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Blends of a diglycidylether epoxy with bisphenol-A polycarbonate or poly(methyl methacrylate): cases of miscibility with or without specific interactions

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Physical and chemical interactions and miscibility in two binary blend systems: diglycidylether of bisphenol-A (DGEBA) with poly(methyl methacrylate) (PMMA) and DGEBA with bisphenol-A polycarbonate (PC), were investigated by differential scanning calorimetry and Fourier transform infra-red (i.r.) spectroscopy. Miscibility was found to exist in both binary blend systems (DGEBA/PC and DGEBA/PMMA blends) before and after heating. Chemical exchange reactions upon heating did not occur between DGEBA and PMMA; however, chemical interactions between the DGEBA and PC components in the blends were proven by evidence of elevation of the glass transition temperatures, shifting of the carbonyl i.r. absorbance peak, and unusual solvent resistance of the blends after heat treatment. The most probable crosslinked structure in the heated DGEBA/PC blend was elucidated. Copyright © 1996 Elsevier Science Ltd.

(Keywords: DGEBA epoxy; blends; miscibility)

INTRODUCTION

Bisphenol-A polycarbonate (PC) mixed with a difunctional epoxy has been briefly mentioned in a recent patent[1]. Subsequently, a few reports on the fracture and Fourier transform infra-red (*FT*i.r.) behaviour of PC blends with difunctional epoxy resins, such as diglycidyl ether of bisphenol-A (DGEBA), have appeared in the literature[2–5]. However, since those studies all focused on physical or macroscopic mechanical behaviour of hardener-cured epoxy blends, the true phase behaviour between the polymer and epoxy resin could be easily masked by the presence of the hardener. Additionally, hardener-cured blends of poly(methyl methacrylate) (PMMA) with DGEBA have also been investigated by Gomez and Bucknall[6]. They reported an initial miscibility in the PMMA/DGEBA blend before curing but distinct phase separation after curing by a hardener (an aliphatic amine). This type of phase evolution is quite typical for many thermoplastic polymers/modified epoxy resin systems. Epoxy resins, in the monomeric or oligomeric forms before being crosslinked by a hardener, are quite good in dissolving or dispersing many amorphous polymers. Many precured mixtures of linear polymers with epoxy resins may form homogeneous blends before curing, but most of these homogeneous liquid blends would turn into multiphase systems with complex phase domains after they undergo crosslinking cure reactions after introduction of curing agents or hardeners[7–12].

Reactions or strong specific interactions between the polymer and epoxy components, if taking place at appropriate temperatures, might prevent or lessen the extent of phase separation at the fully cured state. The aim of this research was to probe the phase behaviour of two binary PC/DGEBA and DGEBA/PMMA blend systems which, upon heat treatment, represented two extreme cases of specific interactions. In this study, an oligomeric epoxy resin was blended with PC or PMMA within a wide composition range. No hardeners of any type were used in order to simplify the phase behaviour and to make it easier to observe changes before and after heating of the binary blend systems. By the use of two binary blends with drastically different specific interactions, this study could focus on the relationships between chemical reactions among the components and phase behaviour of the hardener-free blend systems. By understanding the role of such interactions, the phase behaviour of hardener-cured blends of polymer/epoxy networks may be more easily predicted and controlled.

EXPERIMENTAL

Materials and sample preparation

The epoxy resin used was diglycidyl ether of bisphenol-A (DGEBA; Epikote-828, Shell Corp. USA). The bisphenol-A polycarbonate (PC) was GE Lexan^R HF1130, with $M_w = 23\,000\,\mathrm{g\,mol^{-1}}$. Poly(methyl methacrylate) (a-PMMA) was obtained from a commercial source (Chi-Mei Inc., Taiwan). PMMA and PC were weighed separately and dissolved in the methylene chloride (CH_2Cl_2) or tetrahydrofuran (THF) solvent.

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The resulting polymer solution was then mixed with a predetermined quantity of the epoxy resin at room temperature. The solvent in the polymer/resin solution was vaporized in a circulation oven with an exhaust fan at room temperature, followed by residual solvent removal in a vacuum oven for 24 h at 60°C. Solution blending was performed at room temperature or slightly above room temperature (45–50°C). It was found that film casting at about 50°C yielded the best quality of film samples. A visually transparent film was obtained at the end of this step. The mixtures of various blending compositions were then exposed to several different isothermal temperatures for various lengths of time. Specifically, two temperatures (190 and 220°C, respectively) were used to treat the samples.

Differential scanning calorimetry

The glass transition temperatures and extents of any physical change of the blends before and after exposure to selected temperatures for various times were measured with a power-compensated type of differential scanning calorimeter (Perkin-Elmer DSC-7, equipped with an intracooler and a computer for data acquisition/analysis). All measurements were made at a scan rate of 20°C min^{-1} within the temperature range of −25 to 200°C, and the glass transition temperature (T_g) values were taken as the onset of the transition (the change of the specific heat) in the heat flow curves.

