Blends of Bisphenol A Polycarbonate and Rubber-Toughened Styrene–Maleic Anhydride Copolymers

H. A. STRETZ,[1] P. E. CASSIDY,[1] D. R. PAUL[2]

[1] Department of Chemistry, Southwest Texas State University, San Marcos, Texas 78666

[2] Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712

ABSTRACT: The morphology and mechanical properties of polycarbonate (PC) blends with rubber-toughened styrene–maleic anhydride copolymer materials (TSMA) were investigated and compared with the properties of blends of PC with acrylonitrile–butadiene–styrene (ABS) materials. The PC/TSMA blends showed similar composition dependence of properties as the comparable PC/ABS blends. Polycarbonate blends with TSMA exhibited higher notched Izod impact toughness than pure PC under sharp-notched conditions but the improvements are somewhat less than observed for similar blends with ABS. Since PC is known for its impact toughness except under sharp-notched conditions, this represents a significant advantage of the rubber-modified blends. PC blends with styrene–maleic anhydride copolymer (SMA) were compared to those with a styrene–acrylonitrile copolymer (SAN). The trends in blend morphology and mechanical properties were found to be qualitatively similar for the two types of copolymers. PC/SMA blends are nearly transparent or slightly pearlescent. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1508–1515, 1999

Key words: blends; polycarbonate; toughness; styrene; maleic anhydride

INTRODUCTION

There is a considerable body of literature on polycarbonate (PC) blends with acrylonitrile–butadiene–styrene (ABS) materials.[1–6] These mixtures represent one of the most commercially important series of blend products because of the excellent balance of physical properties and processing characteristics provided for the cost. It is significant to note that commercially available PC/ABS blends do not include a compatibilizer. It has been argued that the thermodynamic interaction between PC and styrene–acrylonitrile copolymer (SAN) that forms the matrix of ABS materials is sufficiently favorable to provide strong

enough interfacial adhesion and a low enough interfacial tension so that commercially useful blends can be formed without a compatibilizer.[7–9]

There has been some; although much more limited, commercial and scientific interest in PC blends with styrenic copolymers that include maleic anhydride (MA) as the comonomer instead of acrylonitrile (AN). For example, PC blends with styrene–maleic anhydride copolymers (SMA) have found some uses in areas such as automotive applications.[10,11] SMA copolymers bring to such blends the advantages of a higher modulus and heat distortion temperature, but the disadvantages of lower inherent toughness relative to SAN copolymers.[12,13] A recent study from this laboratory has compared the interaction of PC with SMA versus SAN copolymers.[8]

In analogy with ABS, there are commercially available rubber-modified SMA products. They have morphologies analogous to ABS products

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Table I   Materials Used in This Study

Polymer[a]	Description	T_g (°C)	M_w/M_n (kg/mol)	Brabender Torque[b] (N m)
PC	Bisphenol A polycarbonate	150	27.1	5.8
SMA 8	Styrene–maleic anhydride copolymer (8% MA)	117	240/120	1.6
SMA 14	Styrene–maleic anhydride copolymer (14% MA)	128	170/90	1.6
TSMA 9	Styrene–maleic anhydride copolymer (9% MA toughened by 15% butadiene rubber)	124	210/90	5.4
TSMA 12	Styrene–maleic anhydride copolymer (12% MA, toughened by 16% butadiene rubber)	130	190/90	4.4

[a] Materials donated by Dow and Arco.
[b] Brabender torque recorded after 20 min at 270°C and 60 rpm.

made by mass polymerization in the presence of butadiene rubber. The mechanical behavior of PC blends with toughened SMA materials, denoted here by the acronym TSMA for convenience, was not explored in the literature to our knowledge.

The purpose of this article is to report the mechanical behavior and morphology of PC blends with SMA and TSMA materials. This study was designed to parallel as nearly as possible a similar study by Lombardo et al.[1] from this laboratory on blends of PC with SAN and ABS materials.

EXPERIMENTAL

All materials employed in this study are commercial products used as received from the manufacturers. Table I describes these materials and some of their properties.

