

Influence of Core–Shell Rubber Particles Synthesized with Different Initiation Systems on the Impact Toughness of Modified Polystyrene

Guanghai Gao,¹ Chao Zhou,² Haidong Yang,¹ Huixuan Zhang^{1,2}

¹Changchun University of Technology, Institute of Chemical Engineering, Changchun 130012, China

²Changchun Institute of Applied Chemistry, Graduate School, Chinese Academy of Sciences, Changchun 130022, China

Received 1 March 2006; accepted 5 July 2006

DOI 10.1002/app.25030

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Core–shell poly(butadiene-*graft*-styrene) (PB-*g*-PS) rubber particles were synthesized with different initiation systems by emulsion grafting polymerization. These initiation systems included the redox initiators and an oil-soluble initiator, 1,2-azobisisobutyronitrile (AIBN). Then the PB-*g*-PS impact modifiers were blended with polystyrene (PS) to prepare the PS/PB-*g*-PS blends. In the condition of the same tensile yield strength on both samples, the Izod test showed that the notched impact strength of PS/PB-*g*-PS(AIBN) was 237.8 J/m, almost 7 times than that of the PS/PB-*g*-PS(redox) blend, 37.2 J/m. From transmission electron microscope (TEM) photographs, using the redox initiators, some microphase PS zones existed in the core of PB rubber particles, which is called “internal-grafting.” This grafting way was inefficient on toughening. However,

using AIBN as initiator, a great scale of PS subinclusion was seen within the PB particle core, and this microstructure increased the effective volume fraction of the rubber phase with a result of improving the toughness of modified polystyrene. The dynamic mechanical analysis (DMA) on both samples showed that the glass transition temperature (T_g) of rubber phase of PS/PB-*g*-PS(AIBN) was lower than that of PS/PB-*g*-PS(redox). As a result, the PB-*g*-PS(AIBN) had better toughening efficiency on modified polystyrene than the PB-*g*-PS(redox), which accorded with the Kerner approximate equation. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 738–744, 2007

Key words: core–shell rubber particles; initiator; polystyrene; toughness; dynamic mechanical analysis

INTRODUCTION

One of the most successful methods developed for modifying plastics is the rubber-toughening process. To improve compatibility between the rubber particles and the plastics matrix, so-called core–shell impact modifiers have been developed.^{1–6} The typical core–shell architecture consists of a soft crosslinked rubber core and a grafted shell designed specifically to interact with the plastics matrix. The chemical composition of the shell can be chosen to impact compatibility or chemical reactivity with the matrix.⁷ It leads to improving dispersion of rubber particles during melt processing, and provides good adhesion with the matrix.⁸ Core–shell modifiers are produced by emulsion grafting polymerization with free-radical initiated systems. The process comprises two basic stages,⁸ as follows:

1. A rubber latex is prepared by emulsion polymerization
2. Monomers are dropped charged into the reactor and polymerized in the presence of the latex.

During the grafting polymerization, a lot of literatures^{9–13} have reported that different factors lead to greatly distinct micromorphology of core–shell modifiers. A core–shell structure is benefited by immiscibility between core polymer and composition forming the shell, or by a low solubility of the shell monomer in the core polymer.⁹ However, the choice of different monomers to form a shell around the rubber core might lead to different morphologies.¹⁰ Hydrophilic monomers have a tendency to remain on the outside of the latex particles and contact with the aqueous phase, whereas hydrophobic monomers tend to penetrate into the core and polymerized. Okubo¹¹ showed how different morphologies could be obtained by taking advantage of hydrophobic–hydrophilic interaction in systems and other investigators^{12,13} have proposed thermodynamic models to predict and controlled desired morphologies in such situation.

The selection of different initiators also affects the core–shell structure of latex particles. Usually, water-soluble initiators tend to produce shell structures, but oil-soluble initiators have a greater tendency to generate subinclusion structure within the core region of particles. As proposed by Williams and coworkers,^{14–16} the observed difference in core–shell

Correspondence to: H. Zhang (zhanghx@mail.ccut.edu.cn).

structure between ABS which were prepared with organic initiators and purely inorganic initiators suggests that the core-shell morphology is determined by the site of initiation rather than the monomer distribution. These different morphologies affect seriously impact toughness of rubber-modified plastics. Furthermore, other influence factors include rubber particles size^{17–20} and the dispersion state of the rubber phase.^{21,22}

Rosen have pointed that only monomer polymerized in the rubber phase can possibly graft establishes an upper limit to the amount of grafting and hence influences the mechanical properties of the product.²³ Some investigators^{24–27} were focused on effect of initiators type on the extent of grafting in emulsion polymerization. Using a two component redox initiators^{24,25} promote grafting at the interface between the hydrophobic natural rubber particles and shell polymer. It has been shown that this process results in significant amounts of both grafted and ungrafted polymer.²⁶ Besides, the redox initiators are found as the better initiating system that gives the highest grafting efficiency.²⁷ Azobisisobutyronitrile (AIBN) has been found to be a poor initiator in promoting the grafting polymerization.²⁸ However, Hourston and Romaine²⁹ found that the grafting of styrene onto NR with AIBN as initiator.