Fourier transform infra-red spectroscopy

Fourier transform infra-red (*FT*i.r.; Bio-Rad FTS-40A spectrometer) spectra were obtained at 4 cm^{-1} resolution and the number of scans was 64. The recorded wavenumber range was 400–4000 cm^{-1}. The measurements were carried out either on thin films case onto potassium bromide (KBr) discs or by a powder mixing technique. Blends of various compositions were prepared by dissolving appropriate amounts of the components in methylene chloride (CH_2Cl_2) to yield 2% (w/v) solutions. Thin films for *FT*i.r. studies were obtained by casting the polymer solutions onto potassium bromide discs at room temperature, then rapidly evaporating the solvent by immediately placing the sample in a vacuum oven at 40°C for 48 h. Another method for preparing the *FT*i.r. sample was by powder grinding/mixing and pellet forming (pressed disc). The epoxy/polymer blend sample (about 2 mg) was intimately mixed with approximately 300 mg of dry, powdered potassium bromide. Uniform mixing of the blend sample with KBr was conducted by thoroughly grinding in a smooth agate mortar. The blend/KBr mixture was then pressed with a special die under a pressure of 600 kgf cm^{-2} into a transparent disc.

RESULTS AND DISCUSSION

Glass transition behaviour of as-prepared binary blends

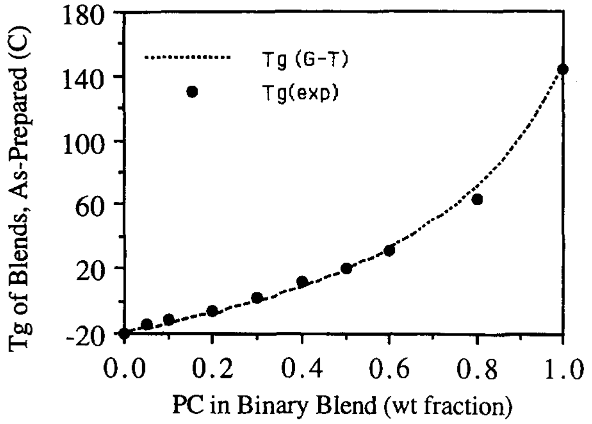


Figure 1 Glass transition temperature–composition relationships for binary DGEBA/PC blends

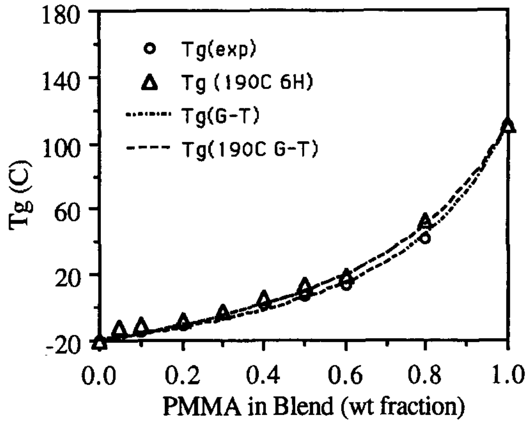


Figure 2 Comparison of glass transition temperatures for PMMA/DGEBA blends before and after heating at 190°C for 5 h

Both binary blends of DGEBA/PC and DGEBA/PMMA were first investigated. The differential scanning calorimetry (d.s.c.) thermograms (not shown for brevity) revealed that only a single T_g was observed in each of the blends within the whole composition range, and both blend systems were judged to be miscible. The composition dependence of blend T_g values were investigated. *Figure 1* shows the T_g–composition curve for the as-prepared (unheated) DGEBA/PC blend system. The T_g dependence on composition for the binary blend system of DGEBA/PC exhibits a negative deviation from the linear relationship described by the equation

$$T_g = w_1 T_{g1} + w_2 T_{g2}$$

Another notable feature in the T_g–composition curves is that the curve for the binary blend system is skewed at the high PC contents (i.e. low DGEBA contents).

Figure 2 shows the T_g–composition curve for the blend system of DGEBA/PMMA. Again, the T_g behaviour for this blend system suggests that the as-prepared blends are distinctly miscible, and the T_g dependence on composition is similar to that of DGEBA/PC, which exhibits a similar negative deviation from the linear relationship described by the equation

$$T_g = w_1 T_{g1} + w_2 T_{g2}$$

This result on the as-prepared DGEBA/PMMA blends of various compositions agreed with that reported earlier by Gomez and Bucknall[6] who stated that the Gordon–Taylor equation[13]

$$T_g = (w_1 T_{g1} + k w_2 T_{g2})/(w_1 + k w_2)$$

best described the T_g–composition relationship, where $k = \Delta C_{p2}/\Delta C_{p1}$ (i.e. ratio of heat capacity change in polymer to the change in DGEBA). They discussed that the low positive value of k (= 0.20) indicated that the interaction forces between DGEBA and PMMA were quite weak. This is also the case for the blend system of DGEBA/PC as well as DGEBA/PMMA, both being in the as-prepared state before being subjected to heat treatment. Note the composition dependence relationship is over-predicted by the Fox equation[13,14]

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

exhibiting a minimum (negative) deviation from the prediction. To better describe the relationships, the Gordon–Taylor equation was again used. The fitted k values for the as-prepared DGEBA/PC and DGEBA/PMMA blends were 0.31 and 0.24, respectively. By comparison, the higher values of k for the DGEBA/PC blends indicates that the interaction force in this blend system may be slightly stronger than that in the DGEBA/PMMA blend system. The difference, however, is not great. Note that the value of k (= 0.24) for the DGEBA/PMMA blend system obtained in this study is in good agreement with $k = 0.2$ obtained by Gomez and Bucknall[6]. The low values of k for both systems suggested that the interaction forces were both relatively weak and probably non-specific, although both blends were miscible.

