

# Core-Shell Structured Latex Particles. III. Structure-Properties Relationship in Toughening of Polycarbonate with Poly(*n*-butyl acrylate)/Poly(benzyl methacrylate-styrene) Structured Latex Particles

I. SEGALL,<sup>1,\*</sup> V. L. DIMONIE,<sup>1</sup> M. S. EL-AASSER,<sup>1,†</sup> P. R. SOSKEY,<sup>2</sup> and S. G. MYLONAKIS<sup>2</sup>

<sup>1</sup>Emulsion Polymers Institute, 111 Research Dr., Iacocca Hall, Lehigh University, Bethlehem, Pennsylvania 18015;

<sup>2</sup>EniChem America Inc., Research and Development Center, Monmouth Junction, New Jersey 08852

## SYNOPSIS

The performance of the designed structured core-shell latex particles in toughening polycarbonate (PC) matrix was examined. Izod impact testing of the PC-core-shell latex blends were used to evaluate the influence of parameters related to the core-shell latex particles on toughening polycarbonate. Among these parameters are the particle size and levels of crosslinking of the core rubber particles, composition and molecular weight of the shell polymer, and weight ratio of shell to core polymers as well as the particle morphology. In this work, core-shell structured latex particles with thinner shells of higher molecular weight polymers were found to improve the impact resistance of polycarbonate. The role of chain entanglements in increased adhesion between the discrete rubbery phase and the continuous glassy matrix and the importance of surface-to-surface interparticle distance for toughening at various temperatures are discussed. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

The deformation processes of most amorphous glassy polymers are described as crazing and shear bending. Polycarbonate (PC) is considered to undergo pseudoductile fracture, where energy dissipation occurs via shear yielding.<sup>1,2</sup> However, at specimen thicknesses above  $\frac{1}{4}$  inch, PC fractures by crazing. Studies on microdeformation mechanisms in coextruded polycarbonate/poly(styrene-acrylonitrile) [PC-(SAN)] composites demonstrated that initiation of microshearbands at the craze tips terminate the craze growth.<sup>3</sup> The interactive shear deformation (interactive crazing and microshear-bending) is responsible for increased ductility and toughness in PC/SAN microlayer composites.<sup>4</sup> The thickness of the PC layer is very important in controlling the crazing behavior of composites.

Toughening of PC by rubber modification is widely used, especially with core-shell-type latex particles. Understanding the mechanism of toughening and the origin of differences in toughening behavior can help design effective impact modifiers. Investigations on the deformation mechanism of rubber-toughened PC at the macroscopic level<sup>5</sup> indicated that impact modifiers with higher cavitation resistance of the rubber phase impart better toughness to blends with PC.

In this part of this series, the structured core-shell latex particles, which were described in Part II, were tested in toughening polycarbonate. Special attention was paid to the influence of the characteristics of the core-shell particles, which are directly related to the toughening mechanism, for example, the level of crosslinking of the rubber core particles which influence the degree of cavitation of the rubber. The size of rubber core particles was considered in light of the proposed change in the failure mechanism from ductile due to shear yielding at room temperature to brittle fracture at subzero temperatures. The influence of the molecular weight and

\* Present address: University of Cincinnati, Department of Materials Science & Engineering, Cincinnati, OH 45221.

† To whom correspondence should be made.

**Table I** Pendulum Izod Impact Resistance of Polycarbonate Blends with 3 wt % Structured Latex Particles

Latex Sample	BA/EGDMA		CTA wt % <sup>a</sup>	BA/BM Wt Ratio	Impact Resistance <sup>b</sup> (ft lb/in.)		
	Wt Ratio	BM/St Wt Ratio			50°C	25°C	-20°C
220	93/7	100/0	1	1/2.6	—	2.4 ± 0.1	2.0 ± 0.1
221	99/1	100/0	1	1/2.6	—	2.4 ± 0.1	2.0 ± 0.1
222	93/7	100/0	1	1/1.1	—	2.8 ± 0.1	—
223	99/1	100/0	1	1/1.1	3.1 ± 0.2	3.0 ± 0.2	2.3 ± 0.0
224	99/1	95/5	1	1/1.1	—	2.8 ± 0.4	—
225	99/1	95/5	0.7	1/1.1	3.5 ± 0.3	3.4 ± 0.2	—
226	99/1	0/100	0.7	1/1.1	13.4 ± 0.6	4.2 ± 0.2	2.4 ± 0.2

<sup>a</sup> Based on monomer used for polymerization of shell layer.

