

Polystyrene/Polycarbonate/Polystyrene-*block*-Polycaprolactone Blends. Emulsification and Mechanical Performance

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SYNOPSIS

Two polystyrene-polycaprolactone diblock copolymers, of differing molecular weights, have been extrusion-blended with polystyrene and polycarbonate. The morphologies of the resultant blends were studied using differential scanning calorimetry and scanning electron microscopy. In all compositions studied, the polystyrene and polycarbonate phases exhibited discrete glass transitions indicative of the immiscibility of these components. However, addition of the copolymer increased the extent of dispersion of the homopolymer components within one another quite effectively. Blend specimens were tested with respect to tensile, flexural, impact, thermal, and flow characteristics to probe the effects of morphology and composition on these factors. In general, the blends were rigid, brittle materials with thermal characteristics in the range between those of the polystyrene and polycarbonate components. Addition of polystyrene-*block*-polycaprolactone polymer to the blends resulted in increased brittleness, reduced thermal performance, maintenance of rigidity, and improved flow.

INTRODUCTION

The use of block copolymers as compatibilizers in blends of immiscible polymers is one approach which is being developed within the larger field of polymer blends and alloys. In recent years, a number of ternary systems composed of two immiscible homopolymers and a diblock copolymer have been investigated.¹⁻¹⁷ These studies have focused primarily on the emulsifying capabilities of the copolymer, with less emphasis being placed on the mechanical performance of the blends.

One commercial aspect of blending polymers is the potential for blending commodity polymers with the more costly specialty materials in the hope of obtaining a favorable cost/performance balance. Our initial attempts in this field have centered on blending polystyrene with engineering resins such as bisphenol A polycarbonate.

For polystyrene/polycarbonate blends aspects

such as viscosity,¹⁸ viscoelastic behavior,^{19,20} morphology,^{21,23,25,26} miscibility,¹⁸⁻²⁶ and mechanical performance²⁴⁻²⁶ have been studied. Polystyrene and polycarbonate are not compatible,^{19,20,23-28} although there is some evidence of partial mixing and adhesion of the two at the blend interface.^{19,25} The extent of dispersion of one polymer within the matrix of the other generally results in particles with diameters of 1 μm and upwards. The tensile²⁴⁻²⁶ and impact²⁶ behavior of these systems have been studied, and although the tensile strength and modulus approximate a linear average of these properties in the component polymers, the impact behavior shows a strong negative deviation from values predicted by linear additivity. Properties such as flexural and thermal behavior (i.e., Vicat softening temperature and distortion temperature under load) do not seem to have been reported in the literature.

In choosing a diblock copolymer to act as a compatibilizer for polystyrene/engineering resin blends, we desired that one block be polystyrene, for miscibility with homopolystyrene, and the other block be such that it would have miscibility with a wide range of engineering resins. Polycaprolactone would seem to be an ideal choice for this second block. It

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Table I Molecular Weights, Polydispersities, and Copolymer Compositions

| Polymer | M_n | M_w/M_n | Wt % PS | Wt % PCL |
|--------------------------|---------|-----------|---------|----------|
| Polysar 201 ^a | 171,400 | 1.690 | | |
| Lexan 121 ^a | 24,130 | 1.761 | | |
| PS-PCL (1) ^b | 114,100 | 1.126 | 83.5 | 16.5 |
| PS-PCL (2) ^b | 59,000 | 1.125 | 80.2 | 19.8 |

^a Determined by size exclusion chromatography using a calibration curve generated from polystyrene standards.

^b Molecular weights for the polystyrene blocks were determined as in (a).

NMR analyses of the copolymers were used in conjunction with SEC data for the PS blocks to calculate the absolute molecular weights of the copolymers.

has demonstrated miscibility with polymers such as phenoxy, SAN (28% AN), polyvinyl chloride, nitrocellulose, polyepichlorohydrin, chlorinated polyether,^{27,28} the Saran copolymers of vinylidene chloride with acrylonitrile (Saran F) vinyl chloride (Saran B) and vinyl acetate (Saran C),²⁹ chlorinated polypropylene, chlorinated polystyrene,³⁰ chlorinated polyethylene,³¹ and bisphenol A polycarbonate.³² By comparison with the aforementioned polymers, polycaprolactone might also be at least partially miscible with various aliphatic polyesters; aromatic polyesters such as polyethylene terephthalate and polybutylene terephthalate; polyvinylidene fluoride; polyvinyl alcohol; and acrylate and methacrylate polymers.

In addition to the wide range of materials miscible (or likely miscible) with polycaprolactone, polystyrene-polycaprolactone diblock copolymers are also attractive as compatibilizers because they can be prepared in a straightforward manner via a two-step living polymerization.³³ Hence, the copolymer architecture and composition can be readily controlled.

Because of the potential for controlling the extent of dispersion in polystyrene/polycarbonate blends by using polystyrene-polycaprolactone diblock copolymers and the lack of information available on the mechanical performance of these blends we have investigated the morphology and mechanical properties of these systems. The results of these studies are presented herein.

EXPERIMENTAL

Materials

Polysar 201 polystyrene (Polysar Ltd.) and Lexan 121 bisphenol A polycarbonate (General Electric Ltd.) were obtained from commercial suppliers. Caprolactone, propylene oxide, styrene oxide, and *sec*-butyllithium were obtained from Aldrich. Styrene and diethylaluminum chloride solution were obtained from in house supplies. All solvents used were obtained from Caledon with the exception of the methanol used in precipitations which was obtained from in house supplies. High purity argon (less than 5 ppm total residuals) was obtained from Matheson.

Size exclusion chromatography was performed on a Hewlett Packard 1090A system. Gas chromatography was done on a Shimadzu GC-9A gas chromatograph. Proton nmr spectra were obtained using a Bruker WM250 nuclear magnetic resonance spectrometer. Water content analyses were carried out on a Metrohm 652 Karl Fischer coulometric titrator.

Polystyrene-polycaprolactone diblock copolymers were prepared by a known route.³³ A brief description of the method follows. Reactions were performed using "bottle" techniques. Bottles were thoroughly rinsed with deionized water, oven baked (180°C for at least 24 h) and then sealed using a

Table II Operating Conditions for Blend Preparation by Twin Screw Extrusion

| Zone Temperatures | Zone 1 ^a | Zone 2 | Zone 3 | Zone 4 | Zone 5 | Zone 6 |
|-------------------|------------------------------------|--------|----------------------------|--------|--------|--------|
| Setting (°C) | | 260 | 240 | 240 | 240 | 240 |
| Actual (°C) | | 200 | 240 | 240 | 240 | 225 |
| | Feed rate 200 mL min ⁻¹ | | Screw rotation rate 50 rpm | | | |

^a Zone 1 was a water-cooled feed zone equipped with a volumetric metering feeding device.

Table III Molding Conditions for the Preparation of Mechanical Test Specimens

| | | | |
|--------------------------|---------|----------------------------|----------|
| Rear zone temperature | 260°C | Forward zone temperature | 245°C |
| Nozzle temperature | 200°C | Mould temperature | 45°C |
| Injection boost pressure | 4.1 MPa | Injection holding pressure | 3.25 MPa |
| Back pressure | 0.3 MPa | | |
| Injection boost time | 1.5 s | Injection holding time | 5 s |
| Mould closed time | 25 s | | |

Teflon layer followed by a nitrile rubber seal (previously extracted with toluene for up to 24 h to remove antioxidant and oil extenders) and finally an aluminum cap. All solvents were dried over CaH_2 , distilled, degassed, and stored under an argon atmosphere. The monomers, styrene and caprolactone, were distilled under vacuum and stored under argon. *Sec*-butyllithium (*s*-BuLi) in cyclohexane and diethylaluminum chloride in hexane were filtered and titrated prior to use. Water contents for all monomers and solvents were less than 20 parts per million (ppm). In some cases, in particular with toluene, H_2O levels less than 10 ppm were achieved.