All blends were prepared in a Killion single-screw extruder with a 2.54-cm diameter and L/D = 30, outfitted with an intensive mixing head, by using materials that had been dried overnight in a vacuum oven at 60°C. Extrusion temperatures varied from 176°C for blends rich in SMA to 260°C for blends rich in PC to accommodate the varying melt strengths of the extrudates for the different compositions. Test specimens were injection-molded by using an Arburg Allrounder 305 screw-injection molding machine at 280°C (mold temperature = 65°C).

Izod impact strength was measured by using a pendulum-type tester for specimens conforming to ASTM D 256. In addition, sharp-notched tests were performed on test bars modified by pressing a new razor blade (that had been cooled in liquid nitrogen) into the notch. Low-temperature impact tests were performed on bars with standard notches. Tensile properties were measured by a Sintech model ID tensile tester for dogbone specimens conforming to ASTM D 638 by using a 25-mm extensometer and a crosshead speed of 5 mm/min.

Ultrathin sections for microscopy were prepared on a cryogenically cooled Reichert–Jung Ultracut E microtome by using a diamond knife at a specimen temperature of −35°C and a knife temperature of −45°C. Sections were stained with OsO_4 for 18 h and then with RuO_4 for 5 min, both from the vapor phase. The thin sections were examined by using a Jeol 200 CX transmission electron microscope.

BLEND MORPHOLOGY

SMA Blends

Figure 1 shows TEM photomicrographs for a series of three blends across a range of compositions for PC and SMA 8. The PC phase appears white, whereas the SMA phase appears grey. As expected, PC forms the matrix for the PC-rich blends, whereas SMA forms the matrix for the SMA-rich blends. These photomicrographs show quite similar morphological features to the corresponding compositions of PC/SAN blends reported by Lombardo et al.[1] At 80% PC, the SMA 8 forms highly dispersed, nearly spherical droplets of about 0.5-μm diameter. Particle sizes range
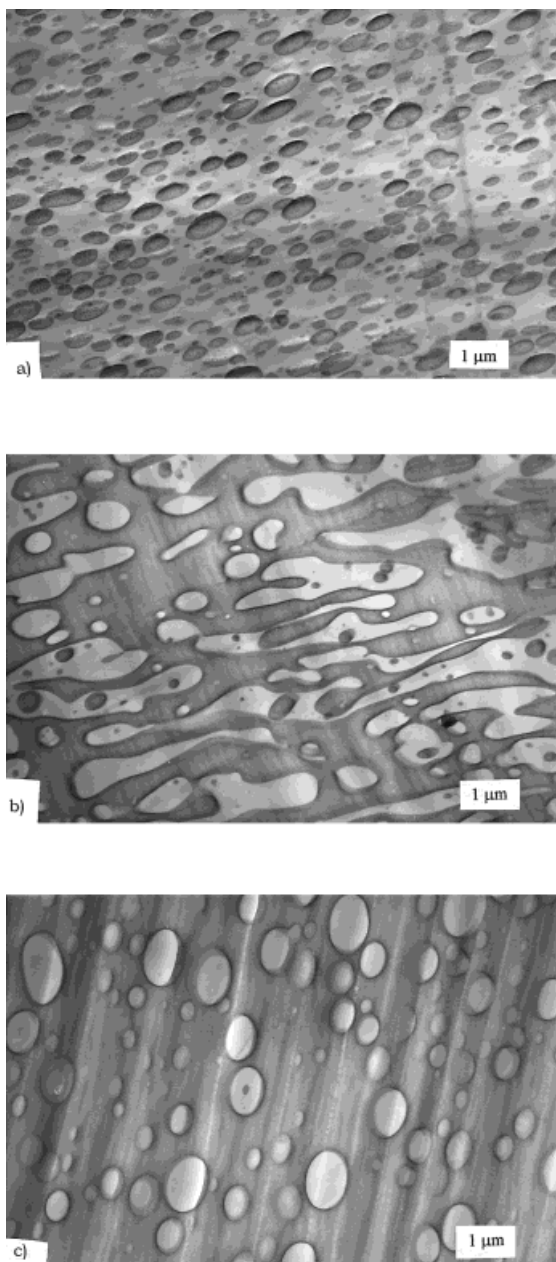
Figure 1 Transmission electron photomicrographs of polycarbonate blends containing (A) 20%, (B) 50%, and (C) 80% of SMA 8.

from about 0.25 to about 0.8 μm, and PC is the matrix phase. These dispersed droplets are larger and more elongated as the amount of SMA 8 in the blend is increased. Phase inversion occurred around the 60/40 (PC/SMA 8) composition. At the 50/50 wt % composition, the SMA is now the matrix, and the dispersed PC domains are very elongated, although not quite a co-continuous morphology.

