

Recycled Acrylonitrile–Butadiene–Styrene Copolymer Resin Strengthened and Toughened by an Elastomer/Inorganic Nanoparticles Complex

Binbin Liu,¹ Hua Lei²

¹Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

²Institute of Applied Mechanics, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China

Correspondence to: H. Lei (E-mail: hualei@zju.edu.cn)

ABSTRACT: The properties of recycled acrylonitrile–butadiene–styrene copolymer (rABS) resin deteriorate because of the aging of the acrylonitrile–butadiene–styrene copolymer (ABS) resin during its lifetime; the impact strength, especially, decreases sharply, and the material is commonly brittle. We studied the toughening of rABS by an elastomer and inorganic nanoparticles incorporated into rABS. The results show that the elastomer could restore toughness of the rABS, but it also caused a decrease in the rigidity (flexural modulus); meanwhile, inorganic nanoparticles enhanced the toughness of the rABS only in a limited range for the coalescence issues but also could increase the rigidity of the rABS. This was just the opposite to elastomer. So, we proposed the solution of using an elastomer/inorganic nanoparticle complex to strengthen and toughen rABS. With the incorporation of a 5–8 wt % powdered ABS grafted composition with a rubber content of 70 wt % (referred to as the ABS graft powder) and 2–3 wt % inorganic nanoparticles into rABS, a synergistic effect between elastomer and inorganic nanoparticles was found to significantly benefit the toughness and strength of the rABS resin at the same time, and effective reusability of the rABS was realized. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: modification; nanoparticles; recycling; rubber; toughness

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INTRODUCTION

Acrylonitrile–butadiene–styrene copolymer (ABS), as a common engineering plastic, is widely used in industries in applications such as auto parts, aircraft parts, electrical and electronic equipment, tools, pipes, and plates. Accordingly, there is plenty of wasted ABS resin when the aforementioned products are discarded. Moreover, ABS is a kind of thermoplastic resin. From the viewpoint of plastic processing, it can be processed repeatedly for reuse, so the wasted ABS from discarded products can be recycled. However, as a result of resin aging during the service period, the mechanical properties of recycled acrylonitrile–butadiene–styrene copolymer (rABS) are usually inferior to virgin ABS, and the impact strength especially decreases evidently, and brittleness is shown. This limits rABS application and reuse. Therefore, it is necessary to explore solutions for improving the properties of rABS.

There is plenty of literature^{1–10} focused on rABS, but little attention has been paid to modifying the properties of rABS, mainly for the reuse of rABS. Wang et al.¹ suggested that the impact strength of rABS could be increased by the addition of a

special toughing agent, but the toughing mechanism and type of additive were not specified. In the patent US2009/00694532,² a method was disclosed in which the mechanical properties of rABS could be recovered by the addition of plenty of virgin ABS; actually, it was just to a method for recycling rABS partly at the expense of the properties of plenty of added virgin ABS. The increased properties of the rABS depended only on the amounts of virgin ABS added; hence, commonly, the amounts of virgin resin are large so the application needs can be met. In all of the published literature,^{1–10} the toughening of rABS is the main focus, but the mechanism of the performance degradation of rABS has not been clarified, and the balance of rigidity and toughness of rABS are ignored. In practical applications, rABS is usually used as a minor component to blend with plenty of virgin ABS or other engineering plastics and is seldom used solely because of its poor mechanical properties.

In this study, the aging mechanism of rABS during its lifetime was studied to analyze the reasons for its performance degradation and to find the method of improving the resin properties. Our aim was to obtain a composite materials system based on

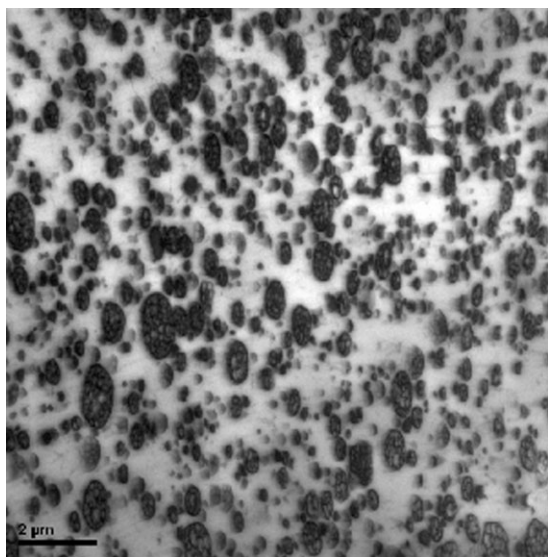


Figure 1. TEM image of the virgin ABS (10,000 \times).

rABS with balanced performance, which could be used to produce industrial products directly. This could not only reduce environmental pollution of plastic waste and petroleum consumption for producing virgin ABS but could also create more economic benefits and value.

EXPERIMENTAL

Materials

The rABS used in this study, which was supplied by Pujiang Jinxin Waste Goods and Material Recycling Co. (Pujiang, China), came from the shell material of wasted electrical apparatuses and was sorted, crushed, cleaned, and granulated before use. ABS graft powder (containing about 70 wt % rubber) was supplied by Daqing Petrochemical Co. (Daqing, China). ABS (type 750, melt flow rate = 28.0 g/10 min) and butadiene rubber (BR) [type BR9000, ML(1+4) $_{100^{\circ}\text{C}}$ = 46] were commercially available from Daqing Petrochemical Co. (Daqing, China). Styrene butadiene rubber (SBR) [type 1502, ML(1+4) $_{100^{\circ}\text{C}}$ = 52] was supplied by Jilin Petrochemical Co. (Jilin, China). Nano-grade silicon dioxide (SiO_2 , precipitated method), zinc oxide (ZnO), and titanium dioxide (TiO_2 ; for all inorganic nanoparticles, the mean diameter of the particles was 50 nm) were supplied by Hangzhou Wanjiang New Material Co. (Hangzhou, China). Aluminate ester (SG-Al821, distearoyl isopropoxy aluminate) was obtained from Nanjing Shuguang Chemical Industry Co. (Nanjing, China).