Preparation of PS-PCL Diblock

Five hundred grams of dry toluene and 80 g of styrene were added to a 1-L capped bottle. The bottle was degassed with argon for 30 min. *s*-BuLi [1.39 M, 0.65 mL (0.898 mmol)] in cyclohexane was added. The deep orange colored solution was agitated in a room temperature orbital shaker bath to maintain the temperature at less than 25°C. Styrene monomer conversion was periodically monitored using gas chromatography and reached over 99% conversion in four hours. A 0.2 mL sample was withdrawn at this time and terminated with a small amount of methanol. The sample was then analyzed by size exclusion chromatography to determine the molecular weight of the PS block. The SEC was calibrated using a series of narrow molecular weight polystyrene standards, thus a reasonably accurate determination of the molecular weight characteristics of the PS block was obtained in this manner.

The reaction mixture was cooled to -10°C after which 0.51 g (4.47 mmol) of caprolactone was added. The lime green solution was shaken for 5 min. Diethylaluminum chloride [1.80 M, 0.50 mL (0.904 mmol)] in hexane was added, followed by 2.5 mL of THF. The solution was heated to 50°C in the orbital shaker bath for 30 min, and 16 g of caprolactone was added. Caprolactone conversion was

monitored by GC and was found to exceed 98% after 17 h. The reaction was quenched with 0.05 mL water.

The molecular weights, polydispersities, and compositions of the diblock copolymers are presented in Table I.

Blend Preparation and Analyses

Blends of the component materials were prepared using a Leistritz LSM 30.34 counterrotating, intermeshing twin screw extruder operating under the conditions presented in Table II. The pelletized blends were molded into mechanical test specimens on a Van Dorn 50-ton injection molding machine using the conditions listed in Table III. Electron micrographs of the room temperature fractured, gold coated surfaces of mechanical test specimens, prepared as above, were obtained using a JEOL JSM-35CF scanning electron microscope. Mechanical properties of these materials were measured in accordance with ASTM procedures which are summarized in Table IV. Differential scanning calorimetry experiments were performed using a DuPont 9900 system. DSC samples were obtained from the

Table IV Mechanical Tests and ASTM Procedure Numbers

| Description of Test | ASTM Procedure |
|--|----------------|
| 3.2 mm, notched IZOD impact strength | D 256 |
| Deflection temperature under load (1.82 MPa) | D 648 |
| Vicat softening point | D 1525 |
| Tensile properties (type I dumbbells) | D 638 |
| Flexural properties | D 790 Method A |
| Melt flow index of thermoplastics (200°C/5.0 kg) | D 1238 |

blend extrudate and were not annealed. The DSC heating rate was $10^{\circ}\text{C min}^{-1}$.

RESULTS AND DISCUSSION

Two key aspects of this work were to determine the extent to which the diblock copolymers could act as emulsifiers for the polystyrene/polycarbonate blends, and to examine the effect of a varying morphology on the mechanical performance of the blends.

The molecular weights of the PS-PCL compatibilizers were selected based on several criteria. In copolymers (1) and (2), respectively, the number average molecular weights of the PS segments were roughly 100,000 and 50,000 g mol^{-1} . These were chosen to be less than the number average molecular weight of the Polysar 201 polystyrene, and comparable to or greater than the critical entanglement length for polystyrene which is roughly 60,000 g mol^{-1} .³⁵ The PCL block in copolymer (1) was chosen to be comparable in molecular weight to the Lexan 121 polycarbonate and thus a number average molecular weight of approximately 25,000 g mol^{-1} was targeted. The weights in copolymer (2) were set at half those in (1), hence the PCL block in (2) had a target number average molecular weight of 12,500 g mol^{-1} . By following these criteria the compatibilizers would presumably have blocks with comparable but lower viscosities than the homopolymers into which they would mix, and provide suitable adhesion into and between these phases by entanglement for PS and heteroatom interactions within the PC/PCL-block phase.

In order to determine the molecular weights of the diblock copolymers with a fair degree of accuracy, the following method was employed. During the copolymer synthesis, at the completion of styrene polymerization, a small sample of the polystyrene solution was withdrawn from the bottle and terminated with methanol. This solution was analyzed by SEC (calibrated with thirteen narrow molecular weight PS standards) to provide accurate molecular weight information about the PS block. Upon completion of the diblock copolymer synthesis the resultant copolymer was analyzed by proton NMR to determine the molar percentages of styrene and caprolactone in the final product. Hence weight percent composition of the copolymer could be calculated and this information in conjunction with molecular weight data for the PS block was used to calculate the overall molecular weights for the copolymers (Table I).

The compatibility of the blend components was examined using differential scanning calorimetry and scanning electron microscopy. PS/PC compositions [30/70 and 70/30 wt %] with varying amounts of the PS-PCL diblock copolymers were examined. Differential scanning calorimetry results for these systems in which 0, 2, and 5 wt % PS-PCL(2) were included are presented in Figure 1. Glass transition temperatures for the homopolymer blend components were Polysar 201 polystyrene, $T_g = 102.9^{\circ}\text{C}$; Lexan 121 polycarbonate, $T_g = 149.4^{\circ}\text{C}$.

If we look first at the figure in general, the sizes

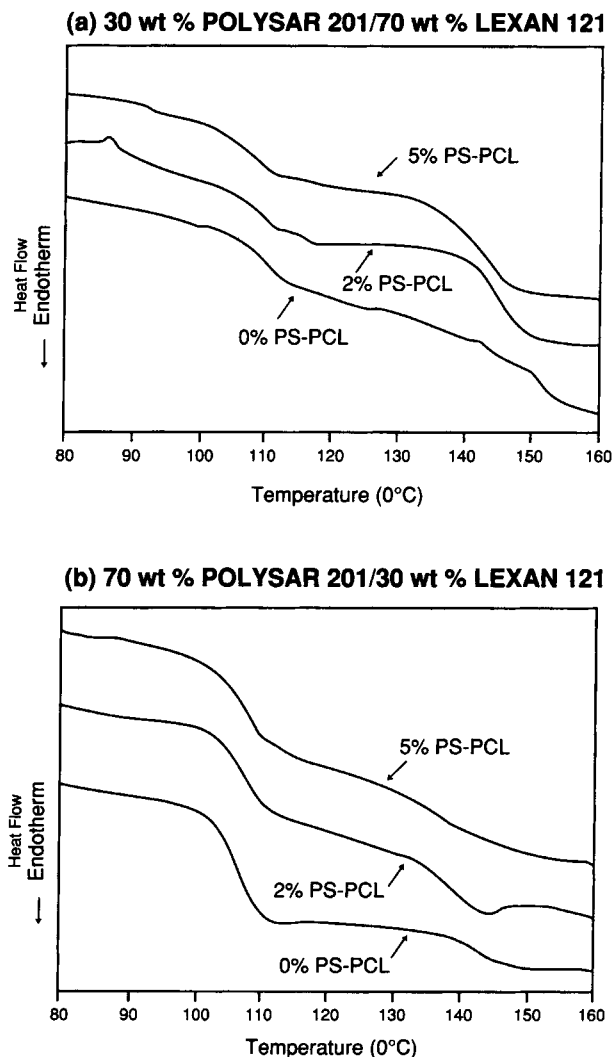


Figure 1 Differential scanning calorimetry for polystyrene/polycarbonate/polystyrene-*b*-polycaprolactone blends: (a) 30 wt % Polysar 201/70 wt % Lexan 121; (b) 70 wt % Polysar 201/30 wt % Lexan 121.

of the transitions roughly correspond to the compositions of the blends (e.g. 70 wt % PS more intense than 30 wt % PS). At each of the polystyrene levels the glass transition temperature for the polystyrene phase is not affected by the addition of the compatibilizer. However, on increasing the polystyrene content the T_g does shift to lower values, moving towards that observed for the pure Polysar 201 polystyrene. The polycarbonate shows this composition dependence in T_g as well and, unlike the polystyrene phase, the polycarbonate glass transition behaviour is strongly influenced by the addition of the polystyrene-polycaprolactone diblock copolymer. In each of the examples depicted it is apparent that on going from 0 to 2 and then 5 wt % PS-PCL loadings the PC glass transition temperature shifts markedly to lower values. This is presumably due to the presence of the low melting polycaprolactone block ($T_m = 59.4^\circ\text{C}$), which is miscible in the polycarbonate phase, and not due to enhanced PS/PC miscibility which should be accompanied by a corresponding shift in the PS T_g as well.

