NOTES

Compatibility Effect of Added Graft Copolymer on Polystyrene and Polyacrylate Rubber Blend

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(Received May 22, 1989)

Rubber-toughened plastics have been studied for many years, but researchers are still interested in such a project.[1] Early work was directed at modifying polystyrene (PS), but simple blend of rubber with PS was hard to improve the impact strength of this glassy polymer. It is now understood that occlusion of PS into the rubber phase plays an important role for high-impact PS(HIPS)[2,3] and the block or graft copolymers could be used as compatibilizers to improve the interfacial situation between the plastic and rubber phases. However, the block copolymers have been more widely used as compatibilizers for these systems than the graft copolymers, because the molecular structures of these graft copolymers, which were usually prepared by chemical grafting reactions, were hard to characterize and the experimental technique for controlling these grafting reactions was limited as well.[4,5]

In this article, well-defined graft copolymers were prepared by copolymerization of butyl acrylate and PS macromonomers which were synthesized by anionic polymerization. These graft copolymers were used as a compatibilizer for PS and polyacrylate rubber (PAR) blend systems. The mechanical properties of these

blends containing different contents of graft copolymer were measured and correlated with microstructures of those graft copolymers as well as the morphologies of the interface between the PS and PAR phases.

EXPERIMENTAL

The graft copolymers having poly(butyl acrylate) (PBA) as backbones and PS as side chains were prepared by free radical copolymerization of butyl acrylate and PS macromonomers which were synthesized by anionic polymerization with n-BuLi as an initiator. All the procedures of synthesis, separation and characterization for these PS macromonomers and graft copolymers have already been described elsewhere.[6] The characterization of these graft copolymers is listed in Table I.

A daily use grade of PS($M_n = 13.8 \times 10^4$) was supplied by Shanghai Gaoqiao Chemical Company, and the PAR(Cyanaeryl L, $M_n = 38.8 \times 10^4$ measured by GPC) was supplied by Cyanamid Company. The binary blend of PS with 20% by weight PAR was prepared by compounding on a heated two-roll mill around 423 K (The PS was milled for

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Table I. Characterization of graft copolymers

Sample No.	MW of PS macromonomer $\times 10^3$	Composition of graft copolymer, wt%		MW of graft copolymer $\times 10^4$	Average number of grafts n
		St	BA		
G-1	3.0	29.9	70.1	9.2	9.2
G-2	5.9	28.0	72.0	10.7	5.1
G-3	6.6	33.6	66.4	/	/
G-4	9.7	37.6	62.4	12.0	4.7
G-5	15.7	35.0	65.0	15.9	3.5

2 min first. Then the PAR was added and milled with PS for another 8 min). The ternary blends of PS with 20% (by wt) PAR containing various proportions of graft copolymers were prepared on the same equipment at about 423 K by the following procedures. The PS was milled first for 2 min and the PAR was added and milled with PS for another 5 min. After that, the graft copolymer was added and milled with them for 5 min. All these blended materials were compressed in a mould at 448 ± 5 K for 10 min (apparent pressure, 4.9 MPa) and at ambient temperature for another 15 min (apparent pressure, 14.7 MPa) to make plates for testing the mechanical properties.

Tensile and bending test specimens were made of these molded plates in accordance with GB 1040-70 and GB 1042-79, respectively, and kept at 298 K for 24 h before testing. The tensile and bending strength measurements were conducted on a Shimadzu AG-200A testing machine at 298 K. The charpy impact test specimens were prepared according to GB 1043-79 and were measured on a charpy tester made by WPM, Leipzig at about 298 K.

Dynamic mechanical properties were measured by using a Viscoelastometer (Rheovibron DDV-III-EA) at 11 Hz and 2 K min^{-1}. Samples were cut from the molded plates ($70 \times 8 \times 3$ mm) and their surfaces were polished. For investigation with a scanning electron microscopy (Stereoscan 250 MK3, Cambridge), the samples were taken from these charpy impact test specimens fractured after impact-

Table II. Mechanical properties of PS/PAR blend systems[a]

Graft copolymer content[b] pph[c]	Impact strength KJm^{-1}	Tensile strength MPa	Bending strength MPa
0	1.65	13.7	32.0
2	3.32	14.3	30.3
4	4.84	14.2	30.4
5	5.64	15.4	33.5
6	8.01	18.8	40.7
7	6.67	17.4	37.1

[a] Impact, tensile and bending strengthes for pure PS were 2.75 KJm^{-2}, 30.5 MPa, and 45.6 MPa, respectively.
[b] MW of PS side chain is 15.7×10^3.
[c] Parts per 100 of base blend.

ing measurements, and cut into $5 \times 5 \times 2$ mm. The surfaces of these samples were coated by gold vapor before examining. The contact angles of water drops on these blend surfaces were measured at ambient temperature with an instrument made by our laboratory.