Instrument and Equipment

We used the following equipment in our experiments: a high-speed mixer (SHR-10 A, Beijing INT Plastics Machinery General Factory, Beijing, China), a twin-screw extruder (TSE-40 A, Nanjing Ruiya Polymer Equipment Co., Ltd., Nanjing, China), an injection-molding machine (HTB110X-1, Ningbo Haitian Plastics Machinery Co., Ltd., Ningbo, China), an electronic universal testing machine (Instron4465, Instron Co., Norwood, MA), an impact test machine (RAY-RAN Test Equipment Co., Warwickshire, United Kingdom), a transmission electron

microscopy (TEM) instrument (JEM-1230, JEOL, Tokyo, Japan), a gel permeation chromatography (GPC) instrument (PL-GPC-50, Waters, Milford, MA), and a scanning electron microscopy (SEM) instrument (SIRON, FEI, Eindhoven, Holland).

Preparation and Characterization of the Samples

Pretreatment of the Nanoparticles. The weighed nanoparticles were added to the high-speed mixer, the low-speed stirrer was started, and the material was heated to 110°C for 30 min. Then, 2 wt % aluminate ester (on the basis of the weight of nanoparticles) was added to mixer, with stirring at high speed for 30 min. Then, the material inside the mixer was discharged and set aside for further use. The purpose of this process was to remove the moisture in the nanoparticles and complete the surface treatment of the nanoparticles.

Dry Mixing. All of the components according to prescribed proportions were added to the high-speed mixer and heated to 110°C for 30 min to remove moisture with stirring at low speed. Then, a small amount of mineral oil was added, which was used to stick the powdered nanoparticles into pelletized ABS. The material was then stirred at high speed for 10 min to mix it uniformly. This process was used to mix the solid material and obtain dry blends.

Extrusion. The extruded blending of the dry blends of all components was carried out with a corotating twin-screw extruder, which had a screw diameter of 36.0 mm and a length-to-diameter ratio of 40. The screw consisted of 10 segmented barrels, in which the temperatures were set as 200, 210, 210, 220, 230, 230, 230, 220, 220, and 210°C . A standard pelletized die plate was installed at the screw end, in which the temperature was set at 200°C . The strand was solidified in a water bath and pelletized. The screw speed was fixed at 120 rpm for all experimental runs. The throughput rate was fixed at 18 kg/h.

Injection. Standard samples for testing were prepared through the single-screw injection molding machine, which had a screw diameter of 30.0 mm and a length-to-diameter ratio of 18.1. The highest temperature of the barrels was set at 230°C . The

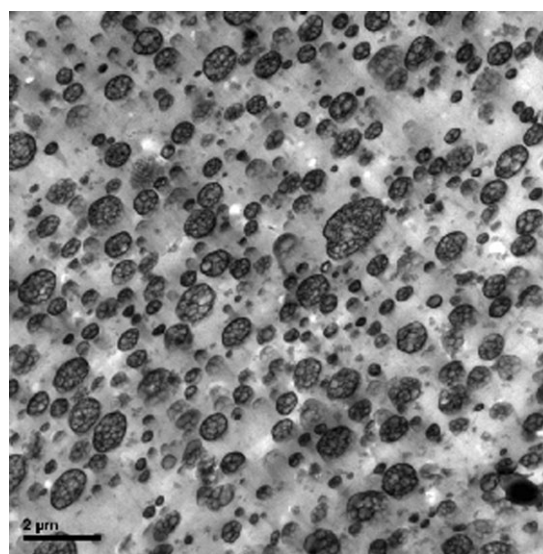


Figure 2. TEM image of the rABS (10,000 \times).

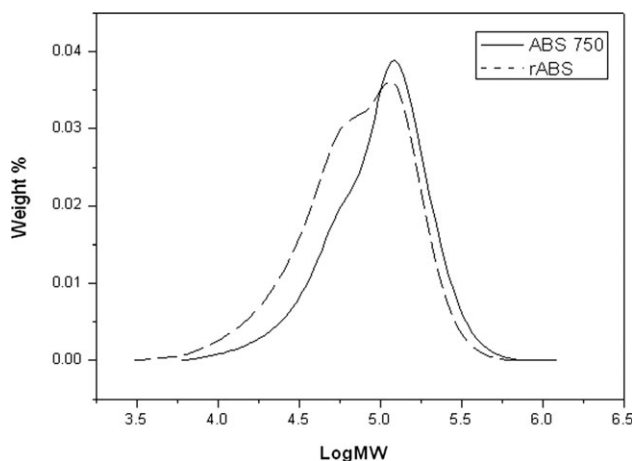


Figure 3. GPC results of the virgin ABS and rABS. MW, molecular weight.

injection pressure was set at 140 MPa, and the dwell time was set at 30 s for every run.

We conducted tensile measurements on the basis of ASTM D 638, Izod impact strength measurements on the basis of ASTM D 256, flexural behavior measurements on the basis of ASTM D 790, and heat deformation temperature measurements on the basis of ASTM D 648, and for all measurements of these mechanical properties, an average value of five replicated specimens was taken for each formula composition. TEM images of the dispersed domains in the ultrathin specimens were directly observed with the JEM-1230. The ultrathin samples were obtained by microtoming of the extruded strands. The dispersed nano-SiO₂ domain within the rABS matrix was studied with the SIRON SEM instrument at an accelerating voltage at 25.0 kV through the freeze-fractured sample surface, which was sputter-coated with platinum.

RESULTS AND DISCUSSION

Aging Mechanism and Property Characterization of the rABS Microstructure Characterization and Property Measurement of the rABS. To determine the aging mechanism of ABS, we first examined TEM images of ultrathin specimens of virgin

Table I. GPC Results of the Virgin ABS and rABS

Sample	Number-average molecular weight	Weight-average molecular weight	PI
Virgin ABS	67,780	115,935	1.7105
rABS	44,767	89,754	2.0049

PI, polydispersity index.

ABS (750) and rABS, as shown in Figures 1 and 2, respectively. Both images showed a rubber phase, and a typical sea-island formation was observed. However, as a comparison, obviously, at the same magnification, Figure 1 indicated a more dense rubber phase distribution than that shown in Figure 2. This means that there was a higher rubber content in virgin ABS than in rABS.

Also, GPC of the virgin ABS (750) and rABS sample was conducted, and the results are shown in Figure 3 and Table I. It can be seen that the molecular weight of virgin ABS was greater than that of the rABS.

Table II shows the test results of the properties of the rABS and virgin ABS (750). The properties of the rABS dropped significantly compared to those of the virgin ABS (750), especially the impact strength, which showed a decrease of 32%. In addition, the heat distortion temperature also decreased.