Electron microscopy was used to examine the morphology of the blends and in particular the emulsifying effects of the copolymers on the blends. Electron micrographs of both PS and PC rich systems with various levels of each of the PS-PCL copolymers are presented in Figures 2-5. In each of these examples, it can clearly be seen that addition of the copolymer produces a decrease in the particle size of the minor component within the matrix of the major component and that the decrease in particle size is sensitive to the amount of copolymer added. It is also apparent, by looking at the systems with 5 wt % copolymer, that the lower molecular weight copolymer, PS-PCL(2), is a more efficient emulsifier. This is indicative of the potential for optimizing the level of dispersion within the system by tailoring certain aspects of the compatibilizer, in this instance the overall molecular weight.

Blends of Polysar 201 polystyrene and Lexan 121 polycarbonate were prepared in composition increments of 10 wt % varying from one pure component to the other. This series was replicated with loadings of 0, 2, and 5 wt % PS-PCL(2), which was the more efficient of the two copolymers as an emulsifier. The blends were prepared, injection-molded, and mechanically tested as described above (Tables II-IV).

The results of tensile testing are presented in Figure 6. The tensile strength at break values [Fig. 6(a)] for the PC-rich, binary blends are comparable to those observed by Rudin and Braithwaite²⁴ and Kunori and Geil.²⁵ For the binary PS/PC blends containing 50 wt % PS or more the values are mark-

edly higher than those reported by Kunori and Geil.²⁵ However, differences in the molding techniques for sample preparation (injection molding—

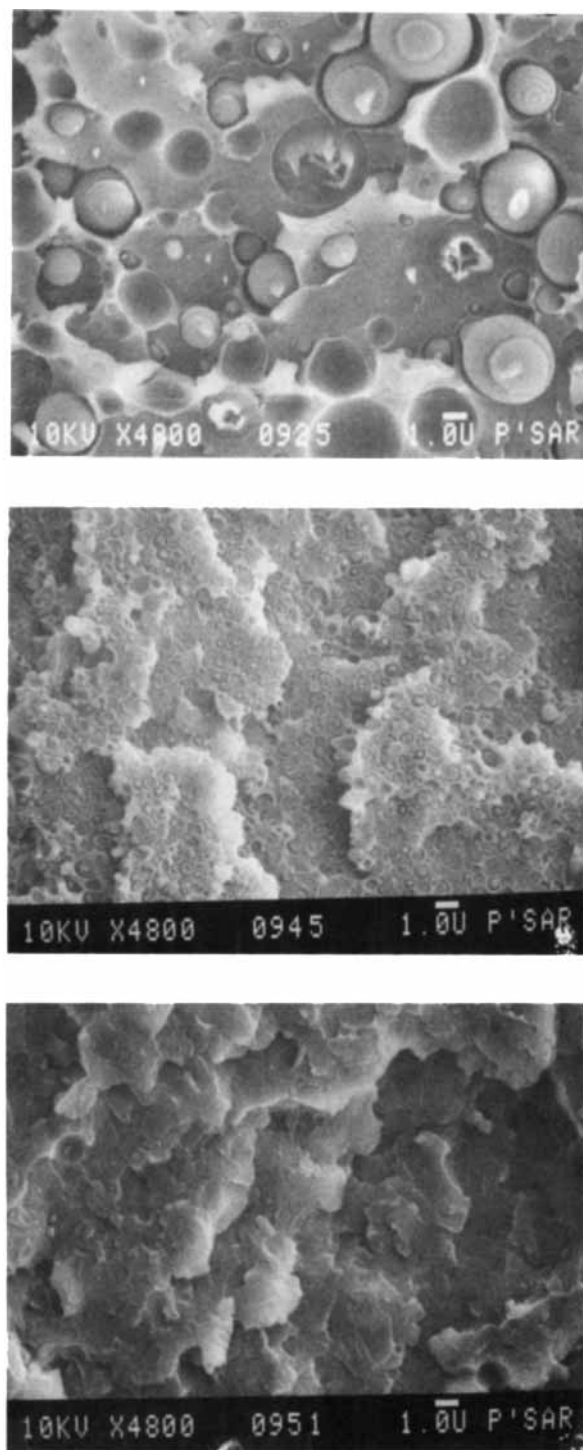


Figure 2 Scanning electron micrographs of polystyrene/polycarbonate/polystyrene-*b*-polycaprolactone blends: 30% PS/70% PC; (a) 0% PS-PCL(1); (b) 5% PS-PCL(1); (c) 10% PS-PCL(1).

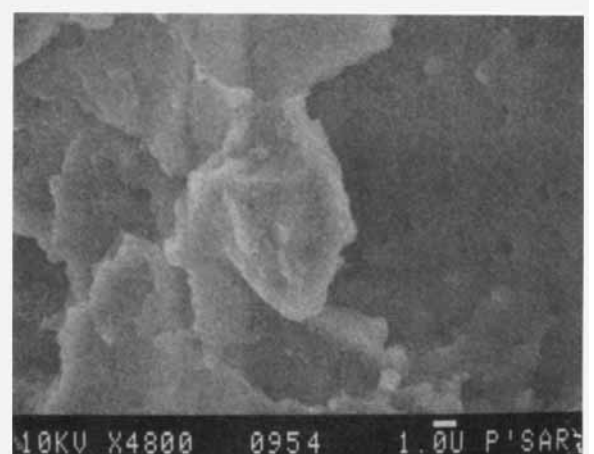
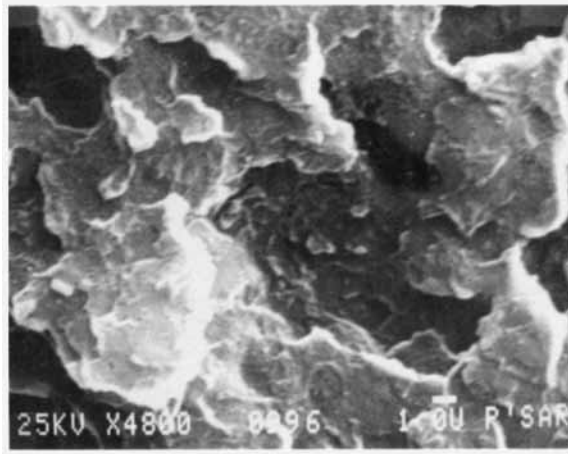
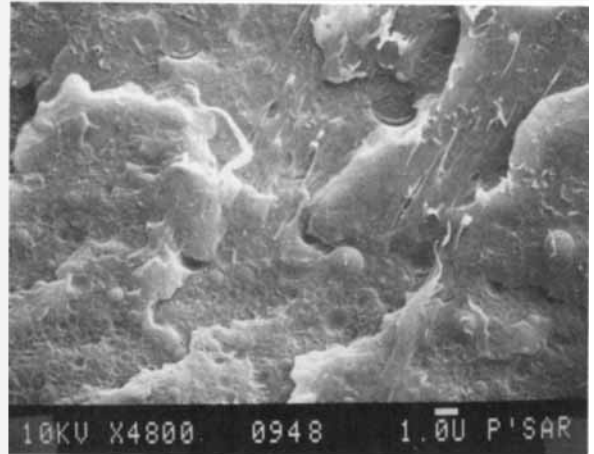
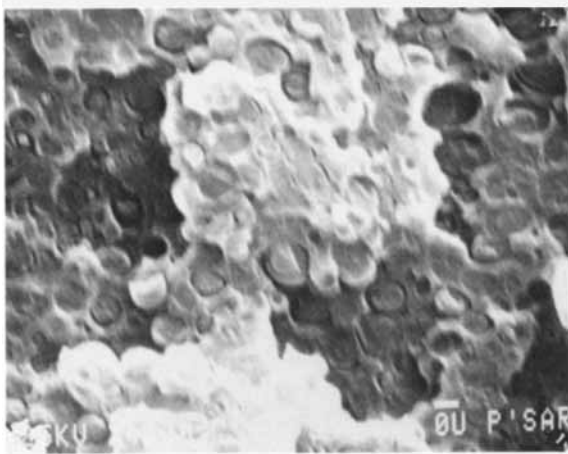
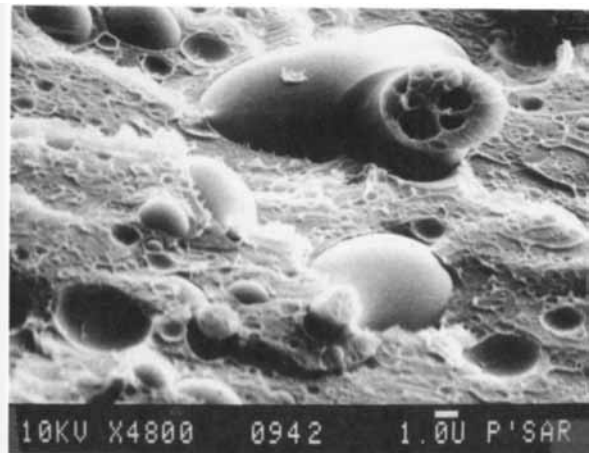
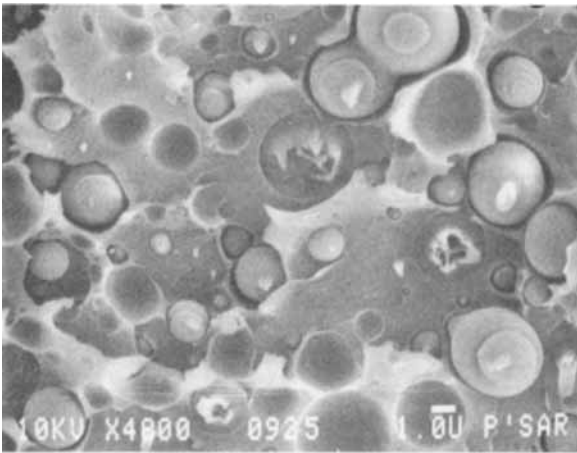