Binary blends subjected to heating

The as-prepared blends were subsequently heated at several isothermal temperatures for various lengths of time ranging from 20 to 200 min. D.s.c. characterization was then performed on these blends to determine their glass transition behaviour. *Figure 2* shows a comparison of the T_g values of the as-prepared DGEBA/PMMA blend (open circle) and heated DGEBA/PMMA blend (open triangle) as a function of composition. After heat treatment at 190°C for 5 h, the blends still exhibited a single T_g, indicating a single-phase behaviour of the blends. However, apparently the heating did not result in any significant changes in the T_g values of the DGEBA/PMMA blends. Additionally, the fitted k value for the DGEBA/PMMA blend increased from 0.24 for the as-prepared DGEBA/PMMA blend to 0.29 for the same blend system after heat treatment. This value for the heated DGEBA/PMMA blend ($k = 0.29$) is only slightly higher than that for the as-prepared DGEBA/PMMA blend ($k = 0.24$), indicating that there might be some changes induced by the heating. The changes in the DGEBA/PMMA blend, however, are insignificant when compared to the corresponding changes in the DGEBA/PC blend system before and after the same heat treatment. The result suggests that there was little or no reaction between the DGEBA and PMMA molecules in the binary blend.

Figure 3 shows a plot of T_g as a function of time of heating at 220°C for the DGEBA/PC blend (composition 50 wt% PC). The T_g values of the thermally treated DGEBA/PC blend sample significantly increased as the heating time was increased. The blend sample heated for 200 min at 220 °C exhibited a T_g of 70°C, which is 50°C higher in comparison to the as-prepared (unheated) DGEBA/PC blend sample of the same composition ($T_g = 20$°C). The increase in T_g of the heated DGEBA/PC blends is likely due to reactions taking place between the two components, which lead to a network-forming structure. This will be discussed in more detail using the *FT*i.r. evidence in later sections.

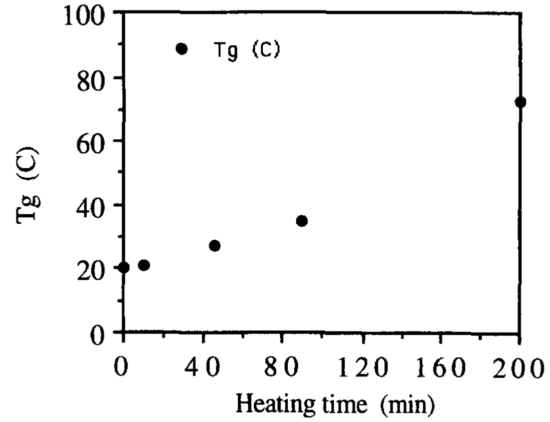
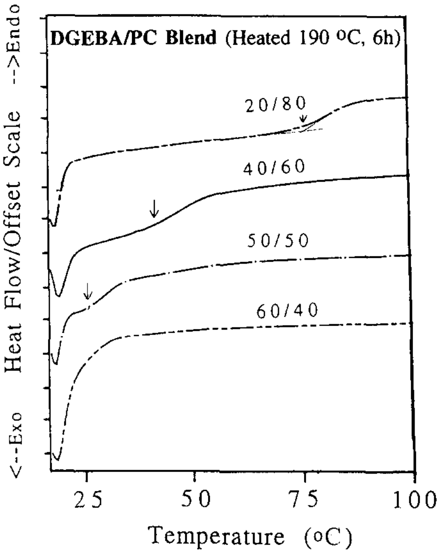


Figure 3 Glass transition temperatures for PC/DGEBA blends as a function of heating time at 220°C



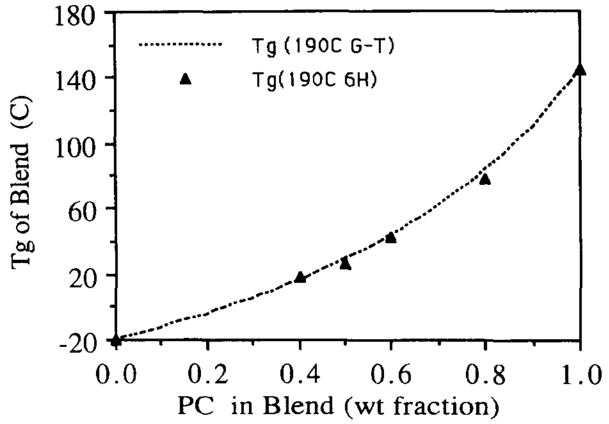


Figure 4 Glass transition temperatures for DGEBA/PC blends before and after heating at 190°C for 6 h: (top) d.s.c. thermograms, (bottom) T_g composition curve

Figure 4 shows (top) the d.s.c. thermograms, and (bottom) the T_g–composition curve with a fitted Gordon–Taylor parameter, $k = 0.42$, for the DGEBA/PC blend after heating at 190°C for 6 h. This value for the heated DGEBA/PC blend system is significantly higher than the k value for the as-prepared DGEBA/PMMA blend system ($k = 0.31$), indicating that there were significant changes in the blend after heating at 190°C. It should be pointed out that when heating was conducted at higher temperatures or for longer times, the changes in the k values for the heated blend samples were increasingly large, suggesting an even greater interaction between the components. For the same blend heated for the same time at a higher temperature of 220°C, a greater value of k resulted; however, the T_g–composition curves began to exhibit a sigmoidal shape. The sigmoidal shape in the T_g curves reflected the fact that the extent of chemical links and network structure varied with the PC content in the blends when heated at high temperatures. Similar behaviour has also been observed in the blend system of PC with tetraglycidyl 4,4'-diaminodiphenylmethane (TGDDM), reported earlier[15].