Proposed Aging Mechanism. To explore how to enhance the performance of the rABS, it was necessary to understand the reasons for that the rABS properties degraded. During their service courses, the wasted products, which contain ABS and are the origins of rABS, are subjected to many physical factors, such as heat, light, mechanical stress, and ultrasonic and high energy radiation, as well as chemical factors, such as oxygen, ozone, metal particles of variable valences, various chemical media (e.g., water, acid, alkali, and salts), and microorganisms. Oxygen, ozone, heat, light, and mechanical stress are the main factors that cause ABS resin material to age and commonly act together on resin. This causes the deterioration of the resin properties. During the aging process, how the chemical structure of ABS resin is changed and how these changes affect the properties of the ABS resin are the keys to

Table II. Comparison of the Properties of the rABS and ABS (750)

Test item	Test standard	rABS	ABS (750)	Relative change
Tensile strength (MPa)	ASTM D 638	38 ± 1	47 ± 1	19.1%
Young's modulus (MPa)	ASTM D 638	170 ± 3	210 ± 4	19.0%
Flexural strength (MPa)	ASTM D 790	53 ± 1	68 ± 1	22.1%
Flexural modulus (MPa)	ASTM D 790	1850 ± 40	2400 ± 50	22.9%
Elongation at break (%)	ASTM D 638	35 ± 1	30 ± 1	—
Izod impact strength (kJ/m ²)	ASTM D 256	17 ± 1	25 ± 1	32%
Heat distortion temperature (°C)	ASTM D 648	72	85	—
Impact retention percentage after UV photodegradation for 100 h (%)	ASTM D 256	71	86	—

ABS (750) is a resin applied to produce household electrical appliances, auto parts, office equipment, and so on by injection molding.

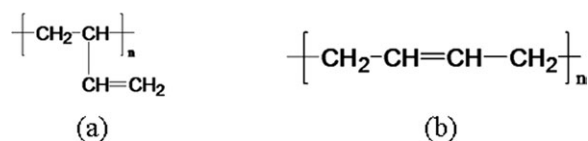


Figure 4. Double-bond structures of the polybutadiene chain in ABS: (a) 1,2-vinyl structure and (b) cis, trans-1,4 structure.

finding the solutions to improve the performance of rABS. In this article, on the basis of our results of characterization and measurement and other researcher's works,^{11–13} we propose a possible aging mechanism of ABS resin as follows.

In the molecular structure of ABS resin, polybutadiene chain segments contained double bonds, as shown in Figure 4. These were vulnerable to a variety of factors during the chemical reactions. The styrene monomer unit and acrylonitrile monomer unit remained relatively stable.

Figure 5 shows that the double bond of the polybutadiene chain segment was saturated during degradation. Then, crosslinking took place, and the rubber phase disappeared. This caused a decrease in the impact strength of the rABS resin. Figure 6 shows broken chains, which caused a decrease in the molecular weight of polymer; at the same time, macroscopically, the elasticity modulus, tensile strength, and heat distortion temperature of the resin all decreased. Figure 7 shows the destruction of the graft chain structures; this made the compatibility of the rubber phase and plastic matrix decrease, and phase separation occurred. Thus, the properties of the resin completely deteriorated. Furthermore, plenty of new substances, such as aldehydes, ketones, and peroxides, were produced during light aging. The carbonyl structures among these new substances led to yellowing of ABS, and peroxide was sensitive to UV radiation, so it would further exacerbate ABS aging and the loss of performance.

In summary, the decrease in the rABS mechanical properties was due to the light aging of polybutadiene chains, which resulted in a reduction of the content of the rubber phase, a decrease in the molecular weight of ABS, and phase separation between the bulk and rubber phase. This led to a decrease in the rABS mechanical properties.

Balance of the Toughness and Rigidity of the rABS

rABS Toughened by the Elastomer. According to the preceding analysis, the primary reason for the decrease in the toughness of the rABS was that the double bonds of the polybutadiene chain

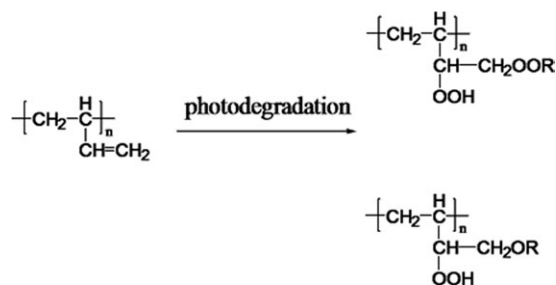


Figure 5. Double bond saturated in the course of photodegradation.

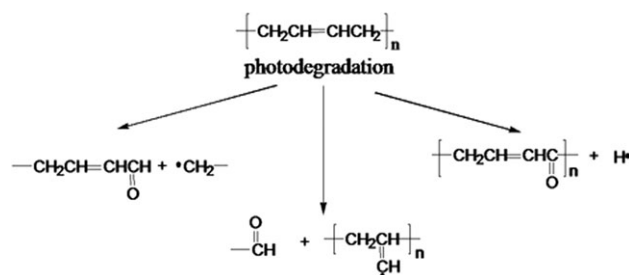


Figure 6. Molecular chains that broke in the course of photodegradation.

segment were degraded. The polybutadiene chain, as the rubber segment of the ABS molecular structure, could provide the toughness of ABS, so the addition of elastomer to rABS could restore toughness to rABS. Table III shows the comparison of properties of the rABSs modified by different elastomers used as toughening agents.

There were some graft units between the polybutadiene chain with other components of the ABS graft powder; their molecular structures are depicted simply in Figure 8. So the ABS graft powder had better compatibility with the rABS matrix, and its toughening effect was superior to the those of the other two kinds of elastomers. Meanwhile, the other properties of the rABS modified by the ABS graft powder were better than those of the rABSs modified by the other two kinds of elastomer. According to the results in Table III, the ABS graft powder was chosen for use as the elastomer toughening agent of the rABS.

As the rigidity and modulus of the elastomer were low, it also existed in the resin matrix as a dispersing phase. The elastomer, as a toughening agent, tended to decrease the tensile strength and flexible modulus while toughening the material; this resulted in toughening without strengthening. Hence, the addition quantities of rubber to rABS were limited. Figure 9 shows the changes in the tensile strength and impact toughness of the rABS modified by different contents of ABS graft powder. Figure 10 shows that the use of different contents of ABS graft powder resulted in different flexural modulus and Izod impact strength values. According to Figure 9, the ABS graft powder could toughen rABS evidently, and the Izod impact strength of the rABS increased greatly with increasing content of ABS graft powder in rABS. When the content of ABS graft powder was 5 wt %, the Izod impact strength increased by about 35%. Meanwhile, the tensile strength and Young's modulus of the rABS decreased with increasing content of ABS graft powder, but the degree of decrease was not large. When the content of ABS graft powder in rABS was 5 wt %, the tensile strength and Young's modulus of the rABS decreased by about 2%. These were

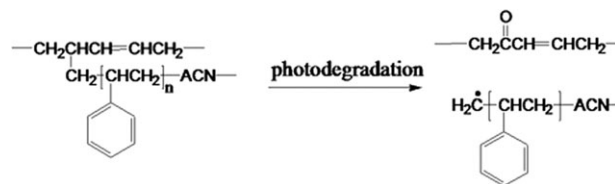


Figure 7. Graft chains destroyed in the course of photodegradation.