<sup>b</sup> Average of 5 specimens.

composition of the shell polymer as well as the ratio of the shell to core polymer and the overall particle morphology were examined because of their importance in the dispersability of the rubber particles in the PC matrix, and in developing the mixing zone between the rubber particles and the PC matrix, which is responsible for anchoring or improving the adhesion between the rubber core particles and the matrix.

## EXPERIMENTAL

### Sample Preparation

The matrix material was a bisphenol-A type PC (Sinvet 251, EniChem). The elastomers were the structured latex particles of poly(*n*-butyl acrylate)/poly(benzyl methacrylate-styrene) [PBA/P(BM-St)] core-shell (prepared as described in Part II of this series and elsewhere<sup>6</sup>), precipitated from the latex with 3/1 volume ratio of methanol and sodium chloride, and then mixed with ground-up PC. The mixture was dried in a desiccating oven for 10 h at 125°C.

Compounding of the elastomers and PC was performed on a Leistritz corotating intermeshing 34-mm twin-screw extruder. Typical operating conditions for the extrusion blending were 250°C barrel temperature, 150 rpm screw speed, 10.7 kg/h feed rate, 7.5 kW drive power, and 260°C melt temperature. The extruded strings were cooled in a water bath and pelletized.

The resulting pellets were dried in a desiccating oven for 5–7 h at 125°C. Impact specimens were produced with an 80-ton Nissei injection-molding machine. Typical operating conditions for the

molding were 290°C barrel temperature and nozzle temperature, 85°C mold temperature, 14,000 psi injection pressure, and 10,000 psi hold pressure.

### Mechanical Testing

Impact testing was performed with a Tinius Olsen pendulum impact testing machine equipped with a low-temperature unit. Notched Izod specimens 6.35 mm thick were prepared and tested according to ASTM D256 specifications.

## RESULTS AND DISCUSSIONS

### Impact Resistance of PC Blends with Structured Latex Particles

#### *Influence of Crosslink Density of Rubber Core*

Pendulum Izod impact test results for ¼-inch notched bars of PC loaded with 3 wt % structured particles are shown in Table I. The characteristics of the structured core-shell particles were discussed in detail in Part II (see Table IV, Part II and associated discussion). All structured latexes were based on small 180 nm poly(*n*-butyl/acrylate-ethylene glycol dimethacrylate) [P(BA-EGDMA)] core particles. The results indicate that at room temperature the impact resistance of PC toughened with 3 wt % small-size structured latex particles is not very sensitive to the extent of crosslinking of the seed and/or to the shell thickness. When comparing samples 220 and 221, which have 7 and 1 wt % crosslinker (EGDMA) in the seed, respectively, and a core-shell ratio of 1/2.6, it appears as if the degree of crosslinking in the seed does not affect the

impact resistance of the composite material at either 25°C (2.4 ft lb/in. for both samples), or at -20°C (2.0 ft lb/in.).

Nevertheless, it must be noted that the shell thickness of these structured latex particles was approximately 50 nm and that such a thick shell may have hindered the effect of the degree of crosslinking of the poly(*n*-butyl acrylate) (PBA) seed. Upon decreasing the shell thickness from 50 to 25 nm, it can be seen that sample 222, with 7 wt % crosslinker yielded a composite impact resistance of 2.8 ft lb/in., while structured latex sample 223, with a 1 wt % crosslinker improved the impact resistance of the PC composite up to 3.0 ft lb/in. Even though the differences in toughening are subtle, there seems to be an improvement in impact resistance by using thinner shells and lower degree of crosslinking. The difference in degree of crosslinking should be viewed in light of its influence on the degree of cavitation of the rubber particles. Higher degree of crosslinking leads to lower cavitation, which seems to be detrimental to toughening.

