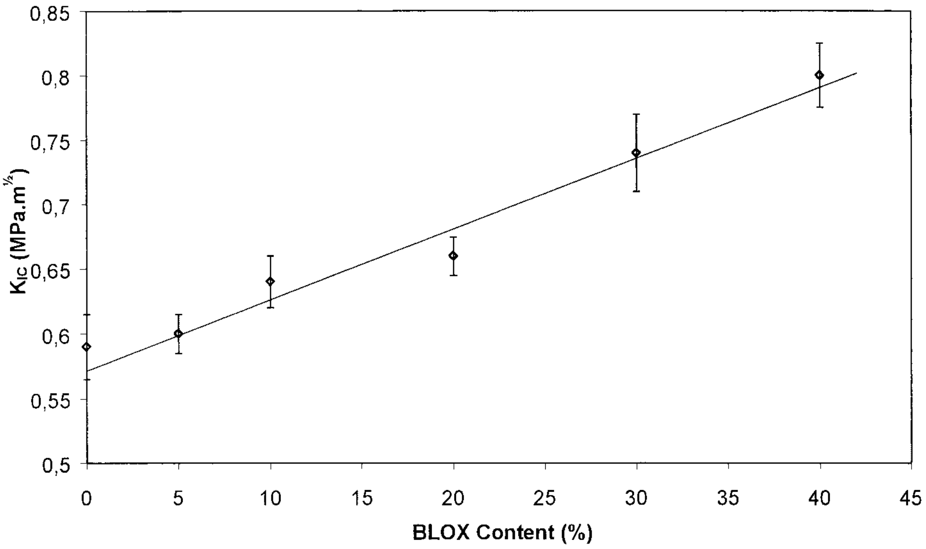


Fig. 5. Fracture toughness vs BLOX content for DGEBA/MCDEA/BLOX00 blends (○).

Conclusions

New thermoset/thermoplastic epoxy blends have been prepared by using a new thermoplastic poly(hydroxy-amino ether). The initial miscibility of the thermoplastic in DGEBA has been studied and an UCST behaviour has been highlighted with a high temperature threshold around 100°C. These results are definitely different from those obtained with Phenoxy/DGEBA system that is miscible over the entire composition range. But heating BLOX/DGEBA blends increases the miscibility. This will be discussed in another publication.[14]

After adding the MCDEA hardener, the thermoplastic was observed to catalyse the epoxy/amine reaction due to the presence of hydroxyl and tertiary amine groups. The higher is the thermoplastic content, the faster is the kinetic. No phase separation is observed during the reaction at 135°C and transparent blends are generated. Whatever the BLOX content, gelation appears for the same gel conversion as the neat system indicating that the pendant hydroxyl groups of the thermoplastic doesn't significantly react with the growing thermoset. Increasing of hydrogen bonds between blend components, few reactions between amine end-groups of BLOX and the growing network and/or the possible formation of epoxy grafted BLOX may explain the final miscibility of this system.

The toughness has been shown to moderately increase with thermoplastic content.

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