Table III. Comparison of the Properties of the rABS Modified by Different Elastomers

Test item	Test standard	Toughening agent		
		ABS rubber power	BR	SBR
Tensile strength (MPa)	ASTM D 638	37 ± 1	30 ± 1	31 ± 1
Young's modulus (MPa)	ASTM D 638	170 ± 3	165 ± 3	168 ± 3
Flexural strength (MPa)	ASTM D 790	53 ± 1	51 ± 1	52 ± 1
Flexural modulus (MPa)	ASTM D 790	1800 ± 40	1780 ± 40	1790 ± 40
Elongation at break (%)	ASTM D 638	30 ± 1	28 ± 1	26 ± 1
Izod impact strength (kJ/m ²)	ASTM D 256	23 ± 1	20±	19 ± 1
Heat distortion temperature (°C)	ASTM D 648	71	68	69

The contents of the three kinds of elastomers in rABS were all 5 wt %.

related to the chemical composition of ABS graft powder. The high butadiene rubber content provided superior impact resistance, and its good compatibility with the rABS matrix led the tensile strength to decrease not strongly. Therefore, it was suitable for modifying rABS. According to Figure 10, the flexural strength and modulus of the rABS decreased significantly with increasing content of the graft powder. When the content of ABS graft powder was 5 wt %, the flexural strength and modulus of the rABS decreased by about 8%. This was due to the dispersal issue of the rubber component as the dispersed phase in the rABS matrix; despite a good compatibility with rABS, additionally, the modulus of butadiene rubber was very low, so the flexural modulus of the rABS decreased evidently. On the basis of the previous results, the proposed content of ABS graft powder went from 5 to 8 wt % to achieve an acceptable increase in the Izod impact strength of the rABS resin. However, from the viewpoint of a balance of rigidity and toughness, if an elastomer is solely used as a toughening agent, it should be considered that the decrease in the rigidity of the resin will be large, and this limits the application of the modified material.

As shown in the TEM images in Figure 11 for the rABS toughened by 4 wt % ABS graft powder, the rubber domain in the added graft powder can be seen with the same dispersion as that of the original rubber domain existing in rABS. Furthermore, most rubber domains were embedded in the continuous rABS bulk, and this indicated strong interfacial interaction between the ABS graft powder and rABS bulk. However, we noticed that the diameter of the large dispersed particles of rub-

ber, which were in a typical sea-island formation, was nearly 0.5–1 μm, so the tensile strength was lowered.

rABS Toughened by Inorganic Nanoparticles. In recent years, studies on polymers modified by inorganic nanoparticle have been a hot spot.^{14–17} The nonsaturated nature of the surface atom of nanoparticles can enhance the interfacial bonding between nanoparticles and resin matrix. Crazes appear in the interface of nanoparticles and the matrix resin when the resin, in which nanoparticles are dispersed uniformly, are subject to impact. Meanwhile, plastic deformation of the resin between nanoparticles occurs, and the impact energy is absorbed. The surface areas of nanoparticles are very large because of the nanolevel of their diameters. This enlarges the contact area of the nanoparticles and matrix resin, and more crazes and plastic deformation occur when resin is subject to impact, and so more impact energy can also be absorbed. Similar to filled particles with ordinary size, inorganic nanoparticles are also rigid and can be used as a skeleton in matrix resin to increase the rigidity of a resin. In summary, with the addition of nanoparticles into a polymer matrix, both the rigidity and toughness of resin can be increased.

Inorganic nanoparticles were applied to toughen rABS, and Table IV shows effect of different types of inorganic nanoparticles

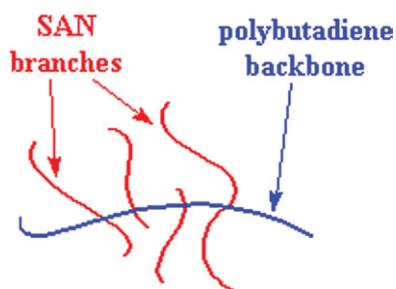


Figure 8. Depiction of the molecular structure of the ABS graft powder. SAN, styrene acrylonitrile copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

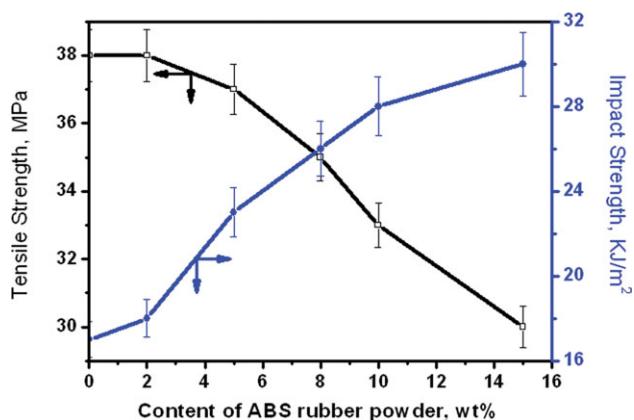


Figure 9. Changes in the tensile strength and impact strength with the ABS rubber powder content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

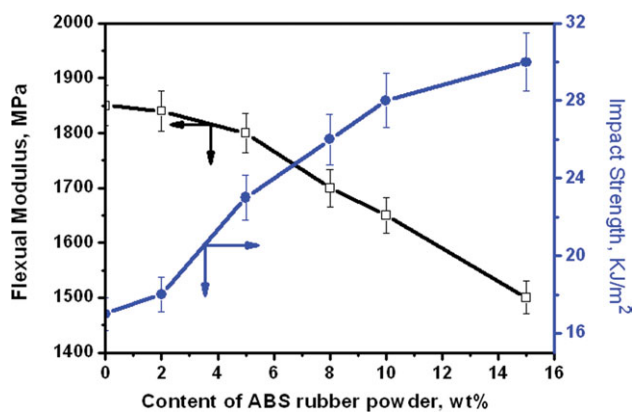


Figure 10. Changes in the flexural modulus and impact strength with the ABS rubber powder content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

on the rABS properties. According to the results, the impact strength of the rABS was increased when the inorganic nanoparticles were added, but the degree of increase was not large and

was not effective compared to that of the elastomer. However, this was different from the toughening by the elastomer in that the flexural strength and modulus of the rABS modified by inorganic nanoparticles increased evidently, which indicated toughening during the addition of rigidity. However, meanwhile, both the tensile strength and elongation at break decreased. The heat resistance of the rABS modified by inorganic nanoparticles increased, and its heat distortion temperature increased a little. In summary, the type of inorganic nanoparticles almost had no difference on the effect on the resin properties, and the particles with same mean particles size almost had the same effect. So, the cost of inorganic nanoparticles should be considered first when the particles are chosen.

