

Polystyrene/Polyethylene Terephthalate/Polystyrene-block-Polycaprolactone Blends: Emulsification and Mechanical Performance

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SYNOPSIS

A polystyrene-polycaprolactone diblock copolymer was extrusion blended with polystyrene and polyethylene terephthalate. The morphologies of the resultant blends were studied using differential scanning calorimetry and scanning electron microscopy. In all compositions studied, the polystyrene and polyethylene terephthalate 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, and thermal performance characteristics to study the effects of morphology and composition on these factors. In general, the blends were rigid, brittle materials with somewhat enhanced thermal characteristics. Addition of polystyrene-block-polycaprolactone polymer to the blends resulted in increased brittleness, slightly reduced thermal performance, and, in some instances, greatly increased rigidity.

INTRODUCTION

In a number of immiscible polymer blend systems, block copolymers have been successfully used as compatibilizing agents.¹⁻¹⁸ The emulsifying effects of the block copolymers have been aptly demonstrated. However, there has been much less attention focused on the mechanical performance of the resultant blends.

Commercial interest in blend materials centers around the potential for achieving favourable cost/performance balances suitable for materials replacement or new market applications. As part of our initial work in this field, we studied blends of polystyrene with polyethylene terephthalate.

Research into polystyrene/polyethylene terephthalate mixtures has been sparse, and the little amount performed is recorded primarily in the Japanese patent literature. The work is focused in the areas of synthetic fibres,¹⁹⁻²² and films,²³⁻²⁸ with other areas of interest being processing aids,²⁹ bot-

ties,³⁰ block,³¹ and graft³² copolymers, heat resistance,³³ adhesion,^{34,35} and composites.³⁶ There does not appear to be any significant North-American-based research into blends of these two materials. No examples pertaining to compatibilization of PS/PET blends were found.

In previous work, polystyrene-*b*-polycaprolactone diblock copolymers were found to be efficient emulsifiers for blends of polystyrene with bisphenol-A polycarbonate.¹⁸ The choice of polystyrene as one block of the copolymer is an obvious one for miscibility with the polystyrene blend phase. The second block was chosen to be one that would be miscible with a wide range of engineering resins (polar polymers). Polycaprolactone is miscible with phenoxy, SAN (28% AN), polyvinyl chloride, nitrocellulose, polyepichlorohydrin, chlorinated polyether,^{37,38} the Saran copolymers of vinylidene chloride with acrylonitrile (Saran F), vinyl chloride (Saran B), and vinyl acetate (Saran C),³⁹ chlorinated polypropylene, chlorinated polystyrene,⁴⁰ chlorinated polyethylene,⁴¹ and bisphenol-A polycarbonate.⁴² Upon examination of this list, we might speculate that the range could be extended to include various aliphatic polyesters and the aromatic polyesters such as poly-

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Table I Molecular Weights, Polydispersities, and Copolymer Composition

Polymer	M_n	M_w/M_n	Wt % PS	Wt % PCL
POLYSAR 201 ^a	171,400	1.7		
KODAPAK PET 7352 ^b	23,000	2.0		
PS-b-PCL-070/071 ^c	58,560	1.1	82.5	17.5

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

^b From product specification sheet.

^c 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.

ethylene terephthalate and polybutylene terephthalate.

Polystyrene-polycaprolactone diblock copolymers are also attractive as compatibilizers because they can be readily prepared in a two-step living polymerization that allows for control of copolymer architecture and composition.⁴³

Due to the lack of information on the mechanical properties of PS/PET blends and our interest in diblock copolymers as compatibilizing agents, we studied the PS/PET/PS-b-PCL blend system to determine the effect of the copolymer on the blend morphology and the resultant mechanical performance.

EXPERIMENTAL

Materials

POLYSAR 201 polystyrene (Polysar Limited) and KODAPAK PET 7352 polyethylene terephthalate (Eastman Kodak Company) were used as obtained. Polystyrene-polycaprolactone diblock copolymers were prepared by a known route.³³ The molecular weights, polydispersities, and diblock copolymer compositions for these materials are presented in Table I.

Sample Preparation and Analysis

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, summarized in Table IV. Differential scanning calorimetry (DSC) experiments were performed using a DuPont 9900 system.

RESULTS AND DISCUSSION

In earlier work involving polystyrene/polycarbonate blends, two PS-b-PCL copolymers of differing molecular weight but identical composition were studied with respect to their emulsifying ability.¹⁸ The copolymer with the lower molecular weight (M_n PS = 48,300 g mol⁻¹; M_n PCL = 10,200 g mol⁻¹) proved

Table II Operating Conditions for Blend Preparation by Twin Screw Extrusion

Zone Temperatures	Zone					
	1 ^a	2	3	4	5	6
Setting (°C)		250	250	250	250	270
Actual (°C)		125	235	250	250	240
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	270°C
Forward zone temperature	265°C
Nozzle temperature	205°C
Mold temperature	45°C
Injection boost pressure	4.5 MPa
Injection holding pressure	3.4 MPa
Back pressure	0.3 MPa
Injection boost time	2.5 s
Injection holding time	10 s
Mold closed time	30 s

to be the more effective emulsifier. Based on this finding, a PS-*b*-PCL copolymer of this composition was used in the work described here.