## RESULTS AND DISCUSSION

Mechanical Properties

The mechanical properties for PS/PAR simple blend (binary blend) and the ternary blends [PS/PAR/P(BA−g−St)] are given in Table II. The simple blend of PS and PAR shows quite poor impact strength, as might be expected, because there is only partial com-

patibility between the PS and PAR phases.[7] The ternary blend systems, however, exhibit better impact strength than the simple blend. The impact strengthes for those three component systems are enchanced with increasing proportion of graft copolymer and it produces the best impact strength at 6 pph addition of graft copolymer among all the samples. In such a case, the impact strength of this ternary system containing 6 pph graft copolymer is approximately 4 times higher than that of specimen without graft copolymer (binary system) and twice that of pure PS. Thus, it seems likely that the adhesion between the rubber particle and plastic matrix may be enhanced by adding graft copolymer so as to increase the toughness for these ternary blends. Improvement in adhesion between the two phases and impact resistance is often achieved by adding some graft copolymers for PS/polybutadiene and PS/low-density polyethylene blend systems.[8-10]

Table II shows that the tensile and bending strengthes of the PS/PAR simple blend are much lower than that of pure PS. This observation is broadly consistent with the observation of other workers for the rubber-toughened plastics.[11] For the ternary blend systems, however, these two mechanical properties are improved and the improvement is greatest for a blend containing 6 pph graft

Figure 1. Impact strength for PS/PAR blends containing graft copolymers having various length of side chains.

copolymer. It is clear that the graft copolymer added here has more marked effect not only on impact strength but on tensile and bending strengthes as well.

Figure 1 shows the relationship between the impact strength and molecular structure of graft copolymers for these ternary blends. It indicates that the impact strength of the blend system increases with increase of PS side chain length of graft copolymer added over the range studied, and there is a discontinuously curved impact strength profile on this plot. The impact strength increases appreciably when the number-average molecular weight (MW) of graft exceeds 6000. Milkovich pointed out that this kind of graft copolymer was easy to reveal microphase separation.[12] However, the so-called microphase separation for the graft copolymer composed of PBA backbone and PS branches was not observed until MW of the grafts was over 6000 and was not complete since the backbone and grafts had partial compatibility as reported previously.[13,14] Thus the plot in Figure 1 for the ternary systems, in which the curve sharply changed at about 6000 (MW), must result from the partial microphase separation of those graft copolymers at the interface. In this case, the PBA backbones exist as a continuous phase and the domains are formed by PS side chains. The partial microphase separation of these graft copolymers at the interface between the two phases could enhance the compatibility between the rubber and plastic phases, and give rise to better impact strength for blend systems. This suggests that these domains formed by PS grafts may have stronger interaction on the PS phase of the blend than those single grafts which have not enough length to cause partial microphase separation and form domains. On the other hand, these graft copolymers having longer PS branches and fewer grafts, as listed in Table I, might be much easier to locate at the interface between the two phases and their backbone (PBA) might also be easier to penetrate into PAR
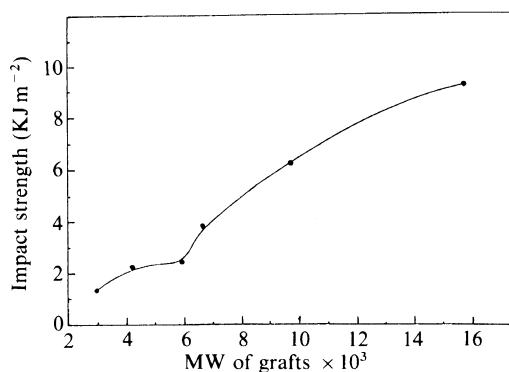
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phase than that having shorter branches and more grafts so as to promote the compatibility between these two phases. Thus, longer grafts, stronger interaction between the two phases and better impact strength should be obtained for those three component blend systems.