Figure 3 Scanning electron micrographs of polystyrene/polycarbonate/polystyrene-*b*-polycaprolactone blends: 30% PS/70% PC; (a) 0% PS-PCL(2); (b) 2% PS-PCL(2); (c) 5% PS-PCL(2).

Figure 4 Scanning electron micrographs of polystyrene/polycarbonate/polystyrene-*b*-polycaprolactone blends: 70% PS/30% PC; (a) 0% PS-PCL(1); (b) 5% PS-PCL(1); (c) 10% PS-PCL(1).

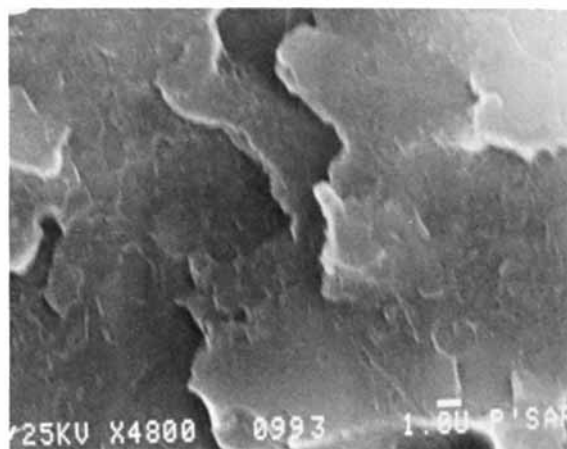
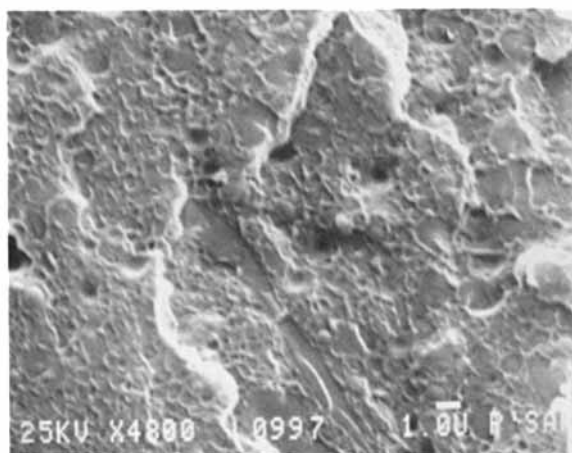
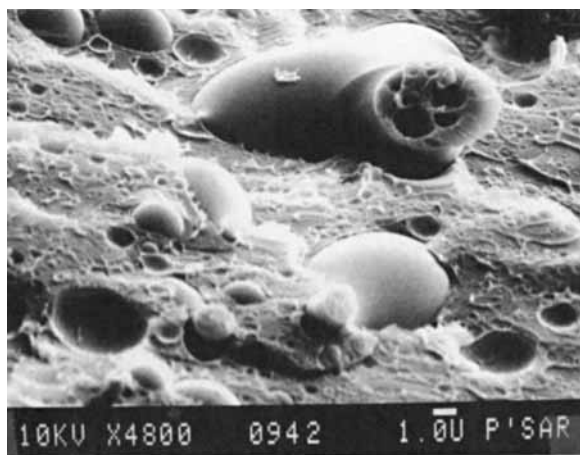


Figure 5 Scanning electron micrographs of polystyrene/polycarbonate/polystyrene-*b*-polycaprolactone blends: 70% PS/30% PC; (a) 0% PS-PCL(2); (b) 2% PS-PCL(2); (c) 5% PS-PCL(2).

this work; compression molding—referenced work²⁵) make comparisons of this sort less than rigorous. The effect of the compatibilizer on the tensile

strength at break is small and follows no apparent trend.

Tensile moduli data are presented in Figure 6(b). Values are generally equal to or greater than those which would be predicted based on linear additivity of the component values. The PS-rich blends exhibit the highest moduli values. These data have been plotted against volume fraction PS in Figure 6(e) and values calculated based on the perfect adhesion case put forth by Paul, as reported by Kunori and Geil,²⁵ have been included. In the work of Kunori and Geil²⁵ several theories on the tensile modulus of composite materials were applied to calculate the tensile moduli for binary PS/PC blends. The values calculated based on the approach of Paul were found to best fit the observed values for their blends. The expression used is an approximate solution which is

$$E = E_1 \frac{E_1 + (E_2 - E_1)\phi_2^{2/3}}{E_1 + (E_2 - E_1)\phi_2^{2/3}(1 - \phi_2^{1/3})}$$

where E is tensile modulus, ϕ is volume fraction, and the subscripts 1 and 2 refer to the matrix and inclusion, respectively.

It is of interest to note that values calculated in this manner correlate very well with those produced assuming linear additivity of the component moduli (correlation coefficient = 0.997). In this work, we found that the measured tensile moduli for binary PS/PC blends were less than those calculated for blends rich in PC and greater than calculated for PS rich blends. This negative deviation of the actual values from the calculated values for PC rich blends was also observed by Kunori and Geil,²⁵ but it is much more pronounced in this work.

Blends with 0 or 2 wt % PS-PCL(2) and up to 40 wt % PS yielded before breaking during tensile testing [Fig. 6(c)], whereas those with 5 wt % of the copolymer broke in all cases without yielding. In the PC-rich blends with little or no compatibilizer failure occurs via a ductile mechanism but upon addition of 5 wt % compatibilizer there is a shift to a brittle failure mechanism. Ultimate elongation data agree with this conclusion [Fig. 6(d)].