#### ***Influence of Molecular Weight and Composition of Shell Polymer***

When comparing the impact resistance of PC toughened by structured latex samples 224 and 225, which differ only in the lower concentration of chain transfer agent (CTA) used during the synthesis of the second stage of the latter sample, it is observed that toughening improved at lower CTA concentrations (2.8 ft lb/in. at 1 wt % isoctyl mercaptopropionate (IOMP) and 3.4 ft lb/in. at 0.7 wt % IOMP). This tendency seems to indicate that longer chains which may interdiffuse and form effective entanglements with the PC matrix enhance the toughening of the composite material by the presence of chemical adhesion forces. It can also be seen that impact toughening is greater for structured latex particles where the polystyrene (PS) content in the shell is greater. Sample 225 and 226 were synthesized under the same polymerization conditions, using the same amount of second-stage monomer. Sample 225 had a shell composition of 95/5 P(BM-St) and an impact resistance of 3.4 ft lb/in., while sample 226 had a shell composition of 100 PS and an impact resistance of 4.2 ft lb/in. The difference in toughening was accentuated when testing was carried out at higher temperatures. At 50°C the Izod impact test of samples 225 and 226 yielded impact resistances of 3.5 ft lb/in. and 13.4 ft lb/in., respectively.

Transmission electron micrographs of structured latex particles (Fig. 2 in Part II) revealed enhanced

tendencies of phase separation (more exposed PBA), with an increase in St content in the shell material. One would expect to achieve poorer dispersability of such particles in a glassy matrix, and hence less toughening. On the other hand, miscibility tests conducted earlier<sup>6</sup> and described in Part I of this series have indicated that factors such as branching and crosslinking, rather than molecular weight alone affect the miscibility of blends. As discussed previously, PBM yields high-molecular-weight polymers, but it is also prone to branching which limits interdiffusion and miscibility.

#### ***Influence of Rubber Loading Level***

Samples 226 and 246 are two batches with low (3 wt %) and high (5 wt %) loading levels of structured latex particles. Both were prepared by using the same structured latex comprised of a 1 wt % crosslinked PBA seed and a 100% PS second-stage synthesized in the presence of 0.7 wt % (based on monomer) CTA. Impact test results given in Table II indicate that a load increase from 3 to 5 wt % of PBA-PS latex particles is responsible for a significant improvement in the impact resistance of the PC composite. A 5 wt % loading had improved the impact resistance of PC at room temperature up to 14.3 ft lb/in., beyond the toughening achieved by 3 wt % loading at 50°C (13.4 ft lb/in.).

#### ***Influence of Particle Size of the Rubber Core Particles and Thickness of the Shell Polymer Layer***

A list of pendulum Izod impact resistance values for virgin PC and PC composites made by blending in the structured latex particles at a 5 wt % loading level is given in Table III as a function of the structured latex particle size and weight ratio of core-shell. The preparation and characterization of the two series of structured latexes (250s with small core rubber and, 260s with large core rubber particles) were discussed in Part II of this series.

A comparison of the Izod impact resistance values for notched bars prepared with the structured latex particles (samples 251 and 252) indicates that both structured latex particles improved the impact resistance of PC at room temperature. The impact resistance of virgin PC at room temperature is 2.9 ft lb/in. The impact resistance of PC after blending with structured latex samples 251 and 252 increased to 4.7 and 14.5 ft lb/in., respectively. Structured latex samples 251 and 252 were synthesized with the same small size of approximately 170 nm, 1% crosslinked PBA seed under the same polymerization conditions. The only difference between these

**Table II Pendulum Izod Impact Resistance of Polycarbonate Blends with 3 and 5 wt % Structured Latex Particles**

Latex Sample	BA-St Wt Ratio	Loading wt %	Impact Resistance (ft lb/in.) <sup>a</sup>			
			50°C	25°C	0°C	-20°C
226	0.91/1	3	13.4 ± 0.6	4.2 ± 0.2	—	2.4 ± 0.2
246	0.91/1	5	—	14.3 ± 0.2	5.6 ± 0.5	3.5 ± 0.4

<sup>a</sup> Average of 5 specimens.

two samples was in the amount of second-stage monomer used for the synthesis of the PBM shell. Sample 252 (the one with a thinner, 11-nm PBM shell) improved the impact resistance of PC three times as much as sample 251, with a thicker, 22-nm PBM shell. Even at 0°C, sample 252, with the thinner shell, appeared to induce a higher impact resistance (4.1 ft lb/in.) than sample 251 (3.7 ft lb/in.), although the difference was not as significant as at room temperature, especially since at low temperatures there was much greater scatter in the experimental results.