Usually, the commercial high impact polystyrene is prepared by the way of bulk or bulk-suspension polymerization. For core-shell rubber particles toughening polystyrene, Guo et al.³⁰ had investigated poly(*n*-butyl acrylate/methyl methacrylate)/polystyrene [P(*n*-BA/MMA)/PS] as impact modifier.

In this study, the principal purpose is to investigate that different initiation systems are used to initiate and synthesize core-shell PB-g-PS rubber particles. The different morphologies of the rubber particles influence seriously the impact toughness modified polystyrene, and the influence factors consist of the micromorphologies, grafting degree, and dynamic mechanical properties of core-shell PB-g-PS modifiers.

EXPERIMENTAL

Materials

Polybutadiene latex was kindly supplied by Jilin Chemical Company, China. The effective diameter was about 300 nm and the polydispersity is 0.056. Polystyrene was supplied as GPPS 525 by Panjin Petrochemistry Company, China. Styrene was purified by washing with 5% sodium hydroxide solution to remove the inhibitor. Cumene hydro-peroxide (CHP, Aldrich Chemical), iron (II) sulfate (Aldrich Chemical), dextrose (DX, supplied by Beihai Starch Factory, China), sodium pyrophosphate (SPP, supplied by

TABLE I
The Recipes for the Preparation of PB-g-PS Synthesized with Different Initiation System

Ingredients	PB-g-PS (redox)	PB-g-PS (AIBN)
Deionized water	1000 mL	1000 mL
Polybutadiene	180 g	180 g
Styrene	420 g	420 g
CHP	2.1 mL	
SPP	1.5 g	
DX	2.1 g	
FeSO ₄	0.03 g	
KOH	0.3 g	
AIBN		4.2 g

Tianjin Chemistry Factory, China) were used as initiators. AIBN was recrystallized from ethanol and dried in a desiccator before using.

Preparation of PB-g-PS

Core-shell PB-g-PS modifiers were synthesized with emulsion polymerization by grafting styrene onto polybutadiene latex particles with the redox initiation systems³¹ and an oil-soluble initiator. The redox initiation system consisted of cumene hydro-peroxide (CHP), sodium pyrophosphate (SPP), dextrose (DX), and iron(II) sulfate (FeSO₄). 1,2-Azobisisobutyronitrile (AIBN) was only selected as an oil-soluble initiator. The recipes for the preparation of PB-g-PS copolymers are shown in Table I.

The emulsion polymerization was performed in a 2-L glass reactor under nitrogen at 70°C. The reaction medium was stirred at 300 rpm and nitrogen gas was purged into the reactor throughout the reaction. The styrene monomer was added in a continuous feeding way to the reaction system in 2 h and then the reaction was carried out for another 2 h. After 10 g antioxidant solution was added, reactor temperature was decreased to 60°C and the reaction was ended. The antioxidant compositions are *n*-octadecyl-β-(4-hydroxy-3,5-di-*tert*-butyl phenyl) propionate (OBP) and 3-methyl-6-*tert*-butyl-phenol (MBP). The latex obtained from emulsion polymerization was coagulated by addition to the magnesium sulfate (MgSO₄) solution to yield loose aggregation of the particles. The final conversion of styrene is shown in Table II. The aggregates were washed thoroughly with water, and then dried at 60°C in the oven for 24 h.

Determination of grafting degree of the PB-g-PS copolymer

The degree of grafting was determined by extracting the ungrafted or free PS of the dried 0.5 g PB-g-PS copolymer by 5 mL methyl ethyl ketone (a solvent for PS but not for PB). After the methyl ethyl ketone

TABLE II
The Grafting Degree and Final Conversion of PB-g-PS
with Different Initiation Systems

Code	Grafting degree	Final conversion of styrene (%)
PB-g-PS(redox)	1.789	93.91
PB-g-PS(AIBN)	1.054	95.36

solutions of the dried PB-g-PS impact modifiers were shaken for 24 h at room temperature, the solutions were centrifuged at 10,000 rpm in a GL-21M centrifugal machine for 40 min with a temperature of -5°C . The degree of grafting was calculated from the following equation:^{32–34}

Grafting Degree

$$= \frac{\text{weight of shell polymer grafted to core}}{\text{weight of core}}$$

Blending and molding procedures

To obtain a constant standard, the PB concentration in the PS/PB-g-PS blend synthesized with different initiation systems was designed at the same content of 20 wt %. The PS/PB-g-PS blends were prepared by roll milling at 160°C for 5 min. The films obtained were then pressed into sheets by compression molding at 180°C for 10 min and these sheets were cut into bars with the thickness of 5 mm for the notched Izod impact tests.