The morphologies of blends of PC with SMA 14 were almost indistinguishable from those of PC/SMA 8 blends, including phase inversion at the 60/40 composition. The melt viscosities of the PC used in this work are significantly greater than that of both SMA materials as judged by the Brabender torque values shown in Table I. Thus, phase inversion should be expected for blends richer in PC than the 50/50 composition.[14]

On a macroscopic scale, blends containing 80% or more PC produced molded specimens that were essentially transparent because of the similar refractive indices of the PC and SMA. Blends with the larger particle sizes showed a pearlescent effect.

TSMA Blends

The morphology of the TSMA 9 and TSMA 12 raw materials differs slightly, as seen in Figures 2 and 3. Most rubber particle sizes for TSMA 9 are estimated to fall within a 0.3–1.5-μm range, whereas those for TSMA 12 are slightly smaller, in the range of 0.25–0.8 μm.

TEM photomicrographs of PC blends with the two TSMA materials (described in Table I) are shown in Figures 4 and 5. Again, PC is white, SMA is grey, and the rubber particles appear black. The blends chosen for imaging in these series all contain >50% PC because of the commercial importance of blends rich in PC.

At 90% PC and 10% TSMA for both blends [Figs. 4(A) and 5(A)], the rubber particles reside inside of an elongated coating of an SMA-dispersed phase. Some rubber particles (especially the larger, more occluded ones) are distorted in the direction of the flow of the material during
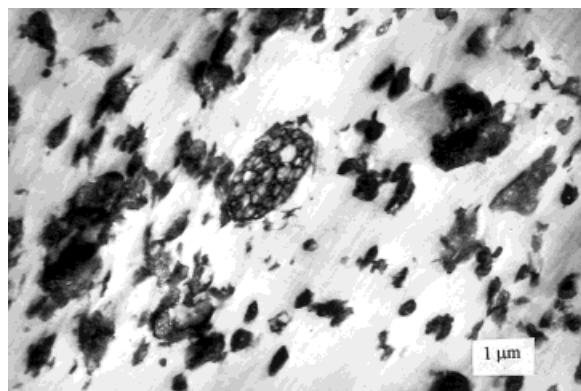

Figure 2 Transmission electron photomicrograph of rubber toughened styrene–maleic anhydride copolymer, TSMA 9.
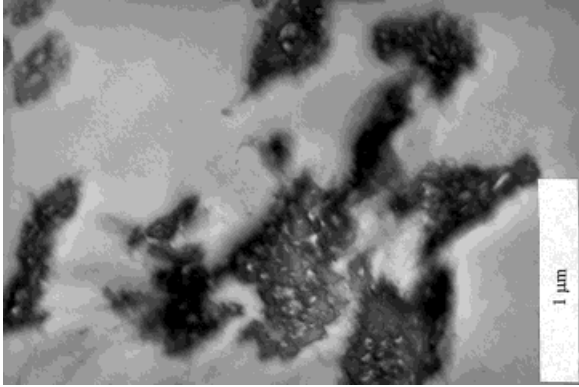
Figure 3 Transmission electron photomicrograph of rubber toughened styrene–maleic anhydride copolymer, TSMA 12.

