Toughening Modification of PS with *n*-BA/MMA/Styrene Core–Shell Structured Copolymer from Emulsifier-Free Emulsion Polymerization

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ABSTRACT: Core–shell structured particles, which comprise the rubbery core and glassy layers, were prepared by emulsifier-free emulsion polymerization of poly(*n*-butyl acrylate/methyl methacrylate)/polystyrene [P(*n*-BA/MMA)/ PS]. The particle diameter was about 0.22 μm, and the rubbery core was uncrosslinked and lightly crosslinked, respectively. The smaller core–shell structured particle–toughened PS blends were investigated in detail. The dynamic mechanical behavior and observation by scanning electron microscopy of the modified blend system with core–shell structured particles indicated good compatibility between PS and the particles, which is the necessary qualification for an effective toughening modifier. Notched-impact strength

and related mechanical properties were measured for further evaluation of the toughening efficiency. The notched-impact strength of the toughened PS blends with uncrosslinked particles reached almost sixfold higher than that of the untoughened PS when 15 phr of the core–shell structured particles was added. For the crosslinked particles the toughening effect for PS was not obvious. The toughening mechanism for these smaller particles also is discussed in this article. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1290–1297, 2003

Key words: core–shell structured particles; emulsifier-free latex; toughening; polystyrene modification

INTRODUCTION

Polystyrene (PS) is a typical example of a brittle thermoplastic, and over the last several decades many efforts have been made to improve its fracture resistance. According to the literature, modifiers for toughening PS can be divided into two classes: (1) blending with rubbery materials, for example, styrene–butadiene rubber (SBR), a styrene–butadiene–styrene copolymer (SBS), natural rubber (NR),[1,2] polybutadiene (PB),[3–5] or ethylene propylene rubber (EPR)[6–9]; however, with this modification method the aging resistance is poor if the modifiers are polybutadiene (PB) or PB-containing copolymers, which have double bonds and are immiscible with PS. Furthermore, there are processing difficulties when a rubber is used as the modifier. (2) Blending with plastics such as polyethylene (PE),[10–17] polypropylene (PP),[18–22] ethylene–vinyl acetate copolymer (EVA),[23] polycarbonate (PC),[24–26] or polyamide (PA).[27,28] The improvement in impact strength for these blending systems is very limited, although many new properties can be provided. Because acrylate elastomers do not have double bonds or the degree of unsaturation is very low, the

aging resistance and processing properties of acrylate/PS blends are very good; thus, adding acrylate elastomer to a toughened system is one of the most promising ways to modify PS.

Emulsion polymerization is used to prepare the toughening of acrylate rubbery particles, which typically comprise rubbery cores and glassy outer layers. This route to rubber-toughened PS has the distinct advantage of allowing independent control of the properties of the matrix PS, composition, morphology, and size of the dispersed rubber phase and the level of inclusion of the toughening particles, compared to other toughened polymers such as poly(methyl methacrylate) (PMMA),[29] poly(vinyl chloride) (PVC),[30,31] polycarbonate (PC),[32–34] and epoxy resin,[35–37] for which there have been relatively few investigations into their preparation, properties, and deformation behavior.[42,44]

Some investigations have already been done on the morphology and dynamic mechanical properties of poly(*n*-butyl acrylate/methyl methacrylate)/polystyrene [P(*n*-BA/MMA)/PS] core–shell particles prepared by emulsifier-free emulsion polymerization.[38] This article explores the possible applications of core–shell particles in the modification of PS as an impact modifier. The preparation, mechanical properties of toughened materials, and toughening mechanism of smaller particles (about 0.22 μm) are described and discussed critically.

TABLE I
Composition of Modifier for the PS System

No.	Step A (g)		Step B (g)
	MMA	BA	styrene
1	4	36	60
2	5	45	50
3	6	54	40
4	7	63	30
5	8	72	20
6	9	81	10

EXPERIMENTAL

Materials

Polystyrene was obtained from Beijing Yanshan Petrochemical General Co. (Beijing, China) in pellet form, with $\rho = 1.05$ g/cm^3; $\bar{M}_{macr};\bar{n}_{macr} = 1.6 \times 10^5$; the antioxygen, 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl) butane, $C_{17}H_{25}O_3$, was produced by the Tianjin Lisheng Chemical Plant (Tianjin, China). Poly(n-butyl acrylate/methyl methacrylate)/polystyrene [P(n-BA/MMA)/PS] core–shell structured particles were synthesized by emulsifier-free emulsion polymerization in our lab.[38] Recipes for the emulsifier-free emulsion polymerization used are shown in Table I.

