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Polycarbonate–epoxy semi-interpenetrating polymer network: 2. Phase separation and morphology

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Bisphenol A-based epoxy resin (DGEBA) was modified with bisphenol A polycarbonate (PC), by either a physical or chemical process, and thermally cured with 4,4'-diaminodiphenyl sulfone, tetraethylenepentamine, and anhydride. The phase separation in the PC/epoxy blends was controlled by varying the composition, and the PC–epoxy reaction, and utilizing curing agents of different reactivity. A single phase morphology was achieved by accelerating the curing reaction, or introducing PC–epoxy reaction, or eliminating crystallization of PC. Under certain conditions, PC spherulites are able to form, in company with the formation of epoxy networks. Curing of the epoxy resin modified the crystallization mechanism, the melting behaviour and the morphology. The nuclei are likely to be pre-existing high molecular weight PC chains and are formed by the special interaction between PC molecules and the primary network. Low molecular weight epoxy resins increase the crystallization rate. The internal fractionation changes by PC chain scission during the melt blending process has an important influence on the crystallization. The spherulite morphology fixed by semi-IPN structure subjected a loss of order by annealing. It is suggested that hydrogen bonding and graft reaction in this kind of PC/epoxy semi-IPN is the key to controlling phase separation and morphology. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polycarbonate; epoxy resin; blend; phase separation; controlling; morphologies)

INTRODUCTION

Tough, high performance thermoplastic modified epoxy resin networks have been shown to have a distinct advantage over elastomeric modified systems, because the fracture toughness can be increased without substantially sacrificing the glass transition temperature (T_g) or modulus of the resulting blend. Since the pioneering work of Bucknall and Partridge[1] on epoxies modified with poly(ether sulfone), there has been much activity in this area, as suggested by the number of articles in the scientific literature[1-15]. Most of the focus of such work addresses the amount of toughness obtained and those material parameters that enhance the toughening effect. The important features of thermoplastics include: the chemical constitution, the T_g, the molecular weight, the mechanical and thermal properties, and the presence of chemically reactive groups at the chain ends or in the polymer backbone or pendant to the backbone.

At present, studies in this field concentrate on the phase separation behaviour, and on toughening mechanisms.

A great deal of controversy exists on the nature of the toughening mechanisms in rubber modified epoxy resin networks[16-18]. Much of the dispute is centered around whether the modifier or the matrix absorbs most of the fracture energy. Generally, it is widely recognized that rubber toughening or hard filler modification cannot induce yielding with highly crosslinked matrices. In view of this inherent problem, it appears that successful

toughening can be achieved only by introducing energy absorption processes that do not depend upon matrix ductility. In other words, morphology will be very important for toughening effects. Unfortunately, there has been little progress made in determining the toughening mechanisms in thermoplastic modified epoxy resin, and even less progress in controlling the morphology.

The phase separation behaviour in a thermoplastic modified epoxy resin network is controlled by the competing effects of thermodynamics, kinetics, and polymerization rate. Yamanaka and Inoue[19] studied the structure development in epoxy resins modified with PES. They achieved control of the morphology by accelerating the approach to the gel point. Almen et al.[20] have reported that the co-continuous morphology, characteristic of spinodal decomposition, results in enhanced fracture toughness in PES toughened resins. Cho et al.[21] found that the cured resin with phase-inverted morphology showed the highest fracture toughness. Pearson and Yee[22] also mentioned the importance of morphology on the fracture toughness of PPO modified epoxy resin.

In our approach, bisphenol A polycarbonate (PC) was used as a modifier in the compounding of epoxy resin for improved toughness. Independently, PC has the following advantages:

1. Good mechanical properties and thermal stability.
2. Good compatibility with epoxy resin.
3. Ability to interact with a resin or amine or network, via hydrogen bonding.

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4. Diepoxides can react with in-chain carbonate groups readily, in the presence of quaternary ammonium salts[23].

Therefore, the purpose of this work is to prepare a new type of thermoplastic modified epoxy resin. The morphology can be controlled by varying the curing agents, composition or catalyst, leading to different degree of hydrogen bonding and a different chemical reaction. In the first part of this work, the preparation, interaction and curing behaviour of PC/epoxy blends have been reported. The results showed that the PC chain scission process occurred through the reaction of carbonate groups with hydroxyl groups in the epoxy resin during the melt blending process, which results in formation of a small amount of epoxy-terminated PC chains. The presence of PC usually remains ineffective, or has a promotive effect on the curing reaction for the amine hardener, because of the *in situ* curing mechanism, except for the diffusion control effect due to the increase in viscosity. The *in situ* curing mechanism results in the formation of PC/epoxy semi-IPN structures. In this article, the phase separation and morphology of PC/epoxy semi-IPNs have been investigated using differential scanning calorimetry (d.s.c.), dynamic mechanical spectroscopy, and transmission electron microscopy (TEM). Additional research regarding chain entanglement structure and dynamic mechanical properties will be reported in the third part of this contribution. It was hoped that these results would aid in designing high-performance materials by the control of structure development in these novel materials.

