Morphologies and tensile properties of elastomer-modified epoxy and polycarbonate blended systems

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The morphologies and tensile properties of an elastomer-modified epoxy (EME)/polycarbonate (PC) binary system and an EME/diglycidyl ether of bisphenol A (DGEBA)/PC ternary system were examined. In the EME system, a continuous elastomer-rich phase formed, while in the EME/DGEBA systems (unblended with PC), a continuous epoxy-rich phase formed. In both of these systems, two-phase structures were observed. In contrast, a microdispersed structure was observed when the PC was blended with either the EME or with the EME/DGEBA systems. It is suggested that blending of the epoxy with PC caused an increased solubility of the former into the elastomer phase. The tensile strength and tensile elongation of both the EME and EME/DGEBA systems were improved by blending with PC. In the EME/PC blend, the tensile elongation reached its maximum value (60%) at a PC content of approximately 10 p.h.r. (parts per hundred resin by weight), with this maximum being approximately one and a half times higher than that of the unblended EME. Tensile strength was also clearly increased by blending with small amounts of PC, but soon reached a steady value. In the EME/DGEBA/PC blends, the tensile properties were dependent on the weight ratio of EME to DGEBA. In the absence of PC, as this ratio increased, the tensile elongation also increased, while at the same time the tensile strength decreased. The tensile properties were also improved in this system, by blending with PC. From the results obtained, it was clear that the improvement in tensile properties was closely related to the changes in morphology. Therefore, blending of the PC induced a microdispersed structure and improved the elongation of the epoxy resin.

(Keywords: elastomer-modified epoxy; morphology; tensile properties)

INTRODUCTION

Epoxy resins are one of the most important types of thermosetting polymers and are widely used as matrix resins for fibre reinforced plastics (FRP)[1,2], adhesives and paints, but they have the disadvantages of being relatively brittle. Recently, the modification of epoxy resins with either elastomers or with thermoplastics has been investigated in an attempt to improve their toughness. In this way, carboxyl-terminated butadiene acrylonitrile (CTBN) rubber[3,4], acrylic elastomers[5,6] and silicone rubbers[7], used as toughening elastomers, and polyimides[8,9] and poly(ether ether ketone)s[10–13], used as toughening thermoplastics, have been successfully blended to improve the toughness of the epoxy resins.

In this paper, we present the results of our investigations on the relationship between the morphologies and the tensile properties in elastomer-modified epoxy resin (EME) and polycarbonate (PC) blended systems. Since PC is used as a ductile engineering plastic, it may be considered to be a toughening thermoplastic[14]. The EME itself and various EME/diglycidyl ether of bisphenol A (DGEBA) blended systems are used as reference materials to compare the morphologies and the tensile properties in the EME/PC binary blended and the EME/DGEBA/PC ternary blended systems.

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EXPERIMENTAL

Materials

The epoxy resin used in this study was a diglycidyl ether of bisphenol A (DGEBA), which was commercially available from Ciba-Geigy (GY-260®), and had an epoxy equivalent weight (EEW) of 190 g. The curing agent, 4,4'-diaminodiphenylmethane (DDM) (HY972®), was obtained from the same company and was used without further purification. The elastomer-modified epoxy resin was prepared by reacting DGEBA with a carboxyl-terminated butadiene acrylonitrile (CTBN) rubber, which was commercially available from the Daitosangyou Daitosaiza Company (8208®), and had an EEW of 408 g. The content of CTBN in the modified resin was 46 wt%. The polycarbonate (Jupilon H-4000®) ($M_v = 1.6 \times 10^4$), was obtained from the Mitsubishi Gas Chemical Company.

Preparation of blended samples and curing procedure

The EME/PC binary mixture and the EME/DGEBA/PC ternary mixture were in each case dissolved in chloroform and stirred, and the resulting homogeneous solution was then evaporated to remove the solvent. The viscous residue formed in this way was heated for 45 min at 170°C. The curing agent (DDM) was then added to this resin (preheated to 120°C) and stirred until a clear transparent mixture was obtained. The latter was finally poured into a mould preheated at 170°C, and after curing

at this temperature for 1 h, thin films (0.2 mm in thickness) were obtained.

