polymer communications

Polycarbonate/polystyrene ABCP: A plastic toughened plastic and novel elastomer

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Mechanical properties of polymers can be modified by the inclusion of a minor dispersed phase of different material. It is commonly assumed that to toughen a brittle plastic, e.g. polystyrene (PSt), the dispersed phase should be rubbery, i.e. its glass transition temperature T_g should be well below ambient[1]. Such composite materials, e.g. high-impact polystyrene (HIPS), have a lower modulus and ultimate strength but greater toughness than the unmodified plastic; increased toughness is usually associated with the appearance of a yield point in the stress–strain curve. In contrast, incorporation of a dispersed phase of high T_g and high modulus, e.g. glass beads, usually increases the stiffness of the plastic but causes further embrittlement with fracture at lower stresses[2].

Block copolymers used, for example, as thermoplastic elastomers are limited in application to relatively low temperatures because of the comparatively low T_gs of the hard segments used, e.g. low molecular weight polystyrene. Synthesis of ABA block copolymers with end-blocks of high T_g is often precluded by the synthetic procedures adopted[3].

In this preliminary communication on the mechanical properties of AB-crosslinked polymers (ABCPs) we report the tensile properties of a polycarbonate (PCarb) modified polystyrene in which a PCarb of high T_g is dispersed throughout a PSt matrix. The data demonstrate that, by suitable choice of components and molecular architecture, it is possible to prepare plastic-modified plastics with good and interesting mechanical properties.

Materials under investigation

The AB-crosslinked polymers used in our studies are prepared by random graft polymerization of monomer B from specific sites (containing reactive halogen) on preformed chains of polymer A; combination termination of the propagating B-chains yields crosslinks between A-chains. The essential chemical processes involved are described elsewhere[4–6]. The crosslinking index is kept sufficiently low that no gel is formed and the average degree of polymerization of the B-chains is controlled by the polymerization kinetics. The final reaction product is normally a blend of unreacted polymer A with a statistical distribution of multicomponent species each containing n A-chains ($n \geqslant 2$) linked by ($n-1$) B-chains; the predominant multicomponent species is that with $n=2$, i.e. A_2BA_2 block copolymers[7]. The average structural parameters of the polymer are calculable. The specific polymer with which this report is concerned had a polycarbonate as A-component and polystyrene as B-component and is described further in the experimental section.

Experimental

Materials. The PCarb ($\bar{M}_n = 16$ kg mol^{-1}) was prepared by condensing 1,1,1-trichloro-bis-2-(p-hydroxyphenyl)ethane with phosgene, using the procedure described elsewhere[8]. Other materials were purified as described in earlier papers[4,5].

PCarb/PSt copolymer synthesis. Graft polymerization of styrene was photo-initiated from specific sites (–CCl_3 groups) on the PCarb by $Mn_2(CO)_{10}$ ($\lambda = 436$ nm[4–6]. The reaction mixture consisted of a dilute solution of PCarb (~ 1% w/v) and $Mn_2(CO)_{10}$ (10^{-3} mol l^{-1}) in styrene. Reactions were performed in a laboratory illuminated with inactive (Na) light.

Rates of photo-initiation were controlled using neutral density filters. The copolymer was synthesized under abnormal reaction conditions (extremely low rates of photo-initiation) chosen specifically to introduce much longer PSt chains compared to PCarb so that a high overall PSt content could be achieved at low degrees of crosslinking.

Extrapolating from kinetic data obtained at higher rates of initiation, the number average molecular weight of PSt was estimated to be 257 kg mol^{-1} and the reaction time corresponded to a relative crosslinking index γ_r of 0.7 (γ_r is the number of crosslinking points per weight average A-chain, $\gamma_r = 1$ at the gel point). Inevitably, under these conditions in bulk styrene the rate of spontaneous thermal initiation must be comparable with the rate of photo-initiation ($\sim 4 \times 10^{-9}$ mol l^{-1} s^{-1}) and chain transfer to monomer would not be negligible[9]. The consequence is that some PSt homopolymer would have been formed and, more important, a large proportion of the PSt would be formed as long branches attached to the PCarb[6]; the true value of γ_r would be less than 0.7. The final polymer, isolated from the reaction mixture by precipitation into petroleum spirit, had an overall composition of 75%(w/w)PSt.