Izod impact test and tensile test

According to ASTM D256, notched impact strength was determined with a XJU-22 impact tester at the maximum speed of 3.5 m/s. The tensile test is measured according to ASTM D638 using Shimadzu AGS-H 5 kN tensile tester at a cross-head speed of 50 mm/min. The test was performed at $(23 \pm 2)^{\circ}\text{C}$, and at least five specimens were tested for each average value given.

Dynamic mechanical analysis measurement

The dynamic mechanical (DMA) measurement for the PS/PB-g-PS blends was made in the single cantilever mode by the Netzsch DMA 242 (Germany) at 10 Hz. The specimen bar was sized $30 \times 10 \times 1 \text{ mm}^3$ and the temperature varied from -150°C to 150°C at a constant heating rate of $3^{\circ}\text{C}/\text{min}$.

Morphology observation

The fracture surface of the sample in the Izod test was observed by a JSM 5600 scanning electron microscope (SEM).

The microstructure morphologies of the samples were observed by using JEM-2000EX transmission electron microscope (TEM). The specimens were cut to 60 nm in thickness using a microtome at -100°C , and the samples were stained with OsO_4 solution for 8 h before observation.

RESULTS AND DISCUSSIONS

Dispersion and morphology of PB-g-PS copolymers

The microphotographs of the PS/PB-g-PS blends by TEM are shown in Figure 1. As can be clearly seen, the rubber particles are well dispersed in the PS matrix. For PS/PB-g-PS(redox) [Fig. 1(a)], the rubber particles almost exist in a state of homogeneous dispersion individually, while that of PS/PB-g-PS(AIBN) cohere together lightly [Fig. 1(b)]. This is related closely with the grafting degree of PB-g-PS copolymers. The grafting degrees are 1.789 and 1.054, due to PB-g-PS (redox) and PB-g-PS (AIBN) respectively, (shown in Table II). Owing to the higher grafting degree of PB-g-PS(redox), the better compatibility between the external grafted shell and the matrix induces the rubber particle dispersion as a homogeneous state. However, the grafting degree of PB-g-PS(AIBN) is so low that several rubber particles cohere lightly together by the van der Waals attraction. For ABS resins, the same phenomenon is drawn by Aoki and coworkers.^{32,33}

For core-shell PB-g-PS modifiers, the PS shell grafted onto the surface of PB particles, which is called "external-grafting." This grafting way influences the dispersion of the rubber particles in the matrix.^{35,36} Another grafting way is "internal-grafting," which determines mainly the interstructure of the rubber particles.

Because of using different initiation systems, there are significantly distinct micromorphologies between both samples. For PS/PB-g-PS(redox), the rubber particles show some microphase PS zones [such as in Fig. 1(c)]. In the system of polybutadiene latex during polymerization, the hydrophobic styrene has a tendency to swell into the PB rubber particles. Using the redox initiators, the tendency to initiate grafting polymerization within the rubber particle core is modified by combining an inorganic reducing salt FeSO_4 with the organic oxidizer CHP. Because of lower activation energy of redox initiation systems, at the beginning of the reaction, the numbers of grafting site within the rubber core are more enough to polymerize easily and form polystyrene microphase zones, which lead to increase of the rubber particles modulus. However, the activation energy of AIBN is so high that quantity of styrene swollen into PB rubber particles and polymerized within the interior of PB rubber. As a result, it has

