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Studies of an epoxy-compatibilized poly(phenylene sulfide)/polycarbonate blend

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Tensile properties, morphology and thermal behaviour of a poly(phenylene sulfide) (PPS)/polycarbonate (PC) binary system and an PPS/PC/epoxy ternary system were investigated. It was observed that the viscosity-average molecular weight (M_v) of the PC fraction was decreased during the melt blending of PC with PPS. This phenomenon was more pronounced as PPS concentration increased. By melt blending PPS and PC with epoxy as a compatibilizer, a shift of glass transition temperature of PC to a lower temperature could be somewhat prevented. It is suggested that epoxy coupled the degraded PC chains generated by blending with PPS. In contrast to PPS/PC binary system, phase separation in the PPS/PC/epoxy ternary system could hardly be observed in the scale of scanning electron micrographs. The tensile strength and tensile modulus of PPS/PC/epoxy system were remarkably improved (more than 100%) compared to those of the epoxy-free system. It was found that the improvement in tensile properties is mainly due to the homogeneous morphology by blending a small amount of epoxy with PPS and PC. © 1997 Elsevier Science Ltd.

(Keywords: blends; poly(phenylene sulfide); polycarbonate)

INTRODUCTION

Poly(phenylene sulfide) (PPS) is a semicrystalline high performance engineering thermoplastic with excellent properties, such as heat resistance, flame retardancy without additives, chemical resistance, electrical insulation, and high dimensional stability. However, the applications of neat PPS have been somewhat limited, owing to its demerits such as a relatively low glass transition temperature (T_g) compared to its high melting temperature (T_m) and the inclination to brittleness. Therefore, commercial grades are usually filled with glass fibre, glass fibre/mineral or carbon fibre[1].

On the other hand, many researchers have focused on polymer blending, in order to make up for those demerits, even though PPS is known to be immiscible with any other polymers. Even though miscibility is not always desirable in polymer blends, at least satisfactory adhesion between the phases must be required to accomplish good mechanical properties in the PPS blends. In this study, several polymers as candidates for a blend component of PPS have been considered. To overcome the low T_g and brittleness of PPS, the candidates are supposed to have a higher T_g and toughness than PPS. In consideration of the above, polycarbonate (PC) was chosen.

However, it was almost impossible to expect good thermal and mechanical properties in the PPS/PC blends, because gases emitted from PPS during melt blending[2] may degrade the other blend component such as polyarylate (PAR), polysulfone (PSF) or PC, which is sensitive to hydrolysis at elevated temperature[3,4]. In addition, the inherent interfacial tension between PPS and PC is high[5], which may affect the mechanical properties of the blends. In order to solve these difficulties, tetrafunctional epoxy was used as a compatibilizer in the PPS/PC blends to reduce the interfacial tension and therefore enhance the adhesion between the phases. Simultaneously, epoxy is thought to react with hydroxyl terminated PC chains[6-8] generated by hydrolysis of PC during melt blending with PPS. In which case, it is expected that better mechanical and thermal properties could be obtained as a result of a good interfacial adhesion and the recovery of molecular weight of degraded PC. Studies on epoxy-compatibilized PPS blends with several polymers including PC were reported in the patent literature[9].

In this paper, we characterize the thermal and mechanical properties and the phase morphology of PPS/PC and PPS/PC/epoxy blends prepared by melt extrusion and subsequent injection moulding. Tensile testing was performed to examine the mechanical properties. Dynamic mechanical thermal analysis (d.m.t.a.) was used for thermal characterization, and scanning electron microscopy (SEM) was used to investigate the morphology.

EXPERIMENTAL

PPS was obtained from Philips Petroleum Co. (Ryton E2480). Polycarbonate, Lexan 141L, was supplied by G.E. Plastics. Materials were dried at 140°C for 4h before extrusion. The expoxy resin used in this study was Epon HPT 1071, available from Shell Chemical Company.