For each type of toughening particle, the latex obtained from emulsion polymerization was coagulated by addition to the magnesium sulfate solution to yield loose aggregates of the particles. These were isolated by filtration, washed thoroughly with water, and then dried at 40°C under vacuum.

Sample preparation

Blends of PS/core–shell structured particles were melt-prepared on a laboratory two-roll mill (made at the Tianjin Mechanical Plant) at 190°C for 5 min, with rotational speeds of the rolls of 21 and 25.5 s^{-1}.

Specimens used for impact and tensile testing were prepared using an SL-45 compression molding machine operated at a temperature of 190°C and a pressure of 19 MPa. The specimens were kept at 23°C ± 2°C for at least 12 h before mechanical testing.

Characterization

The glass-transition temperature (T_g) of the core–shell structured copolymers, from the peaks of the tan δ temperature curve, was investigated by dynamic mechanical analysis (DMA; Netzsch DMA 242 dynamic viscoelastic spectrograph, Germany) at a test frequency of 3.3 Hz, with a heating rate of 2°C/min and a sample size of 2 × 0.2 × 0.020 cm^3.

Notched-impact strength was determined with a Charpy XCJ-500 impact tester. Tensile properties were measured according to ASTM Standard D 1708 using a M500 10AX Testometric universal tester (UK). All mechanical testing was performed at 23°C ± 2°C, and at least six specimens were tested for each value given. Impact fracture surfaces of compression-molded samples were characterized for the phase morphology using a Hitachi X-650 scanning electron microscope (SEM) operating at 20 kV.

RESULTS AND DISCUSSION

Preparation of core–shell structured latex

High-solid-content (60 wt %) core–shell structured emulsifier-free latices for (n-BA/MMA)/St monomers were prepared by a semicontinuous polymerization procedure in the presence of 3-allyloxy-2-hydroxyl-propanesulfonic salt. The design of the toughening particle took into account a number of general requirements. It is important to have an outer glassy layer for each type of toughening particles. There were two aims: to prevent coalescence of primary particles during formation and drying of the coagulum produced from the latices, thus enabling good dispersions of the primary particles to be produced pon blending of the coagulum with the matrix PS; and to mix with the matrix PS, thereby providing a means of stress transfer from the matrix to the particles in the modified PS. A further consideration in the design of the toughening particles is the need for grafting at the interface in the particles and for crosslinking in each of the inter-
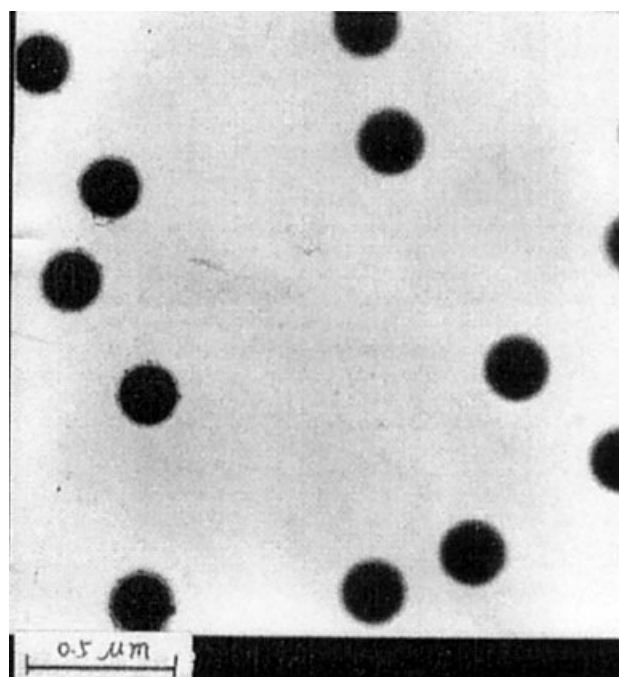
Figure 1 Transmission electron micrograph of poly(n-butyl acrylate/methyl methacrylate)/polystyrene core–shell structured particles (sample 4).
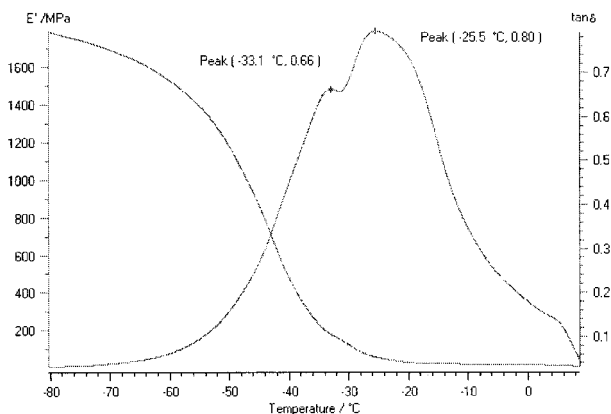
Figure 2 DMA spectrum of the modifier (sample 4).