EXPERIMENTAL

Materials

All materials used throughout this work were from commercial sources and were used as received. The epoxy oligomer, diglycidyl ether of bisphenol-A (DGEBA) was supplied by Guang Zhou East Chemistry Company (E51, molecule weight 392). PC was a Shun De Resin Company product, which has molecular weight of 4.3×10^4 and is a kind of powder, namely PC powder, its structural formula is shown below:
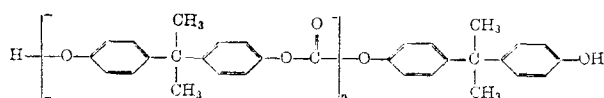
For curing agent, the aromatic amine, 4,4'-diaminodiphenyl sulfone (DDS) was used. Other curing agents, tetraethylenepentamine (TEPA) and anhydride (maleic anhydride/phthalic anhydride = 1/1) were also used to compare with DDS. Tetramethyl ammonium iodide (TMAI) was used as a catalyst to introduce reaction of PC with epoxy resin. The reactivity diluent was glycidyl phenyl ether.

Preparation of PC/epoxy semi-IPN

Resin compositions containing the thermoplastic were firstly prepared by a melting procedure, and then cured to form a semi-IPN structure. The PC was dissolved in epoxy resin at 180°C for 20 min and 200°C for 10 min to give a clear homogeneous mixture. The temperature of the mixture was then allowed to decrease to 150°C and 32 phr DDS hardener was slowly added, with stirring,

over 10 min. The resin was then cast into a preheated mould. Degassing was carried out under vacuum at 150°C for 20 min, followed by curing for 3 h at 100°C, 2 h at 140°C and 2 h at 180°C, with post-curing for 2 h at 200°C. Finally, the oven was switched off and the cured sheet was allowed to cool very slowly to room temperature in order to avoid cracking. According to this procedure an opaque or visually transparent sheet was recovered. Blend compositions containing 0–25 phr of thermoplastic component were prepared. Higher levels of PC could not be incorporated in the PC/epoxy blends, since the resulting high viscosity mixture could not be cast to produce void-free sheets. For the systems containing diluent, 30 phr dilution was added to PC/epoxy mixture before the addition of 44 phr DDS, then they were cured by the same process.

The TEPA hardener and diluent were added to the PC/epoxy melting mixture at room temperature (RT), then the resin was degassed and cured by the following process: 1 day at RT, 2 h at 60°C, 2 h at 80°C and 2 h at 100°C. The melting mixture of PC/epoxy was mixed with anhydride at 100°C and was cured for 4 h at 160°C.

Techniques

Dynamic mechanical spectroscopy measurements were made on Rheovibron model DDV-II viscoelastometer. MS-x infra-red (i.r.) spectroscopy was used to measure i.r. spectra. The melting points of PC crystalline in the network and its enthalpies of fusion were measured on a Perkin-Elmer DSC 2 differential microcalorimeter. The instrument was calibrated with low-melting-point metals and was always flushed with dry nitrogen during the runs. TEM was performed on a JEM-100cx/II microscope. The accelerating voltage ranged between 80 to 100 kV following the contrast of the samples. Ultrathin sections were obtained with a LKB Ultratom 3 device. All samples were stained with osmium tetroxide.

PC was purified by a standard procedure. The PC powder was firstly dissolved in methylene dichloride (CH_2Cl_2) to get a solution with a certain concentration, and the cast film was then obtained from this solution. Purification of PC was achieved by precipitation from the same solution using methanol (CH_3OH) or heptane (C_7H_{16}).

RESULTS AND DISCUSSION

Characterization of PC

Figure 1 shows a typical plot of d.s.c. scans carried out at a heating rate of $10°C\,min^{-1}$ for the PC powder, the cast film and the purification sample. The melting points, enthalpies of fusion and crystallinity of various samples, obtained from d.s.c. testing, are presented in *Table 1*. The results indicate that the PC powder used in this work is a semicrystalline polymer which has a crystallinity level of 32.50%, and exhibits a narrower fusion peak compared with others. This phenomenon implied higher regularity of PC powder. There is also crystallization of PC in the cast film, but the crystallinity level is lower than the PC powder. After purification, both melting point and crystallinity will decrease, especially for the sample precipitated by heptane.

A single phase feature of PC/epoxy/TEPA systems

Dynamic mechanical spectra (*Figure 2*) indicate that

Table 1 Melting points (T_m), heats of fusion (ΔH_m) and crystallinity (X_c), from d.s.c., for PC and its purification

	PC powder	PC cast film	Purified PC precipitation by	
			Methanol	Heptane
T_m (°C)	240.4	242.1	236.0	230.9
ΔH_m (J g^{-1})	35.60	24.76	33.93	26.12
X_c (%)	32.50	22.61	31.09	23.85

$X_c = \Delta H_m / \Delta H_m^c$ pc, ΔH_m pc = 109.50 J g^{-1} (theory heat of transition for 100% crystallinity of PC)
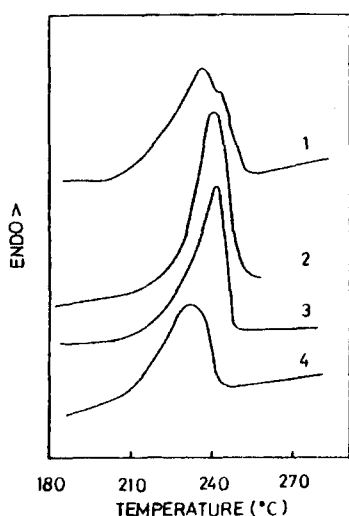