Blends of PPS and PC containing 25, 50, and 75% by weight PPS were prepared. In the case of epoxy

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compatibilized blends, five blend compositions of PPS/PC/epoxy (75/25/2, 5, 8, 11 and 14 phr (parts per hundred of PPS/PC)) were prepared. PPS and PC pellets and epoxy resin were blended in a W&P co-rotating twin screw extruder (model ZSK-30). The screw is 30.7 mm in diameter and 880 mm long. The temperature of the extruder barrel and die was set at 250°C. The screw speed was maintained at 130 rpm. Neat PPS and PC were also extruded under similar conditions, except at a temperature of 300°C. The PPS, PC, PPS/PC and PPS/PC/epoxy blends were dried at 80°C for 24 h after extrusion, then moulded into dumbbell and rectangular bars in an injection moulding machine from Sheffer Corp. (model 6020FF6K). The temperature of the injection barrel and mould was set at 300°C and 70°C respectively. The blend samples were annealed at 140°C for 4 h. D.m.t.a. was done in a machine from Polymer Laboratories (model PL-DMTA) using the dual cantilever bending mode with a scanning rate of 2°C min^{-1} at a oscillating frequency of 1 Hz. Tensile testing was carried out on an Instron (model 4201) at room temperature (ASTM D638). The crosshead speed of the instrument was maintained at 5 mm min^{-1}. The fracture morphology of the tensile test specimens of the blends was investigated using a SEM (model Hitachi 2-2500) operated at 10 kV with a magnification of 8000. Viscosity-average molecular weight (M_v) of the PC fraction of the PPS/PC blended pellets was measured using a Ostwald viscometer at 25°C in order to analyse the dependency of M_v on PPS concentrations. Dichloromethane was used to extract PC and then prepare solution whose concentration was 0.005 g ml^{-1}.

RESULTS AND DISCUSSION

PPS/PC systems

We found that the optimum processing temperature was 250°C for the melt blending of PPS and PC using an extruder. This processing temperature is far below the T_m (285°C) of PPS. The reason why the extrusion had to be performed at such a low temperature is because melt extrusion itself was impossible owing to the drastic decrease in melt viscosity along with bubbles above 250°C. The reason for this is the outgassing from PPS, which may degrade PC during melt extrusion at elevated temperatures. This phenomenon has been discussed in detail in the literature by Golovoy *et al.*[3]. However, despite our efforts to perform extrusion at such a low temperature, the degradation of PC was fundamentally unavoidable, and the higher the PPS concentration, the more pronounced the degradation became. M_v shows an approximately 44% decrease for the PC fraction (*Table 1*).

To characterize the degradation of PC further, the

Table 1 Viscosity average molecular weight of the PC fraction in the PPS/PC blends

PPS/PC (wt%)	η_{rel}	$[\eta]$ ($\mathrm{dl\,g^{-1}}$)	M_v
0/100	1.247	0.458	30 300
25/75	1.229	0.427	27 800
50/50	1.181	0.342	21 000
75/25	1.152	0.290	17 100

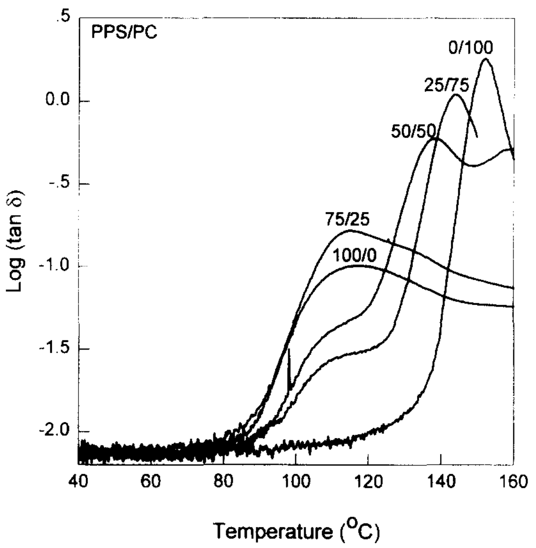


Figure 1 D.m.t.a. thermogram of the PPS/PC blends: log(tan δ)