nal phases. Grafting at interfaces is required for stress transfer between the two layers in the particles. Crosslinking should be necessary for the core component in order to prevent loss of particle integrity upon blending with matrix PS at high temperature. The outer glassy layer does not need to be crosslinked because it is graft-linked to the rubbery core around which it is formed. This has the advantage of making easier and more efficient the mixing of the outer glassy layer with the matrix PS than would be possible for an outer glassy layer that was both graft-linked and crosslinked.

It was thought that the modifiers should be designed to have a rubbery core that used the soft BA monomer as the main component and a glassy shell that used the hard St as the main component. The latex particles prepared in our laboratory were uniform, and the diameter of the latex particle was about 0.22 μm (see Fig. 1).

Dynamic mechanical properties of PS/core–shell structured particle blends

The DMA spectrum of one core–shell modifier is given in Figure 2. It shows that the main relaxations were at
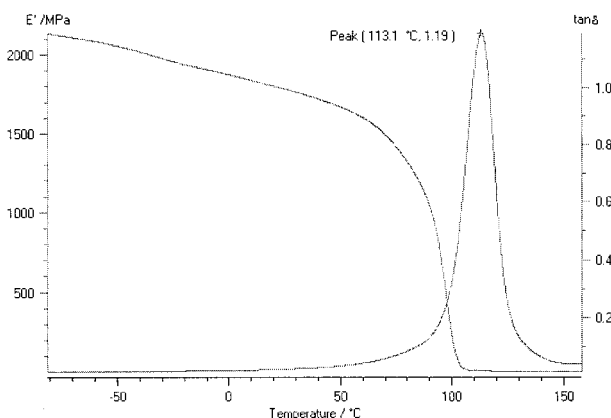
TABLE II
Dynamic Mechanical Properties of the Modified PS system

Modifier content (phr)	T_{g1} (°C)	T_{g2} (°C)
0	113.1	—
5	114.4	−31.1
15	84.4	−34.7
30	74.0	−32.9

−33°C and −26°C, which were related to the movement of chain segments for n-BA/MMA copolymer and n-BA/MMA and a small amount of St copolymer, respectively. Figure 3 shows the dynamic mechanical properties of pure PS, which has one sharp tan δ peak at 113.1°C. The DMA results illustrating the temperature dependence of the storage modulus (E') and loss tangent (tan δ) of the modified blends are shown in Table II. The presence of two peaks in the blends shows that there are two phases in the blends. The T_{g1} peak, in the high-temperature area, can be attributed mainly to the PS chain segments, and the T_{g2} peak, in the low-temperature area, is affected by that of the n-BA/MMA copolymer. Table II and Figures 4 and 5 show that the T_{g1} peak obviously shifted to the low-temperature area with the addition of core–shell structured modifier, with no visible change for the T_{g2} peak, as seen in Figure 6. This demonstrates that chain movement of PS was more easily affected by the rubbery modifier than the rubbery modifier was affected by PS. The chain segments of the rubbery phase, which had great freedom before the movement of the PS chain segments began, can improve the free volume for the blends, resulting in a decrease in T_{g1}. This effect was enhanced with an increase in the rubbery free volume, but not in a linear fashion. For example, for an addition amount in the range of 0–15 phr, the difference in T_g was 30°C; for an addition in the range of 15–30 phr, it was 10°C (as shown in Table I). The
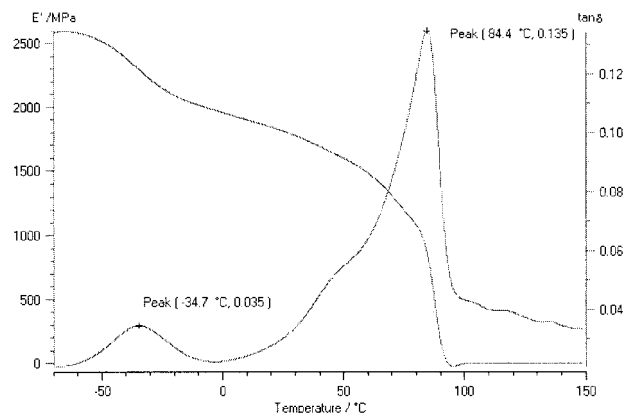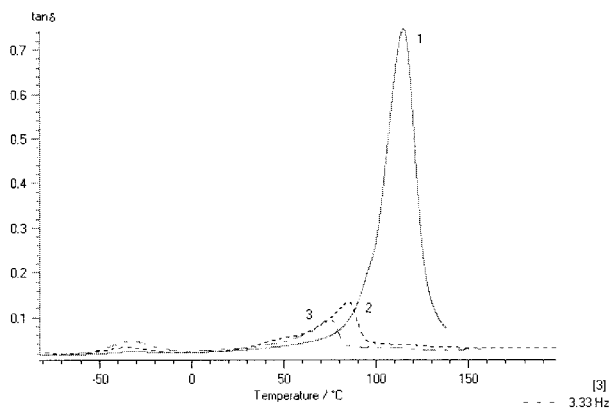