Table 1 Qualitative solvent resistance of heated blends in methylene chloride[a]

Blends/compositions	Dissolution in solvent
DGEBA/PMMA (heated[b])	
20/80	Readily dissolved
50/50	Readily dissolved
80/20	Readily dissolved
DGEBA/PC (heated[b])	
20/80	Most remained intact
50/50	Intact, did not dissolve at all
80/20	Some remained undissolved

[a] All as-prepared (unheated) binary blend systems were readily dissolved in the solvent

[b] Heated at 190°C for 12 h

Solvent behaviour of blends before and after heating

The cast films or plaques of both blend systems were visually transparent. After the prescribed heat treatment, both blend systems were still transparent. Tests of solvent resistance were performed to assess possible effects of heating on reactions or network forming in the blends. Both as-prepared binary blends were readily dissolved in CH_2Cl_2 at room temperature. Their solvent behaviour, however, was found to be significantly changed after the blends were heated at a high enough temperature, say 190°C. The observed changes in the solvent behaviour are summarized in *Table 1*. Binary DGEBA/PC blends of three compositions were tested: 20/80, 50/50 and 80/20. Without being subjected to heating at 190°C, all three as-prepared blends of DGEBA/PC were readily dissolved in the methylene chloride solvent, indicating that the interactions between the components in the miscible blends were typically physical. The binary blends were then heated at 190°C for 12 h before they were immersed in methylene chloride. All three compositions of the heated DGEBA/PC blend displayed drastically different solvent behaviour by becoming indissoluble in the solvent, indicating that chemical links and a network structure were formed between the two components.

Fourier transform infra-red analysis

The d.s.c. and *FT*i.r. results suggested that only slight intermolecular crosslinking reactions were occurring among the DGEBA monomeric molecules when the neat epoxy was heated at high temperatures between 180 and 240°C. Addition of PC or PMMA into DGEBA, however, might result in a completely different situation. This is discussed in the following for the two binary blend systems.

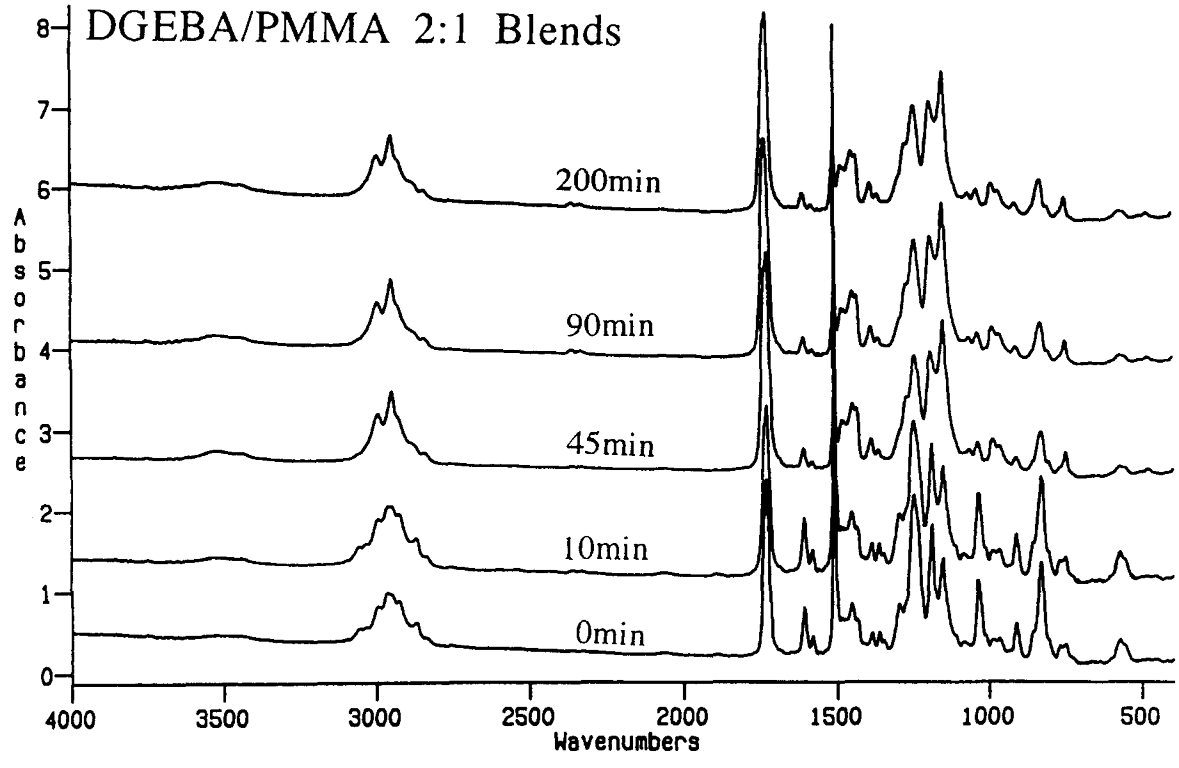


Figure 5 Full *FT*i.r. spectra of the DGEBA/PMMA blend samples heated for various times at 220°C