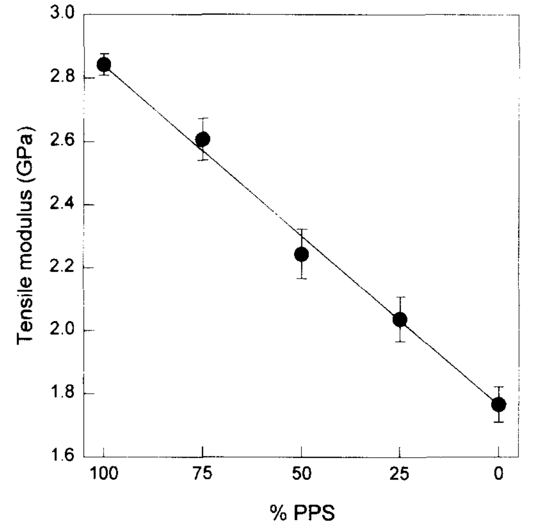


Figure 2 Tensile modulus of the PPS/PC blends as a function of blend compositions

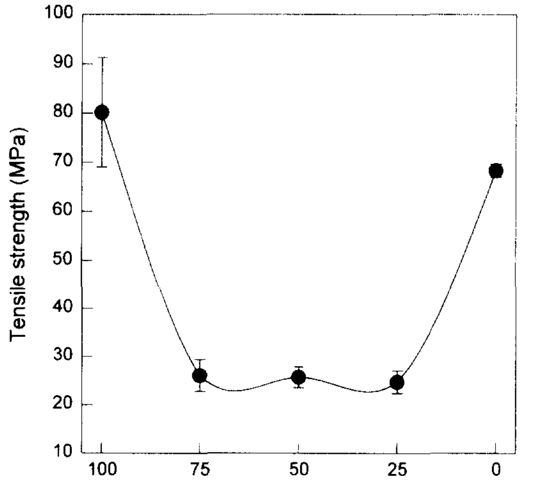


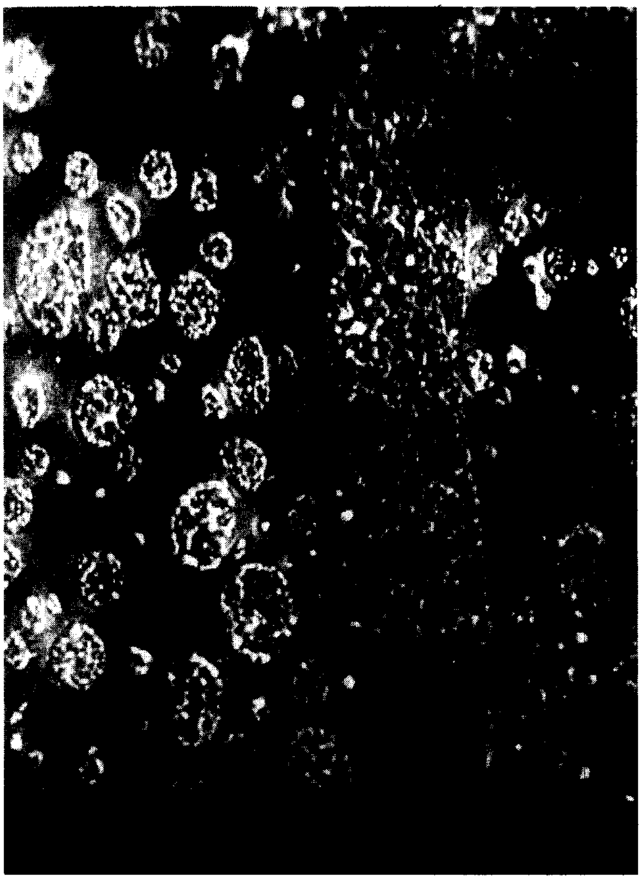
Figure 3 Tensile strength of the PPS/PC blends as a function of blend compositions