Figure 3 DMA spectrum of polystyrene.

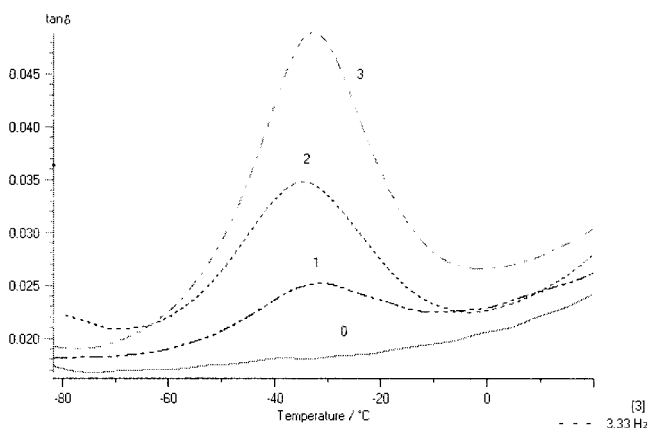
Figure 4 DMA spectrum of modified PS with 15 phr modifier.

Figure 5 Tan δ curves of the modified PS with different amounts of modifier (1: 5 phr; 2: 15 phr; 3: 30 phr).

dynamic mechanical behavior of the core–shell structured particle modified blend system discussed above indicated good compatibility between PS and the particles, which is the necessary qualification for an effective toughening modifier.
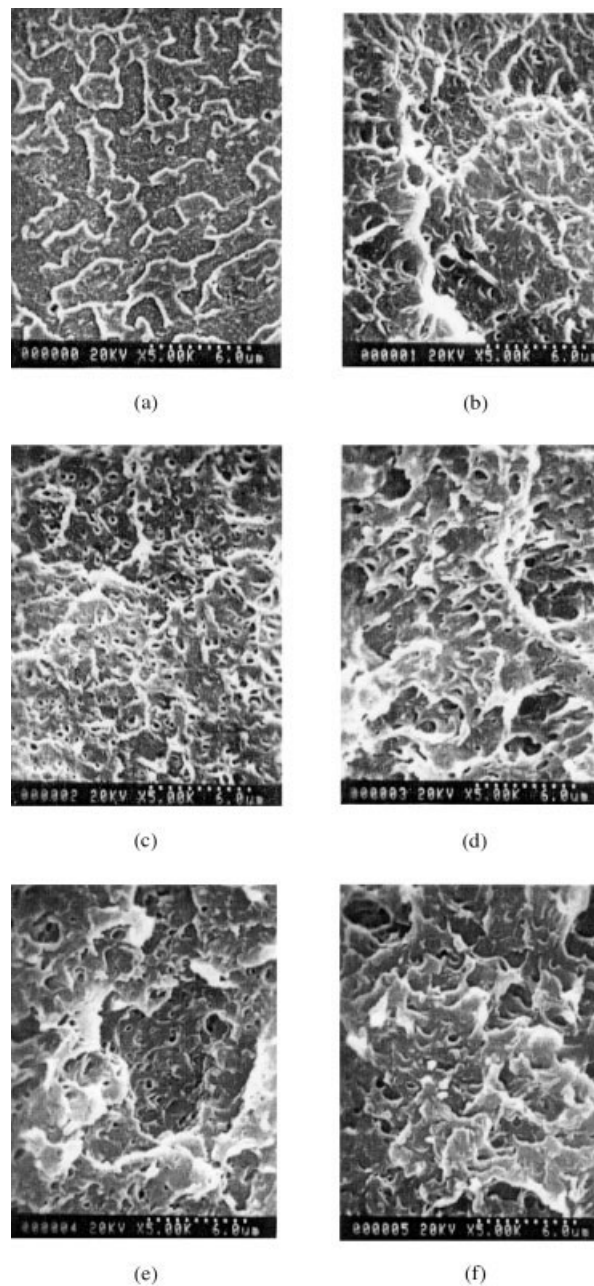
Morphology of PS/core–shell structured particle blends