molding. The SMA particles for 90/10 blends of PC/TSMA range from 0.2 to 1.0 μm. As the percent TSMA is increased for both blends, the dispersed droplets with their imbedded rubber par-
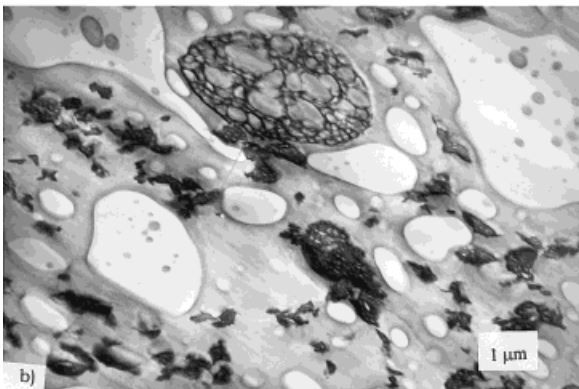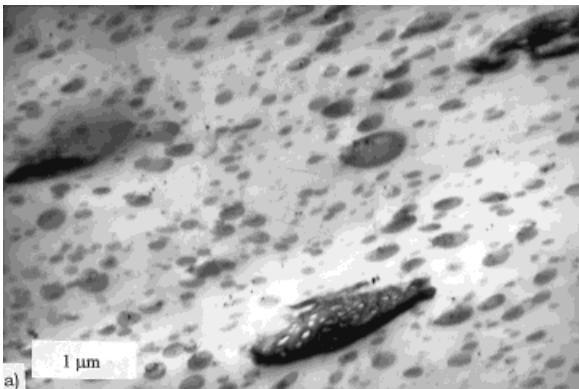

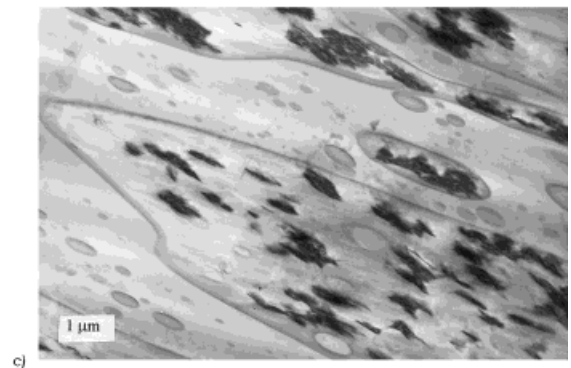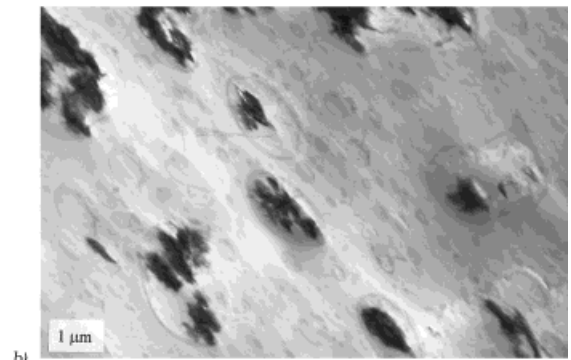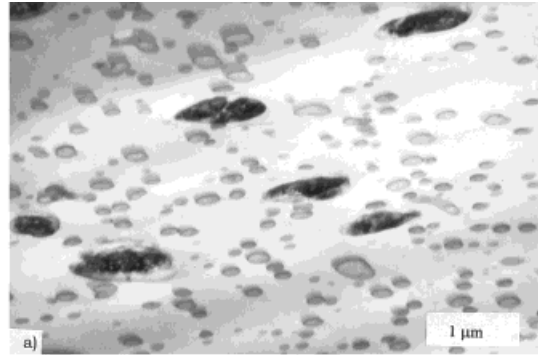**Figure 4** TEM photomicrographs of PC blends containing (A) 10% and (B) 50% of TSMA 12.

Figure 5 TEM photomicrographs of PC blends containing (A) 10%, (B) 30%, and (C) 50% of TSMA 12.

ticles get rounder and larger until a co-continuous morphology is reached at the 50/50 blend. In a comparison of Figures 1(B) and 4(B), the PC/TSMA morphology near the phase inversion was much more rounded and less elongated than that for the unmodified PC/SMA blends.