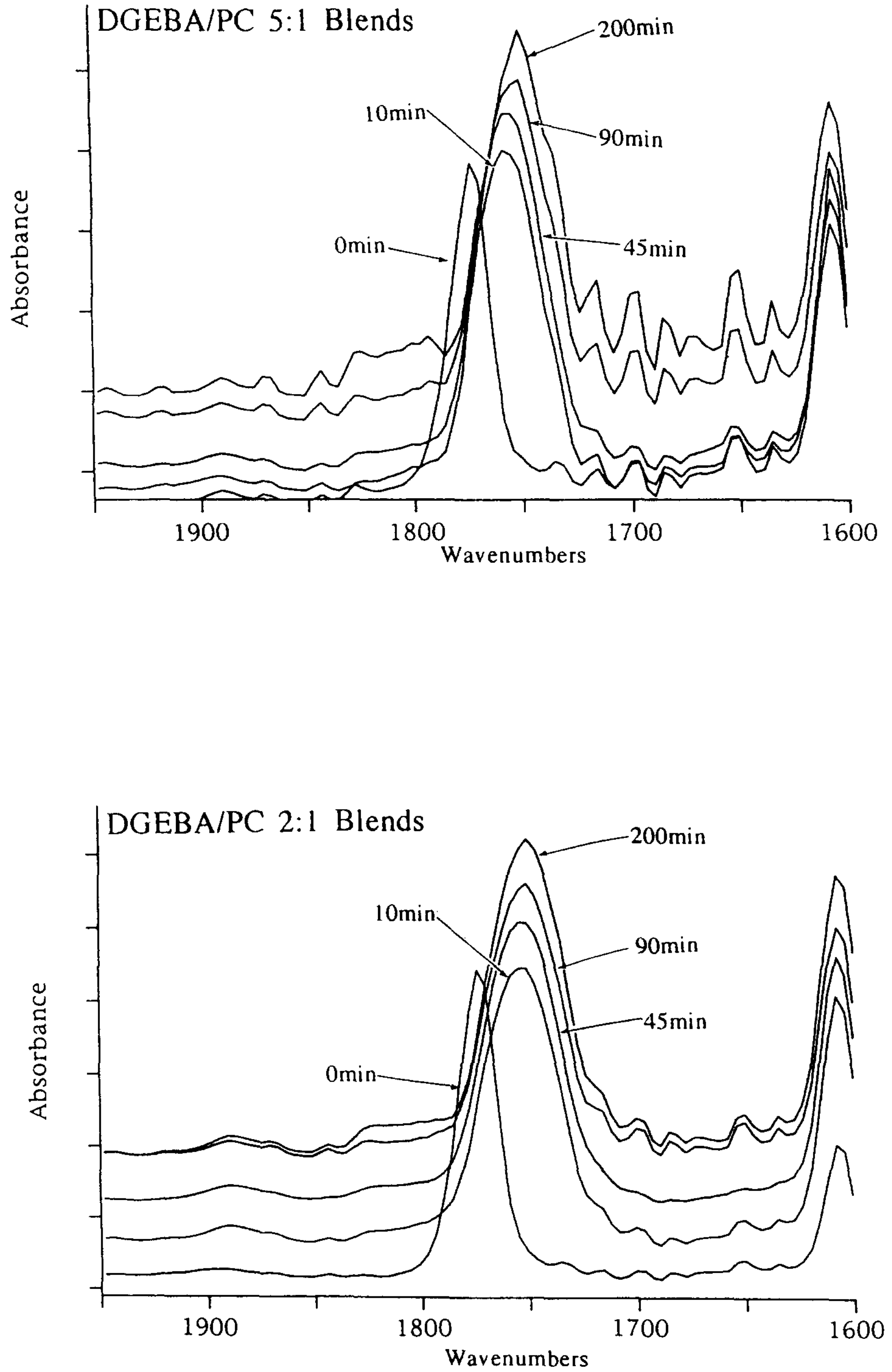


Figure 6 Carbonyl absorbance peak locations in the *FT*i.r. spectra of the DGEBA/PC blend samples heated for various times at 220°C: (a) 16.6 wt% PC; (b) 32.3 wt% PC

DGEBA/PMMA binary blends. Figure 5 shows the full *FT*i.r. spectra (500–4000 cm^{-1}) of the binary DGEBA/PMMA blend samples (PMMA content 33.3 wt%) having been subjected to heating at 220°C for various periods of time. There are several features in the spectra. First of all, the C=O absorption peaks remain at the same position (1725 cm^{-1}). The full spectra also show that there is a slight increase in the broad hydroxyl absorption peak at 3570 cm^{-1} in all the three blend compositions, indicating that there might be homopolymerization of the DGEBA molecules as the heating time was increased. The epoxide peak (943 cm^{-1}) of the DGEBA/PMMA blend diminishes, but does not disappear completely, up to a heating time of 200 min. Furthermore, in order to examine the possibility and extent of homopolymerization by DGEBA itself, a neat DGEBA sample was pelletized with KBr. When heated to 220°C, DGEBA, in presence of KBr, also exhibited a slightly diminishing epoxide peak as the time was increased, indicating partial homopolymerization, causing a broadening of the hydroxyl peak. The extent of such reactions, however, was not great.