Figure 1 Typical d.s.c. thermograms for PC powder (2); cast film (3); purification samples precipitated by methanol (1); and heptane (4)
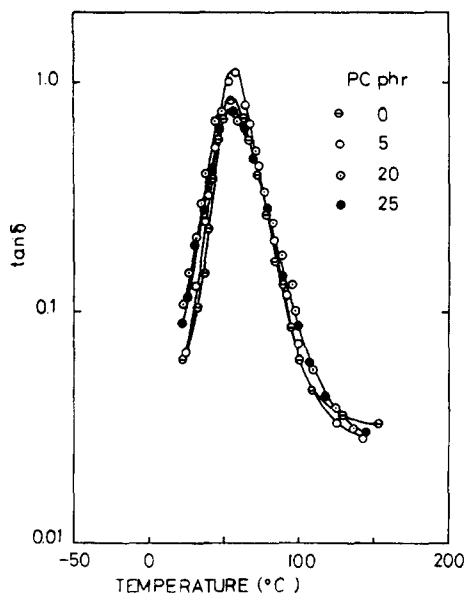
Figure 2 Loss tangent spectra of PC/epoxy/TEPA systems at 3.5 Hz. PC contents (phr) are marked on the curves

no phase separation of PC component occurred in the PC/epoxy/TEPA systems during the curing process. This was confirmed by TEM analysis which showed no evidence of a dispersed second phase in the blends. Attempts to selectively etch the fracture surfaces with a PC solvent (CH$_2$Cl$_2$) did not reveal any feature distinctive of PC removal.
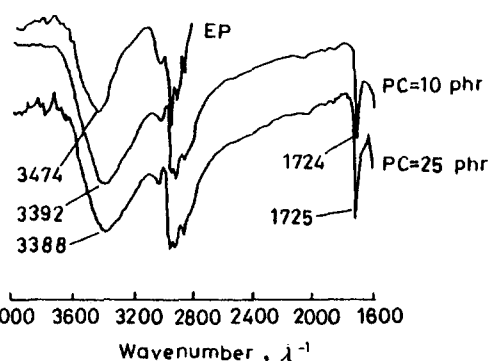
Figure 3 *FT* i.r. spectra of PC/epoxy/TEPA systems. The part associated with hydroxyl and carbonyl groups stretching is shown

For TEPA hardener systems, the curing rate of epoxy resin is very high, even at RT, its gel time being only 0.5 h. Furthermore, there are hydrogen bonding interactions between carbonyl groups in the PC chain and hydroxyl or amine groups in the epoxy resin network judged by Fourier transform i.r. (*FT* i.r.) spectroscopy. Stretching bands of both the carbonyl and the hydroxyl groups in the i.r. spectra of semi-IPNs (*Figure 3*) shift to lower frequencies, the most obvious of which being the carbonyl group stretching band, lowered by as much as 50 cm^{-1} (from 1776 cm^{-1} to 1725 cm^{-1}) due to hydrogen bonding. It has been generally realized that hydrogen bonding in the blends can dramatically enhance compatibility between the two kinds of components with the proton-donor or proton-acceptor. When epoxide groups react with the amine hardener, as a result, stronger and stronger hydrogen bonding between PC and epoxy network can be obtained because of the increase of hydroxyl group content. Therefore, both resistance of hydrogen bonding to the phase separation process, and high curing rate result in there not being enough time for PC to separate from the epoxy network before the gelation point. Systems thus obtained will be transparent and have single phase homogeneous morphologies.

Morphology of PC/epoxy/DDS systems

Dynamic mechanical data for the neat resin and blends containing up to 25% phr of PC, compared in *Figure 4*, show a single relatively narrow glass transition peak indicating that no phase separation of the PC component have taken place during the curing and post curing process. The principal feature in the neat resin curve is the glass transition at 226°C. The addition of PC into the resin tends to broaden and shift the transition to a lower temperature between 212 and 215°C, but shows no systematic dependence upon composition.

It is of interest to note that PC/epoxy blends also exhibit sample opacity or translucency, which is a phenomenon related to a low degree of phase separation or crystallization process of PC. This was confirmed by d.s.c. analysis (*Figure 5*), which showed an endothermic peak in the blends containing 20 or 25 phr of PC. The heat of transitions (ΔH) and melting points (T_m) of PC crystalline in the blends are presented in *Table 2*. Once melted, the PC in the blend is unable to recrystallize even at a very slow cooling rate, as judged by d.s.c.

Having been subjected to annealing treatment at 200°C for 6 h, all blends with incorporation of PC from 5 to 25 phr exhibit two endothermic peaks, which correspond approximately to the T_g and T_m transition
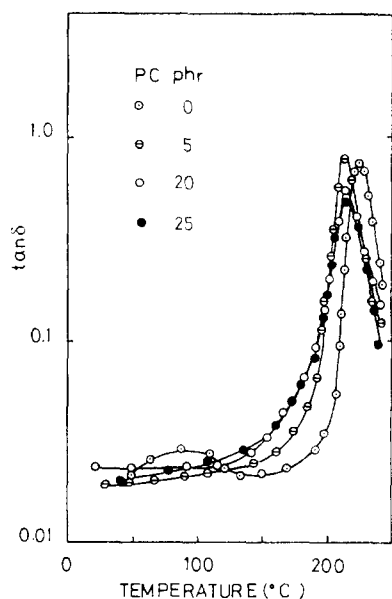
Figure 4 Dynamic mechanical spectra of neat resin and PC/epoxy blends with 32 phr DDS. PC content (phr) are marked on the curves
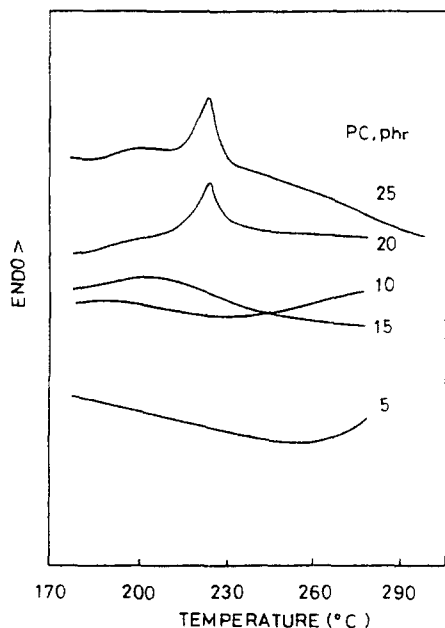