The results for flexural testing are presented in Figure 7. Blends with either 0 or 2 wt % PS-PCL(2) and less than 50 wt % PS yielded before breaking whereas those with more than 50 wt % PS and all of those with 5 wt % of the compatibilizer broke without yielding. This trend is identical to that observed for the tensile test results. The flexural strength at break for blends with 0 or 2 wt % co-

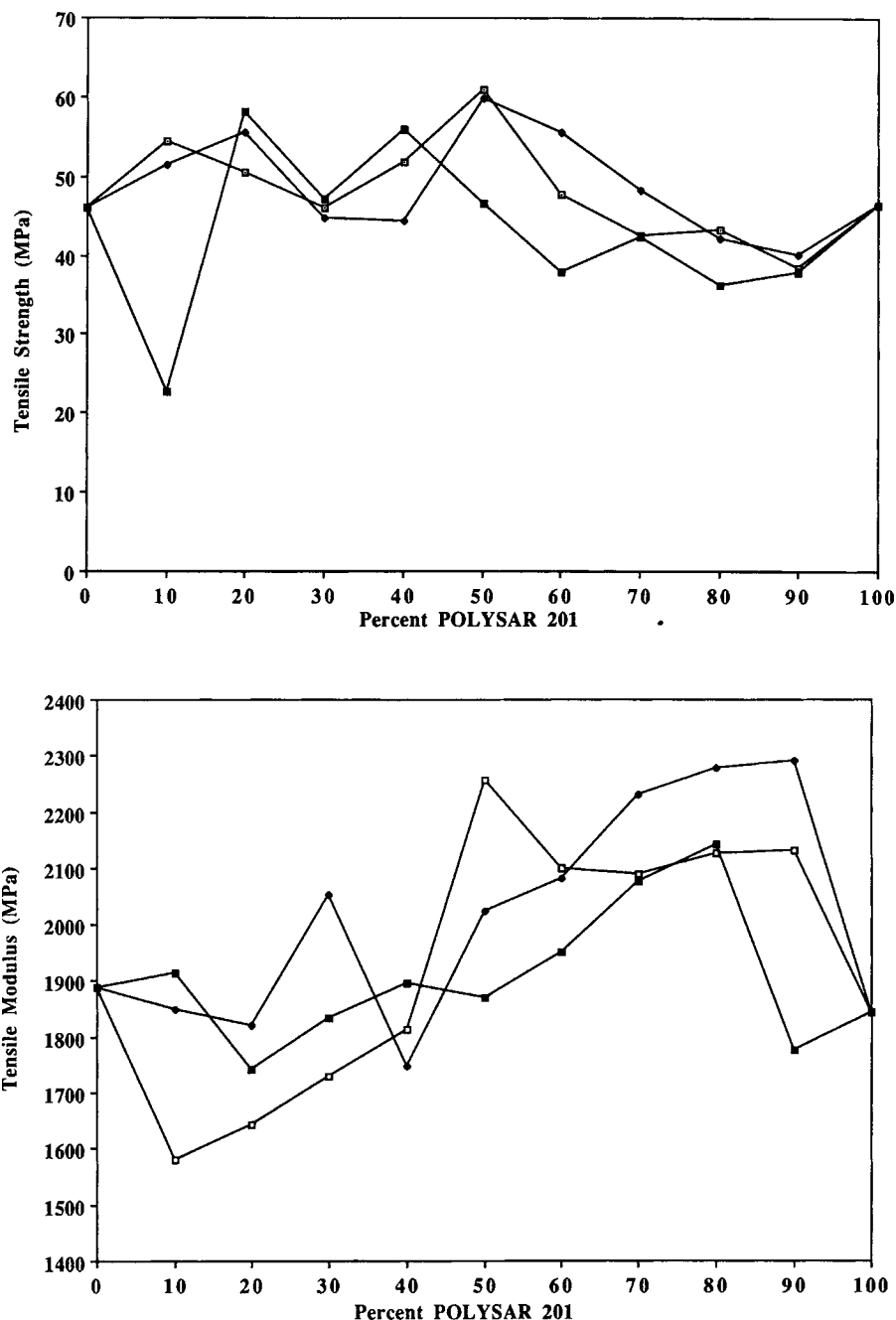


Figure 6 Tensile properties of polystyrene/polycarbonate/polystyrene-*b*-polycaprolactone blends: (a) tensile strength (break) vs. composition; (b) tensile modulus vs. composition; (c) tensile strength (yield) vs. composition; (d) elongation (break) vs. composition; (e) tensile modulus vs. composition; (□) 0% PS-PCL; (◆) 2% PS-PCL; (■) 5% PS-PCL; (◇) Paul (p.a.). Values are plotted against volume fraction polystyrene for comparison with calculated values (◇).

polymer are similar to one another, and greater than linear averaging predicts whereas those for blends with 5 wt % copolymer are lower than the average. Flexural moduli for all of the blend compositions are in excess of those predicted by linear additivity

and are comparable at all levels of compatibilizer loading investigated.

The results of notched IZOD impact testing of 3.2 mm thick specimens for the blends are presented in Figure 8. We have observed that unannealed, in-

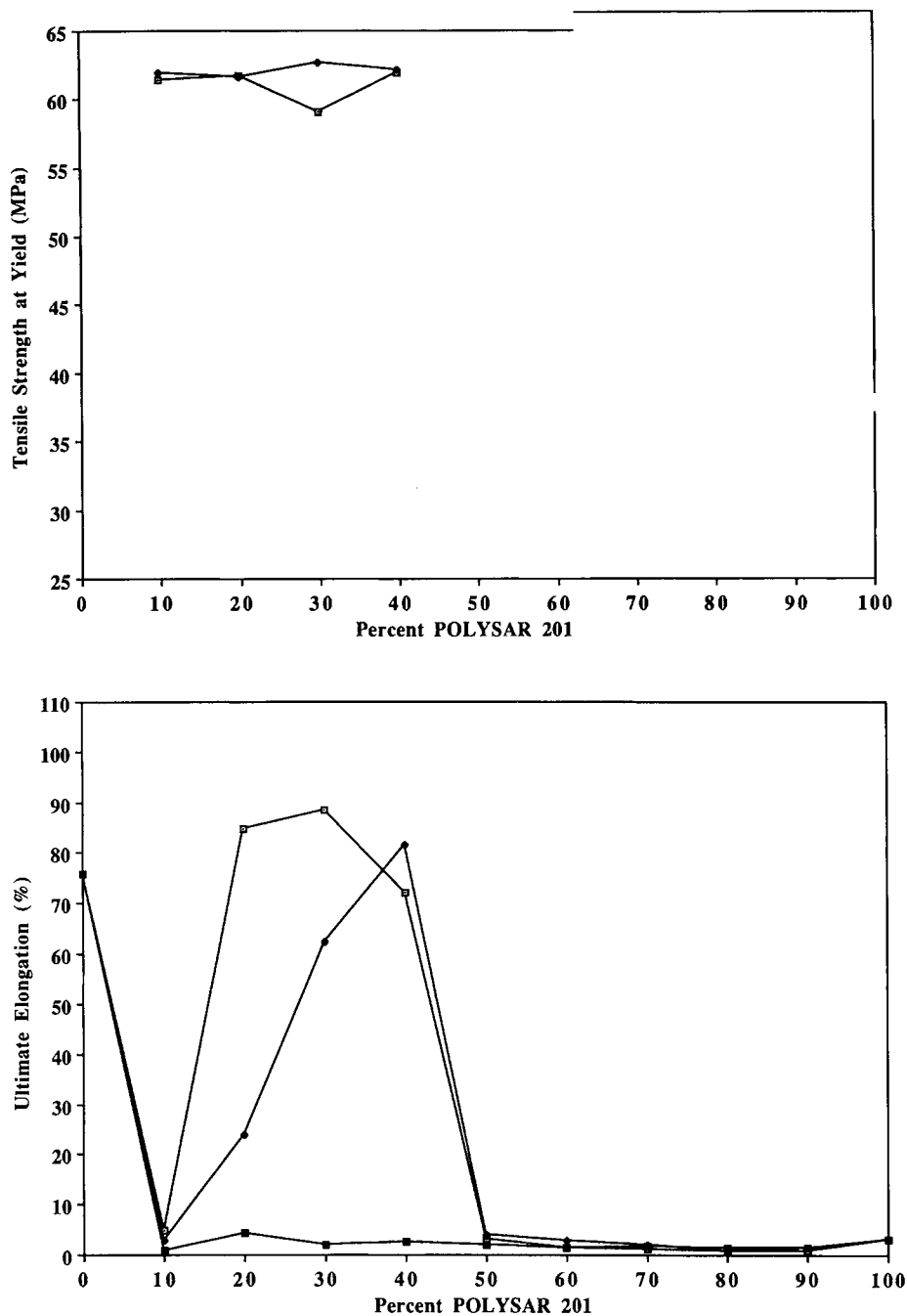


Figure 6 (Continued from the previous page)

jection molded samples of polycarbonate have a high impact strength (roughly 800 J/m) and display ductile failure. Kunori and Geil reported that addition of 2 wt % of PS to PC produced a sixfold decrease in impact strength and upon adding more PS the impact strength declined further.²⁶ In blends with more than half PS the impact strengths were lower than that for pure PS alone. Based upon microscopic examination of the fracture surfaces which

indicated the presence of crazing, Kunori and Geil²⁶ stated:

Presumably, at fast deformation rates as in an impact fracture process, stress concentration occurs in the PS domain, but before it diffuses to other parts of the sample it instantaneously causes the PS domain to crack. This crack in the PS domain travels into the PC matrix by way of the intermixed zone and develops into matrix crazes.