Morphology

In order to examine the influence of graft copolymer on the interface between the phases more directly, it is of interest to observe the impact fracture surfaces of the blend specimen using scanning electron microscopy (SEM). Figure 2 shows both fracture surfaces of the PS/PAR binary blend and ternary blend containing 6 pph graft copolymer. For simple blend of PS and PAR, it shows a typical brittle fracture which is similar to that of metal or

(a)

(b)
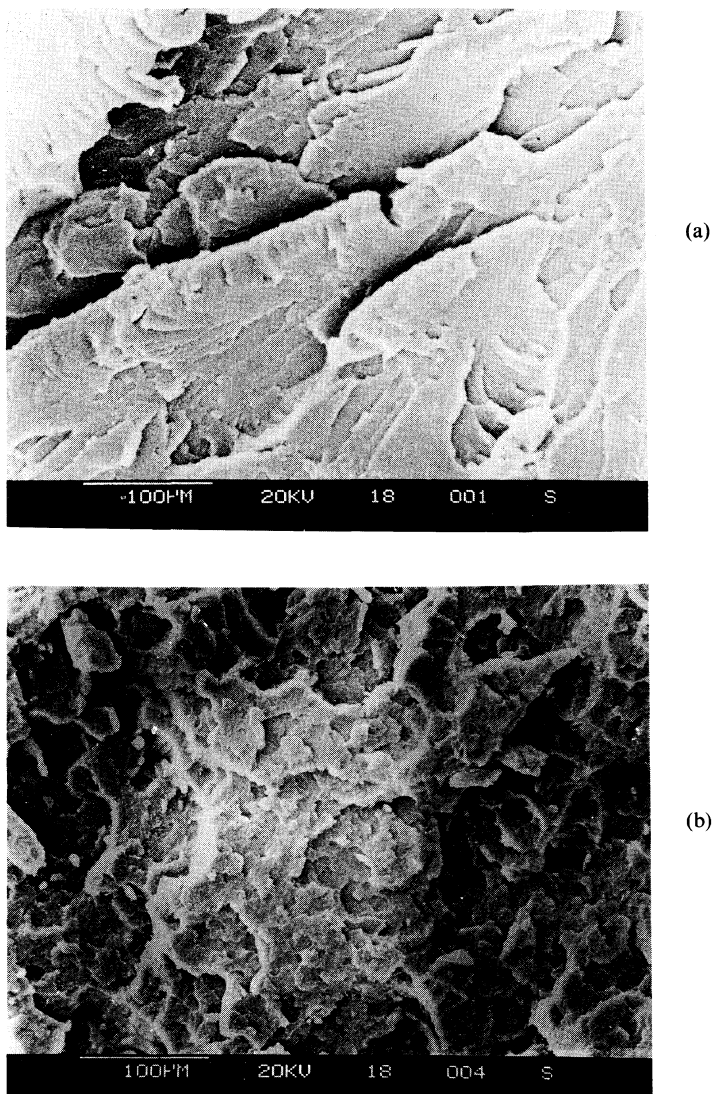
Figure 2. Scanning electron microphotographs of fracture surfaces of PS/PAR blend systems ($\times 250$): (a) without graft copolymer; (b) with 6 pph graft copolymer (MW of grafts, 15.7×10^3).

crystalline materials. For the ternary blend, however, the fracture is not so smooth as that of simple blend and the surface fracture levels become less and their convex fringes are much more rough. All these suggest that such a specimen containing 6 pph graft copolymer exhibits a tough fracture feature which is consistent with its mechanical properties tested and discussed above.

Figure 3 shows the variations in morphologies for these PS/PAR blend systems with the higher magnification SEM. Since the rubber phase was in a forced glassy state under the high rate impact condition, the deformation of rubber particles could be neglected while removal of them from the matrix during the fracture processes left craters. Thus, the morphologies for these blend systems could be

(a)