The diameter of the particles incorporated into the resin was the decisive factor affecting the increasing toughness of the resin. Figure 12 shows the effect of the content of SiO₂ particles filled in rABS on the impact strength with different sizes of inorganic particles. According to the results, the toughness of the rABS filled by SiO₂ particles with an average diameter of 50 nm under appropriate filler contents (<3 wt %) improved, and

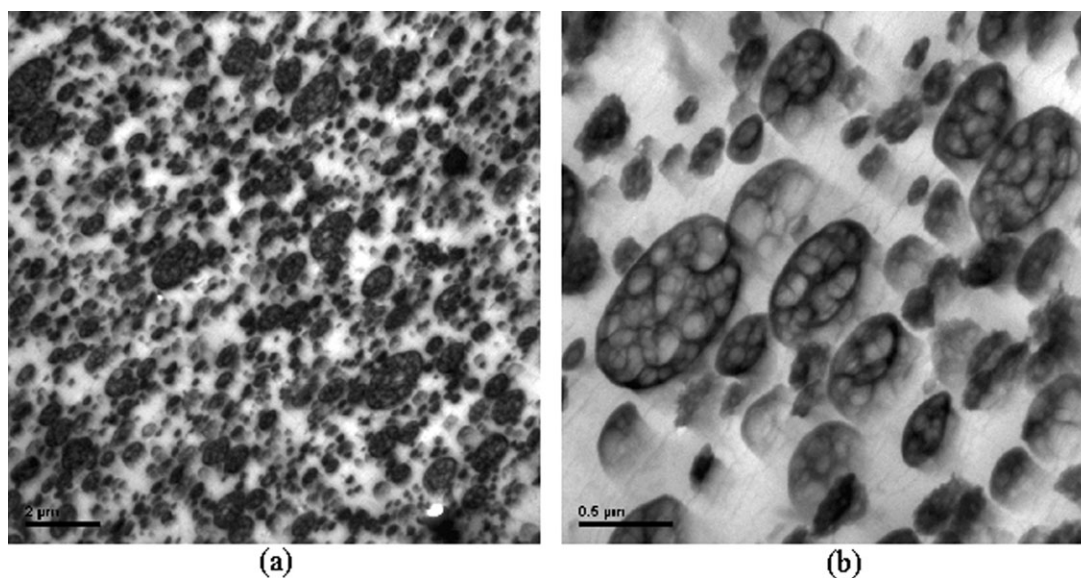


Figure 11. TEM images of the rABS toughened by 6 wt % ABS graft powder at magnifications of (a) 10,000 and (b) 50,000 \times .

Table IV. Effect of the Different Types of Inorganic Nanoparticles on the rABS Properties

Test item	Test standard	Inorganic nanoparticles		
		SiO ₂	ZnO	TiO ₂
Tensile strength (MPa)	ASTM D 638	35 \pm 1	35 \pm 1	36 \pm 1
Young's modulus (MPa)	ASTM D 638	165 \pm 3	166 \pm 3	168 \pm 3
Flexural strength (MPa)	ASTM D 790	58 \pm 1	57 \pm 1	58 \pm 1
Flexural modulus (MPa)	ASTM D 790	1950 \pm 40	1945 \pm 40	1950 \pm 40
Elongation at break (%)	ASTM D 638	25 \pm 1	24 \pm 1	24 \pm 1
Izod impact strength (KJ/m ²)	ASTM D 256	20 \pm 1	20 \pm 1	19 \pm 1
Heat distortion temperature ($^{\circ}$ C)	ASTM D 648	73	72	72

The contents of the three types of inorganic nanoparticles in rABS were all 2%. The average particle diameters of the three types of inorganic nanoparticles were all about 50 nm. The surfaces of all of the inorganic nanoparticles were treated by aluminate ester.

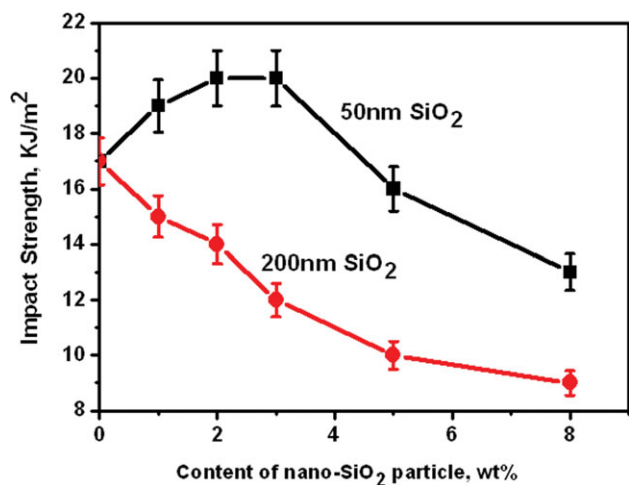


Figure 12. Effects of the diameter and content of SiO₂ particles on the impact strength of the modified rABS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for SiO₂ particles with an average size of 200 nm, the impact resistance of the rABS was not improved.