Comparing samples 252 and 253, which had the same core-shell ratio, it can be seen that sample 252 improved the impact of PC at room temperature (14.5 ft lb/in.) more than sample 253 (7.2 ft lb/in.), probably due to its better dispersability in the matrix, facilitated by the PBM patches spread over the PBA seed surface. The differences in morphologies of these structured latex particles prepared with CTA (253) and without CTA (252) were reported in Part II of this series (see Fig. 4, Part II). Another factor affecting the impact resistance of samples 252 and 253 is the molecular weight of the

glassy polymer. The second-stage polymer in sample 253 was synthesized in the presence of a CTA, while the second stage of sample 252 was synthesized in the absence of CTA, leading to longer polymer chains, which could entangle with the chains of the PC matrix, achieving interpenetration and adhesion between the rubbery discrete phase and the PC continuous phase.

Comparing the impact resistance induced by sample 252 at room temperature (approximately 14 ft lb/in.) to that of the 260 series (15 ft lb/in.), it is observed that there was no significant difference in the impact resistance as a function of particle size (the 250 series had a PBA seed particle size of approximately 170 nm, while the 260 series was based on PBA seed particles of 350 nm in diameter). However, when measuring the impact resistance of the same samples at 0°C, it was observed that the impact resistance was higher for the PC composite bars prepared with the larger seed latex, i.e., at a similar core-shell ratio, sample 264 (2.8/1 core-shell ratio), and sample 252 (2.3/1 core-shell ratio) yielded impact values of 6.5 and 4.1 ft lb/in., respectively. Moreover, comparing the impact of PC

**Table III Pendulum Izod Impact Resistance of Polycarbonate Blends with 5 wt % Structured Latex Particles**

Latex Sample	Seed Size <sup>a</sup>	PBA/PBM Wt Ratio	CTA	Calculated Shell Thick (nm)	Impact Resistance <sup>b</sup> (ft lb/in.)		
					25°C	0°C	-20°C
PC					2.9	2.9	2.9
251	S	1/1	No	22	4.7 ± 0.6	3.7 ± 0.6	—
252	S	1/0.435	No	11	14.5 ± 0.8	4.1 ± 0.4	2.9 ± 0.2
253	S	1/0.435	Yes	11	7.2 ± 1.7	4.0 ± 0.6	—
261	L	1/0.060	No	3	15.4 ± 0.4	9.4 ± 2.2	4.4 ± 0.2
262	L	1/0.123	No	7	15.4 ± 0.6	8.8 ± 1.9	4.8 ± 0.5
263	L	1/0.256	No	14	15.3 ± 0.4	6.2 ± 1.0	4.0 ± 0.4
264	L	1/0.357	No	18	15.5 ± 0.5	6.5 ± 0.6	3.4 ± 0.3

<sup>a</sup> S = small, ~ 173 nm; L = large, ~ 350 nm, based on CHDF analysis.

<sup>b</sup> Average of 5 specimens.

loaded with structured latex particles of similar shell thicknesses, it was seen that sample 252 with a calculated shell thickness of 11 nm had an impact resistance of 4.1 ft lb/in. while sample 262 with a calculated shell thickness of 7 nm and sample 263 with a calculated shell thickness of 14 nm had an impact resistance of 8 and 6.2 ft lb/in., respectively, at 0°C. Clearly, at a similar shell thickness, the larger particle size of the PBA seed had a stronger effect on improving the impact resistance of the PC matrix. Finally, at a temperature of -20°C, the impact of PC "toughened" with small latex particles sample 252 was 2.9 ft lb/in., the same as the impact resistance of virgin PC; while PC blended with the same weight load of structured latex particles, made of the larger PBA seed particles, yielded an impact resistance of more than 4 ft lb/in. The effectiveness of structured latex particles with larger seed size in toughening PC at low temperatures stems from their ability to cavitate and thereby enable the relief of local hydrostatic tension.