Figure 7 shows the SEM photographs of the impact fracture surfaces for the core–shell structured particle-toughened specimens. The white stress stripes in Figure 7(a) are traces of stress in a propagating process for unmodified PS. There is no longitudinal extending for the stress stripes, which display the typical features of brittle fracture. However, there is a large range of stress stripes and cavities in the fracture surface of modified PS. These structural traits can be considered the marks of stress dispersion and longitudinal extension [see Fig. 7(b–d)].

In addition, Figure 7 shows that the average dimension of the dispersed phase of the core–shell struc-


Figure 7 Scanning electron micrographs of PS/modifier blends with different amounts of modifier: (a) pure PS, (b) 5 phr, (c) 10 phr, (d) 15 phr, (e) 20 phr, and (f) 30 phr.

tured particles in the PS matrix was less than 0.5 μm. This demonstrates good dispersion for the toughening particles in the PS matrix.

Mechanical properties
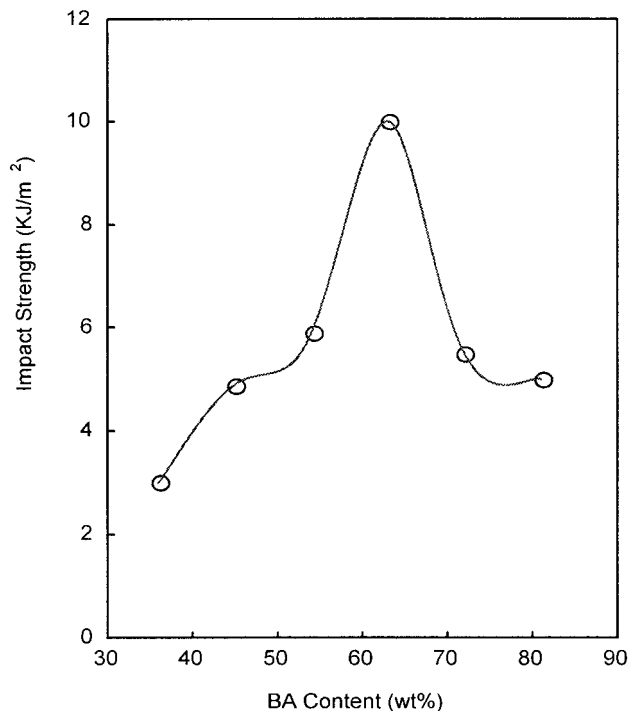
Impact properties

The thinking in the design of the modifiers was to have a rubbery core with the soft *n*-BA monomer as the main component and a glassy shell with hard St as the main component (see Table I). As shown in Figure

Figure 6 Tan δ curves of the modified PS in the low-temperature region with different amounts of modifier (0: unmodified PS; 1: 5 phr; 2: 15 phr; 3: 30 phr).
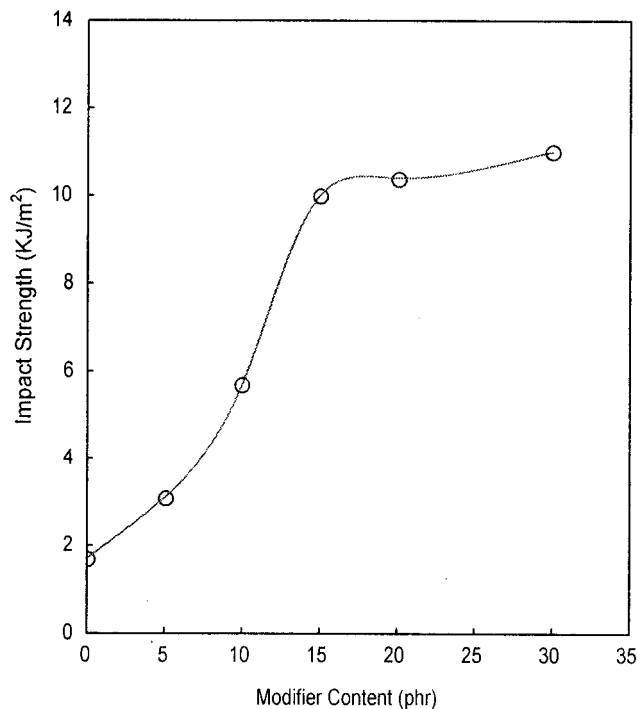
Figure 8 Effect of modifier content on impact strength of modified PS (modifier 4).

