

Toughening Polycarbonate with Core–Shell Structured Latex Particles

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SYNOPSIS

The toughness as a function of temperature of polycarbonate modified by blending with core-shell structured latex particles was evaluated. Comparisons were made among a commercial core-shell latex (MBS), other core-shell (CS) latexes that incorporated a single component rubbery core, and a new class of interpenetrating polymer network (IPN) core-shell latexes with two elastomers in the core. Notched tensile tests differentiated among the blends in terms of their toughness. The most effective modifier at low temperatures was the commercial MBS latex. The CS latexes produced blends that were only slightly less tough than the MBS blends despite better dispersion of MBS and better adhesion to the matrix. The IPN blends were the least tough at low temperatures; however, at 25°C, a blend with IPN had the highest impact strength. Differences between CS and MBS blends were attributed to differences in the percent of butadiene-containing rubber and the chemical nature of the shell. A comparison among the CS latexes showed that increasing the acrylonitrile content of the shell increased the toughness, and increasing the rubber content or the gel fraction of the core increased the toughness. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The notch sensitivity of polycarbonate (PC), especially at low temperatures, can be reduced by blending with a small amount of an elastomer.^{1–3} Core-shell elastomers are designed specifically to produce blends with good dispersion and toughness. The chemical composition and cross-link density of the elastomeric core determine the cavitation resistance of the particle, whereas the composition of the shell is chosen to provide rigidity to the particles during processing and to impart compatibility with the matrix for good dispersion and adhesion.

Core architectures that combine two or more polymers can produce core-shell particles with synergistic properties. An interpenetrating polymer

network (IPN) is defined as a combination of two or more polymers in network form, with at least one polymer synthesized and/or cross-linked in the presence of the other. Control of network composition and morphology makes it possible to optimize a range of physical properties. Latex IPNs can be prepared by emulsion polymerization to form both networks in each latex particle.

Recently, a new class of core-shell structured latex particles with an IPN core and a glassy shell was proposed.^{4,5} The IPN core combines a relatively low T_g polymer for good cavitation and impact toughness with a higher T_g polymer for damping characteristics to improve resistance to slow fracture such as caused by fatigue or vibrations. Synthesis of the IPN core-shell particles was described⁴ and the dynamic mechanical behavior has been characterized.⁵ The present study was undertaken to evaluate the toughness of polycarbonate modified with up to 10% of an IPN core-shell latex. Comparisons were made with a commercial core-shell latex and with other

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Table I Chemical Composition of Core–Shell Structured Latexes

Latex	Core Composition	Shell (S/AN) ^a	Core/Shell Ratio	Rubber Content ^b	Average Particle Size (μm) ^c
MBS	P(Bd/S)	PMMA	N/A	N/A	0.20
CS912	P(Pd/S) (9/1) 95% gel-fraction ^d	72/28	1 : 1	45.0%	0.245 \pm 0.019
CS1011 ^e	P(Bd/S) (9/1) ^f 95% gel-fraction	72/28	1 : 1	45.0%	0.311 \pm 0.016
CS1018	P(Bd/S) (9/1) 10% gel-fraction	72/28	1 : 1	45.0%	0.355 \pm 0.023
CS1025	P(Bd/S) (9/1) 40% gel-fraction	72/28	1 : 1	45.0%	0.306 \pm 0.020
CS1026	P(Bd/S) (9/1) 40% gel-fraction	72/28	2 : 1	60.0%	0.273 \pm 0.017
CS1027	P(Bd/S) (9/1) 95% gel-fraction	75/25	1 : 1	45.0%	0.286 \pm 0.039
CS1028	P(Bd/S) (9/1) 95% gel-fraction	80/20	1 : 1	45.0%	0.306 \pm 0.027
IPN97	P(Bd/S) (9/1) P(BA/MMA) (6/4)	72/28	1 : 1	22.5%	0.432 \pm 0.035
IPN99	P(Bd/S) (9/1) P(BA/S) (5/5)	72/28	1 : 1	22.5%	0.430 \pm 0.064
IPN1013	P(Bd/S) (9/1) P(Bd/S) (5/5)	72/28	1 : 1	22.5%	0.452 \pm 0.056

^a styrene/acrylonitrile ratio.^b as P(Bd/S) (9/1).^c measured by light scattering (Nicomp).^d gelation due to crosslink reaction (4).^e 2% initiator concentration.^f P(Bd/S) = poly(butadiene-co-styrene); P(BA/MMA) = poly(butyl acrylate-co-methyl methacrylate); P(BA/S) = poly(butyl acrylate-co-styrene); S/AN = poly(styrene-co-acrylonitrile); PMMA = poly(methyl methacrylate).

core-shell latexes that incorporated a single component core.