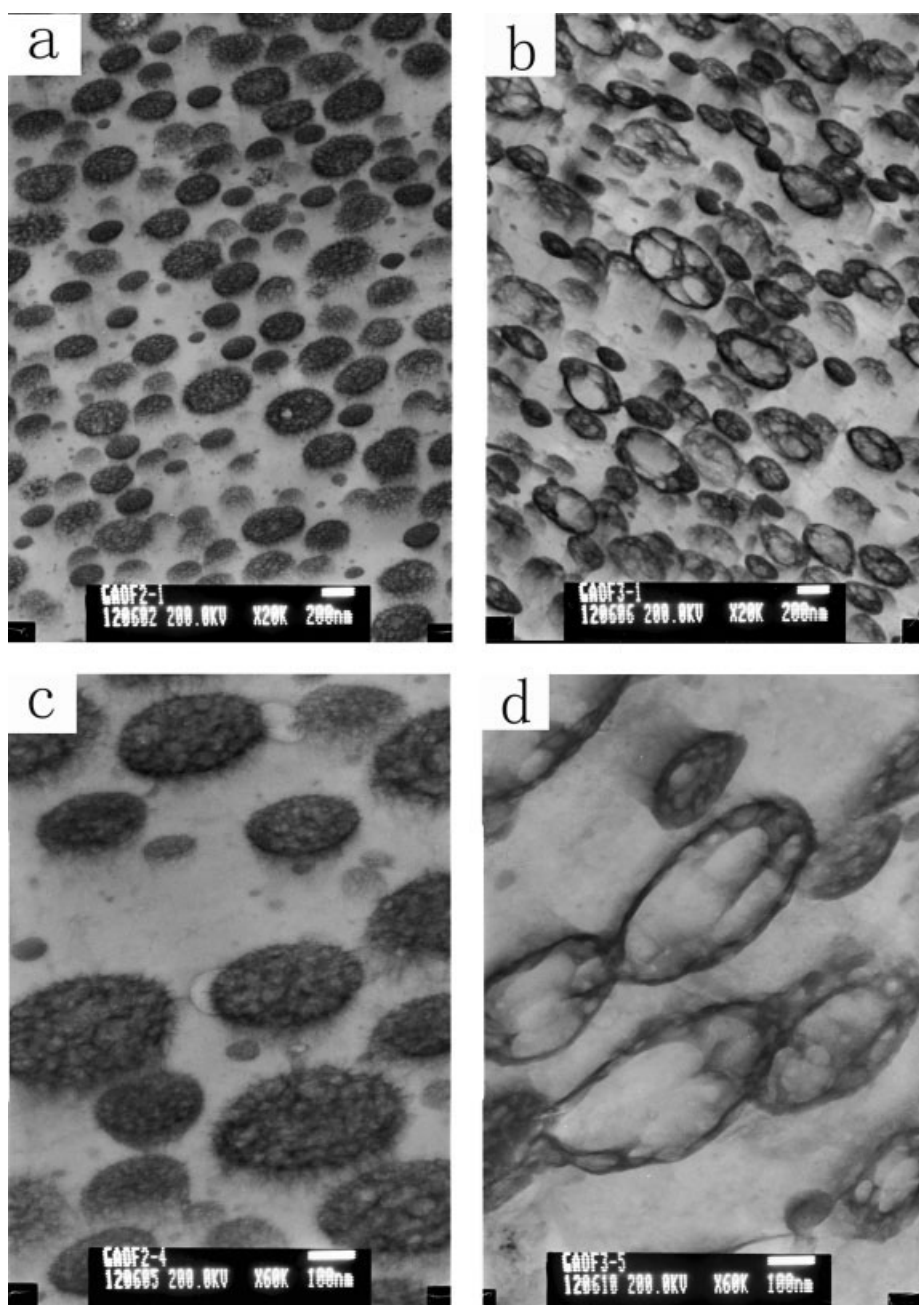


Figure 1 TEM photographs of the PS/PB-g-PS blends: (a) PS/PB-g-PS(redox), $\times 20,000$; (b) PS/PB-g-PS(AIBN), $\times 20,000$; (c) PS/PB-g-PS(redox), $\times 60,000$; (d) PS/PB-g-PS(AIBN), $\times 60,000$.

formed a greater scale of polystyrene subinclusion [Fig. 1(d)] and the subinclusion leads to the increase of the rubber phase volume.

Because of the swelling of styrene monomer into polybutadiene rubber particles, the polymerization of both PB-g-PS copolymers will take place in the core of PB particles. Some occlusions of PS exist in the core of PB rubber particles, which are classified as “internal-grafting” and “subinclusion.” The internal-grafting way tends to produce microphase plastics zones in the rubber particle core and is inefficient

on toughening.^{35,36} However, a great scale of PS subinclusion within the rubber particles increases the effective volume fraction of rubber phase and attributes to promote the toughness of modified polystyrene.

Impact property and fracture surface observation

As for rubber-toughened plastics, in general, the increase of impact strength is contributed from the sacrifice of tensile properties. Therefore, the premise

TABLE III
The Tensile Yield Strength of PS/PB-g-PS(redox)
and PS/PB-g-PS(AIBN)

Code	Tensile yield strength (MPa)
PS/PB-g-PS(redox)	23.8351
PS/PB-g-PS(AIBN)	23.8777

condition of comparing impact resistance is based on the same tensile yield strength on both samples. Table III gives the tensile yield strength of both samples and there is little difference on the yield strength between them.