Two techniques were employed to investigate the compatibility and morphology of the blends: DSC and scanning electron microscopy (SEM).

DSC was used to determine the thermal transitions exhibited by the blends. The results of these experiments are presented in Table V. Potentially observable transitions include the glass transition temperatures for PS and PET, as well as a crystallization exotherm and melting endotherm for the PET. In practice, the PS T_g was too small for observation in the PET-rich samples.

In general, the size of the transitions observed were in proportion to the amounts of each material present in the blends. For example, the PET exotherms and endotherms associated with crystallinity were larger in the traces for samples with 70 wt % PET as opposed to those with 30 wt % PET. Another instance of this was the PS glass transition temperature, which was seen for the PS-rich blends but was too small for observation in the PET-rich blends.

Of perhaps more interest were the lack of effects normally associated with the miscibility of blend components. In a miscible system, the glass transition temperature is an average of those of the components. In systems where partial miscibility is achieved, the glass transition temperatures of the two components are shifted somewhat closer to one another. Neither of these effects was observed in this case. Although the glass transitions of PET and PS are broad, they remain distinct from one another and do not shift closer together upon addition of either 2 or 5 wt % of the PS-*b*-PCL compatibilizer. The small decrease in the PET T_g upon addition of the copolymer was likely due to softening caused by the PET-miscible PCL segment of the copolymer.

In the absence of chemical miscibility between blend components, a diblock copolymer can be used to emulsify and disperse the particles of one phase within the other.¹⁻¹⁸ Success in this sense can normally be observed by taking scanning electron micrographs of fracture surfaces (or microtomed sections) of the blends and observing the morphology, particle sizes, and degree of dispersion. Micrographs for selected PET- and PS-rich compositions with increasing levels of block copolymer are presented in Figures 1 and 2.

Looking first at Figure 1, in which PET-rich blends are depicted, a spherical-domain/matrix morphology is seen. In the absence of copolymer, the PS particle size ranges from roughly 3–30 microns in diameter. Addition of 2 wt % copolymer reduces this size range to 1–10 microns, with most particles being considerably less than 10 microns in diameter. The presence of 5 wt % PS-*b*-PCL produces a morphology that is for the most part visibly homogeneous at this magnification. However, there is evidence of some craters and small particles present.

The micrographs of the PS-rich blends (Fig. 2) show a morphology considerably different from the one discussed above. A domain/matrix morphology is seen, as well as some larger, somewhat continuous, regions. Addition of the copolymer in 2 and 5 wt % levels smooths out this morphology, but a clearcut, stepwise decrease in particle size upon copolymer addition is not seen. It is apparent in the views presented that the blend containing 5 wt % copolymer is the most homogeneous system.

For the PET-rich blend, it is readily apparent that the PS-*b*-PCL copolymer acts as an efficient compatibilizer. Although somewhat less obvious, this also appears to hold true for the PS-rich blends.

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

Table V Summary of Thermal Transition Temperatures for Polystyrene/Polyethylene Terephthalate/Polystyrene-*b*-Polycaprolactone Blends Measured by DSC

Blend Composition (wt %) (%PS/%PET/%PS- <i>b</i> -PCL)	T_g (PET) (°C)	T_g (PS) (°C)	T_c (°C)	T_m (°C)
30/70/0	77.9	^a	124.3	247.1
29.4/68.6/2	72.8	^a	124.8	248.3
28.5/66.5/5	73.8	^a	124.9	248.9
70/30/0	77.2	103.2	128.9	248.1
68.6/29.4/2	78.4	105.1	127.7	248.5
66.5/28.5/5	72.5	105.8	125.7	248.7

^a Transition not observed.

The combination of microscopy and DSC data indicate that although the two major blend components, PS and PET, are immiscible they can be emulsified to a considerable extent by incorporating a polystyrene-polycaprolactone diblock copolymer into the blends.

Blends of POLYSAR 201 polystyrene and KODAPAK PET 7352 polyethylene terephthalate 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 % of PS-*b*-PCL. The blends were prepared, injection molded, and mechanically tested as described above (Tables II-IV).