(b)
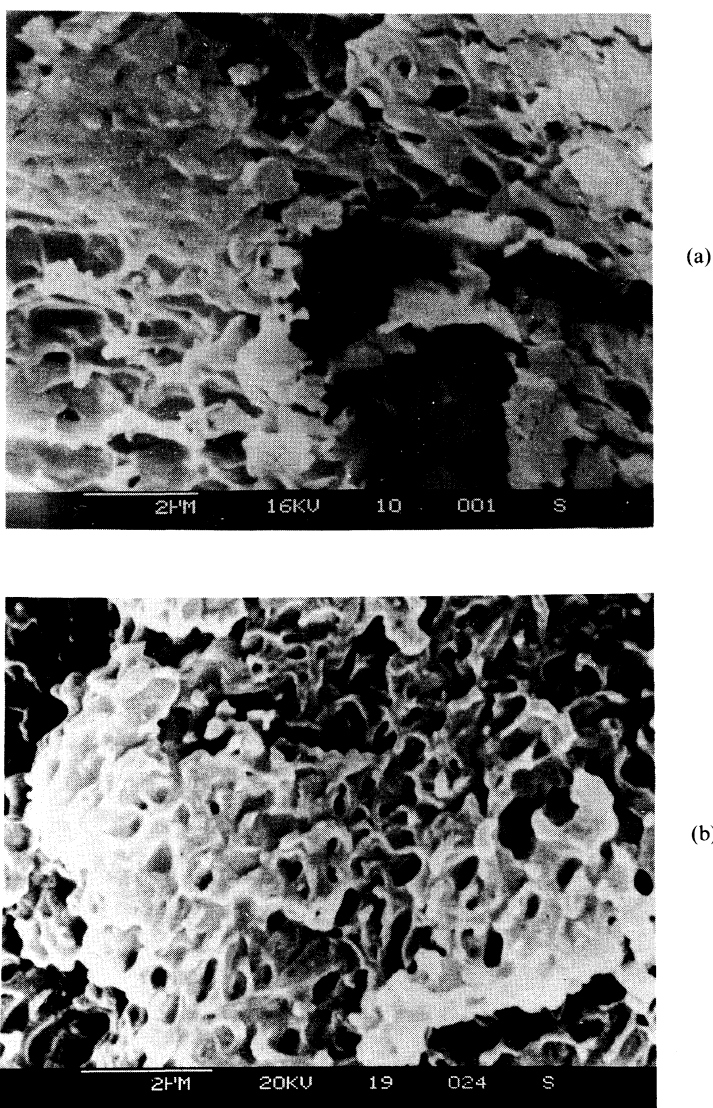
Figure 3. Scanning electron microphotographs of fracture surfaces of PS/PAR blend systems ($\times$ 10000): (a) without graft copolymer; (b) with 6 pph graft copolymer (MW of grafts, 15.7×10^3).

Table III. Second order transition temperatures (T_{g_2}s) of PS/PAR blend systems

Graft copolymer content[a] pph	T_{g_2} K	MW of side chains of graft copolymer[b] $\times 10^3$	T_{g_2} K
0	255	3.0	255
4	257	6.6	257
6	258	15.7	258
7	257		

[a] MW of side chain for this graft copolymer is 15.7×10^3.
[b] The content of graft copolymer is 6 pph.

Table IV. Equilibrium contact angles of water drop on the surface of PS/PAR blend systems at ambient temperature

Content of graft copolymer[a] pph	Equilibrium contact angle θ (°)	MW of side chain of graft copolymer[b] $\times 10^3$	Equilibrium contact angle θ (°)
0	128	3.0	119
2	97	6.6	104
4	96	9.7	99
5	92	15.7	90
6	90		
7	91		

[a] MW of side chain for this graft copolymer is 15.7×10^3.
[b] The content of graft copolymer is 6 pph.

compared by observing the SEM photos. For the ternary system including 6 pph graft copolymer (MW of grafts: 15.7×10^3), the microphotograph shows that the PAR particles are well dispersed through the PS matrix and exhibit little tendency to cluster. An average diameter of 0.3 μm is estimated for the size of these domains. It is generally recognized that the size of the rubber particles has a strong influence upon the toughness of rubber-modified polymers although the critical particle sizes are not the same for all materials.[15] As this ternary blend gives rise to the best impact strength and other mechanical properties over all specimens (see Table II and Figure 1), it seems that a more suitable domain form may be obtained for those PS-PAR blend systems studied here. Furthermore, their interface between the two phases is not so clear as that of simple blend of PS and PAR. Most of the craters are covered with convex shaped pimples which are caused by ductile deformation of the matrix as the rubber particles are pulled away during fracture. This is direct evidence for very strong adhesion between the dispersed and matrix phases, as a result of the existance of a graft copolymer. Additional evidence of interfacial activity of a graft copolymer for these PS and PAR blends is the reduction in domain size. These microphotographs definitively prove that the graft copolymer used here does play an interfacial role and increases the compatibility between

the PS and PAR phases.

Table III shows that the second order transition temperatures of PAR phases (T_{g_2}s) obtained from the peak maxima of loss tangent plots of the blends. The ternary blend with added 6 pph graft copolymer having longer side chains (MW of grafts: 15.7×10^3) has the highest T_{g_2} and gives rise to the best impact strength level among all samples (see Table II and Figure 1), in spite of the small difference between these T_{g_2}s. It is clear that the graft copolymer could only be located at the interface between the two phases for these three component blends and thus have no influence over the T_{g_2} of rubber phase.

Table IV lists the equilibrium contact angles of water drop on these PS-PAR blend surfaces. The agreement between the contact angles and the impact strengthes is excellent. There is the lowest equilibrium contact angle and the best impact strength for the ternary blend incorporating 6 pph graft copolymer (MW of side chains: 15.7×10^3) over all blend specimens. Once more, this indicates that the graft copolymer does improve the compatibility between the PS and PAR phases. The same behavior was also exhibited in a polyurethane-epoxy interpenetrating polymer network.[16]

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