Notched Izod impact strength gives the information about the high-speed failure of the materials. It is one of the most widely used results of the polymer toughness standard. Figure 2 shows the notched impact strength of the PS/PB-g-PS(redox) blend and the PS/PB-g-PS(AIBN) blend. Obviously, in the condition of the same composition with different initiators, there is a great difference on the impact resistance. The impact strength of the PS/PB-g-PS(AIBN) achieved at 237.8 J/m, almost 7 times than that of the blend using redox initiators, 37.2 J/m (shown in Fig. 2).

Besides of the impact strength, the difference of fracture modes can be distinguished from the fracture surface morphologies of the samples. Figure 3 gives the fracture surface photograph of both PS/PB-g-PS blends by the optical microscope. For the PS/PB-g-PS(redox) blend, the stress whitening can be seen at the origin of the notch tip, and there is no yielded zone underneath the fracture surface, while the photograph of PS/PB-g-PS(AIBN) shows that stress whitening is involved in the sample fracture surface and a highly yielding zone is formed.

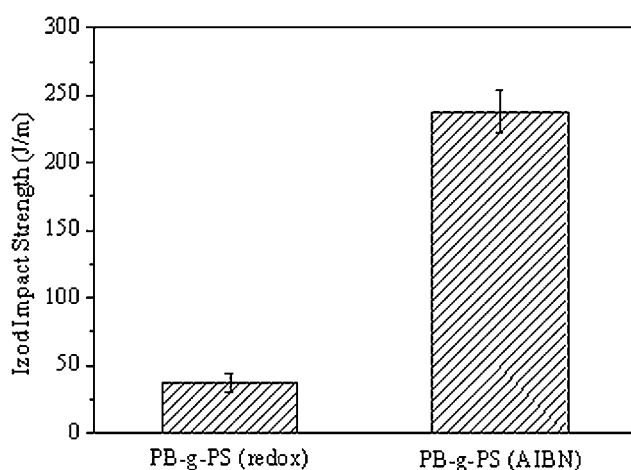


Figure 2 The Izod notched impact strength of PS/PB-g-PS(redox) and PS/PB-g-PS(AIBN).

The toughening information is also given in detail from fracture surface characteristics by SEM (shown in Fig. 4). For the PS/PB-g-PS(redox) blend, the typical brittle fracture characteristics “completely smooth surface” is observed in the Figure 4(a). That is, little energy is absorbed during the Izod test. However, as can be seen from Figure 4(b), the fibril and sign of ductile tearing are easily observed on the fracture surface. This type of plastic deformation implied that shear yielding had taken place in the PS matrix. During the impact test, for PS/PB-g-PS(AIBN), the rubber particles can reduce the detrimental dilatational stress in the bulk polymer without forming cracks in the brittle matrix and encourage the shear deformation in the surrounding matrix, and thus produces the more local ductility extensively. This yielding zone of the matrix can absorb much energy during the deformation process. Therefore, the toughness of modified polystyrene should be improved greatly.

Dynamic mechanical property

For rubber-toughened plastics, there exist normally two glass transition temperatures (T_g), a primary transition above room temperature, due to the matrix component of the composite, and a secondary transition below room temperature, due to the disperse rubber phase. The relationship between the impact strength and the glass transition temperature of the rubber particles is well known.⁸ The rubber particles with lower T_g have higher thermal expansion coefficient, and undergo a hydrostatic dilation stress easily, while the rubber particles having higher T_g are sometimes inefficient on toughening at the same temperature.^{37–40}