The two TSMA materials have melt viscosities similar to the PC as judged by the Brabender torques shown in Table I. Thus, the point of phase inversion is expected to be more nearly at the 50/50 composition than that observed for blends
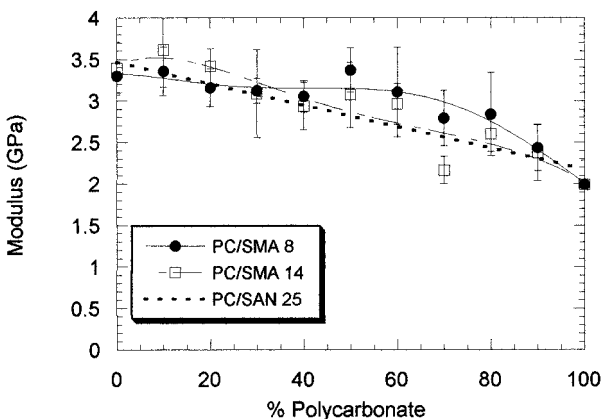
Figure 6 Tensile modulus of PC blends with SMA and SAN copolymers (no rubber).

with the lower viscosity SMA copolymer. Therefore, the co-continuous morphology seen at the 50/50 composition for blends of PC with both TSMA 9 and 12 is to be expected. Note that in all cases, the rubber particles (stained dark) reside entirely in the SMA phase.

TENSILE PROPERTIES

SMA Blends

Virgin polycarbonate is known for its excellent toughness and high tensile strength, around 55 MPa for this molecular weight. Blending with SMA has potential advantages for improving processibility, modulus, and cost, but hopefully not at the expense of losing the high tensile strength of pure PC.

Tensile modulus studies of PC/SMA 8 and PC/SMA 14 blends are shown in Figure 6. Both blends exhibited very similar modulus behavior, with small variation from a linear dependence on percent composition. Each data point is the mean of values measured for 10 specimens, and wide variances were noted specifically for PC/SMA blends without rubber. Any apparent departure from a linear dependence may therefore not be significant. The blend modulus is greatest at high contents of SMA and becomes lower as the amount of PC increases. PC/SAN 24 blends also show a nearly linear compositional dependence of the modulus.[1]

The tensile strength of PC blends with SMA 8 and SMA 14 are shown in Figure 7. The curves are sigmoidal, with maxima and minima. The extremes usually reflect the properties of the con-

tinuous phase. The inflection of the curve should correspond to phase inversion, which is verified in this case by the previously discussed TEM images. In both PC/SMA 8 and PC/SMA 14 blends, these strengths remain high when the amount of PC is >60%. Lower strengths for the blends with <60% PC have an SMA matrix as shown in the TEM images previously discussed. All of the blends containing 60% of more PC have tensile strengths at yield equal to or higher than that of pure PC. The tensile strengths for blends containing <60% PC showed brittle fracture and no yielding; this brittle behavior was most exaggerated for the PC/SMA 14 blends.

Thus, blending PC with SMA 8 and 14 can improve modulus without degrading the tensile strength for compositions above 60% PC. This behavior is very similar to that of PC/SAN 25 blends.

TSMA Blends

Modulus data for blends of PC with TSMA 9 and 12 are shown in Figure 8; results for PC/ABS blends are shown for comparison. The modulus is nearly the same for all three blend systems and is nearly independent of composition. As expected, the addition of rubber reduces the modulus compared to that the PC/SMA blends described earlier. The modulus of the blends with rubber-toughened SMA are about the same as that of pure PC and similar to that of PC/ABS.

The tensile strength of blends of PC with the rubber-modified SMA materials are shown in Figure 9. Data for PC with the analogous mass-made ABS material from the work of Lombardo et al.[1] are shown for comparison. All of the rubber-modified materials showed yielding during tensile
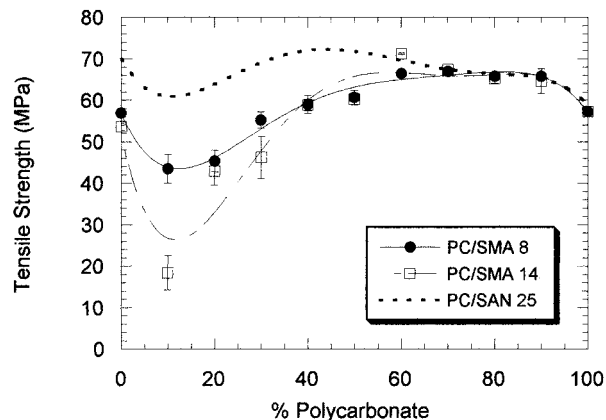