Figure 5 D.s.c. thermograms of PC/epoxy/DDS blends, PC contents (phr) are marked on the curves
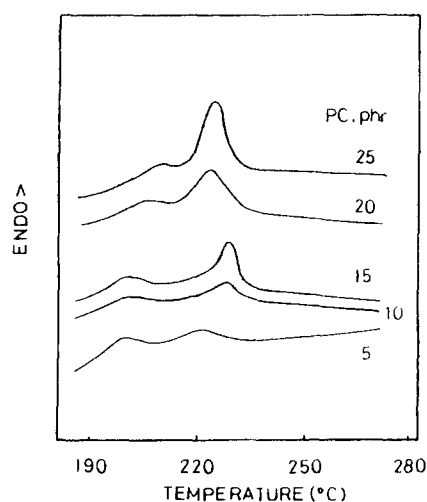

Figure 6 D.s.c. thermograms of annealed PC/epoxy/DDS blends. PC contents (phr) are marked on the curves

respectively (*Figure 6*). Usually, it is believed that at least at higher annealing temperatures, a mechanism of melting the least stable parts of a sample and recrystallizing them around the nuclei provided by the remainder results in two melting endotherm peaks, one of reorganized materials, and one which will have comparatively little reorganization, but may still not be completely unaltered. In these systems, however, PC/epoxy blends containing 5–15 phr PC fail to give any endotherm peak before annealing, moreover, ΔH_1 of the first peak plus ΔH_2 of the second peak give an anomalous high heat of transition, which is false, hence the first peaks were considered to be related to the glass relaxation peak caused by annealing treatment. The first peak seems to be shifted to a higher temperature, with increasing content of PC, and yet the melting points for all blends from the second peak are nearly the same, and remain unchanged by the annealing treatment. The crystallinity in the blends containing 5 to 15 phr of PC increases with annealing process, but for the blends with incorporation of 20 or 25 phr PC, annealing cannot bring about any increase of crystallinity. The ΔH_m and T_m of PC crystalline in blends lie considerably below those of PC powder, disclosing lower crystallinity and higher disorder in the crystalline regions. As compared with PC cast film, T_m is also lower, but the ΔH_m is not lower, even being higher than PC cast film. If the PC was not completely dissolved in the mixture, the T_m and ΔH_m

Table 2 T_g, T_m and ΔH_m for PC/epoxy/DDS blends from d.s.c. measurement

|	Before annealing						After annealing				
	With dilution		Without dilution		With dilution		Without dilution				
	20 phr PC[a]	20 phr PC[b]	20 phr PC	25 phr PC	20 phr PC[a]	20 phr PC[b]	5 phr PC	10 phr PC	15 phr PC	20 phr PC	25 phr PC
T_g (°C)							190.1	201.0	201.6	206.0	210.0
T_m (°C)	233.0	217.9	223.5	223.4	234.7	222.8	220.3	228.0	228.6	223.7	225.0
ΔH_m (J g^{-1})	4.67	1.56	3.66	4.74	3.33	1.38	0.83	1.54	3.29	3.43	4.80
$\Delta H'_m$ (J g^{-1})	45.30	15.13	27.82	29.77	32.30	13.38	22.74	21.87	32.24	26.07	30.14