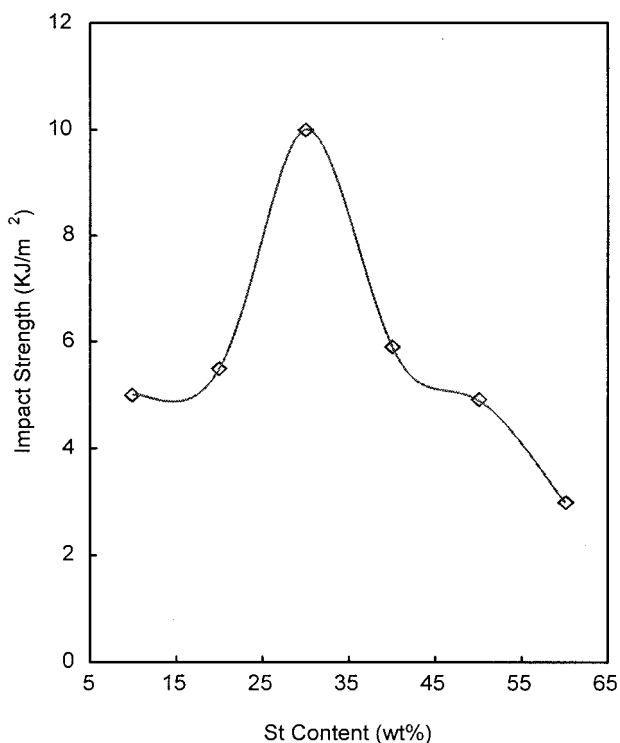**Figure 9** Influence of BA content in the composition of modifier on impact strength of modified PS.

8, the notched-impact strength of the unmodified PS was 1.7 kJ/m^2. The toughness was very poor. However, the impact strength increased dramatically with an increase in the quantity of core–shell structured particles (modifier 4; see Fig. 8). For modifier 4, impact strength was largest, about sixfold higher than that of pure PS, when the amount added was increased to 15 phr. The notched-impact strength increased less obviously when the amount of modifier added was more than 15 phr. Therefore the amount of modifier added was fixed at 15 phr, and the toughening effect of a series of modifiers with different monomer compositions was checked, as can be seen in Figures 9 and 10.

Figure 9 shows that notched-impact strength of the modified PS had its top value with an increase in the amount of *n*-BA component added to about 70 wt %. Additional increases of *n*-BA caused the impact strength to decrease. For the St component in the modifier shell, as shown in Figure 10, the notched-impact strength of the modified PS also had its top value when the St component of the particle was up to 30 wt %. In addition, when the St content of the modifier was high (e.g., modifier 1), the modifier easily blended uniformly with PS, and there were good plastic and flow properties for the blend in its melted state. When *n*-BA content of the modifier was high and St was low (e.g., modifier 6), the melt flow property was poor in the melt-blending processing. This phenomenon shows that when St content of a modifier was high, there was good compatibility between the modifiers and PS. However, if the rubbery phase (*n*-BA com-

ponent) in the modifier was too low to absorb energy effectively in the failure process, then the toughening effect was not enough.

Figure 10 Influence of St content in the composition of modifier on impact strength of modified PS.

TABLE III
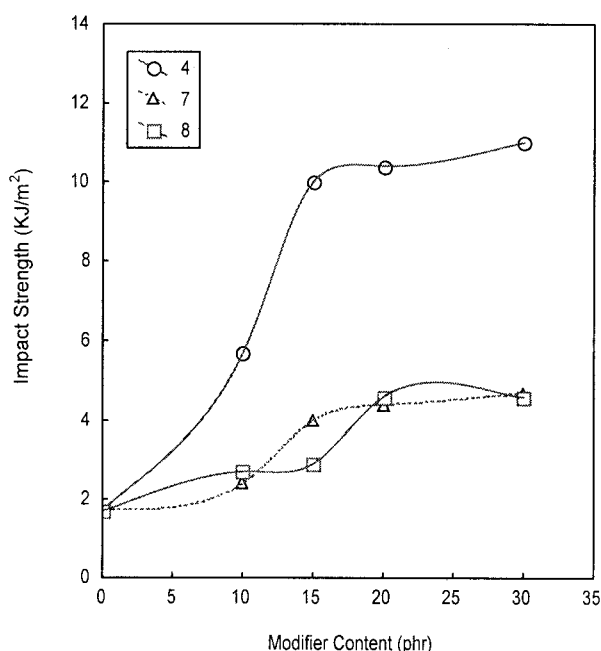**Recipe for the Copolymers that Contained Crosslinker**