MATERIALS AND METHODS

A commercial core-shell impact modifier (MBS) was obtained from Rohm and Haas (Paraloid® 3607). Two types of core-shell structured latex particles were synthesized by emulsion polymerization techniques as described previously.⁴ Antioxidant was added to the latex before it was coagulated with MgSO₄ at 95°C and dried overnight at 60°C and 150 mbar. The CS series consisted of a poly(butadiene-co-styrene) (P(Bd/S)) core and poly(styrene-co-acrylonitrile) (SAN) shell. The CS particles differed from the MBS primarily by having a SAN shell rather than a poly(methyl methacrylate) (PMMA) shell. The IPN series consisted of particles with an interpenetrating polymer network core and a SAN shell. Compositions of all the latexes are given in Table I. The IPN latexes had about half the butadiene content of the other latexes; the other portion of the elastomer had a glass transition of about 10°C. The matrix material was polycarbonate (Lexan® 141 from General Electric Company).

Polycarbonate pellets were blended with 2–10 wt % of the coagulated latex particles by melt mixing in a Leistritz twin screw extruder. Typical operating conditions were 210°C throat temperature, 250°C barrel temperature, 260°C die temperature, 25 rpm

feeder speed, and 100 rpm screw speed. The extrudate was quenched in water and pelletized.

Pellets were dried at 120°C overnight prior to molding. A plunger-type Morgan Press injection molding machine was used to prepare 3 mm thick tensile bars (ASTM D638 Type I). Typical operating conditions were 220°C barrel temperature, 230°C nozzle temperature, and 50°C mold temperature. Unnotched tensile bars were tested in uniaxial tension at ambient temperature with a strain rate of 10%/min in an Instron Model 8510 mechanical testing machine.

An Izod notch was cut in one edge of some of the tensile bars following ASTM D256. The notch angle was 45 degrees with a radius of 0.25 mm and depth of 2.54 mm. Notched tensile bars were cryofractured at liquid nitrogen temperature, coated with 90 Å of gold and examined in a JEOL 840A scanning electron microscope (SEM) to observe particle size and dispersion. Izod impact tests were conducted on some of the notched specimens. Tests were carried out on a TMI Testing Machine with a 5 lb hammer at ambient temperature following ASTM D256. Notched specimens were also tested in tension with a crosshead speed of 500 mm/min at temperatures from 25 to –70°C. Specimens were equilibrated at temperature in the environmental chamber of the Instron for 10 min before testing. Fracture surfaces from the high speed tests were coated with 90 Å of gold and examined in the SEM.

RESULTS AND DISCUSSION

Morphologies of three representative blends of PC with 10% latex are compared in Figure 1. The 0.2 μm MBS particles were uniformly dispersed in the blend with good adhesion to the matrix owing to good compatibility between the PMMA shell and PC. The IPN latex particles were also uniformly dispersed; however, separation of the particles from the matrix indicated that particle–matrix adhesion was not as good as with MBS particles. The IPN particle size measured from scanning electron micrographs of the blends, 0.34–0.40 μm , was the same as obtained previously from transmission electron micrographs of the latex (Table I). The CS latexes had a particle size of 0.28–0.30 μm . All of them showed poor adhesion relative to MBS and some level of particle aggregation. The amount of aggregation did not correlate with any of the latex compositional variables; possibly, aggregation of CS

Table II Notched Izod Impact Strength at Ambient Temperature

Sample ^a	Impact Strength (ft-lb/in)
PC	14.9 \pm 1.0
10% MBS	10.2 \pm 0.2
10% CS912	11.4 \pm 0.8
10% CS1026	11.0 \pm 1.3
10% CS1027	11.1 \pm 0.1
10% IPN97	12.5 \pm 0.0
10% IPN1013	11.0 \pm 0.3

^a Three specimens for each sample.

particles reflected use of less-than-optimum processing parameters for preparing the blends.