[a] PC was partially dissolved in the mixture
[b] PC was completely dissolved in the mixture
$\Delta H'_m = \Delta H_m / PC\%$ (wt% in the blend)
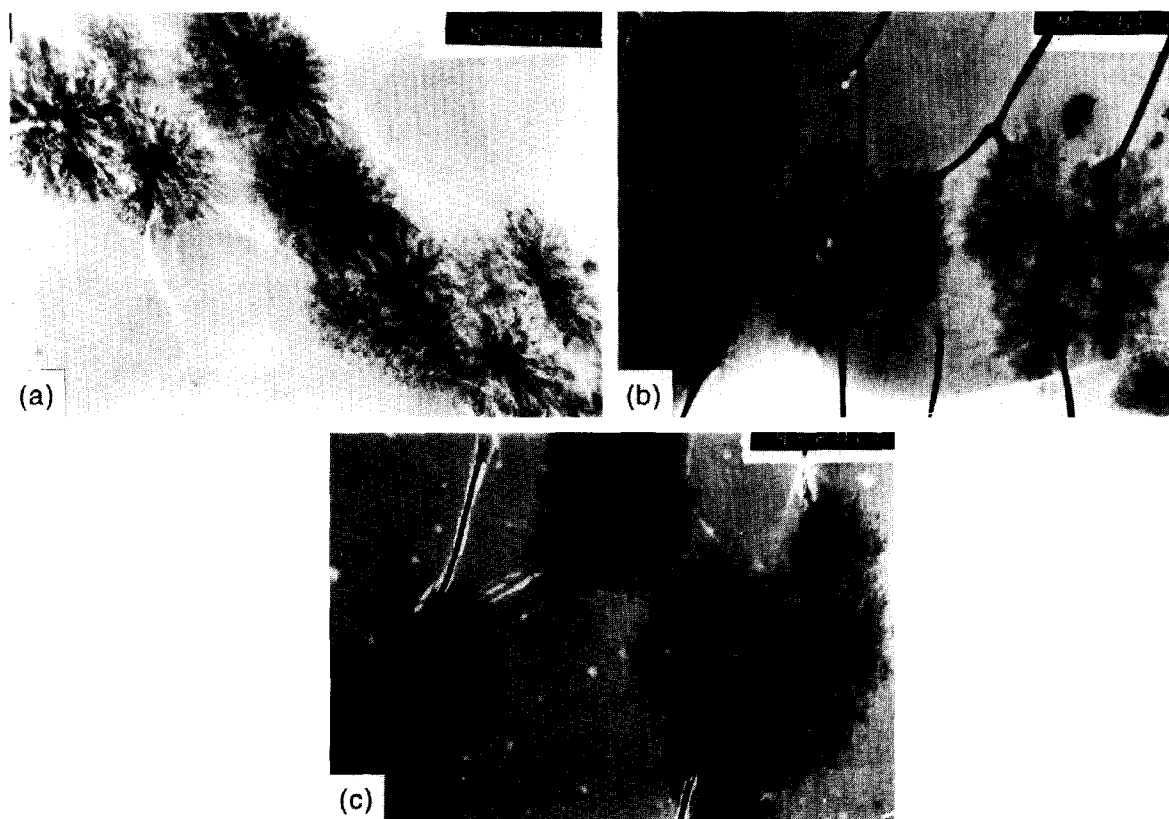
Figure 7 TEMs of PC (25 phr)/epoxy/DDS blend, showing the morphology of PC spherulite (a), a loss of the order in morphology after annealing (b), no evidence of spherulite after quenching (c) at 4800× magnification
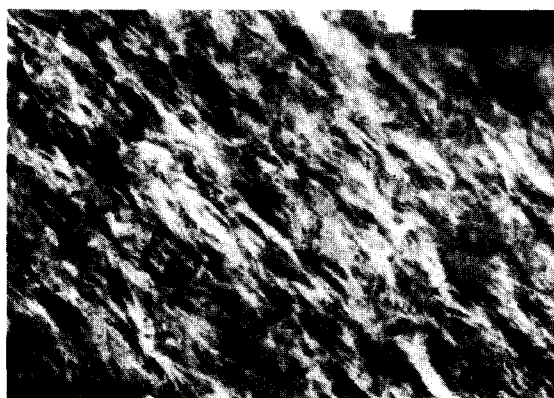
Figure 8 TEM of PC cast film showing a multilayer aggregation, at 4800× magnification

will be higher because of the remainder of PC particles (*Table 2*). Its morphology also showed great difference from blends obtained from homogeneous mixtures, illustrated as follows.

The essential morphology feature attributed to spherulites in the blends may be inferred from their appearance in *Figure 7*, illustrating specimens of PC/epoxy semi-IPN containing 25 phr of PC, before and after being annealed and quenched, observed by TEM. *Figure 7a* exhibits what may be called a classic spherulite in size of about 3.5 μm, which is completely different from that of PC cast film (*Figure 8*) which showed multilayer aggregates. For the blend in which the PC was not completely dissolved, the remainder of PC particle

could also be identified clearly in the TEM, but there is no trace of spherulite, indicating that the unique spherulite morphologies are really formed from a homogenous mixture, with the formation of the epoxy network. Although the space of the spherulites have been uniformly filled by branched fibrils, the spherulites still remain in an immature stage of growth, with open texture. It should be noted that no amorphous PC domain could be observed in PC/epoxy semi-IPNs by TEM. Both phase separation of PC and its crystallization may take place at the same time with the increase of epoxy resin molecular weight. Once gelation of epoxy network is realized, the other parts of uncrystallizable PC cannot be separated from epoxy networks, and interpenetrate with epoxy networks to form a semi-IPN structure. The morphology fixed by the epoxy resin network is easily observed by TEM, without noticeable electron damage.

For the blend of 10 phr incorporation of PC, since there is not enough time for a small amount of PC molecules to aggregate before the gelation of epoxy network, the growth of the spherulite has come to a halt at an early stage. Some molecules of PC may be in a non-crystalline phase, but a meso-form with a two-dimensional ordering[24], which may be made crystalline by annealing treatment. However the spherulite in blend containing 25 phr of PC subjected to melting process shows a clear loss of order in *Figure 7b* after annealing treatment, in this situation, there is not obvious recrystallization by reason of the lower annealing temperature, which may appear to lie below the melting range (209–235°C), as well as the fixed effect of the network structure. This material when quenched from

the temperature above T_m to RT shows no evidence of the spherulite structure feature (*Figure 7c*).

A few of the PC/epoxy mixtures of the same composition as above, PC content is up to 40 phr, but obtained by direct dissolution of the components in mixed solvent (CH_2Cl_2/DMF = 20/1) were used as a reference system. It has been demonstrated that there was not crystallization of PC in the cured reference systems before and after annealing by both TEM and d.s.c. measurements. This phenomenon reveals the influence of molecular mass changes on crystallization by PC chain scission process occurring through reaction of carbonate groups with present hydroxyl groups in the epoxy resin during the high-temperature melting process. Fractionation is inevitable if the composition of a growing crystal differs from that of its environment. Both kinetic and thermodynamic factors are involved in fractionation, the two being related by the theory of rate processes[25]. It can be estimated that the decrease of PC molecular mass by chain scission improves the crystallization rate, but lowers the melting points of PC spherulites.