No.	Step A (g)			Step B (g) styrene
	MMA	BA	TAIC	
4	7	63	0	30
7	7	63	0.49	30
8	7	63	0.70	30

The microstructure of core–shell structured particles has a strong impact on toughening effectiveness. Therefore, core–shell structured particles with different degrees of crosslinking for the core part were prepared in our laboratory. The recipe for the copolymers containing a crosslinker is shown in Table III. Figure 11 shows that in this case notched-impact strength decreased with the introduction of crosslinker in the core part. This can be attributed to the decrease in chain movement ability. Deformation is very difficult for small crosslinking rubbery particles, which cannot initiate and stop crazes effectively; thus, impact strength decreases.
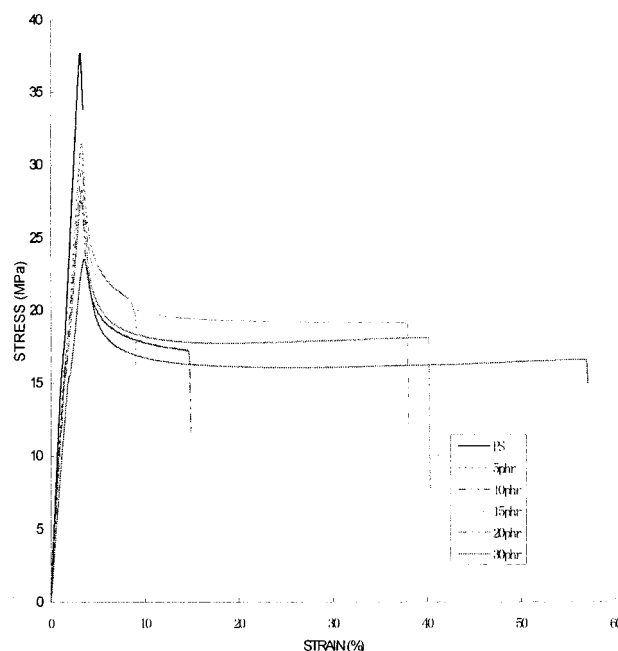
Stress–strain behavior of toughened PS

The stress–strain behavior of the toughened PS blends is listed in Figure 12. Multiple crazes (stress whitening) were formed for the toughened PS blend when strain reached 1.5% (see Fig. 12) in the tensile process.

Experimental results indicate that the yielding stress and elastic modulus for the toughened PS blend, as seen in Figures 13 and 14, were all decreased to some
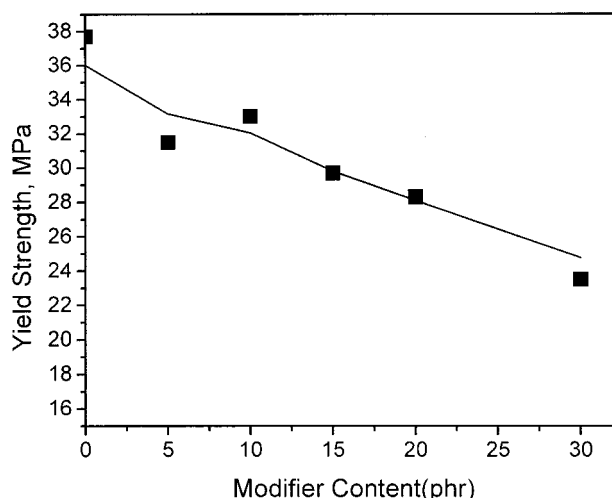
**Figure 12** Strain–stress curves of modified PS systems with different contents of modifier.

extent with increases in the amount of core–shell toughening modifiers. More stress concentration points will be formed with the addition of modifier, which initiates and stops the craze-forming process. Thus, deformation energy was assimilated, and the yield stress decreased (Figs. 13 and 14).

Toughening mechanism of smaller particles

This article has focused on the toughening effect of smaller core–shell particles (average diameter was about 0.22 μm) on polystyrene because small particles (<1 μm) can be obtained easily and economically on

Figure 11 Influence of crosslinking of the core component of the modifier on impact strength of modified PS.