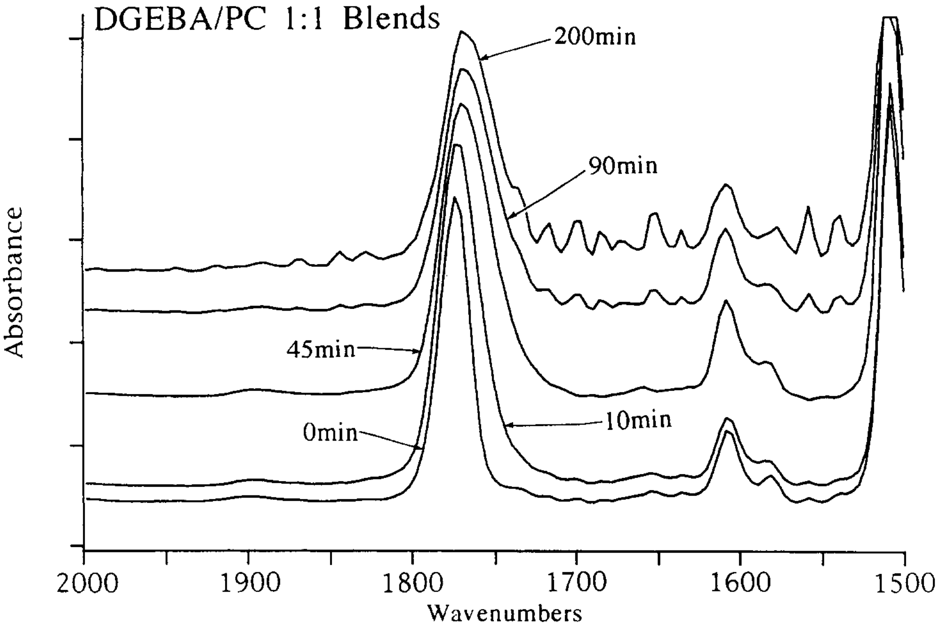


Figure 7 Carbonyl absorbance peak locations in the *FT*i.r. spectra of the DGEBA/PC blend (50 wt% PC) samples heated for various times at 220°C

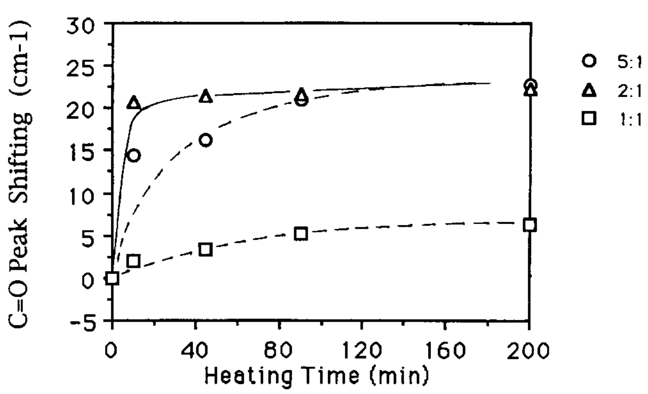


Figure 8 Comparison of carbonyl peak shifting for the DGEBA/PC blend system of three different compositions as a function of heating time. The carbonyl peak for the DGEBA/PMMA blend does not shift at all regardless of the heating times or composition

DGEBA/PC binary blends. *Figures 6a* and *b* show the partial *FT*i.r. spectra (1600–1950 cm^{-1}) of two binary DGEBA/PC blend samples (PC contents 16.6 and 33.3 wt%, respectively, for *Figures 6a* and *b*) after heating at 220°C for various periods of time from 0 to 200 min. For both compositions, the C=O absorption peak is apparently shifted to lower wavenumbers as the heating time is increased for the three different compositions. Additionally, the C=O peak is more broadened (as measured by the half-height width of the peak) for the two DGEBA/PC blends heated for longer times. The peak of the original C=O group in the PC chains is located at 1774 cm^{-1}. However, a *trans* reaction turned some of the carbonate C=O groups into an aliphatic-linked C=O, which absorbs i.r. at lower frequencies. Since it is not possible that all the C=O groups in PC were transformed, the reaction resulted in mixed C=O groups of aliphatic and aromatic linkages. The peak broadening phenomenon may be associated with this partial transformation after heat treatment on the blends. Similarly to the DGEBA/PMMA blend system, the magnitude of the broad–OH i.r. absorption peak of the DGEBA/PC blend system in the full i.r. spectra (not shown for brevity) is seen to increase as a function of the heating time. This indicates that the concentration of the –OH groups in DGEBA molecules might have been enhanced during heating of the blend.

A third composition of the DGEBA/PC blend with an even higher PC content was examined. *Figure 7* shows the *FT*i.r. spectra (1600–1950 cm^{-1}) of the binary DGEBA/PC blend samples (PC contents 50 wt%) after heating at 220°C for various periods of time from 0 to 200 min. The original trend of increasing shift as a function of increasing PC contents is now reversed.