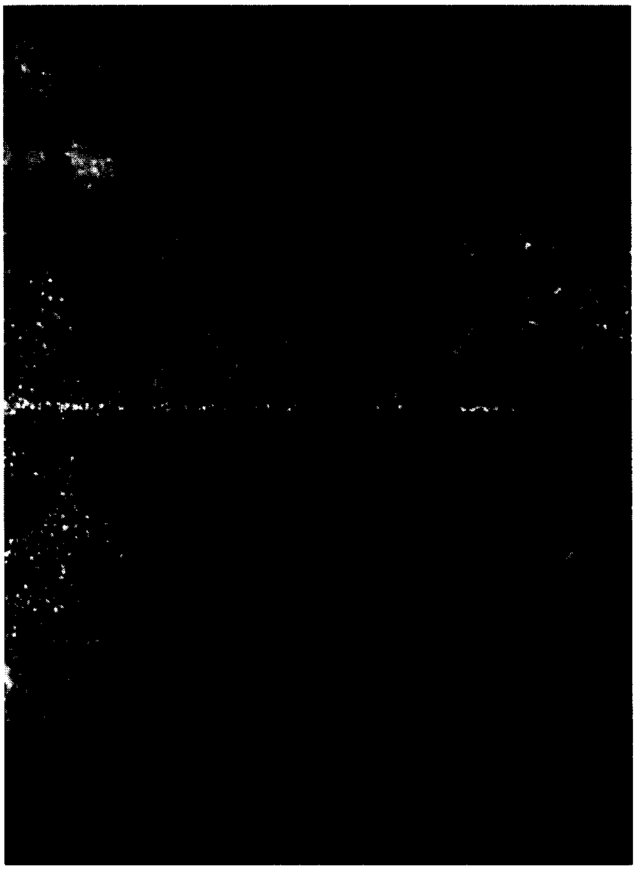
Figure 4 SEM of the fracture surfaces of PPS/PC blends. (a) PPS/PC = 25/75 wt%. (b) PPS/PC = 50/50 wt%. (c) PPS/PC = 75/25 wt%

d.m.t.a. was used as a characterization tool. The d.m.t.a. thermogram for the PPS/PC blends is shown in *Figure 1*. Assuming that temperature at the maximum in $\tan\delta$ is the T_g, the T_g of PPS remained constant at about 110°C regardless of concentration while that of PC shifted to a lower temperature, from about 150°C for neat PC to 130°C for 25% PC. The decrease in the T_g of PC can clearly be explained by the decrease in molecular weight caused by degradation[10].

Figures 2 and *3* show the tensile modulus and tensile strength of the blends respectively. The tensile modulus of the blends followed the simple additive rule of mixtures. On the other hand, the tensile strength showed sharp decrease when PPS and PC were blended. To investigate the severe decrease in tensile strength of PPS/PC blends, phase morphological characterization was undertaken using a SEM.

Figure 4 shows the SEMs of the fracture surfaces for 25/75, 50/50 and 75/25 PPS/PC. At 25% PPS, shown in *Figure 4a*, there is evidence for poor interfacial adhesion between dispersed PPS phase and continuous PC phase, in which case there is minimal stress transference from a continuous phase to a dispersed one, through the interface. Therefore, the dispersed phase surrounded by cavitation might have acted like a void which reduces the tensile strength. In addition to their inherent interfacial tension, the de-adhesion may be due to the contraction of the PPS domain after annealing at 140°C for 4 h, which is above the T_g of PPS and below that of PC. *Figures 4b* and *4c* show the fracture surfaces of 50% and 75% PPS. PPS which appears to contain the PC subinclusions, is





becoming a co-continuous phase (*Figure 4b*). The phase inversion is observed between 50% and 75% PPS. At 75% PPS, the size and shape of PC domains are irregular (*Figures 4c*). The low tensile strength at 50% and 75%