Considering the scatter in Izod impact resistance results observed at a temperature of 0°C, it appears that the fracture mode of PC composite bars varied randomly from ductile to brittle fracture, indicating that 5 wt % loading is near the limit of toughening for PC notched bars at a temperature of 0°C.

A comparison of 5 wt % loading of PBA-PS (sample 246, Table II) and PBA-PBM (all samples in Table III) shows that at room temperature PBA-PS synthesized in the presence of CTA was as good for toughening (14.3 ft lb/in.) as PBA-PBM of thinner shell thickness synthesized in the absence of CTA (14.5 ft lb/in.). At 0°C, toughening by PBA-PS (5.6 ft lb/in.) was greater than the impact resistance of PBA-PBM of comparable particle size (sample 252, 4.1 ft lb/in.), indicating that at lower temperatures adhesion between the discrete rubbery phase and the continuous glassy matrix gained importance. PBM, which is prone to branching, limits the interdiffusion between the shell polymer and the PC matrix preventing the formation of sufficient entanglements to provide adhesion forces.

At -20°C the impact resistance of the small size seed, PBA-PS latex particles (3.5 ft lb/in.) was within the toughening range achieved by the large size seed, PBA-PBM latex particles (260 series, between 3.4 and 4.8 ft lb/in.). It is worth noting that all comparisons are made as a function of total loadings and not in terms of rubber contents. However, for the cases of similar core-shell ratios, comparison can be made in terms of matrix ligament thickness (surface-to-surface distance). When structured latex particles are dispersed in a matrix, for the same

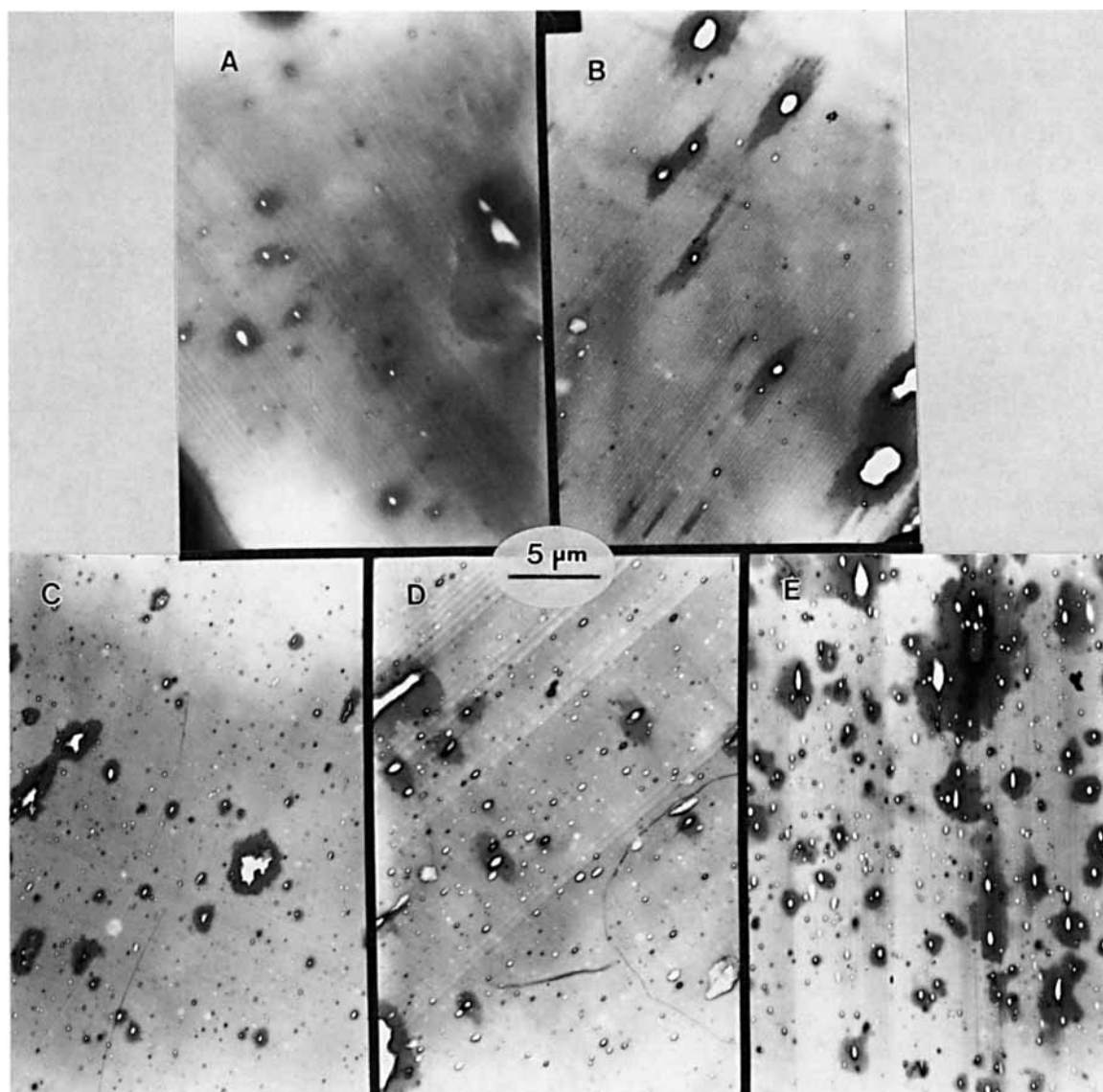
volume fraction of additive, the use of smaller size particles results in shorter surface-to-surface distances. It was observed that at lower temperatures a thin matrix ligament was not sufficient to dissipate the impact energy, and a minimum particle diameter was critical for improved impact toughness.