The extent of shift is clearly dependent on the composition of PC in the blends. To show the changing trend of the magnitude of shift for blends with various PC contents, a quantitative comparison was made by plotting the magnitude of shift as a function of heating time for all three blend compositions. *Figure 8* shows a comparison of the magnitudes of peak shifting of the C=O absorbance for these two binary blend systems. For the DGEBA/PC binary blend system (two blend compositions with 16.6 and 50 wt% PC), shifting of the C=O peak as a function of heating time is apparent and obviously dependent on the blend compositions. The increase of peak shifting as a function of heating time at 220°C is clearly associated with the increase in the reaction extent as time increases. The greater magnitude of shift of the C=O peak for the DGEBA/PC blend with a lower PC content (16.6 wt%) in comparison with that with a higher content (50 wt%) can be explained in terms of the available –OH sites for the *trans* reaction to occur. At lower PC contents (high DGEBA concentration), there are a relatively large number of –OH sites in the epoxy available for reaction with the carbonate groups in PC. The magnitude of shift with time of heating was found to increase with PC contents and was greatest for the blend with a PC content of up to 33.3 wt% in the blend, while the magnitude of shift decreased as the PC content increased beyond 33.3 wt%. At higher DGEBA concentrations (i.e. lower PC content) in the blends, there were apparently comparatively more –OH groups for the PC chains to react with. In contrast with the apparent peak shifting observed in the PC/DGEBA blend system after heating, shifting of the C=O group in the DGEBA/PMMA blend system is not observed at all, regardless of the heating time or blend composition.

Shifting of the carbonyl absorbance peak has also been reported to occur in polymer pairs where H-bonding interactions and/or *trans*-ester reactions are considered likely, such as in blends of phenoxy–poly(ϵ-caprolactone)[16], PC–phenoxy[17], and PC–poly(ethylene terephthalate)[18,19]. H-bonding interactions may exist in the blends between the carbonate group in the PC chain segments and the hydroxyl group in the oligomeric DGEBA molecules. The carbonyl shifting in DGEBA/PC blends as a function of heating, however, might not be accounted for solely by changes in the H-bonding interactions between the species after heating. The prospect of heating-induced chemical links between the PC and DGEBA molecules was likely. The possibility of reactions between PC and DGEBA was also further substantiated by the increase of T_g of the DGEBA/PC blend system as a function of heating time. Additionally, a crosslinked structure, reflecting a highly reacted state, of the DGEBA/PC blend after heating is demonstrated by the insolubility of the blend in CH_2Cl_2. By contrast, the T_g behaviour and the result of quick dissolution in CH_2Cl_2 of the heated DGEBA/PMMA blend suggested that the reactions between DGEBA and PMMA were probably negligible.

Discussion on network forming of DGEBA/PC blend

From the *FT*i.r. data and the above analysis, a mechanism for the reactions in the DGEBA/PC blend system is proposed. The main reactions are primarily bond exchanges between the hydroxyl group (–OH) in oligomeric DGEBA and the carbonate group (O–CO–O) in PC. Upon heating in the DGEBA/PC blend, some of the PC molecular chains are fractured at the carbonate linkages, followed by grafting of the fragmented PC chains onto the hydroxyl sites of the DGEBA epoxy molecules. As a side product, molecules of shorter PC chains with an exchanged hydroxyl end group are liberated and remain free at early stages of the reaction. At high extents of exchange reaction, all originally free PC chains are eventually grafted. It should be noted that some of the DGEBA oligomeric molecules have multiple –OH sites, thus the exchange reactions between PC and DGEBA have a natural tendency to develop a network structure. In addition, at high enough temperatures, the epoxide rings at the end of DGEBA molecules will start to homopolymerize, which further helps extend the network. The phenomena found in this DGEBA/PC blend system are similar to those reported earlier for a blend system of PC with TGDDM[15].

It is quite difficult to judge from the *FT*i.r. data whether PMMA underwent reactions with DGEBA since the C=O absorption peak did not change position at all as a result of heating of the DGEBA/PMMA binary blend samples. The reason for no shift occurring is simple. Even if there were a *trans* reaction similar to that occurring in the DGEBA/PC pair, C=O peak shifting would not be expected. This is because the carbonyl group in the PMMA molecules is originally aliphatic-linked, while a *trans* reaction with DGEBA, if taking place, still results in an aliphatic-linked C=O structure. Although the *FT*i.r. results did not yield unambiguous evidence, the T_g and solvent resistance behaviour of the heated DGEBA/PMMA blend systems, discussed in earlier sections, strongly suggested that chemical links did not develop between the components in the DGEBA/PMMA system.

A *trans* reaction between C=O in PC with DGEBA, however, would result in different linkages. The C=O in PC was originally carbonate-linked (i.e. ϕ–O–CO–O–ϕ) groups that absorb at higher i.r. frequencies, while the reaction might turn the carbonate linkages into aliphatic/aliphatic-linked carbonyl groups that absorb at lower frequencies. A shift of the C=O absorption peak to lower frequencies indicates that such reactions are likely.

Schematic network structure in heated DGEBA/PC blends

From the above discussion, the resulting structure of the binary DGEBA/PC blend after heat-induced reactions along with the possible products and/or unreacted species are depicted in *Figure 9*. At low extents of exchange reactions, not all the PC and DGEBA molecules were grafted or interlinked. Depending on the extent of reaction, greater or lesser amounts of DGEBA and PC remained in the unreacted state. Note that the pendent epoxide groups from the grafted DGEBA may also be opened and further reacted by an appropriate curing agent if introduced into the blend system. As proposed in the mechanisms, the reactions of the hydroxyl group (–OH) of the DGEBA epoxy with the carbonate group in PC lead initially to the formation of a graft copolymer of DGEBA and PC with an aliphatic–aromatic carbonate link. Finally, upon extended heating with further opening of the epoxide groups in DEGBA, a highly linked structure of DGEBA/PC was formed. These chemical bondings helped ensure the observed miscibility in the blends after heating at 180–220°C. Additionally, the interlinked network resulted in the observed elevation of the glass transition temperatures of the DGEBA/PC blends upon heating. The intractability of the heated blends in the CH_2Cl_2 solvent provided a clear indication of the formation of a crosslinked rigid structure in the PC/DGEBA blends after the reactions.