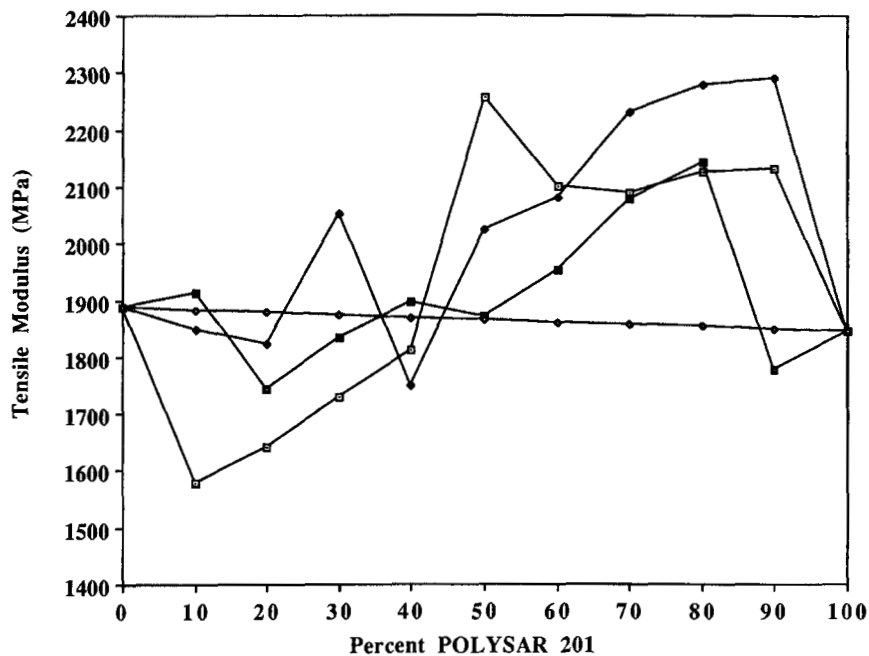


Figure 6 (Continued from the previous page)

In this manner, addition of even small amounts of PS causes the blends to fail by a brittle mechanism. If PC is subjected to annealing prior to impact testing, the mechanism of failure observed is brittle and the impact strength is now roughly 20 times lower than that observed for unannealed samples.

Although the blend samples were not annealed prior to testing, we have used the value obtained from an annealed sample of PC in the construction of Figure 8 in order to provide a comparison between materials which all fail in a brittle manner.

In these comparisons, for results obtained at room

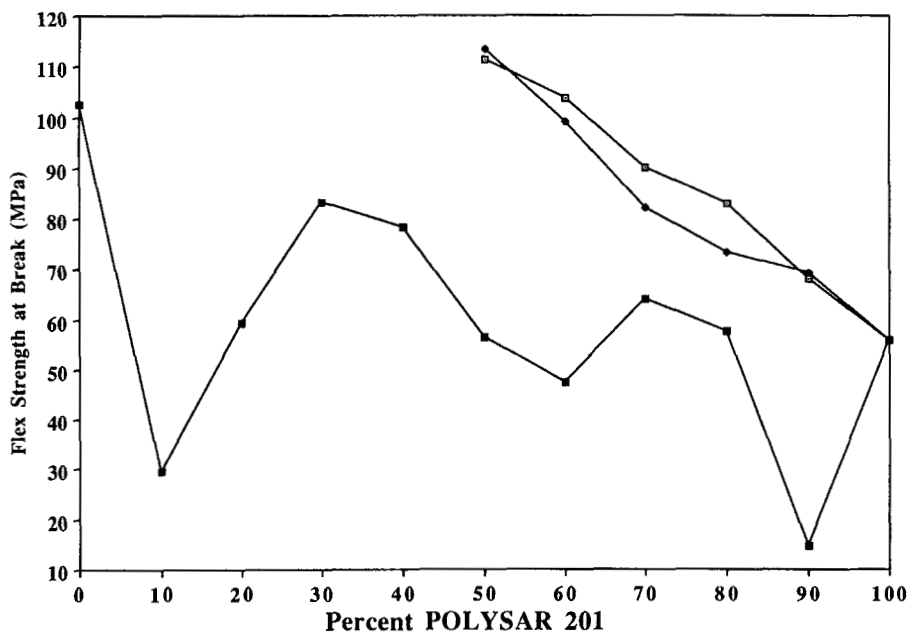


Figure 7 Flexural properties of polystyrene/polycarbonate/polystyrene-*b*-polycaprolactone blends: (a) flex strength (break) vs. composition; (b) flex modulus vs. composition; (c) flex strength (yield) vs. composition; (□) 0% PS-PCL; (◆) 2% PS-PCL; (■) 5% PS-PCL.

temperature and at -30°C , there is a distinct trend that increasing the level of the compatibilizer decreases the impact strength of the blend. In particular, PS rich blends with 5 wt % PS-PCL(2) have extremely low notched impact strengths. If we follow the rationale of Kunori and Geil, presumably the presence of the copolymer at the PS/PC interface facilitates the propagation of crazes, initiating in the PS phase, into and through the PC phase, thus enhancing the brittle failure of the material.

Vicat softening temperature and heat distortion

under load data are summarized in Figures 9 and 10, respectively. Vicat data for each level of compatibilizer loading (i.e., 0, 2, or 5 wt %) appear as S-shaped curves with greater than tie line values for PC-rich blends and less than tie line values for PS-rich blends. For PC-rich blends addition of the compatibilizer produces a stepwise decrease in the Vicat temperature of roughly 5°C per step on going from 0 to 2 and then 5 wt % copolymer loading. These differences decrease to a range of roughly 2°C for the PS rich blends which is of marginal significance.