## DISPERSABILITY OF STRUCTURED LATEX PARTICLES IN POLYCARBONATE

Microtomed sections of PC composites made with 5 wt % PBA-PBM structured latex particles were examined by transmission electron microscopy (TEM). Micrographs of microtomed sections preferentially stained with ruthenium tetroxide ( $\text{RuO}_4$ ) vapors are displayed in Figure 1. PC and PBM stain similarly by the  $\text{RuO}_4$  vapors. Therefore, it is difficult to differentiate between the shell layer and the continuous phase or to observe the morphology of the structured latex particles. Nevertheless, a dark cloud is observed surrounding the particles, and its presence is intensified in the microtomed section of the PC blended with PBA in the absence of a PBM shell material. Trent et al.<sup>7</sup> reported that boundaries of stressed material, which were subsequently exposed to  $\text{RuO}_4$  vapors, were heavily darkened by the stain. Such an observation indicates that the PBA particles which are not protected by a shell polymer material are more prone to being stressed and deformed either during the melt processing stage in the extruder and injection of the composite bars or during the microtoming procedure. It is more likely for deformation to have occurred during the processing of the composite material and not during the microtoming because the orientation of the cloud does not always follow the direction of the microtoming knife. It is hard to evaluate the extent of clustering as a function of toughener composition since particles are microtomed at different positions relative to their centers and appear to be of different particle sizes. Nevertheless, some clustering was observed for all the PC composites.

## FINAL REMARKS

Glass transition temperatures ( $T_g$ ) for a range of St-BM compositions were determined and reported earlier<sup>6</sup> as described in Part I of this series. The results demonstrated a certain miscibility between PBM homopolymer and PC, as indicated by an intermediate  $T_g$ , and no miscibility at all for other St-BM copolymer compositions, including PS homo-



**Figure 1** Transmission electron micrographs of microtomed PC composites preferentially stained with  $\text{RuO}_4$  vapors. Loadings in PC composites are 5 wt % in micrographs (A) through (D) of PBA-PBM structured latex particles with core-shell ratios of (A) 1/0.435, PBM synthesized in the presence of CTA (sample 253); (B) 1/0.435, PBM polymerized in the absence of CTA (sample 252); (C) 1/0.357 (sample 264); (D) 1/0.060 (sample 261); and (E) PBA without shell.

polymer. Nevertheless, it was shown in this article that at constant loading, PBA-PS structured latex particles improve the impact resistance of PC more than PBA-PBM of comparable particle size and core-shell ratios. These seemingly contradictory results can be explained in terms of polymer chain length and chemical structure.