The hydroxyl-terminated PC chains formed by chain-scission of PC can further react with epoxy groups forming epoxy-terminated PC chain which will take part in the crosslinking reaction, thus incorporating the PC backbones with the epoxy network. But the formation of crystalline in PC/epoxy blends (melting mixture) is an indication that the extent of the reaction between PC and epoxy is not considerable, because of the short reaction time (0.5 h) and lower reaction temperature (< 200°C). When the quaternary ammonium salts (TMAI) were added into the mixture to catalyse the epoxide–carbonate reaction, then the obtained transparent systems show no evidence of crystalline PC, revealing that incorporation of PC chains within the epoxy network do not favour phase separation and crystallization of PC during the curing process. In fact, introducing reaction between the PC and the epoxy resin can result in a single phase homogeneous PC/epoxy hybrid networks of semi-IPNs and A-B networks, which will be discussed in the third part of this work.

A further analysis of the influence of molecular length on the crystallization of PC in PC/epoxy blends has been performed by purification of PC in order to eliminate both the longest and the shortest molecules. For this purpose the PC solution was firstly filtered and then PC was precipitated from the solution by methanol or heptane. It is interesting to find that the blends of purified PC/epoxy resin cured under the same process give a transparent sample which showed no evidence of PC crystalline by TEM and d.s.c. No matter whether nucleation is heterogeneous or homogeneous, it is still strongly affected by molecular weight, with longer molecules usually initiating crystallization of the polymer. In the PC/epoxy blend case, this is presumably because the longer a molecule is the greater the chance of being able to be separated from the homogeneous mixture at a very early stage of the curing reaction, otherwise there will not be enough time for the PC chain to adopt a suitable conformation in nucleation before the gelation of the epoxy network. It is worth noting that no evidence of amorphous PC domains in the blends could be found. This phenomenon implies that the phase separation of PC component from epoxy resin network is really hindered by hydrogen bonding between the two components, but the hydrogen bonding may be related to the formation of PC spherulites.

The effects of epoxy resin network on the formation of PC spherulites can be deduced from the influence of crosslink density on the crystallinity and morphology of PC crystal in the blends reported in *Table 2* and *Figure 9a*. It should be noted that a decrease in the crosslink density (the calculation of molecular weight between crosslink points increases from 344 to 746 by adding active diluent to the systems) resulted in both an increase in crystal perfection, and a concomitant decrease of crystallinity by a factor of about 2. The size of the spherulite is about 8 μm and its morphology is not affected by annealing treatment (*Figure 9b*). This fact demonstrates that a lower viscosity and a lower crosslink density caused by addition of diluent to the mixture favour spherulite growth rather than nucleation. It is reasoned that the nuclei are formed by the special interaction between PC molecules and the primary network. The sol may act as a foreign material, which induces heterogeneous nucleation, or several molecules to come together to form a nucleus forced by preliminary formation of epoxy network and stabilized via hydrogen bonding between the two components. The similar size of spherulites observed by TEM revealed that heterogeneous nucleation has a leading role. The hydrogen bonding may cause the aggregation of PC chain on the surface of sol to form nuclei. During the curing process, the epoxy networks formed acting as 'impurities', accompanying the crystallization of PC, are localized by
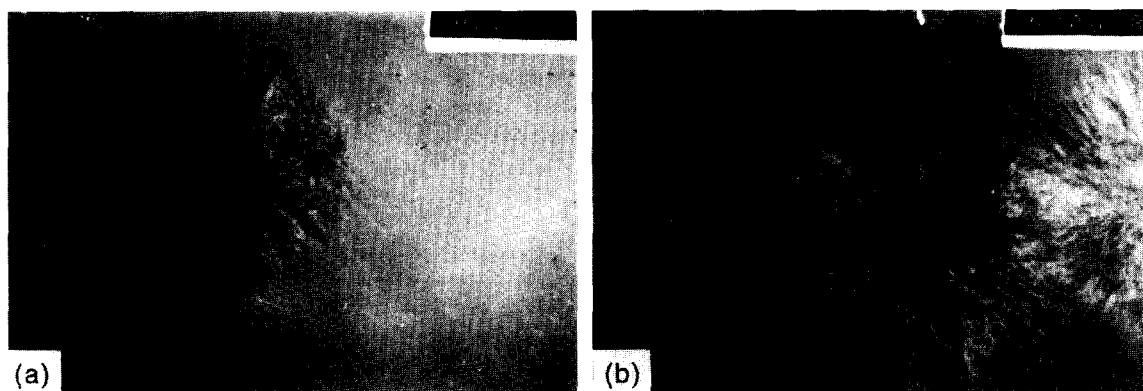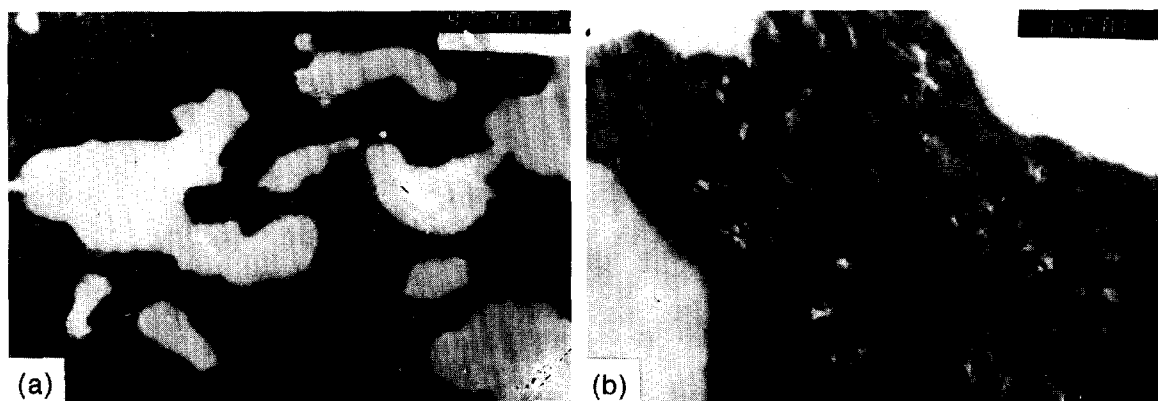