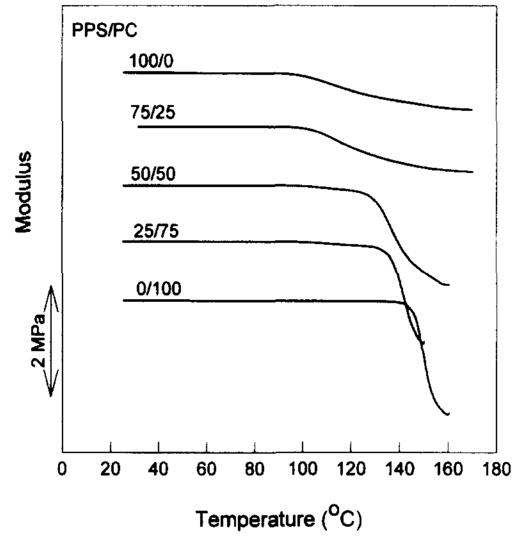


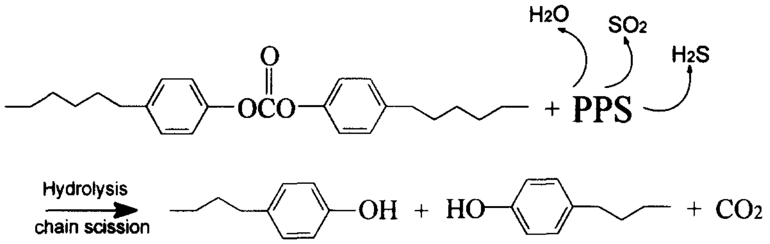
Figure 5 D.m.t.a. thermogram of the PPS/PC blends: modulus

PPS is thought to be due to the decrease in molecular weight of PC fraction as well as the inherent interfacial tension.

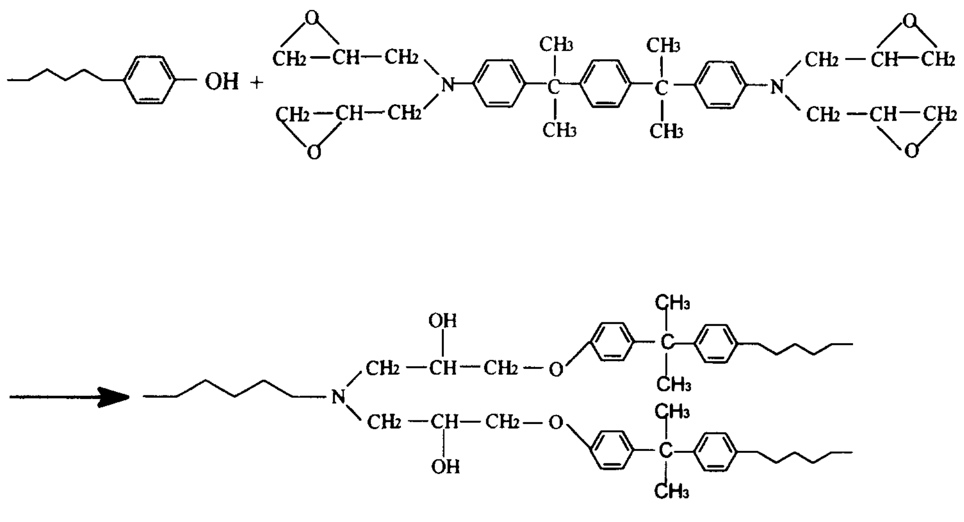
A thermogram of storage modulus as a function of temperature is presented in *Figure 5*. The most prominent feature of this figure is the change in the modulus between 50 and 75% PPS. The change in modulus indicates that the phases were inverted between 50 and 75% PPS, which confirms the conclusion about phase inversion drawn from the SEMs.