In unnotched tensile tests, PC failed in a ductile manner with necking and cold drawing. The unnotched tensile properties were not strongly affected by the latex. The addition of 10% latex to PC caused

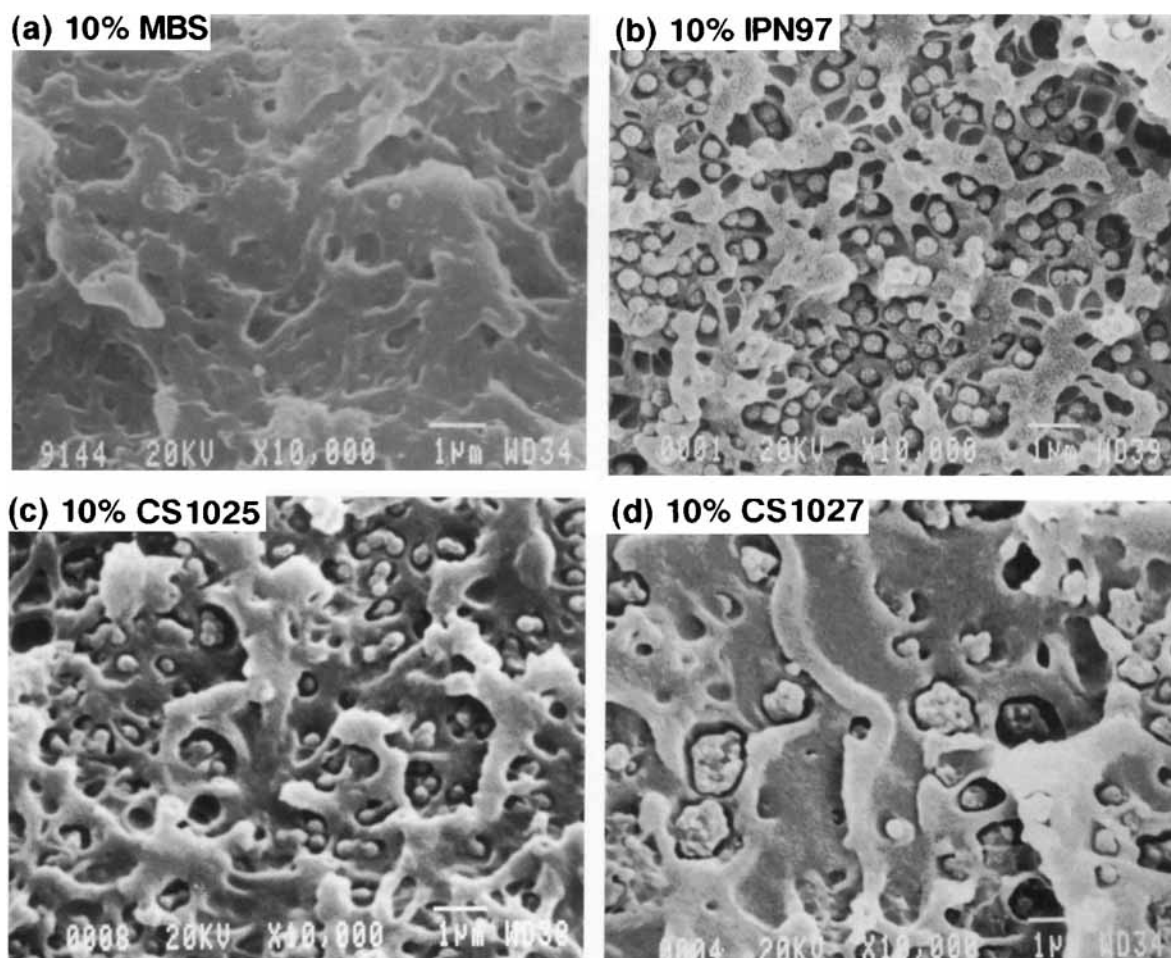


Figure 1 Cryogenic fracture surfaces of PC blends: (a) PC with 10% MBS, (b) PC with 10% IPN97, (c) PC with 10% CS1025, and (d) PC with 10% CS1027.