Figure 13 Effect of modifier content on yield strength of modified PS.
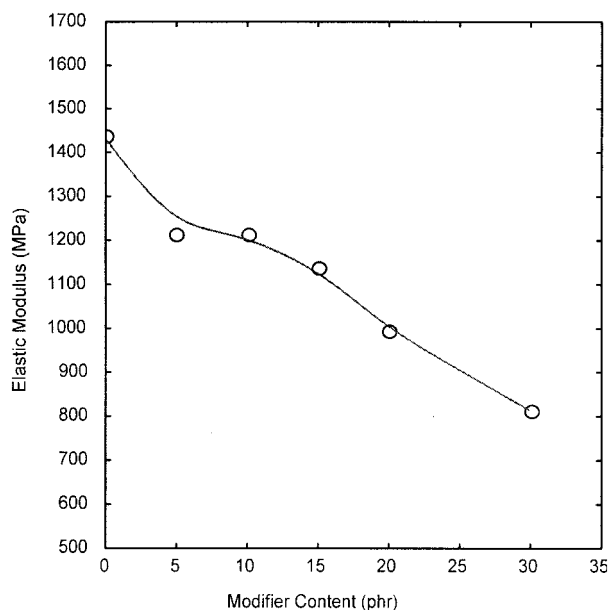
Figure 14 Effect of modifier content on elastic modulus of modified PS.

an industrial scale and do not need specialized techniques.

Much work has been done on the particle-size effects in rubber-toughened materials. Donald and Kramer[39] showed that crazes rarely nucleated from particles of less than 1 μm in diameter in HIPS. Because the crazing region in polystyrene must be initiated approximately three fibril spacings, or about 0.75 μm, from the surface of the particle, they argued that the particles must be larger than 1 μm in diameter for effective craze nucleation. They also speculated that the toughening process might be dependent on internal particle morphology.[40]

Wu[41] investigated the effect of particle diameter on nylon–rubber blends and found that impact energy decreased markedly as particle size increased at a constant rubber volume. He suggested that particle spacing must not exceed a critical distance for optimal toughness. And Wu's work demonstrated that the smallest-diameter rubber particles appear to be the most effective in shear-yielding polymers.

Recently, the work of Okamoto et al.[42] showed evidence of craze initiation and termination from smaller particles (0.2 μm) during the fracture process, and Grocela and Nauman[43] found that small particles could toughen polystyrene because craze initiation would occur from smaller particles during a fracture event.

The results of a study by Cook[44] suggested that large rubber particles (> 2 μm) with a lightly crosslinked rubber core and outer polystyrene shell were necessary for both initiating and controlling craze breakdown in polystyrene.

The above information implies that: (1) rubber particle size plays an important role in the toughness of polymer rubber blends, and both large particles and small particles have the capability of initiating and terminating crazes; (2) many factors, apart from rubber particle size and size distribution, determine the degree of toughening, including rubber phase/matrix adhesion, rubber content and phase volume, relaxation behavior of rubber (T_g), and composition of the matrix; (3) theoretical models on rubber particle–toughened polystyrene are effective only for special systems and special conditions.

The experimental results in our laboratory indicated an obvious toughening effect of uncrosslinked small particles in polystyrene, implying that those small particles can initiate and terminate craze processing. Although initiating and stopping effectiveness may be very low for a single rubbery core–shell particle, the number is much larger at a given rubbery content for small particles. Thus, initiating and terminating effectiveness are still very high. For crosslinked small particles, if the chain movement of the rubbery core part was limited to some extent, then the capacity to initiate, stabilize, and stop the generation and growth of crazes in the polystyrene matrix was decreased.

CONCLUSION

The dynamic mechanical behavior of the core–shell structured particle modified blend system indicated good compatibility between PS and the particles, which is the necessary qualification for an effective toughening modifier.

The impact strength of the toughened PS was considerably improved by the amount of the poly[(n-BA/MMA)/St] core–shell structured particles added. When the amount of core–shell particles added was 15 phr, impact strength was almost 6 times higher than that of the untoughened PS. A BA component in the core of about 70 wt % and St in the shell of 30 wt % was the optimum composition of core–shell particles to produce an excellent toughening effect. This indicates that smaller core–shell particles (0.22 μm average diameter) without core phase crosslinking also have obvious toughening effectiveness for polystyrene.

The SEM showed that the fracture surface of pure PS was smooth and neat, the typical feature of brittle fracture. For the toughened PS, widespread stress stripes and cavity structures, the traits of a typical toughening fracture, were evident in the SEM micrographs.

For the toughening mechanism of uncrosslinked small particles, although the initiating and stopping effectiveness may have been very low for a single rubbery core–shell particle, but the number was much larger at a given rubbery content for small particles.

Thus, initiating and terminating effectiveness were still very high.

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