Figure 9 TEM of low crosslink density PC (20 phr)/epoxy/DDS blend, showing an increase in crystal perfection (a), and inefficient annealing (b), at 4800× magnification

Figure 10 TEM of phase inversion PC/epoxy 50/50 system, showing the sheaving shapes of immature PC spherulites, at 4800× (a), and 14 × 10³ (b) magnification

Table 3 T_m and ΔH_m for phase inversion PC/epoxy/DDS solution blends from d.s.c. test

	Before annealing			After annealing	
	33.3/66.7 PC/epoxy (w/w)	50/50 PC/epoxy (w/w)	75/25 PC/epoxy (w/w)	50/50 PC/epoxy (w/w)	75/25 PC/epoxy (w/w)
T_m (°C)	215.3	221.0	217.3	217.0	222.0
ΔH_m (J g⁻¹)	3.26	12.13	17.44	10.69	20.16
$\Delta H'_m$ (J g⁻¹)	11.93	28.12	25.16	24.83	28.84
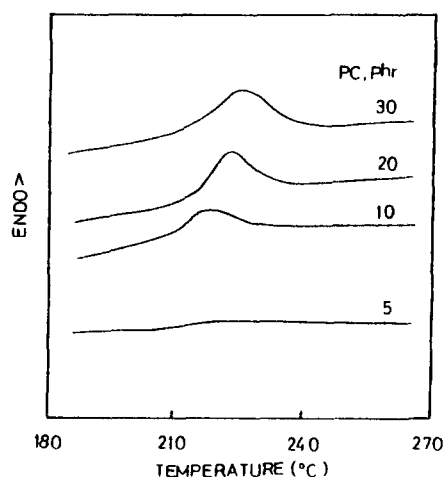
Figure 11 D.s.c. thermograms of PC/epoxy/anhydride blends, PC content (phr) are marked on the curves

being unable to diffuse away from an interface at large rates compared to the crystalline growth rate. Spherulites result, therefore, just because the uncrystallizable network is segregated between PC, resulting in fibrillation and small-angle branching.

In the reference system (solution mixture), at high wt% incorporation of PC, above the phase inversion composition, the PC continuous phase exhibits a crystallization process when cast from a solution mixture similar to PC cast film. After the same curing process as the PC/epoxy melting blend, the semi-IPN has nearly the same crystallinity as PC cast film, but its melting point is lower (*Table 3*). The phenomenon that both melting point and crystallinity remain unchanged by the annealing treatment reveals the 'fixed effect' of epoxy network

on the morphology of the PC phase attributed to semi-IPN structure, even though the epoxy resin exists as a discrete phase. When PC/epoxy = 33.3/66.7, the lower crystallinity indicated that the epoxy resin has a 'dilution effect' on the crystallization of PC phase, nevertheless, the 'dilution effect' becomes less obvious as PC content increases. The morphology of the PC phase (*Figure 10*) resembles the sheaving shapes of immature spherulites, which is quite different from multilayer aggregates of PC cast film grown from solution (*Figure 8*). Spherulites by comparison are believed to be collections of much narrower lamellae. The Keith and Padden theory[25] relates this to the respective values of δ, which in solution are much greater than the crystal dimensions, so that morphological instability underlying a fibrous habit has not set in. However, in the situation of PC/epoxy solution mixture, the interaction between two components and the formation of epoxy network phase may change the conformation of PC chains. The morphology difference between PC cast film and PC phase in PC/epoxy semi-IPNs with phase inversion supported the deduction about the effect of epoxy resin network and inter-molecular interaction on the formation of PC spherulite.

PC/epoxy/anhydride systems

As compared with the amine curing system, the anhydride, which will reduce the degree of hydrogen bonding in the systems, has also been used as a curing agent to illustrate the effect of interaction between the two components on the formation of spherulites. The d.s.c. analysis showed that there exists PC crystalline in the blend (*Table 4, Figure 11*), although ΔH_m and T_m, similar to those of DDS curing systems, remained nearly unchanged by annealing, the T_m seems to be increased. There exist crystals of PC even in the blend of 10 phr PC content which showed some immature spherulites by TEM in *Figure 12*. The ability of PC phase separation and growth of spherulites become stronger because of both the higher curing temperature (160°C vs 100°C for DDS curing systems) and the weaker hydrogen bonding interaction. However, both the broad melting peaks in d.s.c. spectra and the high disorder in spherulite morphology (*Figure 13*, compared with *Figure 7*) indicate that hydrogen bonding interactions, which are stronger in the DDS system than in the anhydride system, really play an important role in the formation of PC spherulites. Nevertheless, the formation of the epoxy resin network