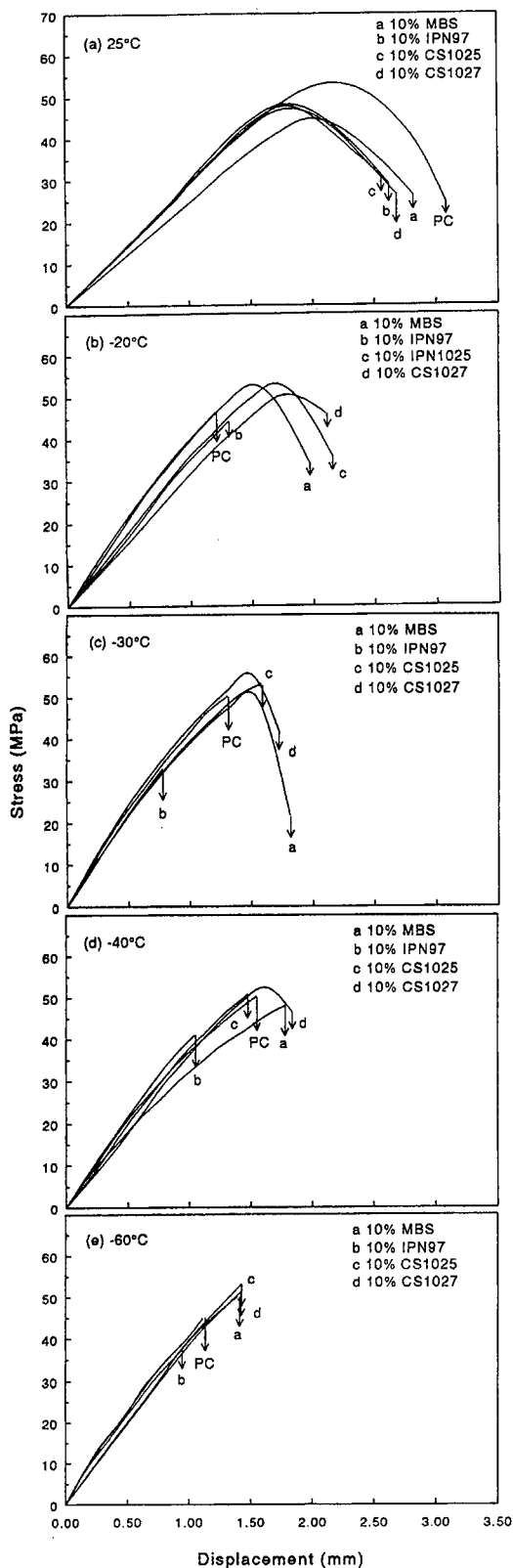


Figure 2 Stress-displacement curves of PC and PC blends: (a) 25°C, (b) -20°C, (c) -30°C, (d) -40°C, and (e) -60°C.

a decrease in the modulus from 1.5 to about 1.3 GPa and a decrease in the yield stress from 62 to about 55 MPa but did not significantly alter the fracture strain of 80%.

Ductile failure of PC was observed in notched Izod tests on 3 mm thick bars, and ductile failure accompanied by stress whitening was observed for all the blends. The lower failure energy of the blends compared to PC (Table II) reflected the lower modulus and yield stress.¹ Of the blends, the MBS blend had the lowest ductile failure energy. It is characteristic of notched PC that the failure mode at ambient temperature changes from mostly plane stress ductile failure in thinner (3 mm) specimens to mostly plane strain brittle failure in thicker (6 mm) specimens. Impact modifiers reduce the notch sensitivity by promoting cavitation, which relieves the triaxiality and changes the failure mode from plane strain to plane stress. The specimens used in the Izod tests were too thin to reveal this effect.

Because the specimens were not thick enough for the Izod test to reveal the effect of the latexes on notch sensitivity of PC, 3 mm thick specimens with the V-shaped Izod notch were tested in tension and the test temperature was varied in order to obtain transitional behavior that would differentiate the toughness of the blends.^{6,7} The stress-displacement curves of PC and four blends with 10% latex are shown in Figure 2. At 25°C, PC and all the blends were ductile: a maximum in the stress-displacement curve was accompanied by yielding at the notch root. All the materials remained ductile at -20°C, except PC and the IPN97 blend. Brittle fracture was inferred when the stress-displacement curve did not exhibit a maximum. Below -20°C, lower fracture stresses of the IPN97 blend compared to PC indicated that IPN97 particles actually embrittled PC. At -30°C, the CS1025 blend yielded only slightly before it fractured. The MBS and CS1027 blends remained ductile at -30°C, although the ductile fracture strain gradually decreased as the temperature was lowered. At -40°C, only the CS1027 blend exhibited a yield maximum in the stress-displacement curve. At -60°C, all the materials fractured in a brittle manner but varied in the fracture stress or strain.