Tensile strength at break and modulus vs. composition graphs are presented in Figure 3. Tensile strength values lie below the tie-line levels in all cases. Without added PS-*b*-PCL copolymer, the negative deviations from average linearity are small, but addition of copolymer (2 or 5 wt % similar results) produces marked negative deviations most pronounced in the 50/50 PS/PET composition region. In contrast, the tensile moduli are, for the most part, greater than values expected from additivity, with the exceptions being the compatibilized, PET-rich blends (more than 70 wt % PET + copolymer). Here, as with the tensile strengths, the presence of the compatibilizer has a negative effect on the blend performance. Elongation at break values are all quite small and the blends break at elongations less than that for either of the components. In all cases, this is indicative of brittle failure via cracking. Copolymer addition further decreases the elongation at break to 0.5% in the middle of the composition window (40-70 wt % PS).

The trends in the flexural behaviour (Fig. 4) are quite similar to those seen for the tensile perfor-

mance, i.e., the strengths are less than tie-line and the moduli are above, with the compatibilizer producing a negative effect. However, there are notable exceptions in the region from 50-70 wt % PS. In this region, the modulus increases stepwise from roughly 4 to 5.5 to 6.2 GPa for blends with 2 wt % PS-*b*-PCL, as compared to a relatively steady value of 2.9 GPa for the blends with either 0 or 5 wt % copolymer. The flexural strengths at break are also notably above tie-line expectations for the blends with 60 and 70 wt % PS and 2 wt % PS-*b*-PCL. It is interesting to compare these performance characteristics with the observed fractured-surface morphologies of the 70 wt % PS blends (Fig. 2). In the noncompatibilized blend, both particulate and larger more continuous structures are seen, but adhesion between phases appears to be poor, as evidenced by the sharp, well-defined holes and fracture surfaces seen in the micrograph. Addition of 2 wt % copolymer does not appear to alter the overall structure. However, there is a softening of the features in the fracture surface that is usually associated with enhanced compatibilization and adhesion between phases. At the 5 wt % copolymer level, the morphology is quite different from that of the noncompatibilized blend. It is a much finer and more homogeneous structure. It appears that the coarse, partially compatibilized morphology exhibited by the blend with 2 wt % PS-*b*-PCL copolymer results in significant increases in flexural performance relative to the blends with either more or less copolymer.

Notched IZOD impact strengths (Fig. 5) for both of the components are quite low. Upon blending, either with or without compatibilizer, there are no significant improvements in impact strength. For the most part, values less than predicted by additivity are seen. The effect of added copolymer is