Table 4 T_m and ΔH_m for PC/epoxy/anhydride blends from d.s.c. measurements

	Before annealing			After annealing			
	10 phr PC	20 phr PC	30 phr PC	5 phr PC	10 phr PC	20 phr PC	30 phr PC
T_m (°C)	216.2	222.1	224.7	227.9	227.3	230.4	234.2
ΔH_m (J g^{-1})	2.46	3.55	5.44	0.79	2.56	3.70	4.62
$\Delta H_m'$ (J g^{-1})	38.13	29.29	31.73	23.70	39.68	30.53	26.95
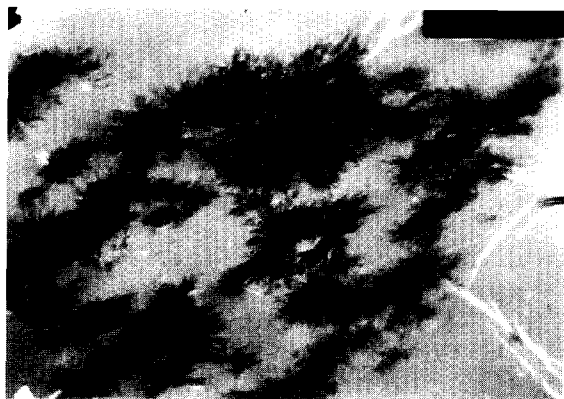
Figure 12 TEM of PC (10 phr)/epoxy/anhydride blend, showing immature spherulite morphology, at 4800× magnification
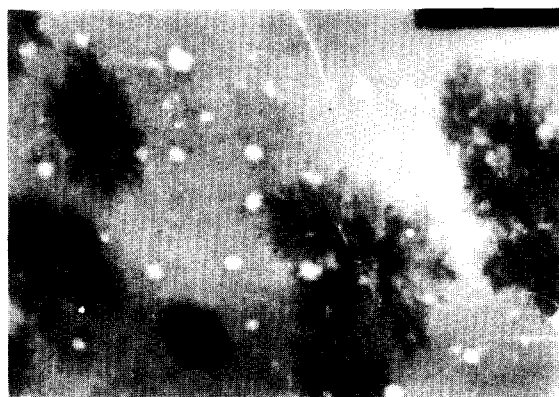
Figure 13 TEM of PC (20 phr)/epoxy/anhydride blend, showing high disorder in spherulites morphology, at 4800× magnification

gives the main spurring force to the nucleation and growth of spherulites in PC/epoxy semi-IPNs.

CONCLUSION

PC/epoxy semi-IPNs formed by a melting blend process displayed an unusual phase separation behaviour and morphology, which is associated with 'compatibility enhancement effect' of semi-IPNs via molecules entanglement, intermolecular forces via hydrogen bonding between the two components, and semi-crystalline features of PC polymer.

The phase separation and crystallization of PC in the PC modified epoxy network is controlled by varying the composition, and the PC–epoxy reaction and by utilizing curing agents of different reactivity. For TEPA hardener, both resistance of hydrogen bonding to phase separation and high curing rate result in a single phase PC/epoxy semi-IPNs. A single phase morphology was also achieved

by introducing PC–epoxy reaction or by eliminating crystallization of PC in PC/epoxy/DDS systems. It is found that phase separation and crystallization of PC occur at the same time, indicating that hydrogen bonding hinders phase separation rather than formation of spherulite.

In certain conditions, spherulite is able to form in company with the formation of the epoxy resin network. The introduction of highly mobile low molecular weight epoxy resin results in a very high rate of crystallization in comparison with that from polymer melts. The systems of epoxy and hardener are not ordinary solutions because both molecular weight and viscosity increase with increasing conversion of epoxy resin network. Once the development of the network structure reaches the stage of gelation, phase separation and crystallization of PC is halted and the morphology is fixed.

From the dependence of the crystallization on the PC purified or not, it is suggested that the nuclei on which the crystallization starts are likely to be pre-existing high molecular weight PC chains. During the formation of epoxy resin network, either homogeneous or heterogeneous stable nuclei formed by the special interaction between PC chains and primary network chains. The longest PC chains may be firstly excluded by the epoxy resin network to form nuclei. It is estimated that the sol may act as a foreign material which induces heterogeneous nucleation, and the hydrogen bonding between the two components is responsible for accelerating the nucleation process. In PC/epoxy melting blends, heterogeneous nucleation may be the main mechanism, because of the similar size of spherulites. Nevertheless, there is another possible homogeneous nucleation, that is several molecules come together to form a nucleus forced by preliminary epoxy network and stabilized via hydrogen bonding.

In anhydride curing systems, the stronger ability of PC phase separation and growing of crystalline can be attributed to the weaker hydrogen bonding, but its higher disorder in spherulite morphology, in comparison with that in DDS curing systems, may imply the influence of intermolecular interaction.

The morphology of PC/epoxy (PC > 20 phr, impure) blends are characterized by spherulites with a very coarse and open texture, because of the 84% uncrystallizable epoxy resin acting as impurities. The melting points of the spherulites lie considerably below that of crystal from solvent, but the crystallinity is not lower, being even higher than that of PC cast film. Although the spherulites were full of thick fibrils, which in fact contains a large amount of epoxy resin network with the gross morphology, there seems to be some kind of unequilibrium stress on the boundary around the spherulite, which results in a destruction of the crystal under annealing process. If the content of PC is low (<15 phr), the PC will aggregate to

form a mesoform microdomain which could be changed into crystal by annealing treatment.

The influence of internal fractionation changes by PC chain scission during high temperature melting process on the growth of spherulite is also important. When a single phase morphology was achieved by introducing PC-epoxy reaction or by making PC unable to crystallize, a real segment entanglement structure obtained gives an opportunity to study entangled structure at molecular level. These investigations will be reported in another paper.

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