PPS/PC/epoxy systems

The results we have obtained from the PPS/PC binary systems were not disappointing, but rather predicted, because our ultimate aim of this experiment has lain not in obtaining good mechanical properties by blending only PPS and PC, but in improving the mechanical and thermal properties of the PPS/PC blends by using a suitable material as a compatibilizer. However, we had two difficult tasks awaiting solution in order to improve those properties of the PPS/PC blends. First, either the degradation of PC itself should be prevented, or the already degraded PC chains should be connected. Second, the interfacial tension between PPS and PC should be reduced to improve miscibility. If the first were accomplished, the T_g of PC would not be decreased as much as in the results we have obtained so far. Even though it is rarely possible for an immiscible system to be a miscible one, it is essential to improve miscibility to a certain degree by introducing a compatibilizer[11] because better mechanical properties could be observed in a homogeneous system. The first is a prerequisite for the second, because we cannot expect excellent mechanical and thermal properties if PC is degraded during melt blending. To satisfy both of them, epoxy with four functional groups was chosen.



Scheme 1



Scheme 2

As presented in *Scheme 1*, the hydroxyl-terminated PC chains were generated by hydrolysis or transesterification of carbonate groups. Simultaneously, the hydroxyl terminated PC chains reacted with epoxy molecules. In other words, epoxy molecule itself can become a connection site, as presented in *Scheme 2*[6]. Epoxy,

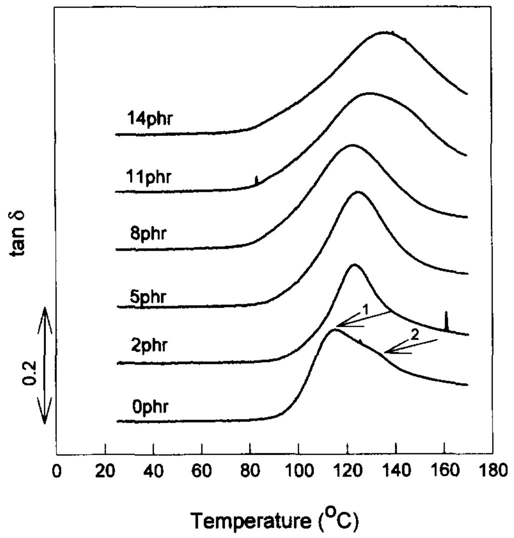
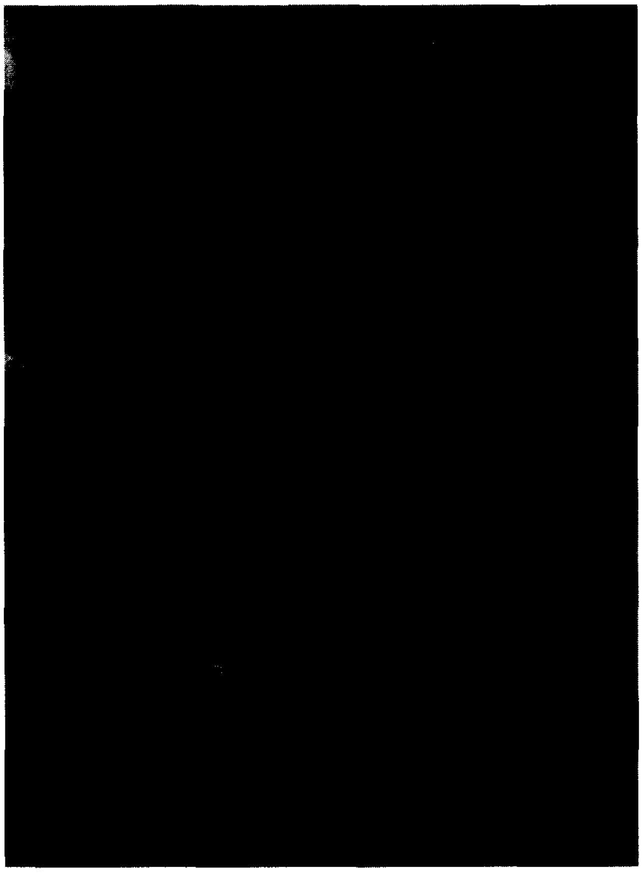