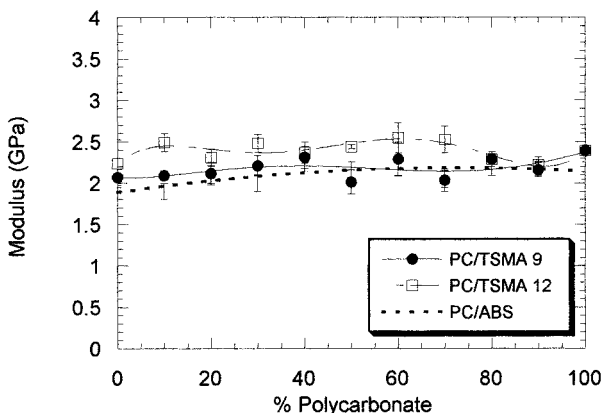**Figure 7** Tensile strength of PC blends with SMA and SAN copolymers (no rubber).

Figure 8 Tensile modulus of PC blends with ABS and TSMA materials (with rubber).

testing; blends without rubber showed brittle fracture when the PC content was <60%. The relationship between tensile strength and composition is nearly linear for blends containing rubber, not sigmoidal like the blends without rubber particles. Both TSMA 9 and TSMA 12 blends have similar absolute tensile strengths when compared at the same composition. The rubber-containing blends tend to have slightly lower tensile strength than those without rubber. Slightly higher values but similar trends were reported for blends of PC with ABS. The ABS material used by Lombardo et al.[1] has a similar composition and morphology as the TSMA materials (16% rubber, salami structure morphology of the rubber particles, and similar particle sizes); the exception, of course, is the presence of acrylonitrile versus maleic anhydride as the comonomer in the styrene copolymer backbone.
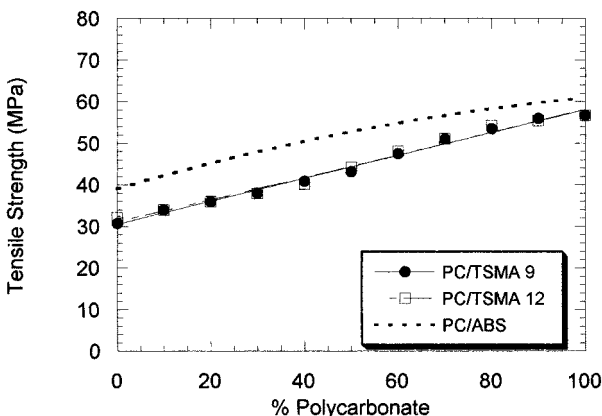
In summary, the introduction of the rubber particles has a leveling effect on the modulus and tensile strength behavior of both types of blends. For blends containing more than 60% PC, this means tensile strengths and moduli comparable to the original PC. Of course, rubber-containing blends are opaque, which is a liability in some applications. Blends of PC with TSMA have similar tensile strength and modulus as blends with ABS.

IMPACT PROPERTIES

Polycarbonate is well known for its high impact strength, which is a necessary property for many applications. Interestingly, PC may not be tough under certain conditions. The triaxial stress state generated in thick sections inhibits shear yielding and leads to a more brittle fracture.[15] This phenomenon also happens when there is a sharp notch like that formed by a razor blade. Blends of PC with SMA and TSMA were tested via the standard-notched Izod impact method and with a razor notch as a model for toughness in thicker parts. The temperature dependence of the impact properties was determined to assess the ductile/ brittle transition temperature.