The content of inorganic nanoparticles incorporated in the resin was another key factor affecting the mechanical properties of the resin. Figures 13 and 14 show the effect of different contents of nano-SiO₂ that was 50 nm in mean diameter on the mechanical properties of the rABS. According to the results, with increasing content of nanoparticles incorporated in the rABS, the impact strength first increased to a maximum and then declined quickly. The results indicate that the nanoparticles played the role of toughening the rABS under appropriate contents, but when the content was further increased, because of the coalescence of inorganic nanoparticles, shown in Figure 15 in the SEM image for the 4 wt % nano-SiO₂ filled rABS, the impact strength decreased rapidly. The flexural modulus and strength of the modified rABS increased with increasing content of nano-SiO₂. This reflected the rigid nature of the inorganic nanoparticles. Therefore, the inorganic nanoparticles synchro-

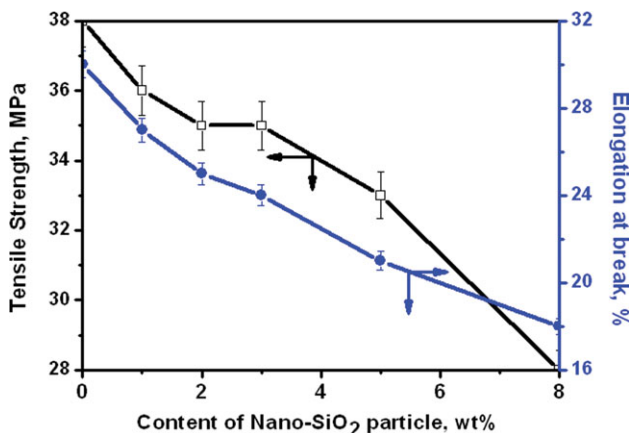


Figure 13. Effects of different contents of nano-SiO₂ (50 nm) on the tensile strength and elongation at break. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

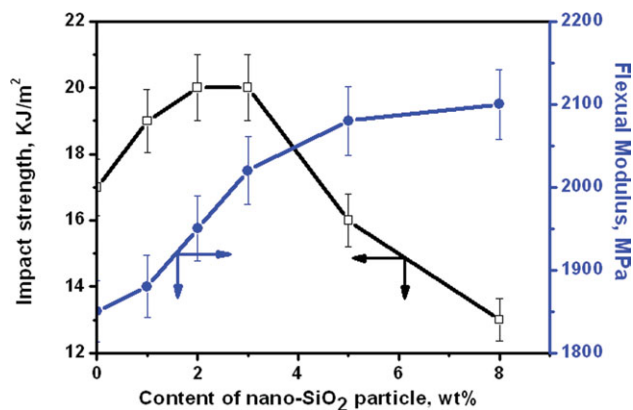


Figure 14. Effects of different contents of nano-SiO₂ (50 nm) on the impact strength and flexural modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nously increased the rigidity and toughness of the rABS under appropriate contents; this was different from the rABS toughened by the elastomer. Meanwhile, the incompatibility between the inorganic nanoparticles and resin matrix caused decreases in the tensile strength and elongation at break, but under low content, the extent of the decrease was acceptable. In a summary, it was better that the content of inorganic nanoparticles, when they were used solely to modify rABS, was 2 wt %.

Figure 16 shows the TEM images of the rABS strengthened by 2 wt % nano-SiO₂ particles. It can be seen that nanoparticles dispersed uniformly in the rABS bulk. However, it can also be observed that the diameter of the dispersed domain of nano-SiO₂, although there was some coalescence, was less than that of the rubber domain existing in the rABS bulk, so the tensile strength was not affected, but it could play the role of a skeleton and was beneficial to the rigidity of the rABS.

rABS Strengthened and Toughened by the Elastomer/Inorganic Nanoparticle Complex. According to the preceding results, the elastomer increased the toughness of the rABS evidently but decreased the rigidity of resin. Although the

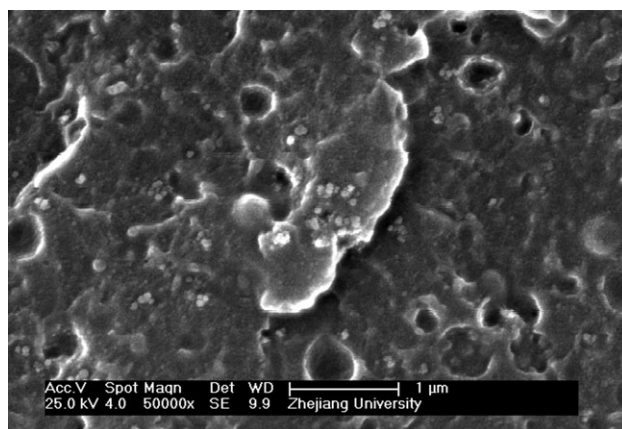


Figure 15. SEM images of the rABS filled with 4 wt % nano-SiO₂ particles (50 nm).

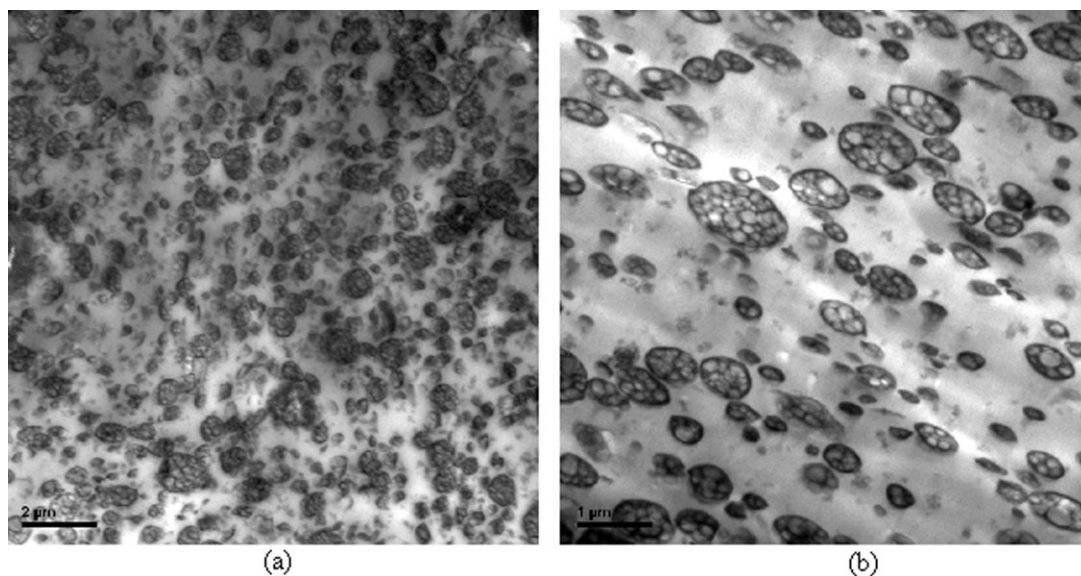


Figure 16. TEM images of the rABS strengthened by nano-SiO₂ particles (50 nm) at magnifications of (a) 10,000 and (b) 20,000 \times .

inorganic nanoparticles had a certain toughening effect, which was less evident than that of the elastomer, the inorganic nanoparticles could increase the rigidity of the rABS. Obviously, the elastomer and inorganic nanoparticles both contributed to the toughening of the rABS and complemented each other to increase the rigidity of the rABS. So the complex system of the elastomer and inorganic nanoparticles could be used to increase the integrated properties of the rABS, and a balance of rigidity and toughness in the rABS was achieved.