Because there was ambiguity in determining the fracture mode from the stress-displacement curve, especially in the ductile-to-brittle transition (D/B transition) region, the fracture mode was also identified fractographically. Ductile fractures were characterized by shear tearing, sucking in of the fracture plane, and stress whitening. Brittle fractures showed characteristics of craze fracture, no

Table III Fracture Mode Determined from Fractography of PC Blended with Latex^a

Sample	25°C	0°C	-20°C	-30°C	-40°C	-60°C	-70°C
PC Blended with 10% Latex ^a							
PC	DD	DDBB	BB				
MBS					DD	TT	BB
CS912					DD	BB	
CS1011				DD	TT	BB	
CS1025				DD	DTT	BB	
CS1026					DD	BB	
CS1027					DD	BB	
CS1028				DD	TT		
IPN97	DD		TD	BB			
IPN99			DD	BB			
IPN1013			DD	TBBB			
PC Blended with 5% Latex							
PC	DD	DDBB	BB				
MBS					DD		
CS912			DD	BB			
CS1011			DD	DBBB	BB		
CS1018			DD	BB			
CS1025			DD	BB			
CS1026				DD	DTBB	BB	
CS1027			DD	DBBB	BB		
CS1028			DD	BB			
IPN97	DD		BB				
IPN99			BB				
IPN1013			BB				
PC Blended with 2% Latex							
PC	DD	DDBB	BB				
MBS	DD		DBBB	BB			
CS1025			DBBB	BB			
CS1026			BB				
CS1027			B				
IPN97	DBBB		BB				

^a The failure mode of each specimen tested in the temperature region of the D/B transition is indicated as ductile (D), brittle (B), or transitional (T).

sucking in, and were not stress-whitened. The fracture mode of each specimen tested in the temperature region of the D/B transition is tabulated in Table III. Due to the high notch sensitivity, PC fractured either by ductile tearing (D) or in a brittle manner by crazing (B). Above 0°C, PC showed only ductile fractures; below 0°C, all the fractures of PC were brittle. The two modes are illustrated in Figure 3 with fracture surfaces from tests at 0°C, where PC showed bimodal behavior with a mix of ductile and brittle failures. This temperature was taken as the D/B transition temperature.

In contrast to PC, the blends sometimes showed transitional fracture surfaces that contained both a

ductile region beginning at the notch root and a brittle region further from the notch root. A fracture was considered to be transitional when the region of ductile fracture occupied more than 10% of the fracture surface area. Fracture surfaces of the 10% MBS blend in Figure 4 illustrate the characteristic features of ductile (D), brittle (B), and transitional (T) fracture. The stress-whitened surface obtained at -40°C shows ductile tearing and sucking in and, when viewed at higher magnification, profuse cavitation and matrix shear deformation. Fracture surfaces obtained at temperatures above -40°C exhibited these same features. The surface obtained at -60°C is transitional, as indicated by the abrupt

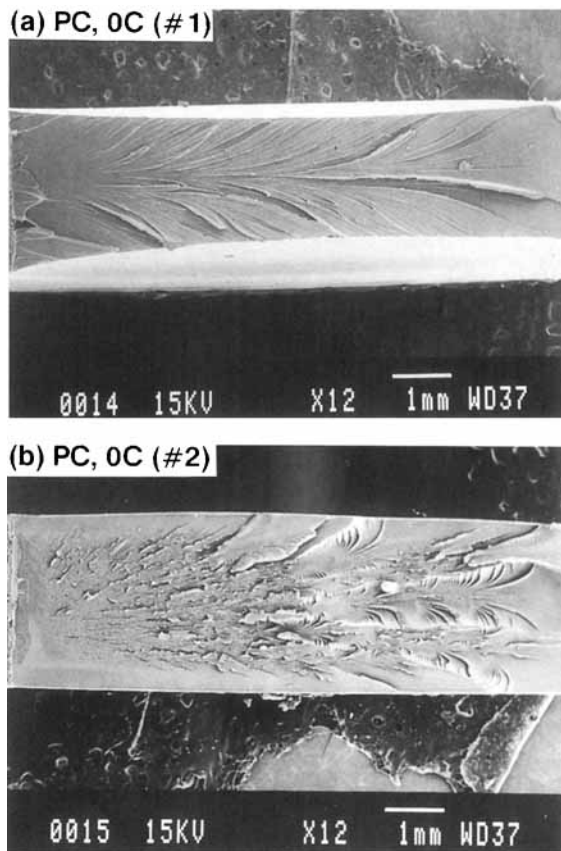


Figure 3 Fracture surfaces of notched PC tested at 0°C: (a) a ductile tearing fracture and (b) a brittle craze fracture.

change from tearing fracture to brittle fracture as the crack propagated from left to right. The fracture surface at -70°C is brittle, with the same features as the brittle region of the transitional fracture.