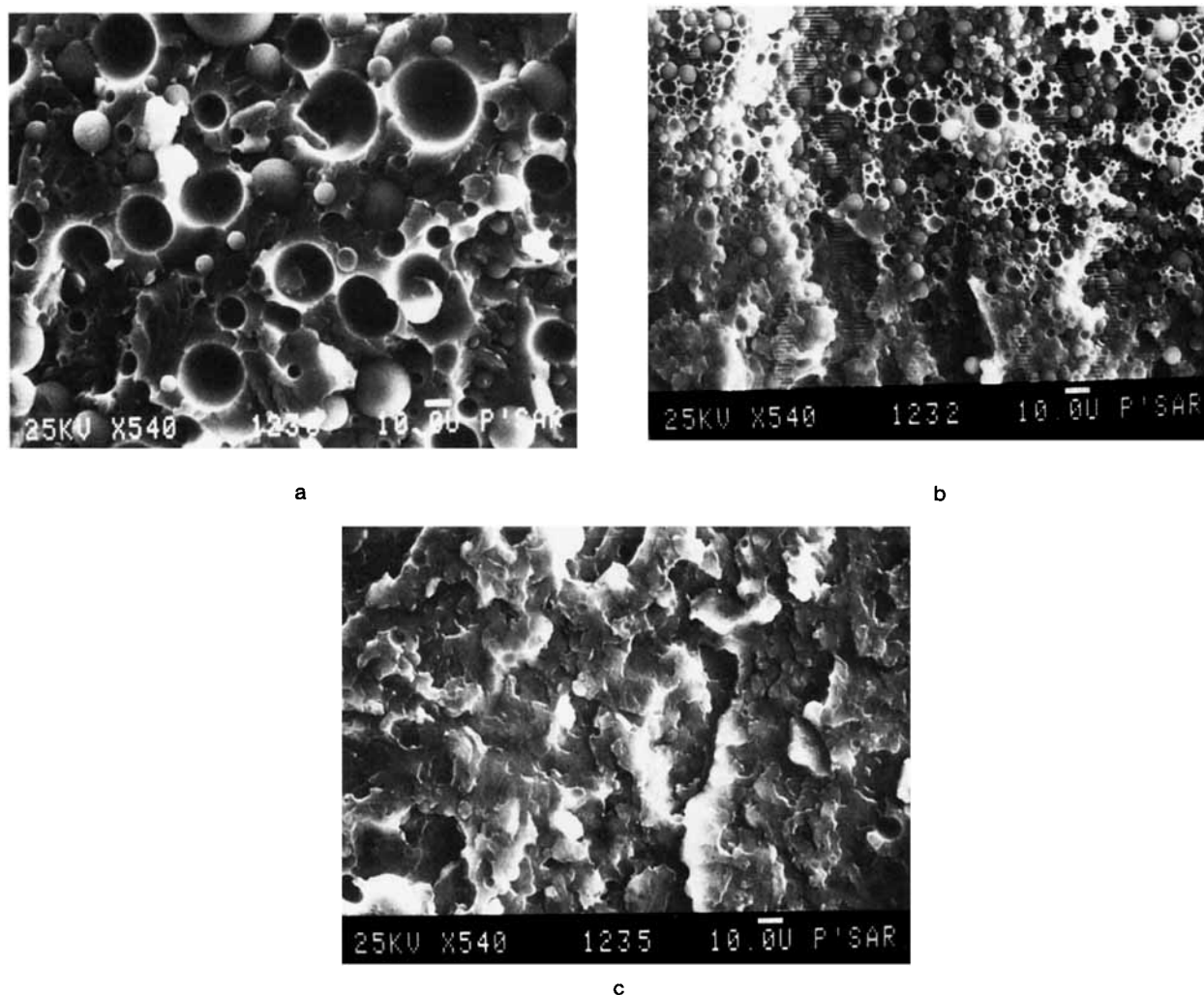


Figure 1 Scanning electron micrographs of polystyrene/polyethylene terephthalate/polystyrene-*b*-polycaprolactone blends. 30% PS/70% PET. (a), 0% PS-PCL; (b), 2% PS-PCL; (c), 5% PS-PCL.

small, and there is no clearcut trend of positive or negative deviations from the control blends (without copolymer). In all cases, observation of the fracture surfaces indicated brittle failure.

Thermal testing of the blend materials produced some interesting results (Fig. 6). Vicat softening temperatures for the binary PS/PET blends for unannealed samples follow the same S-shaped curve seen for PS/PC blends,¹⁸ i.e., Vicat softening temperatures are less than tie-line for the PET-rich blends (unannealed PET has the lower Vicat temperature) and greater than tie-line for the PS-rich blends (PS has the higher Vicat temperature). This type of behaviour presumably relates to which of the components is the matrix and which is found in the domains. Vicat temperatures for the compati-

bilized, unannealed blends follow this S-shaped curve, for the most part, with notable exceptions in the 50/50 composition range. At this point, the Vicat temperatures were 25–30°C higher than the value for the noncompatibilized blend (for which a near tie-line value was found). In this region, the copolymer must be increasing the rate of PET crystallization, thus leading to higher levels of crystallinity in the molded specimens and the higher observed Vicat temperatures for the unannealed samples. Upon annealing the samples for 30 min at 180°C, all Vicat temperatures for the PET-rich blends exceeded 200°C, the limit of our testing machinery; hence, useful data could not be obtained. However, this does indicate that, with proper annealing, PET-rich blends can withstand surface deformation to at