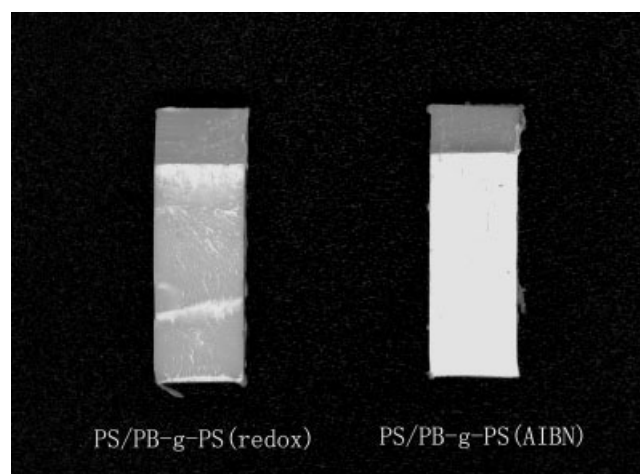
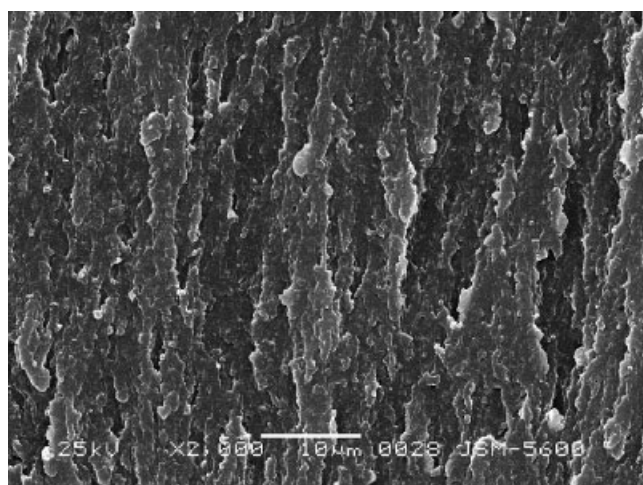
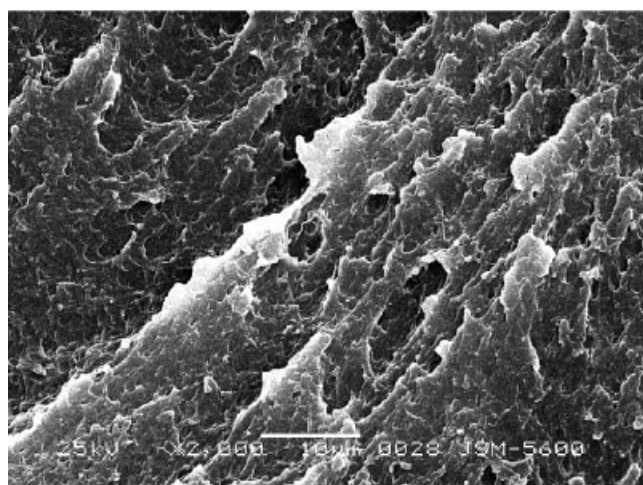


Figure 3 The fracture surface photographs of PS/PB-g-PS blends by the optical microscope.



PS/PB-g-PS(redox)

(a)



PS/PB-g-PS(AIBN)

(b)

Figure 4 SEM photographs of fracture surface of PS/PB-g-PS blends: (a) PS/PB-g-PS(redox); (b) PS/PB-g-PS(AIBN).

In both samples, the matrix phase of them is polystyrene, corresponding simultaneously to about 100°C. Therefore, for the purpose about revealing the effects of core-shell rubber particles on toughened polystyrene, we only give the diagram of storage modulus and loss tangent as a function of the temperature below the room temperature for both PS/PB-g-PS blends (Fig. 5).

Figure 5(a) gives the tendency of storage modulus (E') versus temperature of the rubber phase. Obviously, the E' of PS/PB-g-PS(AIBN) is lower than that of PS/PB-g-PS(redox). This phenomenon is explained by the Kerner⁴¹ equation about the relationship between the storage modulus of two-component composites and the volume fraction of dis-

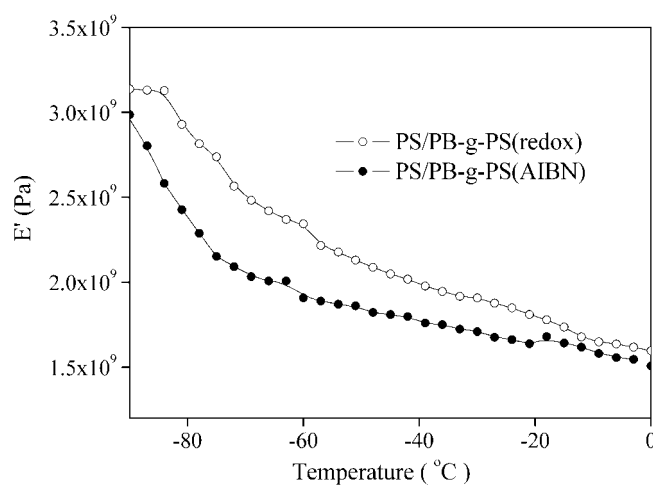
persed phase. This approximate expression is given by

$$\frac{E_0}{E_1} = \frac{\frac{\phi_2 E_2}{(7-5\nu_1) + (8-10\nu_1)E_2} + \frac{\phi_1}{15(1-\nu_1)}}{\frac{\phi_2 E_1}{(7-5\nu_1) + (8-10\nu_1)E_2} + \frac{\phi_1}{15(1-\nu_1)}}$$