Unmodified Blends

Figure 10 shows standard-notched Izod impact strength results for PC/SMA 8 and PC/SMA 14 blends. Additional small amounts of SMA caused embrittlement; blends of PC with SAN 25 show similar behavior, but toughness is retained up to 20% added SAN. The current blends were not
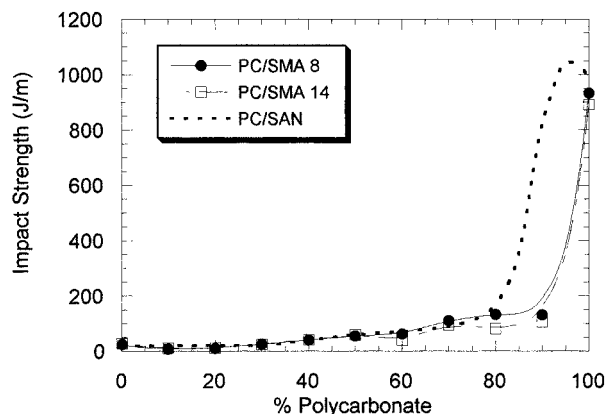

Figure 9 Tensile strength of PC blends with ABS and TSMA materials (with rubber).

Figure 10 Izod impact strength (standard notch) of PC blends with SAN and SMA copolymers (no rubber).
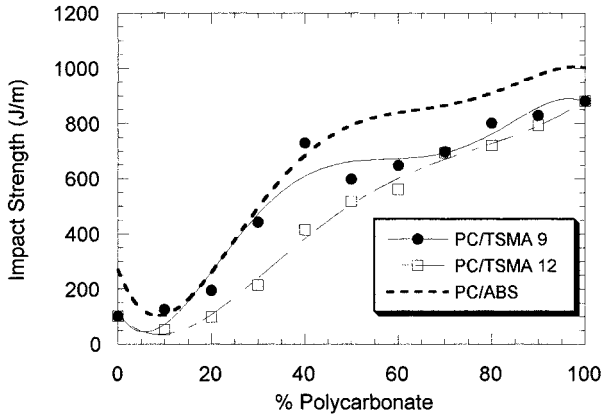
Figure 11 Izod impact strength (standard notch) of PC blends with ABS and TSMA copolymers (with rubber).

Figure 13 Izod impact strength (standard notch) as a function of temperature for selected PC/TSMA 9 blends.

tested by using a sharp notch or as function of temperature because they were all found to be brittle at room temperature.

Rubber-Modified Blends

Figure 11 shows the standard-notched Izod impact strength of PC blends with TSMA 9 and P/TSMA 12 (and with ABS for comparison). Introduction of rubber particles greatly improves the notched Izod behavior in comparison to the results shown in Figure 10. There is a gradual decline in impact strength as the amount of TSMA in the blend increases; blends with ABS show slightly higher impact strength for the very ductile PC-rich blends. All three types of blends show much better toughness than the blends without rubber.
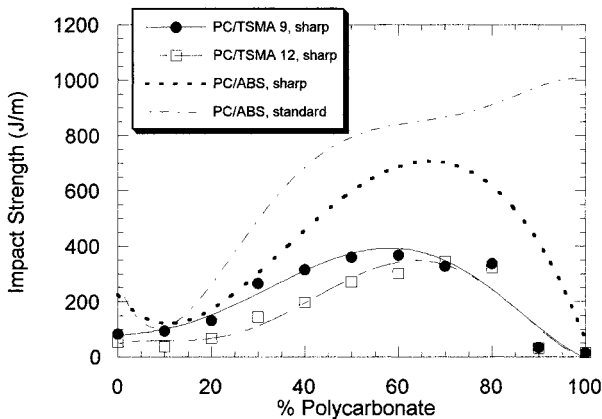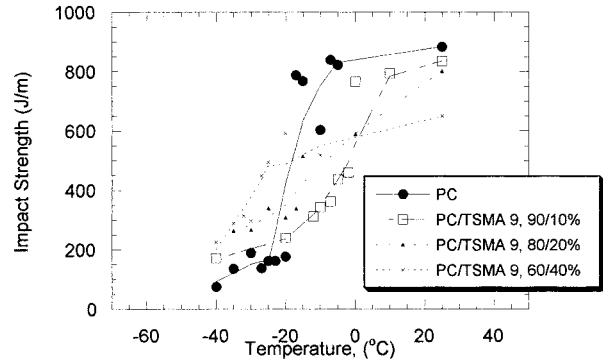
Figure 12 shows results for the more severe

condition with a sharpened notch. The sharp-notched Izod impact strength of pure PC is very low compared to the standard notch value of around 900 J/m. The presence of the rubber particles in the TSMA provides some recovery of the sharp-notched Izod impact strength of these blends across a wide range of compositions. The optimal composition contains about 60% PC where a sharp-notched Izod impact strength of around 400 J/m is achieved. This represents a significant synergism relative to the two pure components. Polycarbonate blends with ABS show somewhat higher levels of toughness, as seen in Figure 12, than the blends with either TSMA 8 or TSMA 12.