Figure 5 shows fracture surfaces of the 10% CS1025 blend from tests at -40 and -60°C . One of the specimens tested at -40°C fractured in a ductile manner; the second exhibited transitional behavior. This temperature was taken as the D/B transition temperature of the 10% CS1025 blend. Fracture of the specimen tested at -60°C was considered as brittle because the ductile, stress-whitened region at the notch root was less than 10% of the fracture surface. Fractured specimens of blends with 10% CS1011 and CS1028 also exhibited transitional behavior at -40°C . All the blends with 10% of a CS latex exhibited a D/B transition at -40°C or lower. Transitional fracture surfaces were not observed for blends with 10% CS912, CS1026, and CS1027. All the specimens of these blends tested at -40°C exhibited ductile fracture, and all the specimens tested at -60°C fractured in a brittle manner. Therefore

the D/B transition temperature of these blends was taken as -50°C .

Fracture surfaces of a 10% IPN97 blend specimen tested at 25°C and two specimens tested -20°C are shown in Figure 6. Shear tearing fracture was observed at 25°C . One of the specimens exhibited transitional fracture and the other brittle fracture at -20°C , which was taken as the D/B transition temperature. Only subtle differences were observed among the IPN latex blends. The 10% IPN99 fractures were ductile at -20°C and brittle at -30°C , so -25°C was chosen as the D/B transition tem-

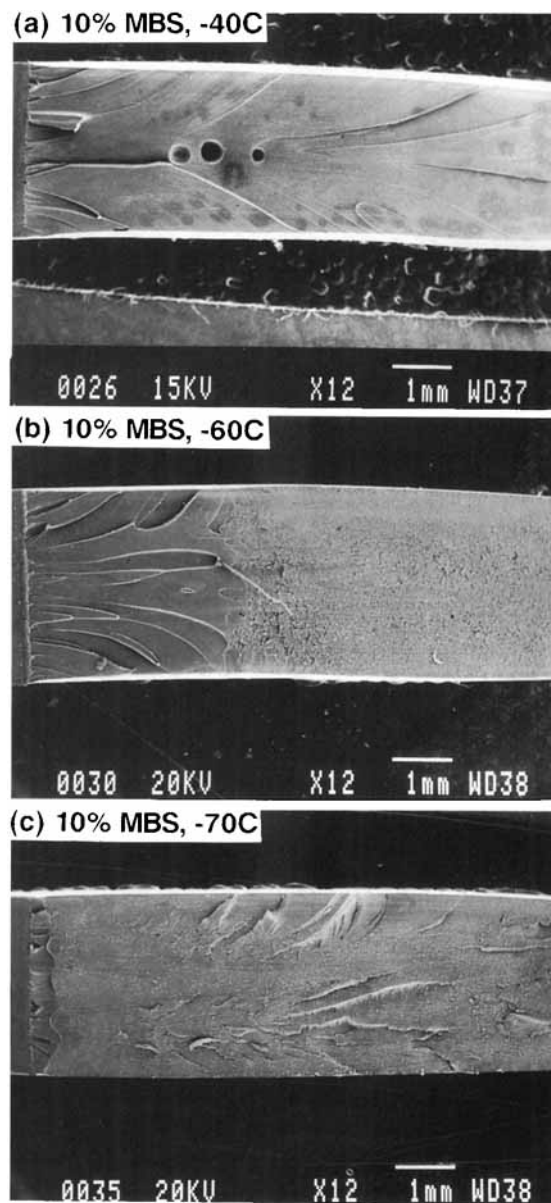


Figure 4 Fracture surfaces of notched PC with 10% MBS: (a) ductile fracture at -40°C , (b) transitional fracture at -60°C , and (c) brittle fracture at -70°C .