Tensile tests

Tensile tests were carried out on a Mini-Max Tensile Tester (Custom Scientific Instruments) at room temperature, using rectangular-shaped sample test pieces ($5.0 \times 25.0 \times 0.2$ mm). A number of determinations (>5) were carried out for each sample and the average value used. The crosshead speed of the instrument was kept constant at 9.8 mm min^{-1}.

Morphological observations

The morphologies were examined by the use of a scanning electron microscope with an accelerating voltage of 20 kV, using samples that had been stained with osmium tetraoxide (OsO_4), with magnifications of 500–5000.

RESULTS AND DISCUSSION

EME/PC binary systems

The effect of PC content on the tensile properties of the EME/PC system is shown in *Figure 1*. The tensile properties of the EME, namely the tensile strength and the tensile elongation, were improved by blending with PC, when compared to that of the EME on its own. In particular, its tensile strength was clearly increased by blending with a small amount of PC (e.g. 6 p.h.r.), eventually reaching a steady value above a PC content of 10 p.h.r. On the other hand, the tensile elongation reached its maximum value (i.e. 60%) at a PC level of approximately 10 p.h.r., with values decreasing at higher PC contents. This maximum value was approximately one and a half times higher than that of the EME itself.

It is reasonable to expect an increase in the tensile strength of the EME by blending with PC because the tensile strength of the polycarbonate used in this study (Jupilon H-4000) is 60–70 MPa. In this respect, PC appears to play the role of an organic filler. However, if the PC is just simply dispersed in the EME matrix, without any interactions at the interface region between the PC and the EME, it is difficult to understand why the tensile elongation at a PC content of approximately 10 p.h.r. is improved, when compared to that of the EME on its own. In addition, the reason for the decrease of tensile elongation above a PC level of 20 p.h.r. remains unclear. It might therefore be suspected that interactions between the PC and EME are generated by the blending process.

The effect of the PC concentration on the morphology in this system is shown in *Figure 2*. All of the samples were stained with OsO_4 to provide good contrast between the phases. In the cured EME system, it was observed that the CTBN-rich phase formed a continuous matrix along with a dispersed epoxy-rich phase (see *Figure 2a*), with the size of the dispersed spherical particles being approximately 1.5 μm in diameter. Since the CTBN modifier constitutes 46 wt% of this system, this morphology is not unreasonable. The change in tensile properties, namely a decrease in tensile strength and an increase in tensile elongation, is attributed to differences in the morphology when compared to that of cured (unmodified) DGEBA. In the cured EME/PC blended system containing 6 p.h.r. PC, the CTBN-rich phase formed a continuous matrix, similar to that observed in the cured unblended system. However, in this case the size of the dispersed epoxy-rich spherical particles is smaller (0.5 μm in diameter) (see *Figure 2b*). Moreover, in the cured blended systems with a PC $\geqslant 13$ p.h.r., the