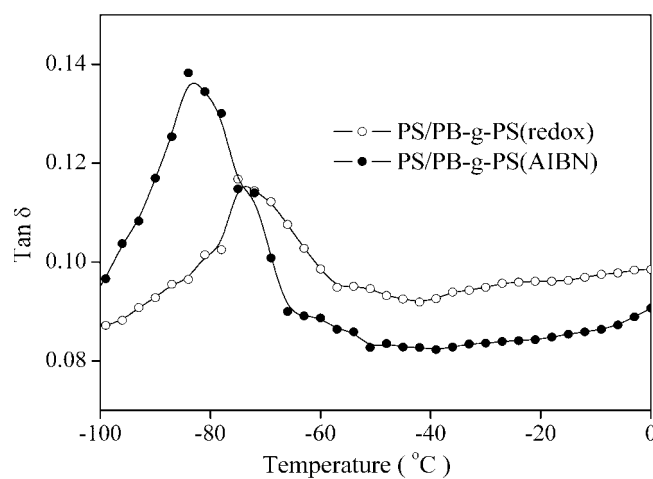
where the E_0 is the shear storage modulus of the sample. E_1 , ν_1 , Φ_1 are the modulus, Poisson ratio, and volume fraction of the matrix plastics, respectively. And E_2 , Φ_2 are the modulus and volume fraction of the rubber phase. Comparing the moduli between the matrix and the rubber particles, $E_1 > E_2$, so ignoring E_2 , the Kerner equation is simplified by

$$E_0 = E_1 \frac{1}{1 + \frac{15(1-\nu_1)\phi_2}{(7-5\nu_1)\phi_1}}$$

Applying this approximate expression to both PS/PB-g-PS blends here, the increased volume fraction



(a)



(b)

Figure 5 The storage modulus E' , and $\tan \delta$ as a function of temperature at 10 Hz for PS/PB-g-PS samples.

of rubber particles owing to the PS subinclusion in PS/PB-*g*-PS(AIBN) decreases the storage modulus of the PB-*g*-PS copolymer.

Figure 5(b) shows the $\tan \delta$ versus temperature curves for both PS/PB-*g*-PS samples. The maximum $\tan \delta$ value represents the glass transition temperature (T_g) of the rubber phase. The T_g of PS/PB-*g*-PS(AIBN), -83.3°C , is lower than that of PS/PB-*g*-PS(redox), -73.8°C . It is well-known that the grafting and cross-linking reactions take place simultaneously during the emulsion polymerization.^{8,42} For the redox initiation system, the internal-grafting produces large numbers of grafted polystyrene chains within the rubber core and forms microphase PS zones. It induces the $\tan \delta$ peak to shift to higher temperature. Simultaneity, the internal-grafting alters the relaxation behavior of the rubber chain sections. As a result, the toughening ability of the PB-*g*-PS(redox) modifier is not operated in toughened polystyrene. As for the PB-*g*-PS(AIBN), a large scale of PS subinclusion zones have little effect on the T_g of the rubber phase. It should contribute to increase the rubber phase volume and improve the toughening efficiency of the PB-*g*-PS modifiers.

Besides, the maximum $\tan \delta$ of PB-*g*-PS(AIBN) is further larger than that of PB-*g*-PS(redox), which result from the difference on the effective volume fraction of the rubber particles. Owing to the a large area of PB subinclusion in the rubber particles of PB-*g*-PS(AIBN), the rubber phase volume increases so highly that the maximum $\tan \delta$ is improved greatly.

CONCLUSIONS

Core-shell PB-*g*-PS impact modifiers were synthesized with emulsion polymerization by grafting styrene onto the PB latex particles with different initiation systems. These initiation systems included the redox initiators, CHP-FeSO₄, and an oil-soluble initiator, AIBN. Then the modifiers were blended with PS to prepare the PS/PB-*g*-PS blends.

In the condition of the same tensile yield strength on both samples, the Izod notched impact strength of PS/PB-*g*-PS(AIBN) was 237.8 J/m, almost 7 times than that of PS/PB-*g*-PS(redox), 37.2 J/m. From TEM photographs, the rubber particles of PS/PB-*g*-PS(redox) included some microphase PS zones, which was classified as "internal-grafting." This internal-grafting way improved the modulus of rubber particles, which were inefficient on toughening polystyrene. However, the rubber particles of PS/PB-*g*-PS(AIBN) showed a large scale of PS subinclusion, which was able to increase the effective volume fraction of rubber phase and attributed to promote the toughness of modified polystyrene.

The DMA results suggested that the storage modulus of rubber phase of PS/PB-*g*-PS(AIBN) was lower than that of PS/PB-*g*-PS(redox). This result was accorded

with the Kerner approximate expression. Combining with impact strength of samples, the results showed that the rubber with lower E' had a great tendency to release triaxial dilatational stress during deformation in the impact test and had a better toughening ability.