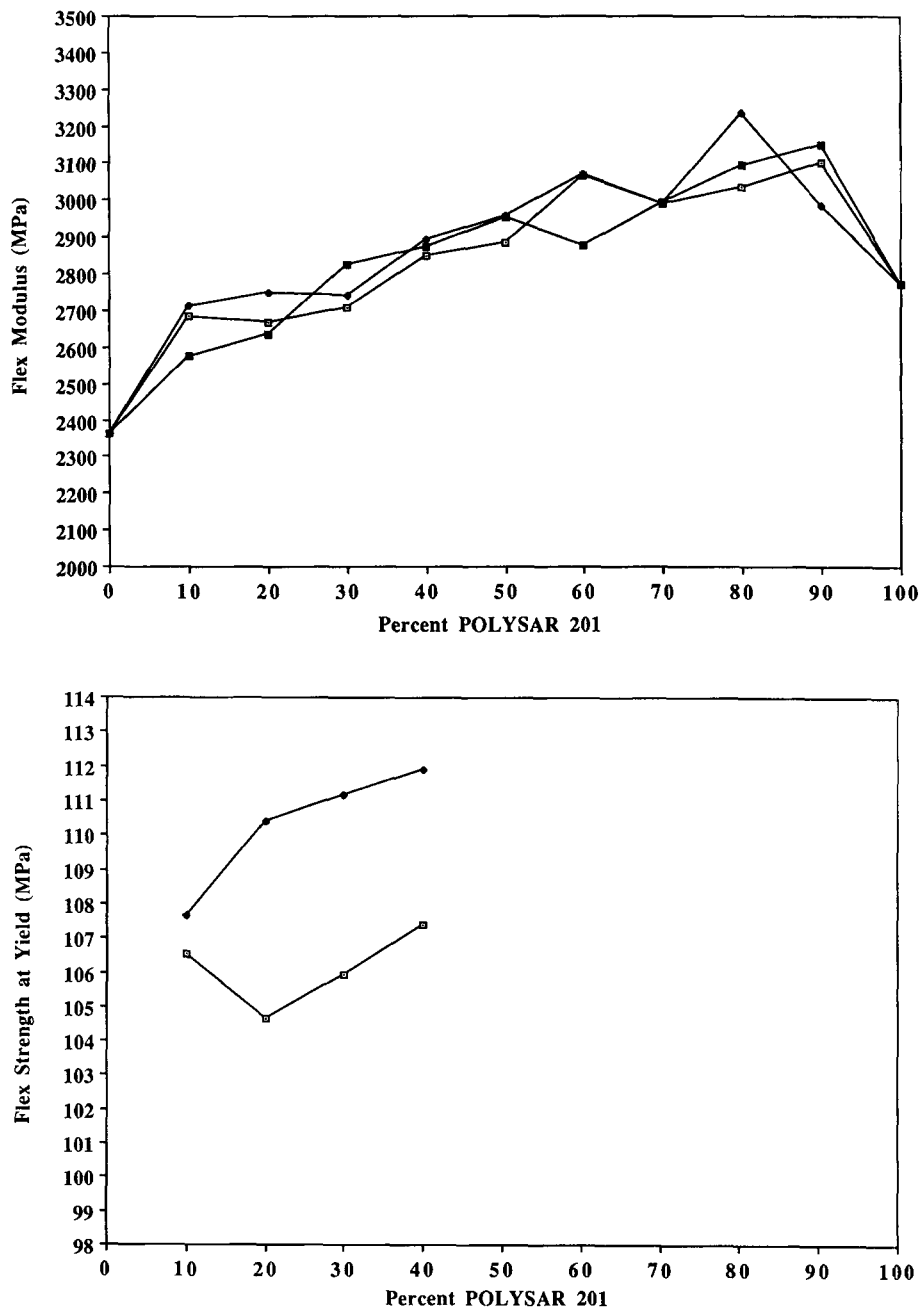


Figure 7 (Continued from the previous page)

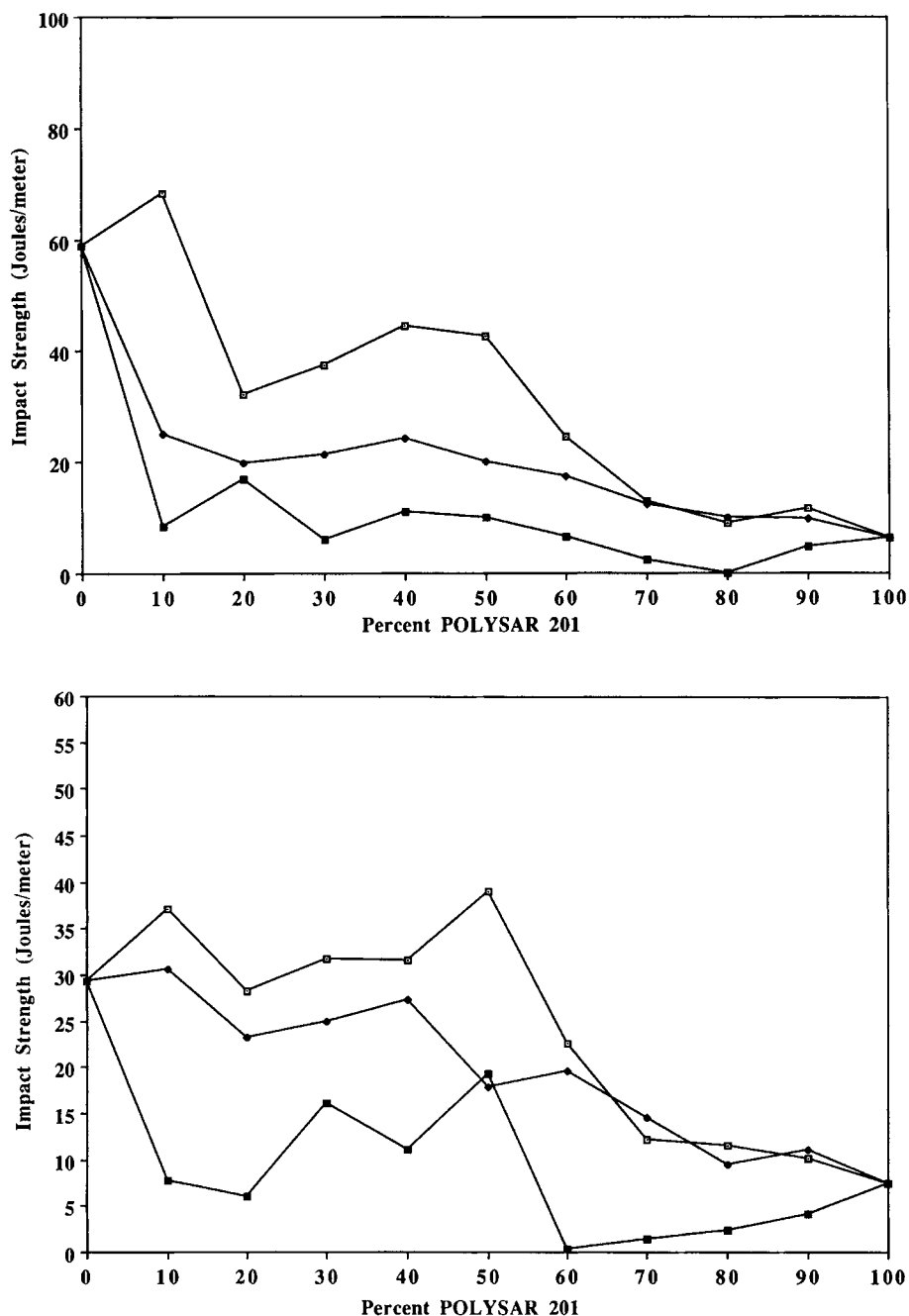


Figure 8 IZOD impact strength (3.2 mm notched) for polystyrene/polycarbonate/polystyrene-*b*-polycaprolactone blends: (a) impact strength vs. composition at room temperature; (b) impact strength vs. composition at -30°C ; (\square) 0% PS-PCL; (\blacklozenge) 2% PS-PCL; (\blacksquare) 5% PS-PCL.

The behavior here is most likely related to the matrix-domain structure of the blends. When PC is the matrix, the PS inclusions are somewhat shielded and hence the softening temperature is greater than the linear average. When PS becomes the matrix, values lower than the average are seen.

Addition of the compatibilizer affects the PC softening temperature through plasticization by the

polycaprolactone segments which penetrate into the PC phase. Increasing levels of PS-PCL, in which the PCL block is liquid at temperatures greater than 66°C , produce the stepwise decreases in Vicat softening temperature for the PC-rich blends. In contrast, the effect of compatibilizer on the softening temperature for the PS-rich blends is quite small. This is due to the presence of the PS block of the

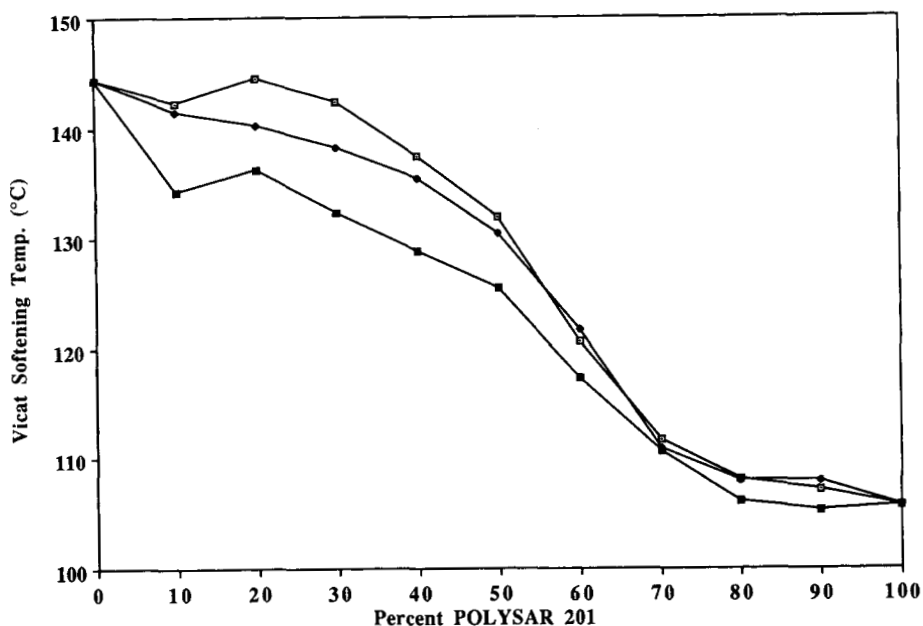


Figure 9 Vicat softening temperature for polystyrene/polycarbonate/polystyrene-*b*-polycaprolactone blends: Vicat softening temperature vs. composition. (□) 0% PS-PCL; (◆) 2% PS-PCL; (■) 5% PS-PCL.

copolymer penetrating into the PS phase. In the compatibilizer the PS block has a molecular weight of roughly $50,000 \text{ g mol}^{-1}$ and as such would be expected to soften at temperatures somewhat lower than those for the higher molecular weight homopolystyrene. However, the difference in thermal be-

havior between two polystyrenes of varying molecular weight is not of the same order of magnitude as the difference between PC and PCL.