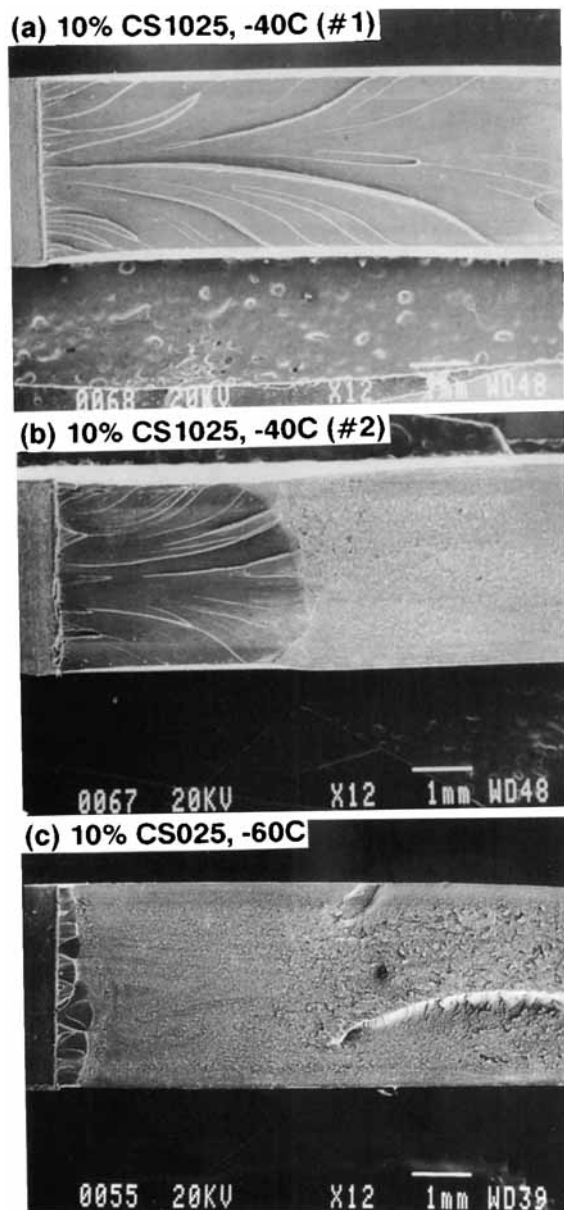


Figure 5 Fracture surfaces of notched PC with 10% CS1025: (a) ductile fracture at -40°C , (b) transitional fracture at -40°C , and (c) brittle fracture at -60°C .

perature. There was one transitional fracture of the 10% IPN1013 at -30°C ; therefore, this was taken as the transition temperature. The higher D/B transition temperature was anticipated with the IPN latexes because they had only about half the low-temperature elastomer of the CS latexes.

When viewed at low magnification, ductile fracture surfaces of the IPN blends were very similar in appearance to ductile fractures of MBS and CS blends. However at higher magnification, the MBS surface was relatively smooth compared to the

roughness created by pulled out matrix on an IPN surface (Figure 7). Coalescence of voids created by the latex particles during yielding, and subsequent pull-out and fracture of the matrix ligaments between coalesced voids, created the characteristic surface texture of the IPN blend.¹⁸ Coalescence of voids into critical-size flaws would have had a detrimental effect on the low temperature toughness of IPN blends.

All the blends exhibited a lower D/B transition temperature than PC (Table IV). The IPN blends

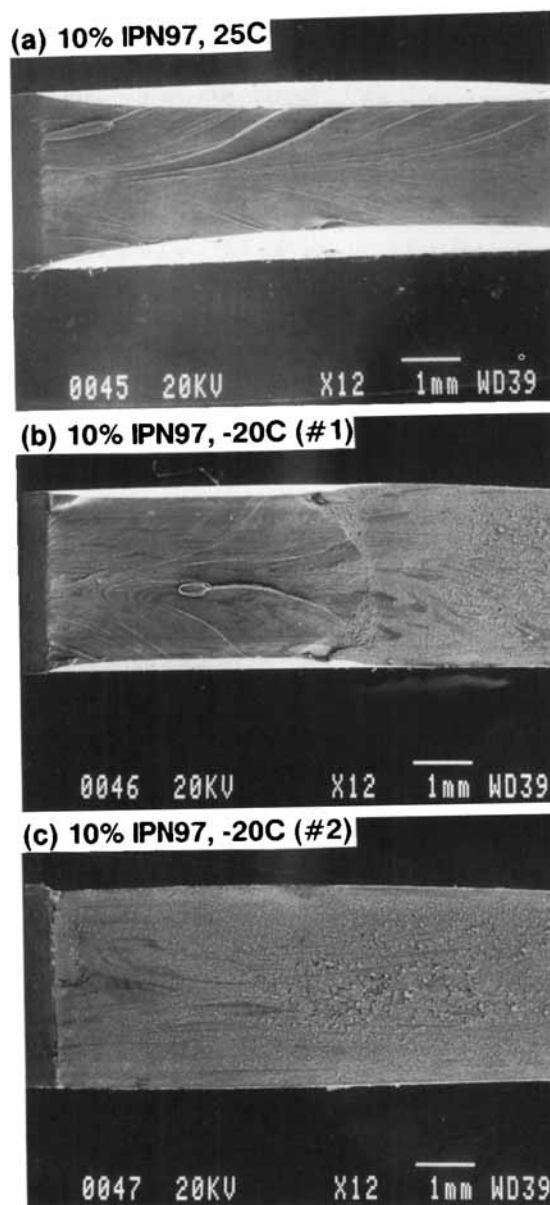


Figure 6 Fracture surfaces of notched PC with 10% IPN97: (a) ductile fracture at 25°C , (b) transitional fracture at -20°C , and (c) brittle fracture at -20°C .