When the "shell systems" (St-BM latex particles) were polymerized, CTAs were introduced into the system to obtain a targeted molecular weight of

100,000 g/mol. In the presence of a CTA the polymer chain length is decreased, and very short polymer chains are not able to efficiently interdiffuse and interact with other polymer chains or polymer phases. Therefore, domains of miscibility, where both polymers coexist, are hard to find. It was discovered during the kinetic studies of St and BM polymerizations,<sup>6</sup> which are detailed in Part I of this series, that BM is not as susceptible to CTA, therefore, despite the presence of CTA, BM yielded higher

molecular weights than PS, which translate into longer chains, enabling interdiffusion and creating domains of miscibility with the PC.

When a monomer is polymerized as a second stage on a preexisting seed (as in core-shell structured latex particles), the kinetics of reaction as well as the final molecular weight differ from those resulting when carrying out a "single-stage" polymerization (as in the shell system study). In the case of toughening, not only is it necessary to achieve interdiffusion between the dissimilar polymers in the blend, but it is also necessary to obtain sufficient entanglement to provide adhesion between the continuous and the discrete phases. Chains with bulky pendant groups have greater difficulty in forming effective entanglements and therefore are unable to provide the necessary adhesion with the PC matrix. In PBM, the pendant group attached to the polymer backbone is larger ( $-\text{COO}-\text{CH}_2-\text{C}_6\text{H}_5$ ) than the pendant group attached to the polymer backbone in the case of PS ( $-\text{C}_6\text{H}_5$ ), and although interdiffusion of PBM and PC polymer chains is possible, the large pendant group restricts the flexibility and therefore the ability of the polymer backbone to bend and form effective entanglements. The large pendant group may also act as a plasticizer between the PBM backbone chains and the PC polymer chains, favoring slippage during deformation under applied stress. Also, we reported in Part I of this series that PBM is prone to branching and those branching are a limiting factor for interdiffusion.

## SUMMARY AND CONCLUSIONS

Pendulum Izod impact tests of composite PC notched bars revealed that higher impact resistance is induced by structured latex particles for which the shell was synthesized in the absence of a chain transfer agent indicating that the chain length and chemical structure of the interfacial layer play an important role in providing adhesion between the PBA discrete phase and the PC continuous phase. Also, a greater improvement in the impact resistance

when using particles with thinner shell layers indicates that an optimum shell thickness is necessary for the shell material to provide adhesion without restricting the ability of the rubber to induce ductility or to cavitate.

The effectiveness of impact toughening by structured latex particles is decreased as the testing temperature is lowered from room temperature. At room temperature, the toughening by small and large particles is of the same order of magnitude. However, at lower temperatures, higher impact resistance is achieved by using larger structured latex particles, i.e., at low temperatures thin matrix ligament alone is not enough for toughening of  $\frac{1}{4}$ -inch notched PC composite bars and a minimum particle size is required in order to improve the impact resistance.

Transmission electron micrographs of microtomed sections of preferentially stained PC composites indicate increased deformability of the particles at lower shell thickness.

This work was supported in part by EniChem America Inc.

## REFERENCES

1. M. Ma, K. Vijayan, J. Im, A. Hiltner, and E. Baer, *J. Mat Sci.*, **24**, 2687 (1989).
2. G. Cigna, C. Maestrini, L. Castellani, and P. Lomellini, *J. Appl. Polym. Sci.*, **44**, 505 (1992).
3. D. Haderski, K. Sung, J. Im, A. Hiltner, and E. Baer, *J. Appl. Polym. Sci.*, **52**, 121 (1994).
4. K. Sung, D. Haderski, A. Hiltner, and E. Baer, *J. Appl. Polym. Sci.*, **52**, 135 (1994); **52**, 147 (1994).
5. C. Cheng, A. Hiltner, E. Baer, P. R. Soskey, and S. G. Mylonakis, *J. Appl. Polym. Sci.*, **52**, 177 (1994).
6. I. Segall, Structured Latex Particles for the Toughening of Polycarbonate, Ph.D. Dissertation, Lehigh University (1992).
7. J. S. Trent, J. I. Scheinbein, and P. R. Couchman, *Macromolecules*, **16**, 589 (1983).

Received September 12, 1994

Accepted November 16, 1994