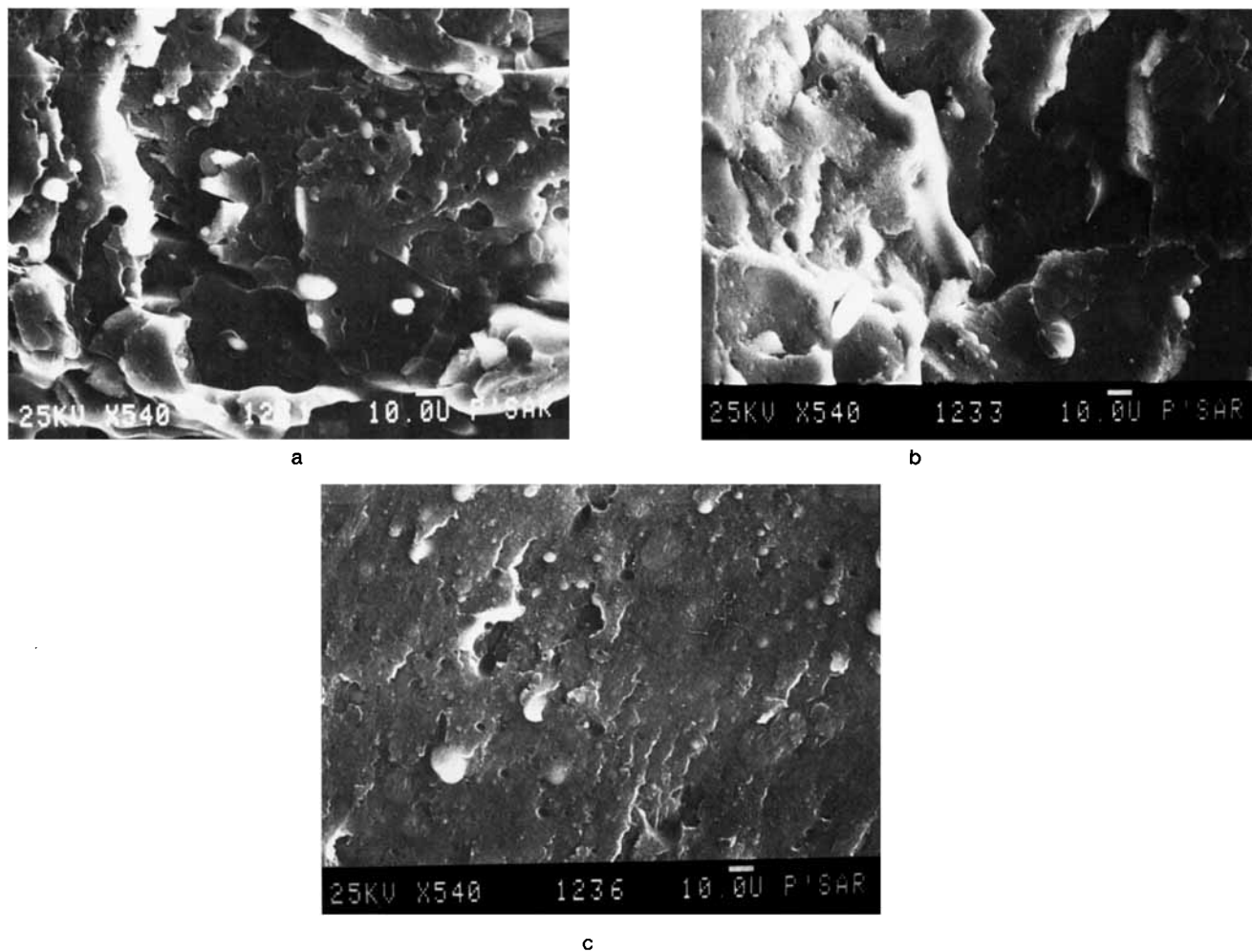


Figure 2 Scanning electron micrographs of polystyrene/polyethylene terephthalate/polystyrene-*b*-polycaprolactone blends. 70% PS/30% PET. (a), 0% PS-PCL; (b), 2% PS-PCL; (c), 5% PS-PCL.

least 200°C even with appreciable polystyrene contents (up to 50 wt %).

Distortion temperature under load (DTUL) (1.82 MPa) data were obtained for both unannealed and annealed samples. These results are presented in Figure 6. DTUL values for unannealed (as molded) samples remain fairly constant on going from pure PET to 50/50 PS/PET blends, with the compatibilizer having a negative effect (roughly -5°C). From the composition midpoint to pure PS, the values rise stepwise through a range of about 20°C , with the compatibilizer having a small positive effect (roughly 1°C).

The annealed samples behave differently. Annealing does not affect the DTUL value for non-crystallizable polystyrene, but it does raise the

DTUL for PET from 63–79.5°C. Annealing at 180°C for 30 min has a profound effect on the blends. All blends had DTUL values 5–10°C greater than those for either of the pure components. The presence of the compatibilizer has a small negative effect on the performance of the PET-rich blends and little or no effect on the PS-rich blend performances.

Each of the component plastics, on their own, are rigid materials with good tensile and flexural levels and low-impact strength. Therefore, the observation of similar behaviour for blends of the two is not altogether unexpected. Addition of particles of one plastic within the matrix of the other could be viewed as a similar case to employing a filler such as glass beads or the various mineral fillers. The high yield and compressive strengths of these materials pre-