Figure 17 shows that the impact strength of the rABS modified by 5 wt % ABS graft powder increased with increase content of incorporated nano-SiO₂ and reached a maximum value when the content of nano-SiO₂ was 2 wt %. After that, the impact strength decreased with increasing content of incorporated nano-SiO₂. The previous results indicate that nano-SiO₂ increased the toughness of the rABS toughened by ABS graft

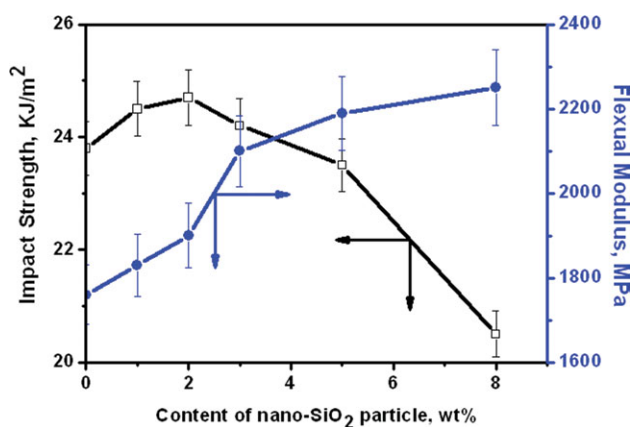


Figure 17. Impact strength and flexural modulus of the rABS toughened by 5% rubber powder as a function of the content of nano-SiO₂ (50 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

powder when the content was low, but the increased extent of toughness of the resin was not great. Meanwhile, the flexural modulus and strength of the rABS toughened by ABS graft powder increased with increasing content of nano-SiO₂. This demonstrated the rigid nature of the inorganic nanoparticles.

Figure 18 shows that the impact strength of the rABS modified by 2 wt % nano-SiO₂ increased with increasing content of incorporated ABS graft powder, and the extent of increased toughness was large. This demonstrated the characteristic of toughening of the elastomer. The flexural modulus of the rABS decreased with increasing content of incorporated ABS graft powder, and the decreased extent of the flexural modulus of the rABS was small when the content of ABS graft powder was low, such as less than 5 wt %. When the content of ABS graft powder was more than 5 wt %, the decreased extent of the flexural modulus increased. The previous results indicate that the

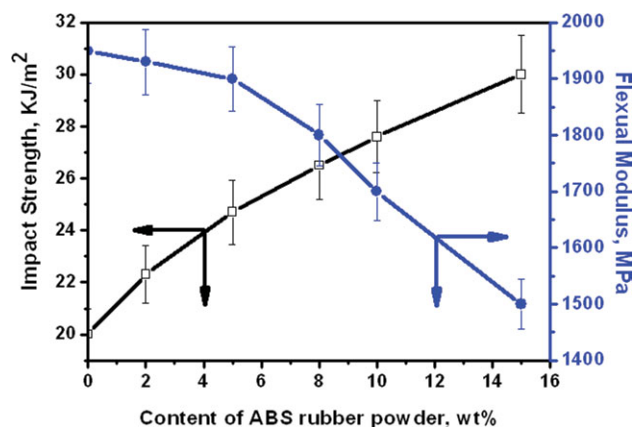


Figure 18. Effect of the content of the ABS rubber powder on the impact strength and flexural modulus of the rABS modified by 2 wt % nano-SiO₂ (50 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Properties of the rABS Modified by the ABS Rubber Powder and Nano-SiO₂ Complex System

Test item	Test standard	ABS rubber powder/inorganic nanoparticles	rABS	ABS (750)
Tensile strength (MPa)	ASTM D 638	37 ± 1	38 ± 1	47 ± 1
Young's modulus (MPa)	ASTM D 638	170 ± 4	170 ± 4	210 ± 4
Flexural strength (MPa)	ASTM D 790	63 ± 1	53 ± 1	68 ± 1
Flexural modulus (MPa)	ASTM D 790	2100 ± 40	1850 ± 40	2400 ± 50
Elongation at break (%)	ASTM D 638	33 ± 1	35 ± 1	30 ± 1
Izod impact strength (kJ/m ²)	ASTM D 256	24 ± 1	17 ± 1	25 ± 1
Heat distortion temperature (°C)	ASTM D 648	74	72	85

rigidity of the inorganic nanoparticles played a role in making the rABS more rigid and that the inorganic nanoparticles had a synergistic effect on the toughness of the rABS with the elastomer when the content of ABS graft powder was low. The flexural modulus of the rABS decreased greatly when the content of ABS graft powder was high. At this time, the deteriorating effect of the rubber phase on the rigidity of the rABS was greater than the rigidizing effect of the nanoparticles on rABS, and the rubber phase was the decisive factor in the rigidity of the rABS. Therefore, a low content of ABS graft powder is recommended to ensure that toughening agent has a synergistic effect with inorganic nanoparticles and to gain a balance of strengthening and toughening for rABS.

Table V shows the properties of the rABS modified by 6 wt % ABS graft powder and 3 wt % nano-SiO₂. According to the results, the complex modification system of inorganic nanoparticles and ABS graft powder not only increased the impact strength of the rABS evidently, which approached the level of the virgin ABS impact strength, but also increased the flexural modulus of the rABS greatly. The previous results indicate that

the components of the complex modification system complemented each other and had a synergistic effect on increasing the mechanical properties of the rABS. The system could also increase the heat distortion temperature of the rABS a little, but it had no contribution on increasing the tensile strength of the rABS.

Figure 19 shows the TEM images of the rABS modified by the ABS graft powder/nano-SiO₂ particles complex. It can be seen that the microstructural morphology was almost same as that of the rABS strengthened solely by nano-SiO₂ particles. The only difference was a denser rubber domain. Still, it was also observed that the diameter of the dispersed domain of nano-SiO₂ was less than that of the rubber domain existing in the rABS bulk and ABS graft powder, so these two component synergistically acted on the properties of the rABS.

In summary, to increase the integrated properties of rABS to meet demands of application, a complex modification system of inorganic nanoparticles and ABS graft powder should be considered first, and the recommended content of graft powder and inorganic nanoparticles are 5–8 and 2–3 wt %, respectively.