Figures 13 and 14 show the standard-notched Izod strength for selected PC/TSMA blends. For comparison, Figure 15 shows similar data for PC/ABS blends from the work of Lombardo et al.[1] The addition of 10% TSMA 9 to PC causes a slight increase in the ductile/brittle transition tempera-
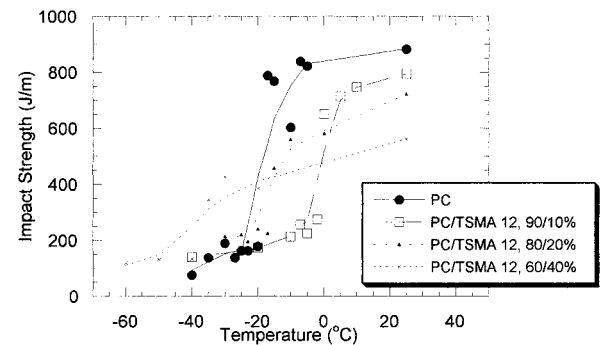

Figure 12 Izod impact strength (sharp notch) of PC blends with ABS and TSMA copolymers (with rubber).

Figure 14 Izod impact strength (standard notch) as a function of temperature for selected PC/TSMA 12 blends.
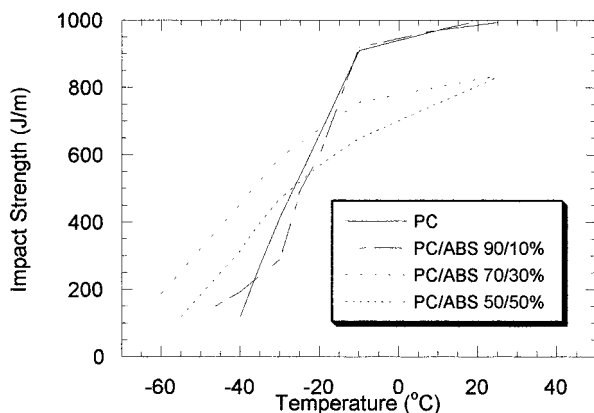
Figure 15 Izod impact strength (standard notch) as a function of temperature for selected PC/ABS blends (data from Lombardo et al.[1]).

ture. However, blends with larger amounts of TSMA 9 have a lower ductile/brittle transition temperature than pure PC. The TSMA 12 blends show similar trends; the 60/40 PC/TSMA 12 blend has a lower ductile/brittle transition temperature than the corresponding TSMA 9 blend. The PC/ABS blends show qualitatively similar trends; however, because the pure PC used by Lombardo et al.[1] had a lower ductile/brittle transition temperature than the pure PC used here, due primarily to molecular weight differences, more quantitative comparisons are not possible.[16]

CONCLUSIONS

The purpose of this work was to determine how blends of polycarbonate with SMA copolymers (with and without rubber modification) compare to the corresponding blends with SA copolymers (with and without rubber modification). In general, the trends are very similar. Both SAN and SMA cause an increase in stiffness when added to PC. Because of the more brittle nature of SMA than SAN, the tensile strength is inferior for SMA blends compared to SAN blends except for very high levels of PC where the two blends are quite similar. The Izod impact strength decreases more rapidly with the addition of SMA than SAN to PC. Rubber-toughened versions of these copolymers, ABS and TSMA, lead to much higher levels of impact strength for blends with PC. Polycarbonate specimens with sharp notches are quite brittle; however, the addition of either ABS or TSMA

greatly increases toughness under these more plane strain conditions. It appears that, in general, ABS provides better toughness in blends with PC than rubber-modified SMA or TSMA. This is not surprising in view of the lower fracture resistance of the styrenic matrix when the comonomer is MA rather than acrylonitrile.[12]

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