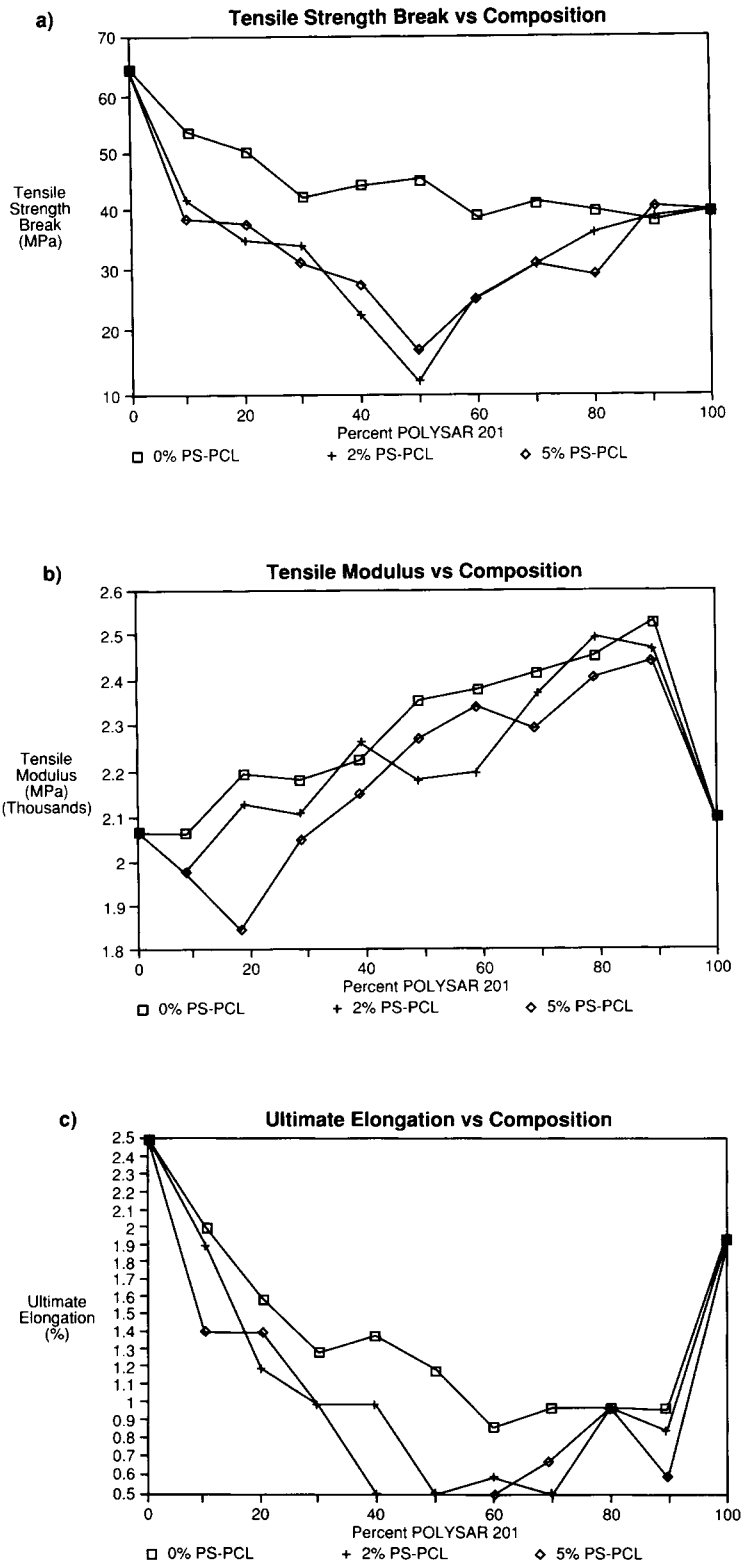


Figure 3 Tensile properties of polystyrene/polyethylene terephthalate/polystyrene-b-polycaprolactone blends. (a), tensile strength break vs. composition; (b), tensile modulus vs. composition; (c), ultimate elongation vs. composition.

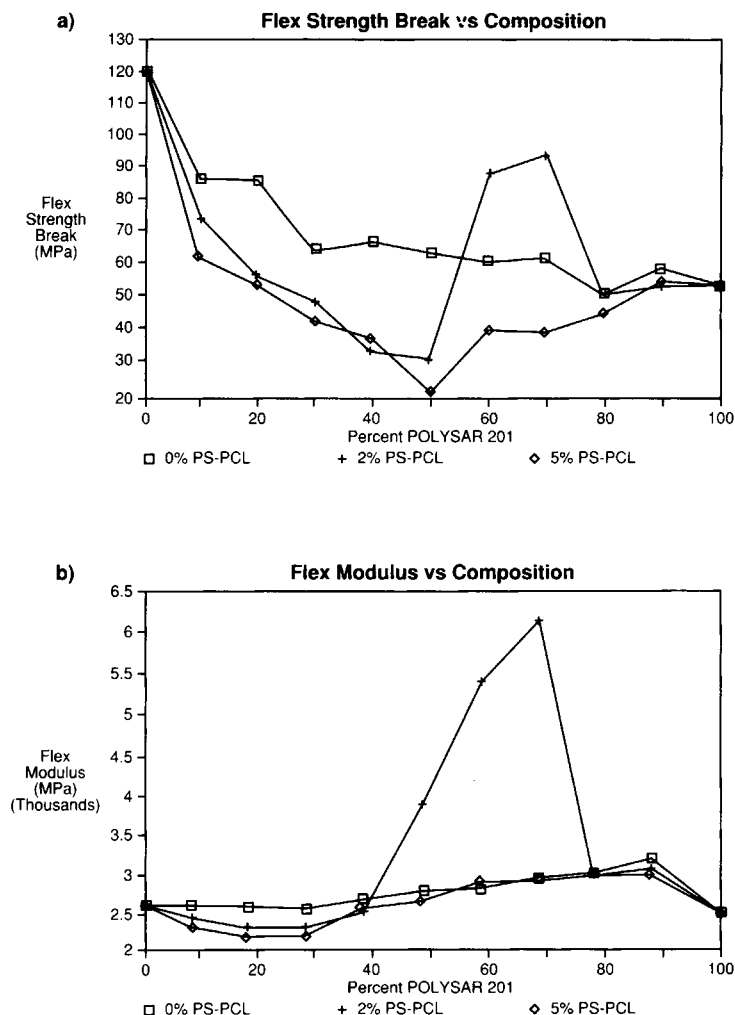


Figure 4 Flexural properties for polystyrene/polyethylene terephthalate/polystyrene-b-polycaprolactone blends. (a), flex strength break vs. composition; (b), flex modulus vs. composition.