Deflection temperatures under load were all less than predicted by additivity and addition of the compatibilizer produced a negative effect on the re-

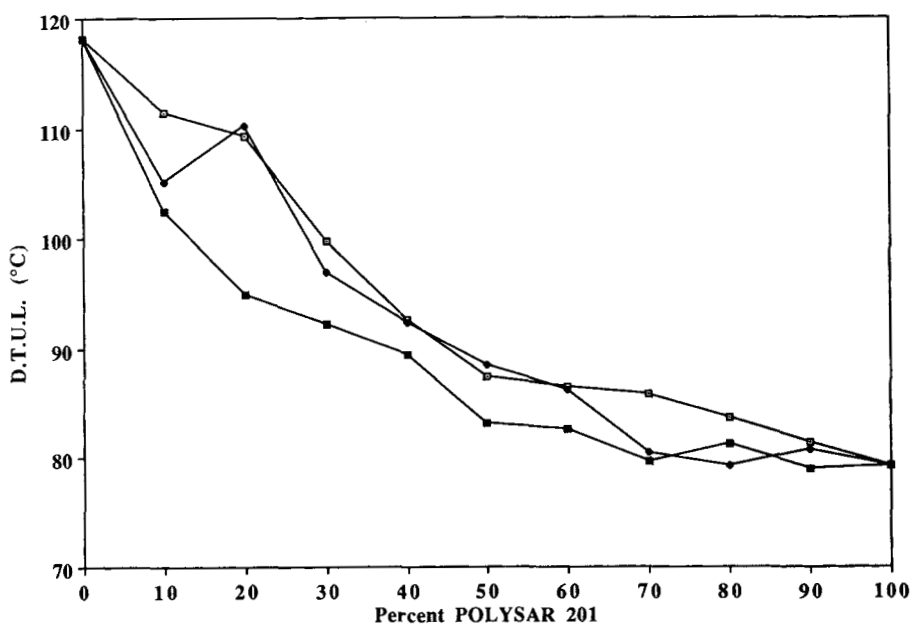


Figure 10 Distortion temperature under load for polystyrene/polycarbonate/polystyrene-*b*-polycaprolactone blends. DTUL (1.82 MPa) vs. composition. (□) 0% PS-PCL; (◆) 2% PS-PCL; (■) 5% PS-PCL.

sults. As with the Vicat softening temperatures, the compatibilizer produced a greater effect in the PC-rich blends than for the PS-rich blends, presumably due to the softening effects of the polycaprolactone blocks. The DTUL values decrease by roughly 30°C on going from pure PC to the 50/50 PS/PC blend and then only a further 5°C throughout the second half of the composition range ending with pure PS. For reasons which are not clear the presence of PS within a PC matrix has a much more pronounced effect on the DTUL behavior than does the reverse case of PC in a PS matrix.

Melt flow index results are presented in Figure 11. All MFI values for the blends are greater than tie line predictions and addition of the copolymer increases the flow. The most prominent exceptions to tie line behavior are evident for the PS rich blends with 5 wt % PS-PCL(2) for which the melt flow indices are two to three times greater than those predicted by additivity. The melt flow index behavior of the blends agrees with observations of the extruder power requirements during blending. Those blends with the higher MFI values tended to require less power input during mixing. Based on these most tentative observations, it appears that the compatibilizer acts as a processing aid which is most effective in the PS-rich blends.

Visual inspection of the molded blend samples indicated that all of the materials were transparent, with those containing compatibilizer having a

slightly greater level of haze than those without compatibilizer. Blend transparency can result either from close matching of the refractive indices of the components or from achieving a fine dispersion of one component within the other such that the particle size is small enough so as not to interfere with light in the visible spectrum (i.e., roughly five times less than the wavelength of visible light²). In this instance, the refractive indices of the two component polymers (PS = 1.592 and PC = 1.585)³⁴ are very similar and transparency results from refractive index matching. It is apparent from the electron micrographs presented in Figures 2-5 that the particle sizes present in these blends cover the range from several times less than to several times greater than the wavelength of visible light. Hence the refractive indices of the components must match sufficiently well to result in transparent blends for all compositions studied.

CONCLUSION

The PS/PC/PS-PCL mixtures consist of incompatible PS and PC phases which are effectively dispersed by the addition of the PS-PCL block copolymer. The lower molecular weight copolymer employed in this work was a fairly efficient emulsifying agent in that 2 wt % of the material reduced the

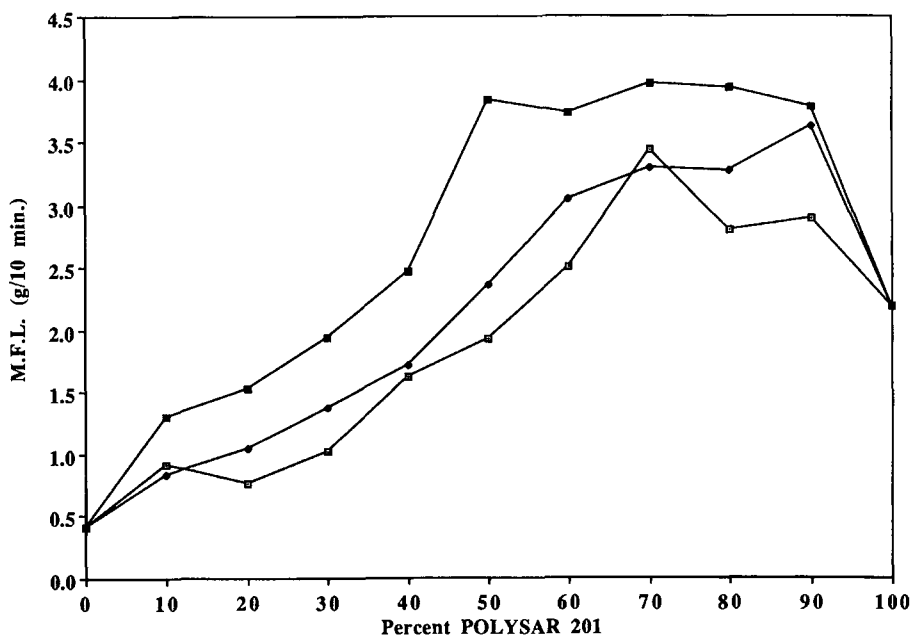


Figure 11 Melt flow index for polystyrene/polycarbonate/polystyrene-*b*-polycaprolactone blends. MFI (200°C, 5.0 kg) vs. composition. (□) 0% PS-PCL; (◆) 2% PS-PCL; (■) 5% PS-PCL.

particle size by a factor of 10, and 5 wt % copolymer produced at least a 100-fold decrease in particle size.

Reduction of the particle size, through compatibilization, has not resulted in any commercially significant enhancement in the physical performance of these blends as compared to the uncompatibilized ones. Addition of the compatibilizer produced moderately negative effects on the flexural, and impact strengths, as well as the Vicat softening and DTUL behavior of the blends versus their PS/PC counterparts.

Essentially small and random effects on tensile strength and flexural modulus and somewhat positive effects on tensile modulus and melt flow index were produced by incorporating the compatibilizer into the blends. The general trend was to produce increased brittleness and reduced thermal performance upon incorporating the PS-PCL copolymers into these blends.

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