References

1. Ayre, D. S.; Bucknall, C. B. *Polymer* 1998, 39, 4785.
2. Cho, K.; Kang, J.; Park, C. E. *Polymer* 1998, 39, 3073.
3. Abu-Isa, I. A.; Jaynes, C. B.; O'Gara, J. F. *J Appl Polym Sci* 1996, 59, 1957.
4. Memon, N. A. *J Polym Sci, Part B* 1998, 36, 1095.
5. Yu, Z. Z.; Ou, Y. C.; Qi, Z. N.; Hu, G. H. *J Polym Sci, Part B* 1998, 36, 1987.
6. Lin, K. F.; Shieh, Y. D. *J Appl Polym Sci* 1998, 70, 2313.
7. Wakker, A. *Polymer* 1991, 32, 272.
8. Bucknall, C. B. *Toughened Plastics*; Applied Science Publishers: London, 1977.
9. Silverstein, M. S.; Talmon, Y.; Narkis, M. *Polymer* 1980, 30, 416.
10. Landfester, K.; Boeffel, C.; Lambla, M.; Spiess, H. W. *Macromolecules* 1996, 29, 5972.
11. Okubo, M. *Makromol Chem, Macromol Symp* 1990, 35/36, 307.
12. Chen, Y.-C.; Dimonie, V.; El-Aasser, M. S. *J Appl Polym Sci* 1991, 42, 1063.
13. Durant, Y. G.; Sundberg, D. C. *J Appl Polym Sci* 1995, 58, 1607.
14. Grancio, M. R.; Williams, D. J. *J Polym Sci A1* 1970, 8, 2617.
15. Williams, D. J. *J Polym Sci Chem Ed* 1974, 12, 2123.
16. Keusch, P.; Graff, R. A.; Williams, D. J. *Macromolecules* 1974, 7, 304.
17. Moore, J. D. *Polymer* 1971, 12, 478.
18. Donald, A. M.; Kramer, E. J. *J Appl Polym Sci* 1982, 27, 3729.
19. Donald, A. M.; Kramer, E. J. *J Mater Sci* 1982, 17, 2351.
20. Okamoto, Y.; Miyagi, H.; Mitsui, S. *Macromolecules* 1993, 26, 6547.
21. Keskkula, H.; Kim, H.; Paul, D. R. *Polym Eng Sci* 1990, 30, 1373.
22. Kim, H.; Keskkula, H.; Pual, D. R. *Polymer* 1990, 31, 869.
23. Rosen, S. L.; *Fundamental Principles of Polymeric Materials*; Wiley: New York, 1993.
24. Anstey, J. F.; Subramaniam, N.; Pham, B. T. T.; Lu, X.; Monteiro, M. *J Macromol Symp* 2000, 150, 73.
25. Lamb, D.; Anstey, J. F.; Fellows, C. M.; Monteiro, M. J.; Gilbert, R. G. *Biomacromolecules* 2001, 2, 518.
26. Kangwansupamonkon, W.; Fellows, C. M.; Lamb, D. J.; Gilbert, R. G.; Kiatkamjornwong, S. *Polymer* 2004, 45, 5775.
27. Kangwansupamonkon, W.; Gilbert, R. G.; Kiatkamjornwong, S. *Macromol Chem Phys* 2005, 206, 2450.
28. Cameron, G. G.; Qureshi, M. Y. *J Polym Sci* 1980, 18, 2143.
29. Hourston, D. J.; Romaine, J. *J Appl Polym Sci* 1991, 43, 2207.
30. Guo, T. Y.; Tang, G. L.; Hao, G. J.; Song, M. D.; Zhang, B. H. *J Appl Polym Sci* 2003, 90, 1290.
31. Sohn, S.; Kim, S.; Hong, S. I. *J Appl Polym Sci* 1996, 61, 1259.
32. Aoki, Y. *Macromolecules* 1987, 20, 2208.
33. Hasegawa, R.; Aoki, Y.; Doi, M. *Macromolecules* 1996, 29, 6656.
34. Donald, A. M.; Kramer, E. J. *J Appl Polym Sci* 1982, 27, 3792.
35. Xu, X. F.; Yang, H. D.; Zhang, H. X. *J Appl Polym Sci* 2005, 98, 2165.
36. Xu, X. F.; Wang, R.; Tan, Z. Y.; Yang, H. D.; Zhang, M. Y.; Zhang, H. X. *Eur Polym J* 2005, 41, 1919.
37. Bucknall, C. B.; Street, D. G. *SCI Monogr* 1967, 26, 272.
38. Matsuo, M.; Ueda, A.; Kondo, Y. *Polym Eng Sci* 1970, 10, 253.
39. Borggreve, R. M. J.; Gaymans, R. J. *Polymer* 1989, 30, 71.
40. Borggreve, R. J. M.; Gaymans, R. J.; Eichenwald, H. M. *Polymer* 1989, 30, 78.
41. Kerner, E. H. *Proc Phys Soc B* 1956, 69, 808.