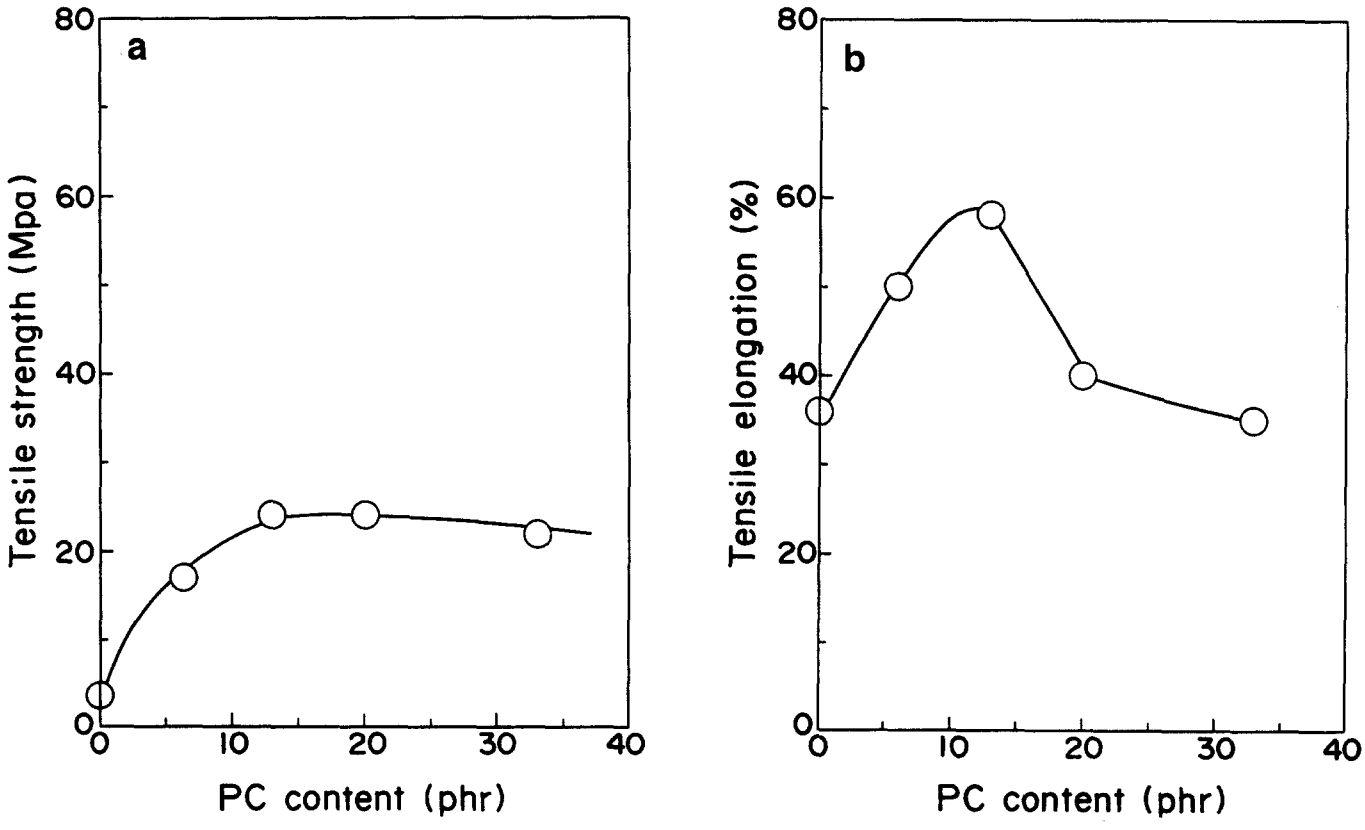

Figure 1 Effect of PC content on the tensile properties of the EME/PC system: a, tensile strength and; b, tensile elongation