had the highest transition temperatures. This was anticipated because the IPN latexes had only about half the low-temperature elastomer of the CS latexes. The IPN core also contained a higher T_g polymer for damping characteristics. Resistance to slow fracture, such as is caused by fatigue or vibrations, of PC blends with IPN latexes is a subject of future studies. The blend with MBS had the lowest D/B transition temperature although the CS blends had transition temperatures that were only 10–20°C higher. The core of both CS and MBS was nominally poly(butadiene-*co*-styrene), although there may have been differences in rubber gel fraction, crosslinking, and overall rubber content. Important differences between CS and MBS blends were better dispersion of MBS and better adhesion to the matrix. These characteristics are determined primarily by the shell composition. There is evidence that PMMA, the shell polymer of MBS, is thermodynamically miscible with PC.^{9,10} Although SAN also exhibits excellent interfacial adhesion to PC,^{11,12} separation of particles from the matrix in cryogenic fracture surfaces indicated that particle–matrix adhesion was not as good as with MBS particles.

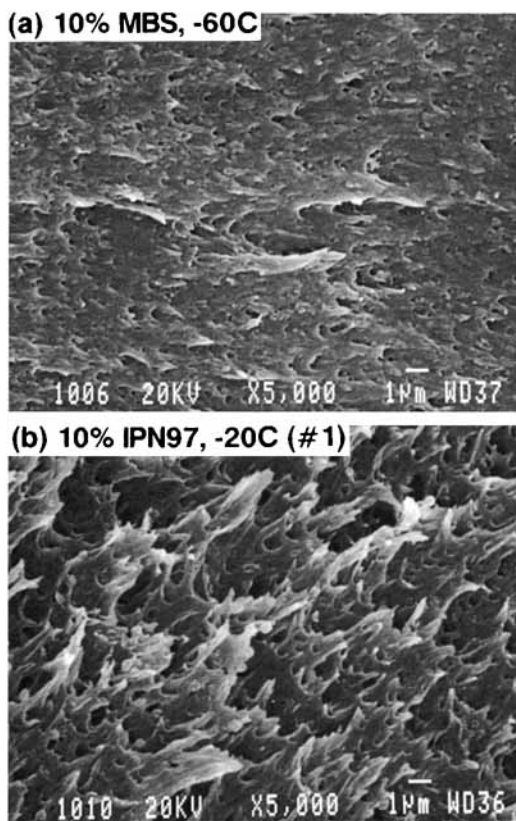


Figure 7 Higher magnification of ductile fracture surfaces: (a) PC with 10% MBS at -60°C and (b) PC with 10% IPN97 at -20°C .

Table IV Ductile-to-Brittle Transition Temperature of PC Blended with 10% Latex

Sample	Transition Temperature ($^{\circ}\text{C}$)
PC	0
MBS	-60
CS912	-50
CS1011	-40
CS1018	N/A
CS1025	-40
CS1026	-50
CS1027	-50
CS1028	-40
IPN97	-20
IPN99	-25
IPN1013	-30

Among the CS latexes, it was possible to compare the effects of several variables. The effect of AN content in the shell was examined by comparing blends of CS1028 (20% AN) with CS1027 (25% AN) and CS912 (28% AN). All had a core with 95% gel fraction and 45% rubber content. The latex with the lowest AN content exhibited the highest D/B transition temperature, -40°C , compared to -50°C for the other two. This is consistent with the general consensus that the maximum adhesion between PC and SAN is achieved with an AN content of 25–27%.¹³ Two core characteristics were varied: the rubber content and the gel fraction. Comparing CS1025 (45% rubber) with CS1026 (60% rubber), increasing the rubber content lowered the transition temperature from -40 to -50°C for blends with 10% latex and from -25 to -40°C for blends with 5% latex. The effect of gel fraction was obtained from a comparison of CS1025 (40% gel fraction) with CS912 (95% gel fraction). The latex with the higher gel fraction had a lower transition temperature, -50°C , compared to -40°C . Higher crosslinking may increase the cavitation resistance of the latex particle. It is thought that impact modifiers with higher cavitation resistance impart better toughness to PC.¹ This suggests that there is an optimum level of core crosslinking yet to be determined.

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