Figure 6 D.m.t.a. thermogram (tan δ) of the PPS/PC/epoxy blends with different epoxy concentrations: composition of PPS/PC is 75/25 wt%



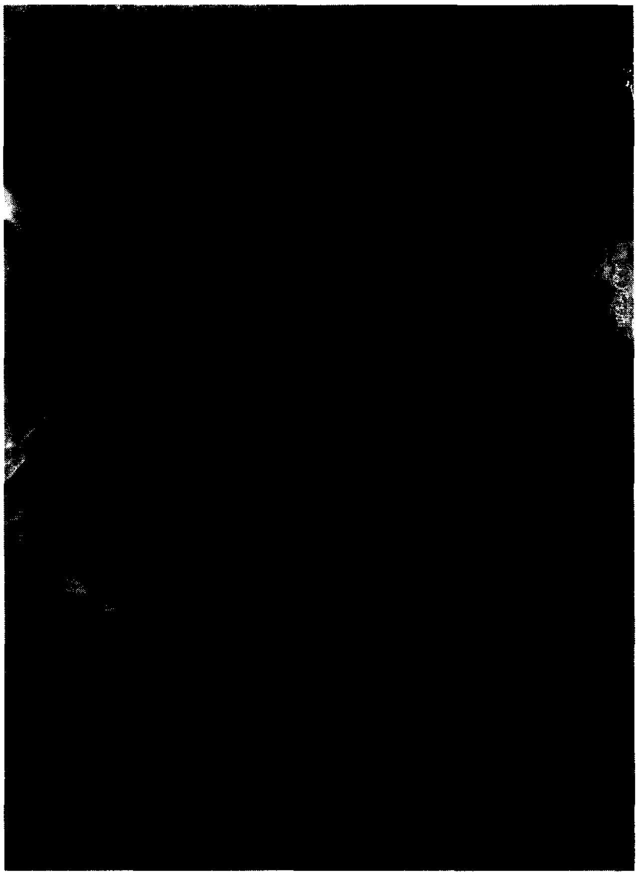


Figure 7 SEM of the fracture surfaces of PPS/PC/epoxy blends after etching (PPS/PC = 75/25 wt%). (a) Epoxy = 0 phr. (b) Epoxy = 2 phr. (c) Epoxy = 11 phr

consequently, prevented a sharp decrease in the molecular weight of PC, by connecting the degraded PC chains. *Figure 6* shows the d.m.t.a. thermogram of the uncompatibilized 75/25 PPS/PC blend and the epoxy-compatibilized 75/25 PPS/PC blends containing 2, 5, 8, 11 and 14 phr. The reason why 75/25 PPS/PC composition was selected as an epoxy-compatibilized system is because PPS is supposed to be the matrix in order to provide the blend its excellent properties[12]. Moreoever, the effect of connecting the degraded PC chains seemed to be more pronounced because we have found that at high PPS concentration such as 75% PPS, chain scission

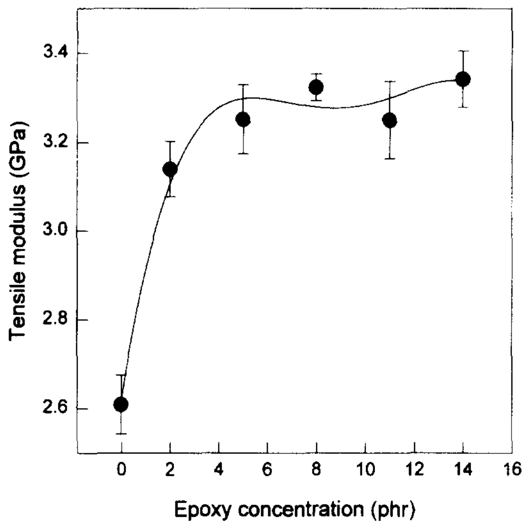


Figure 8 Effect of epoxy concentration on the tensile modulus of the PPS/PC(75/25)/epoxy blends