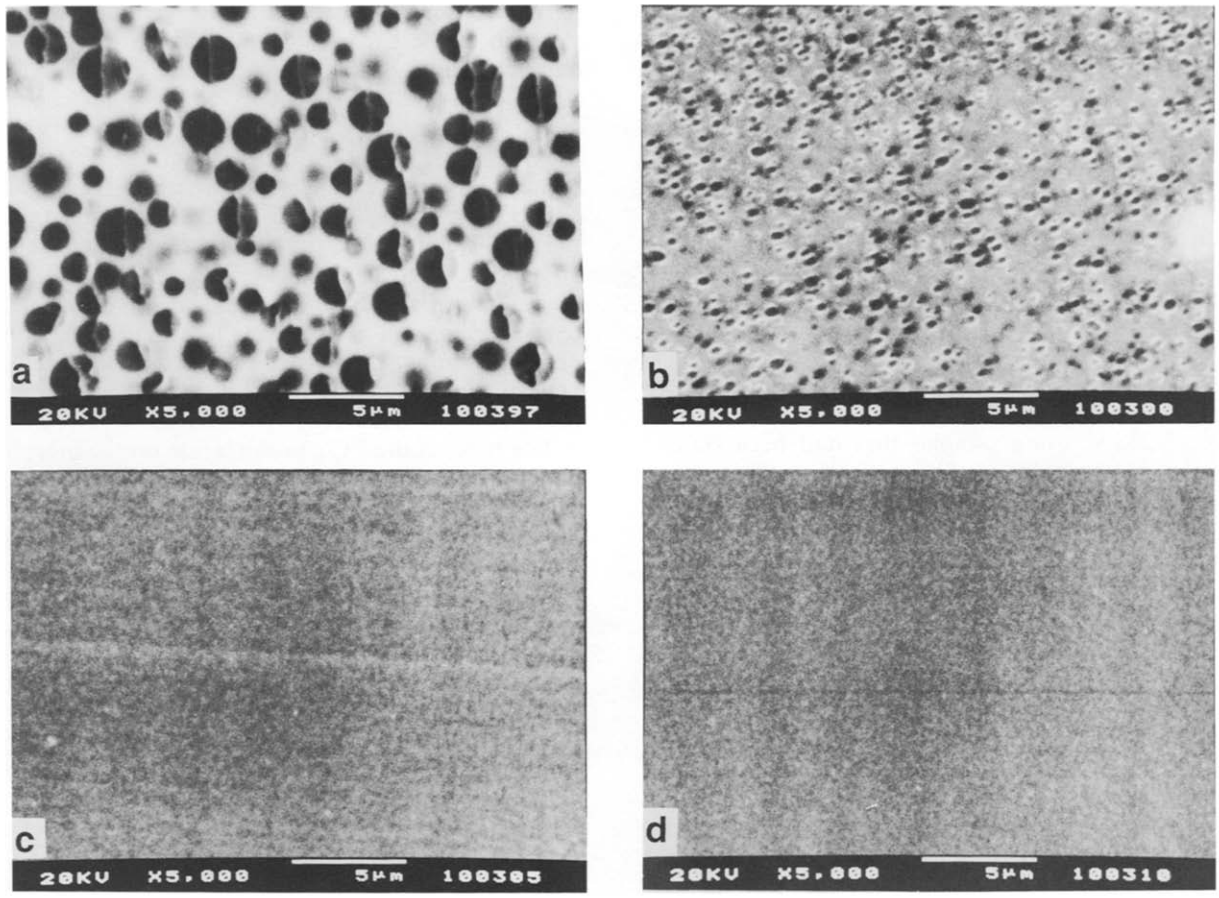

Figure 2 Scanning electron micrographs of the fracture surface of thin films of EME/PC blends: a, no PC present; b, 6 p.h.r. PC; c, 13 p.h.r. PC and; d, 20 p.h.r. PC

size of all of the dispersed epoxy particles is less than 0.1 μm, and obvious phase separation is not seen (see *Figures 2c* and *2d*). The reason for the change in morphology is considered to be as follows. The epoxy phase (in the EME) and the PC either react or are miscible, with improvements in the miscibility of the CTBN phase in the EME induced by the preheating treatment (170°C for 45 min). It has been reported that the miscibility of DGEBA and PC is increased by melt blending[15–18]. It was also observed that the molecular weight of the PC decreased and the concentration of phenolic OH groups increased, in proportion to the blending time, when heating DGEBA with PC[15–17]. From these results, it is suggested that some type of chemical degradation, such as hydrolysis or transesterification, take place during melt blending, which generates lower-molecular-weight PC, and consequently, increased numbers of OH groups. Since phenolic OH groups can react with glycidyl groups, the degraded PC presumably reacts with the epoxy resin, and thus behaves as a compatibilizer in the epoxy/PC/CTBN system.