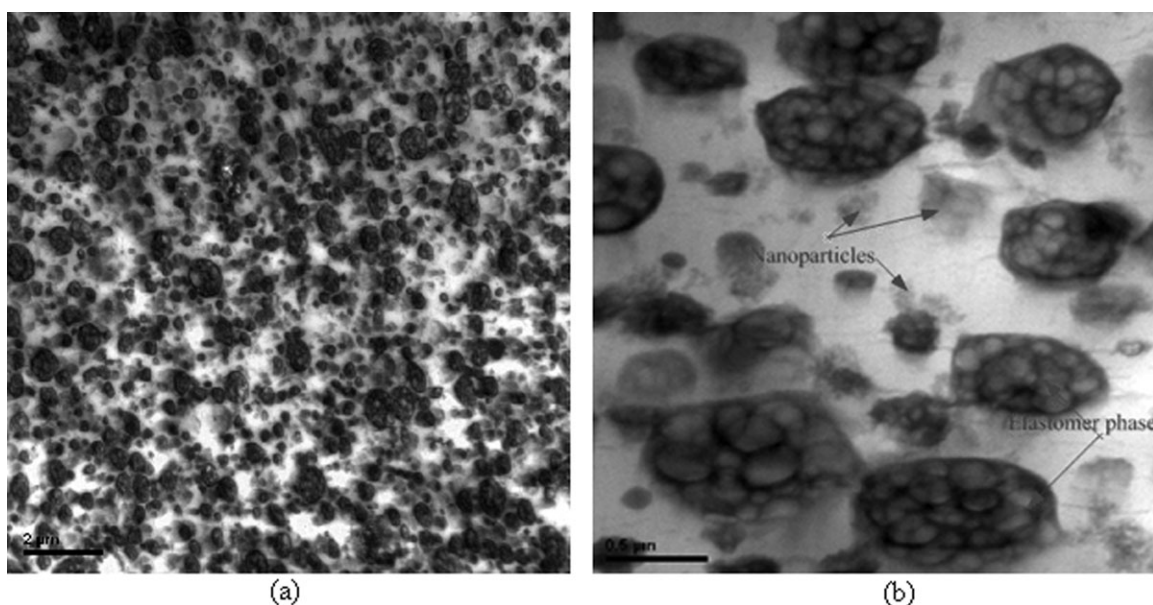


Figure 19. TEM images of the rABS modified by the ABS graft powder/nano-SiO₂ complex: (a) 10,000 and (b) 50,000×.

CONCLUSIONS

The aging of double bonds in the butadiene chain segment in the ABS molecular structure resulted in a reduction in the content of its rubber phase, decreased the molecular weight of ABS, and caused phase separation between the bulk and rubber phase. Thus, the mechanical properties of rABS decreased. Specifically, the impact strength decreased greatly, and the tensile strength, flexural modulus, heat distortion temperature, and weather resistance all decreased to a certain extent.

An elastomer restored the toughness, but it decrease the rigidity (flexural modulus) of the rABS. Inorganic nanoparticles toughened rABS partly, but their toughening effect was limited, and they also increased the rigidity.

An elastomer/inorganic nanoparticle complex had a synergistic effect, and the complex system increased the toughness of the rABS greatly. Both the stiffness and toughness of the resin were improved at the same time. By incorporating contents of 5–8 wt % ABS graft powder and 2–3 wt % inorganic nanoparticles into the rABS together, we achieved strengthening and toughening of the rABS.

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REFERENCES

1. Wang, J. K.; Ou, Z. H.; Zhou, Y. Q.; Jin, X. C. *Shang Hai Plast. (Chin.)* **2005**, *3*, 16.
2. Daisuke, H.; Yasuhito, I.; Haruo, W.; Masahiro, S. (to Sony Co.). U.S.Pat. 20,090,069,453 (A1; **2008**).
3. Chen, S. C.; Liao, W. H.; Hsieh, M. W.; Chien, R. D.; Lin, S. H. *Polym. Plast. Technol. Eng.* **2011**, *50*, 306.
4. Yeh, S. K.; Agarwal, S.; Gupta, R. K. *Compos. Sci. Technol.* **2009**, *69*, 2225.
5. Garcia, D.; Balart, R.; Sanchez, L.; Lopez, J. *Polym. Eng. Sci.* **2007**, *47*, 789.
6. Reig, M. J.; Segui, V. J.; Ferrandiz, S.; Zamanillo, J. D. *J. Polym. Eng.* **2007**, *27*, 29.
7. Liu, X. D.; Boldizar, A.; Rigdahl, M.; Bertilsson, H. *J. Appl. Polym. Sci.* **2002**, 1986, 2535.
8. Mantaux, O.; Lorriot, T.; Chibalon, L.; Aurrekoetxea, J.; Puerto, A.; Arostegi, A.; Urrutibeascoa, I. *J. Mater. Sci. Technol.* **2004**, *20*, 135.
9. Liu, X. D.; Bertilsson, H. *J. Appl. Polym. Sci.* **1999**, *74*, 510.
10. Rybnicek, J.; Lach, R.; Lapcikova, M.; Steidl, J.; Krulis, Z.; Grellmann, W.; Slouf, M. *J. Appl. Polym. Sci.* **2008**, *109*, 3210.
11. Jouan, X.; Gardette, J. L. *J. Polym. Sci. Part A: Polym. Chem.* **1991**, *29*, 685.
12. Jouan, X.; Gardette, J. L. *Polym. Degrad. Stab.* **1992**, *36*, 91.
13. Magali, P.; Agnes, R. *Polym. Degrad. Stab.* **1997**, *55*, 147.
14. Ren, J. F.; Wang, J. Q.; Wang, H. G.; Zhang, J. Y.; Yang, S. G. *J. Macromol. Sci. Phys.* **2009**, *48*, 1069.
15. Shi, G.; He, L. J.; Chen, C. Z.; Liu, J. F.; Liu, Q. Z.; Chen, H. Y. *Adv. Mater. Res.* **2011**, *150–151*, 857.
16. Song, J. R.; Shen, Z. G.; Chen, J. F.; Chu, G. W.; Wang, G. Q. *Polym. Mater. Sci. Eng. (Chin.)* **2004**, *20*, 126.
17. Jiang, L.; Lam, Y. C.; Tam, K. C.; Chua, T. H.; Sim, G. W.; Ang, L. S. *Polymer* **2005**, *46*, 243.