Sample preparation. The PCarb/PSt ABCP was cast into a thin film (0.2 mm thick) from dilute solution [< 5% (w/v)] in dichloromethane after filtering through a

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Table 1 Tensile properties of polymers

Sample	Temperature °C	Initial modulus GN m^{-2}	Yield stress MN m^{-2}	Ultimate tensile strength MN m^{-2}	Extension at break %	Comments
PCarb	20	2.40	52.5	52.1	91	
ABCP	20	2.43	55.9	54.6	3.7	crazes
	93	1.45	18.6	11.8	140	necks and stress whitens
PSt	20*	3.33	–	51.0	2.3	crazes
	75.5	0.80	10.5	3.9	83	necks
	90	0.007	0.98	–	–	flows
HIPS^{+}	20	1.60	17.5	21	40	

* Typical data from references 1, 11

$^{+}$ Data from ref 1

Millipore filter. The film was dried over a period of days. Residual solvent was removed by heating under vacuum, raising the temperature by 5–10°C per hour, finally maintaining the temperature at 90°C for one day. The film was optically almost clear. Films of PCarb and PSt homopolymers were prepared under comparable conditions.

Instruments. A Metropolitan-Vickers EM6 electron microscope was used to determine the polymer morphology. Ultra-thin sections were cut using an LKB Ultratome III. Tensile tests were performed on an Instron TSM Universal Tensile Tester using an initial jaw separation of 3.3 cm with a crosshead speed of 0.5 cm min^{-1} at temperatures below 100°C and 5 cm min^{-1} at higher temperatures. Test pieces, stamped from cast films, had a standard dumb-bell shape with a parallel sided mid-section (4 mm wide, 28 mm long).

Results and discussion

Morphology. The morphology of the ABCP was established by transmission electron microscopy of ultra-thin sections, using natural contrast to distinguish the components[8], and by examination of replicas of etched surfaces. The etch technique employed was an extension of the alkaline hydrolysis method developed for polyblends[10]; details of the technique will be presented in a subsequent publication. The sample consisted of a PSt matrix with small dispersed PCarb spheres, average diameter 44 nm, with occasional large PCarb regions (presumably homopolymer), about 1.5 μm diameter.

Tensile properties at 20°C. Representative stress–strain curves for PCarb and PCarb/PSt ABCP are shown in *Figure 1* and average values of derived parameters, together with typical values for PSt homopolymer[1,11], are given in *Table 1.* Difficulties were encountered in preparing damage-free samples of PSt homopolymer from the brittle films prepared by solvent-casting under the conditions used in this study. The stress–strain curves for PCarb and the derived parameters are comparable with those for conventional poly(bisphenol-A carbonate)[11,12].

Although the ABCP has a PSt matrix its stress–strain curve shows a definite yield point. The derived parameters for this polymer are intermediate between those of the component PCarb and PSt homopolymers, a siutation which parallels the rubber-modification of brittle plastics. The significant feature of these data is the development of a yielding process, indicating an increase in toughness, even though a plastic of high T_g is incorporated into PSt. While we were unable to perform impact tests it is notable that the area under the stress–strain curve for the ABCP is greater than that for conventional PSt. Although the extension to break is much less than that for HIPS (*Table 1*) the use of PCarb as the dispersed phase produces a smaller decrease in modulus than does rubber-modification.

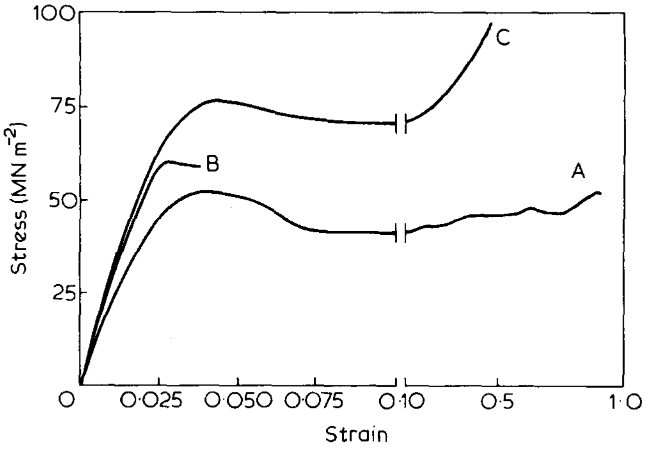

Figure 1 Stress–strain curves for: (A) PCarb; (B) PCarb/PSt ABCP (unorientated); (C) strain-orientated PCarb/PSt ABCP. Note change in scale at strain = 0.1

Properties at elevated temperatures — a polystyrene elastomer. At temperatures above ambient the properties of the ABCP are superior to those of PSt. Approaching T_g of PSt, where PSt loses its dimensional stability, the ABCP retains a considerable modulus and strength and fails by fracture rather than flow (*Table 1*).

Above T_g of PSt, where PSt is rubbery, the ABCP behaves as a low modulus rubber. Data in *Figure 2* demonstrate that at elevated temperatures the ABCP has a low initial modulus (about 2.1 and 0.9 MN m^{-2} at 121 and 141°C, respectively) but strain hardens at high extensions. Extensions of 700% (the maximum using the environmental chamber) were achieved without fracture. Recovery of samples cut under extension was rapid and complete. At 140°C complete recovery from 418% extension with some hysteresis was observed (*Figure 2*), using a cross-head speed of 5 cm min^{-1}; no hysteresis was observed from extensions of 200% using a cross-head speed of 0.5 cm min^{-1}.