CONCLUSION

The d.s.c. and *FT*i.r. results indicated that miscibility existed in the as-prepared (unheated) binary blends of DGEBA/PC and DGEBA/PMMA. A single T_g, indicating the existence of miscibility, was found in as-prepared (unheated) blends in the complete composition range. Additionally, a single T_g was found in the blends after heating at various temperatures between 190 and 220°C for various times. The T_g of the heated blends, however, increased with the temperature and duration of heating for the binary DGEBA/PC blend systems, suggesting possible reactions. On the other hand, the T_g increase in the binary DGEBA/PMMA blend system after heating at comparable temperatures for the same time was negligible, implying a lack of

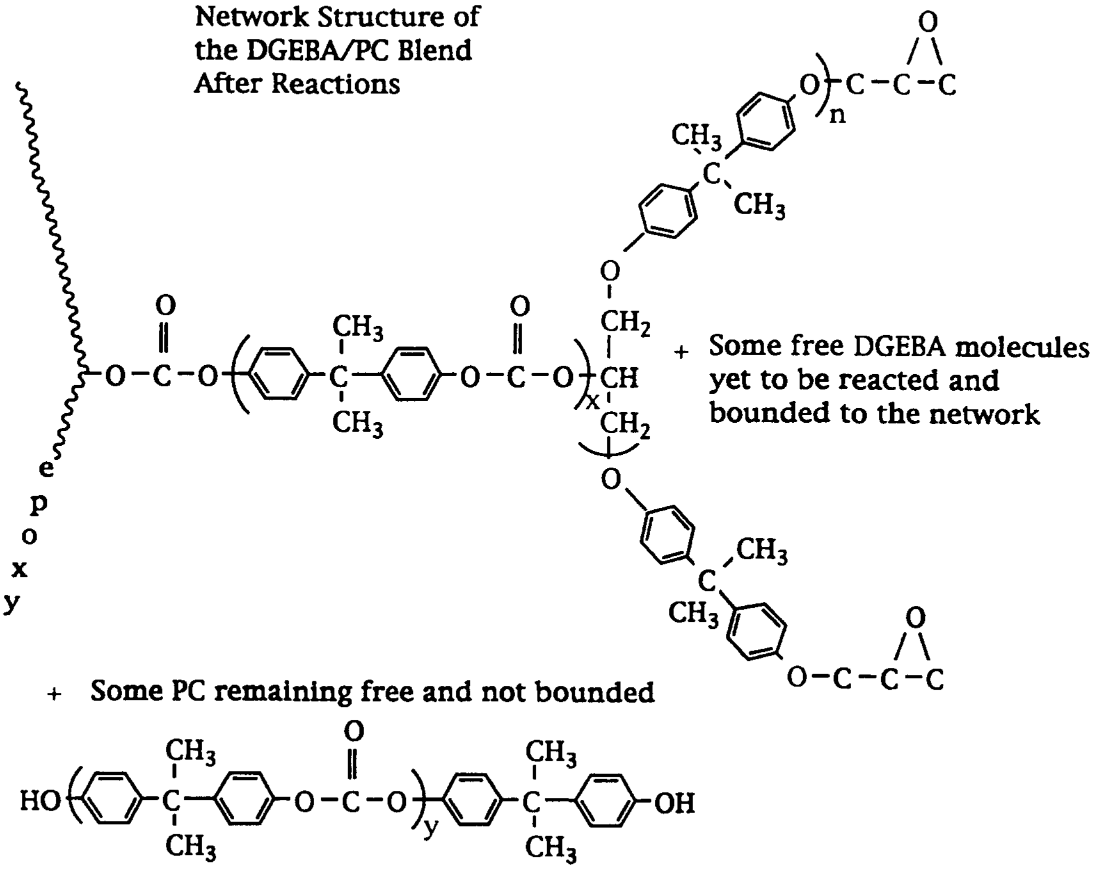


Figure 9 Schematic drawing of the final networking structure showing the products of the DGEBA/PC blend system after heating

reaction between PMMA and DGEBA components in the blend. The solubility behaviour of the heated PMMA/DGEBA blend system also indicated that exchange reactions between PMMA and DGEBA did not occur or progress to any significant extent.

The possible reactions between the components and resulting structures after the heat treatments were probed by *FT*i.r. in order to investigate the detailed mechanisms. In all DGEBA/PC blends, the carbonyl peaks were found to shift to lower frequencies with increasing extent of reaction. The –OH and carbonate exchange was the main type of reaction in the binary DGEBA/PC blends upon heating. The extents of chemical links and distribution of different links and product species were obviously dependent on the relative contents of PC in the DGEBA/PC blends. It was this composition-dependent distribution that caused the asymmetry in the T_g–composition curves discussed in earlier sections. Finally, upon extended heating with further opening of the epoxide groups in DEGBA, a highly linked structure of PC/DGEBA was formed.

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