EME/DGEBA/PC ternary systems

In these systems, the tensile properties were dependent on the weight ratio of EME to DGEBA and the presence of PC (*Figure 3*). As this weight ratio increased, the tensile elongation increased, although there was a corresponding decrease in the tensile strength. These results may be understood by taking into account the change in the CTBN content and crosslink density. It was also clear that blending PC into the EME/DGEBA could improve the tensile properties when compared to those of the PC-free system, as previously observed in the binary system described above. For example, the blending of 13 p.h.r. of PC into EME/DGEBA (75/25 wt%) led to an increase in the tensile strength from 5 to 29 MPa, and in the tensile elongation from 10 to 40%.

From morphology investigations, it was recognized that a two-phase structure was present in this EME/DGEBA (75/25 wt%) system. An epoxy-rich phase formed the continuous matrix, with a dispersed CTBN-rich phase (see *Figure 4a*), in contrast to that of the EME system on its own. Moreover, the dispersed particle size of the CTBN-rich phase was relatively large (10–15 μm in diameter). From these results it is suggested that the miscibility of DGEBA and CTBN was not good enough to form a microdispersed structure under these conditions, and phase inversion might take place at a DGEBA content of less than 25 wt% DGEBA. On the other hand, the morphology of EME/DGEBA (75/25 wt%) blended with 13 p.h.r. of PC showed a microdispersed structure (see *Figure 4b*), in which the size of the dispersed particle was less than 0.1 μm, similar to that found in EME blended with PC at contents greater than 13 p.h.r. (c.f. *Figure 2d*). The change in morphology of these systems was thought to be due to the PC (or decomposed PC) acting as a compatibilizer between the epoxy and the CTBN phases, as previously suggested for the EME/PC binary systems described above.