The ABCP above the T_g of PSt, therefore, is an elastomer and behaves in a similar manner to an ABA block copolymer with a long elastomeric mid-block and short hard end-blocks[3]. In this case the short PCarb

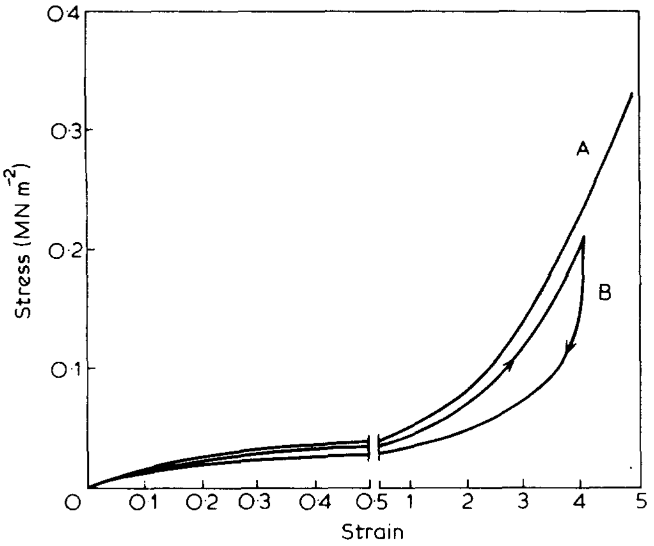

Figure 2 Stress–strain curves for PCarb/PSt ABCP at elevated temperatures: (A) 118°C; (B) 140°C. Note change in scale at strain = 0.5

chains in hard domains provide physical crosslinks between the PSt chains. Thus, the material is a block-copolymer type material with a high upper working temperature; the use of a mid-block of lower T_g would increase the temperature range of the polymer as a functional elastomer.

The absolute stress required to produce a strain in the ABCP used in this work is low compared with that required to produce the same strain in a St–butadiene–St (SBS) copolymer of equivalent composition[3] or in a PCarb/polychloroprene ABCP with a polychloroprene matrix[13], at ambient temperature. This result may appear surprising since the temperatures used here are only slightly in excess of the PSt T_g and PSt chains are inherently stiffer than those of polydienes. However, the result is understandable in view of the structure of the polymer.

According to the theory of rubber elasticity the stress required to produce a given elongation is proportional to the number v of effective network chains per unit volume, when allowances are made for filler particles and network defects[14]. In the present context we expect v to be low because the PSt in the form of branches and homopolymer are not true crosslinks between the PCarb domains; the excellent recovery observed is consistent with extremely long PSt branches being entangled and acting as partial crosslinks.

Strain orientation. Samples stretched to 400% extension at elevated temperatures and allowed to stress relax for 30 min were cooled at constant length. The room temperature properties of the strain-orientated samples are given in *Table 2* and a stress–strain curve for the sample strain-orientated at 121°C is shown in *Figure 1*; the specimen drawn at 159°C failed at 3.8% extension due to a flaw in the sample. In calculating the properties of the strain-orientated polymers the sample dimensions after strain-orientation were used; the crosshead speed was maintained at 0.5 cm min^{-1} so that the actual rate of strain was 0.25 times that of the unorientated samples.

Strain-orientated samples exhibit higher moduli and greater extensions to break (in the strain direction) than does the unorientated material. The magnitudes of the various properties decrease with increasing orientation temperature. This trend is no doubt due to the more facile stress relaxation at the higher temperatures during which initially extended branches and homopolymer chains recoil towards their original conformations; primarily the crosslinks retaining significant extensions in the original stress direction. Unlike the original ABCP the strain-orientated samples do not craze on extension but fibrillate in the stress direction. The large extensions observed demand significant deformation of the PSt matrix at ambient temperatures in contrast to the very small deformations possible in unorientated PSt homopolymer; the stresses involved could also deform the PCarb domains. It is notable that PSt can be deformed more extensively when crazing is precluded, e.g. in tension under high hydrostatic pressures[15] and, more notably, in compression[16]. Moderate increases in extension to break (×3, approximately) have been reported for biaxially orientated PSt films[17].

When strain-orientated samples were heated above the PSt T_g they exhibited almost instant recovery to the original unorientated dimensions.

The PCarb domains, acting as physical crosslinks at high temperature, permit strain orientation of the PSt chains to be 'frozen in' to give a strong, tough polymer at room temperature. By strain-orientating at relatively low temperatures the modulus and yield stress can be increased significantly and the ultimate strength increased by almost 80%. This combination of properties gives a large area under the stress–strain curve and, hence, a large work to fracture. The extension to break is similar to HIPS but the modulus is much higher (compare *Tables 1* and *2*).