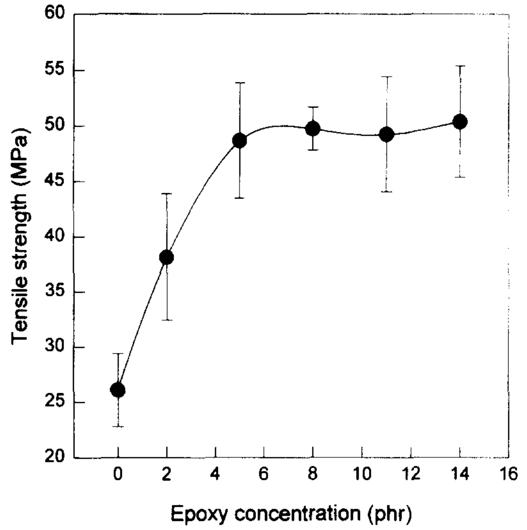


Figure 9 Effect of epoxy concentration on the tensile strength of the PPS/PC(75/25)/epoxy blends

of PC would take place more than other blend compositions during melt blending. The most intriguing thing in this figure is that the blend without epoxy has two T_gs at 110°C for PPS (Arrow 1 in *Figure 6*) and 130°C for degraded PC (Arrow 2 in *Figure 6*) while the blends containing epoxy seem as if they had single T_g which can be seen in a homogeneous system. Generally, the miscible system shows the symmetrical tan δ peak shape[7]. Moreover, the single T_g of the ternary blend shifts to a higher temperature as epoxy composition increases. In the case of 14 phr of epoxy, the T_g reaches almost 140°C. This phenomenon could be explained by the recovery of molecular weight of already degraded PC.

The SEM micrographs in *Figure 7* show the characteristic morphology of the PPS/PC blends with various epoxy compositions. The SEM samples were prepared using a selective solvent etching method where dichloromethane was used as a solvent. Lots of hollows with various size are the traces of PC domains in the uncompatibilized blend (*Figure 7a*), while the PC domains are rarely observed in the blend with 2 phr of epoxy (*Figure 7b*) and finally disappear like a homogeneous system in the blend with 11 phr of epoxy (*Figure 7c*).

The tensile modulus and tensile strength of the PPS/PC/epoxy blends are shown in *Figures 8* and *9*. As expected from the phase morphology, a remarkable improvement in mechanical properties was achieved. Even a small amount of epoxy introduced higher modulus than neat PPS. The cause for this is that higher crystallinity could be obtained in PPS/PC/epoxy than in PPS along[11]. Also, 5 phr of epoxy gave rise to almost 100% higher tensile strength than uncompatibilized 75/25 PPS/PC. Both tensile modulus and tensile strength reached a steady value above 5 phr, which indicates that the amount of epoxy required to improve tensile properties was saturated at about 5 phr in the 75/25 PPS/PC.

CONCLUSIONS

PPS and PC could be blended at 250°C which is far below the T_m of PPS. It was observed that M_v of PC fraction was decreased as PPS concentration increased. This is thought to be due to the degradation of PC by the gases emitted from PPS at elevated temperature. Epoxy was used as a reactive compatibilizer in the 75/25 PPS/PC to couple the degraded PC chains and reduce the interfacial tension between PPS and PC. Epoxy-compatibilized PPS/PC blends seemed as if they were miscible from the analysis of d.m.t.a. thermograms and SEM micrographs. In addition, its T_g shifted to higher temperature as epoxy concentration increased. The tensile properties were greatly improved by a small amount of epoxy and reached their steady value at 5 phr.

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