clude toughening due to their inability to yield and initiate either brittle or ductile mechanisms of energy dissipation during failure.

Fillers are often used in conjunction with additives that assist in their dispersion and adhesion within the plastic matrix. A proper choice of these materials can lead to improvements in tensile and flexural performance. By analogy, the PS-b-PCL copolymer fills the role of the additive for dispersion and adhesion of either PS or PET within the other. For the mechanical specimens prepared in this study, it is evident that use of the copolymer yields some marked flexural improvements while being, on the whole, detrimental to tensile performance. This may well be due to anisotropy in the morphology of the test specimens for which nonspherical particles have been observed. Hence, when under elongational

stress in the direction of mold flow (tensile testing) some loss in strength is observed, whereas strength in the direction perpendicular to mold flow (flexural testing) is enhanced.

The improvement in DTUL behaviour of the annealed samples is an interesting phenomenon. This is a truly synergistic result in that none of the blend components displays this high a distortion temperature under load. At this time, even a speculative reason for this behaviour is not known.

CONCLUSION

Polystyrene and polyethylene terephthalate have been demonstrated to form an immiscible blend system. Addition of a polystyrene-block-polycapro-

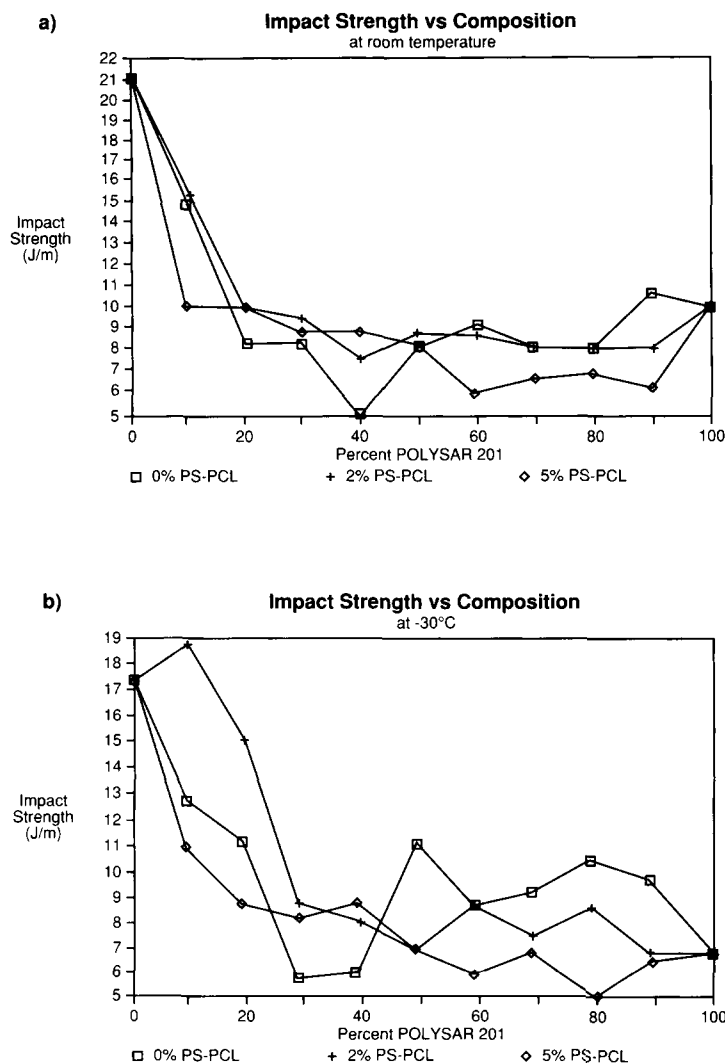


Figure 5 Notched IZOD impact strength for polystyrene/polyethylene terephthalate/polystyrene-*b*-polycaprolactone blends. (a), impact strength vs. composition; (b), impact strength vs. composition.

lactone diblock copolymer in low levels has been shown to effectively emulsify these blends. The particle sizes in the blends, whether emulsified or not, are roughly 10 times larger than those found in the corresponding polystyrene/polycarbonate blends.¹⁸

A common criterion for assessing the mechanical performance of a blend is to look at the observed level of performance in comparison to the value predicted by taking a linear combination of the performance levels for the pure component materials. Within this framework, tensile strength, IZOD impact strength, elongation at break, flexural strength, and unannealed DTUL values for the blends were generally less than additivity predicts. Unannealed Vicat softening temperatures followed an S-shaped

curve that lies close to tie-line values. Tensile modulus, flexural modulus, and annealed DTUL values were greater than predicted by linear additivity.