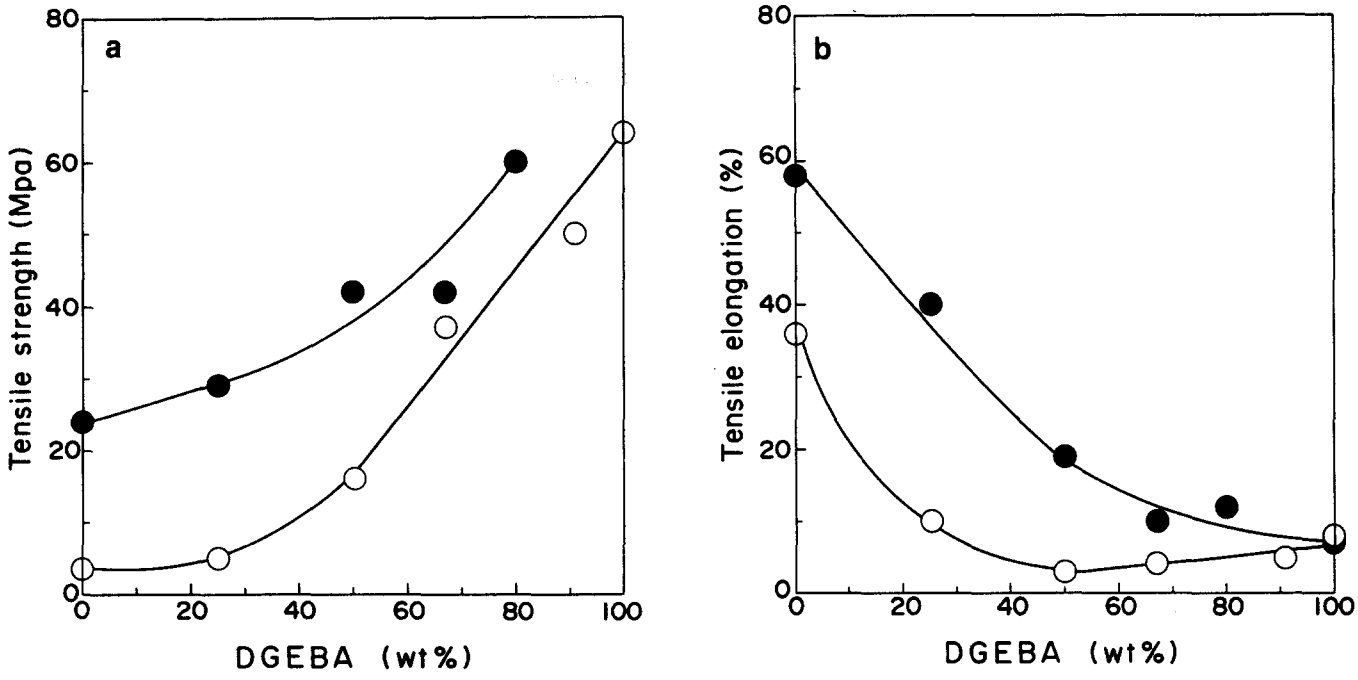

Figure 3 Effect of PC on the tensile properties of the DGEBA/EME system: a, tensile strength and; b, tensile elongation. ○, in the absence of PC and; ●, with a PC content of 13 p.h.r.

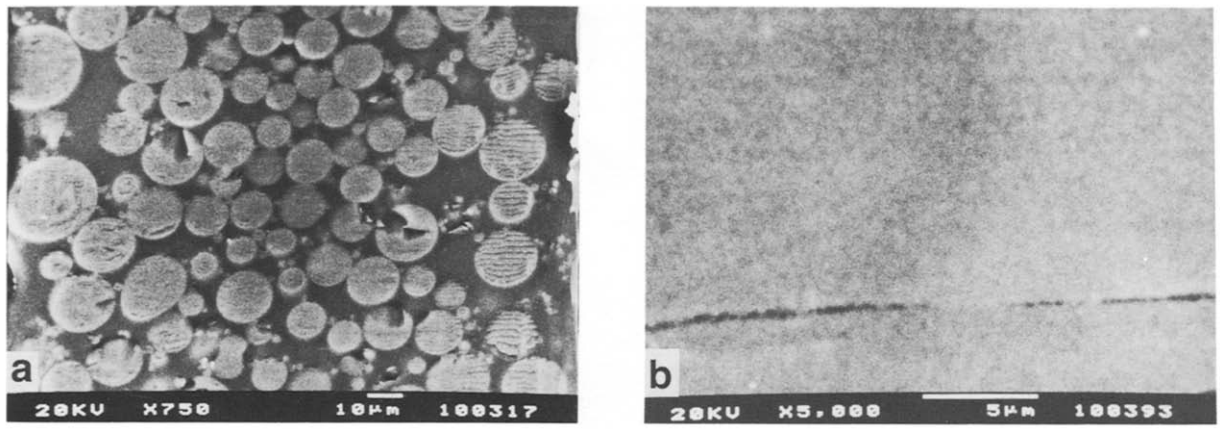

Figure 4 Scanning electron micrographs of the fracture surface of thin films of the DGEBA/EME system: a, in the absence of PC and; b, with a PC content of 13 p.h.r.

CONCLUSIONS

It was observed that blending of PC into EME or EME/DGEBA systems could effectively improve the tensile properties in both cases, with the improvements corresponding well to the changes in morphology. Although the morphology in the EME and EME/DGEBA (75/25 wt%) systems showed different two-phase structures, a microdispersed structure (particle size <0.1 μm) was formed by blending a small amount of PC (13 p.h.r.). Since the blended systems that formed microdispersed structures exhibited good tensile properties, it was suggested that PC sequences were introduced into the epoxy matrix, i.e. a PC-modified epoxy was produced, and this played an important role as a compatibilizer, leading to improvements in the miscibility of the CTBN and epoxy phases. It was concluded that an increased resistance to tensile stress was a consequence of the microdispersed structure in the PC blended systems. It is well known that phase structure has a significant effect on the toughness of materials. In this case, the morphological change to a microdispersed structure, and the resulting improvements in tensile properties indicate an improvement in toughness of the epoxy resin. The effect of the molecular weight of the PC on the morphology and mechanical properties of these EME and EME/DGEBA systems will be reported in a future paper.

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