Conclusions

The data presented demonstrate that in order to introduce a yielding process into a brittle plastic it is not necessary to incorporate a minor rubber component. It is possible to achieve the same effect, perhaps smaller in magnitude, by incorporating a polymer of high T_g if that polymer itself yields on deformation. Also, use of a high-modulus modifier maintains a high modulus for the composite.

ABCPs behave similarly to linear block copolymers. If relatively short end blocks have a higher T_g than the long central block the domains of the former act as physical crosslinks between the latter. At temperatures above T_g of the central blocks, but below that of the end blocks, the ABCP behaves in a manner similar to SBS block copolymers at room temperature. The present combination gives a material with a high upper limit to the working temperature range.

Because T_g of the central block is above ambient the PCarb/PSt ABCP can be permanently strain-orientated

Table 2 Tensile properties of strain-orientated ABCP

Orientation temperature °C	Initial modulus GN m^{-2}	Yield stress MN m^{-2}	Ultimate tensile strength MN m^{-2}	Extension at break %
121	2.96	75.9	96.6	48.2
141	2.75	72.6	86.2	47.4
159	2.56	64.0	–	–

to produce a strong tough polymer which can rapidly retract to its original dimensions on heating above the PSt T_g. Potentially such ABCPs could be used as heat shrink materials if fabricated into some appropriate shape and subsequently deformed to larger dimensions at elevated temperature.

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Dilatometric studies on PVC-Cu composite

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Impregnation of metallic fillers in the polymer matrix enhances the strength and electrical conductivity of the resulting metal-polymer composite[1-8]. In a previous paper[6] we have shown that better coalescence of the matrix markedly enhances the strength and electrical conductivity of poly(vinylchloride)-copper (PVC-Cu) composites. However, no systematic investigation has so far been made to explain the nature of interaction between the phases. Unlike fibre reinforced composites for which the strength of the interfacial adhesion is normally determined by the single fibre pull out experiment, there is no direct method in the particulate composites to measure the magnitude of the strength of the interfacial bonding and mechanism of failure under applied stress. In the present investigation, an attempt has been made to understand the strengthening mechanism through dilatometric studies of PVC-Cu composites.

Commercially available poly(vinylchloride) powder (NOCIL, Bombay) of average particle size 126 μm and copper powder (Assam Carbon Company) of average size 7 μm were used here. Details of the preparation of PVC-Cu composites has been given elsewhere[4,5].

Glass transition temperature (t_g) was measured using a quartz dilatometer. The rate of heating was 1°C min^{-1}. The range of temperature studied was 32-100°C.

Figure 1 shows that glass transition temperature of pure PVC is increased from 85° to 88°C for 5 volume % and to 90°C for 10 volume % metal concentration. Beyond 10 volume % t_g is hardly affected. This is presumably because of the complete formation of segregated network around 10 volume % beyond which increase in metal content does not improve the metal-metal contact condition significantly[5,9,10]. Similar observations have been made by a number of authors in this field[11-16]. Increase in t_g proves segmental immobilization of the pure

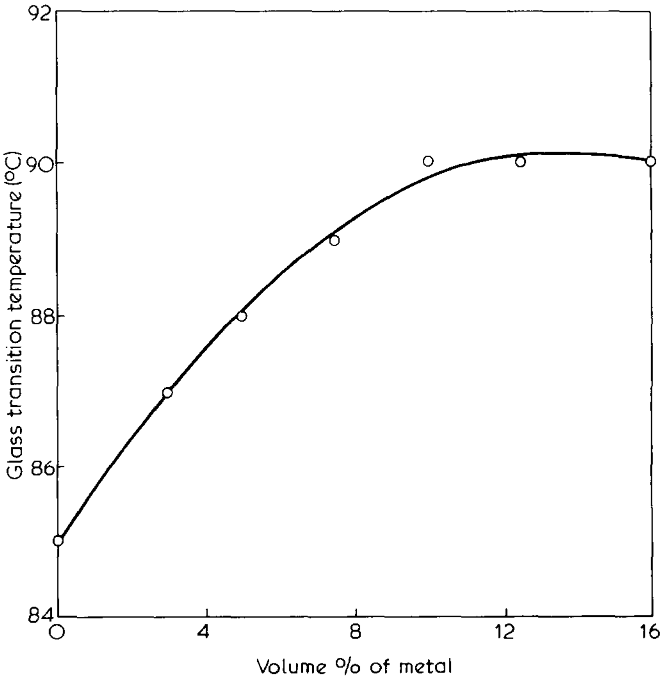

Figure 1 Glass transition temperature of PVC—Cu composite as a function of metal concentration

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