In the majority of blends, the addition of the copolymer had a small negative effect on the performance of the blend relative to the performance of the corresponding noncompatibilized blend. However, a region of greatly enhanced flexural performance upon incorporation of a low level of copolymer was observed. Unfortunately, the balance of properties in this region is not positive.

Overall, there is an increase in the rigidity and thermal performance of the blends and a decrease in their toughness relative to either pure polystyrene or polyethylene terephthalate.

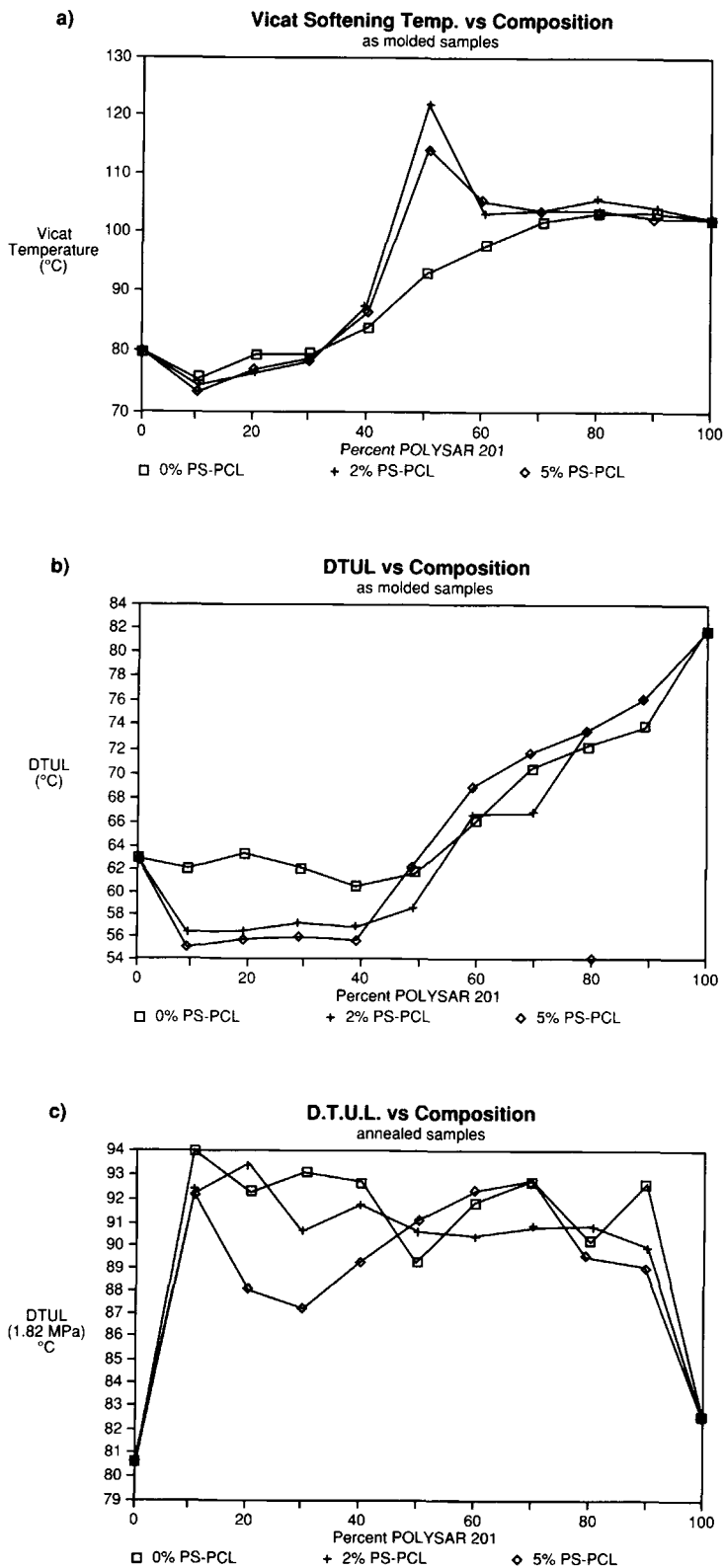


Figure 6 Thermal behaviour of polystyrene/polyethylene terephthalate/polystyrene-*b*-polycaprolactone blends. (a), vicat softening temp. vs. composition; (b), DTUL vs. composition; (c), DTUL vs. composition.

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