

A Study on Functionalizing SEBS Through Ozone Treatment and the Mechanical Properties of its Blend with Polyamide 6

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ABSTRACT: Two types of styrene-*b*-(ethylene-*co*-1-butene)-*b*-styrene triblock copolymer (SEBS) were functionalized through ozone treatment. The structure and properties of ozonized SEBS and the mechanical properties of their blend with Polyamide 6 (PA6) were studied by FTIR spectroscopy, gel permeation chromatography, gel content measurement, contact angle measurement, SEM, and mechanical properties measurement. The experimental results show that through ozone treatment, some oxygen-containing groups (mainly carbonyl groups) are introduced onto the molecular chains of SEBS. The polarity of SEBS is thus improved. Compared with star-shaped SEBS602, SEBS503 of linear shape is more susceptible to ozone oxidation. The polarity of ozonized SEBS503 is higher than that of ozonized SEBS602. The improvement of mechanical properties of PA6/ozonized SEBS blend is attributed to the improve-

ment of the dispersion of ozonized SEBS in PA6 matrix and the interfacial adhesion between PA6 and ozonized SEBS. Compared with that of PA6/ozonized SEBS602 blend, the size of dispersed phase in PA6/ozonized SEBS503 blend is smaller, and the interfacial adhesion is stronger. The notched Izod impact strength of PA6/ozonized SEBS503 (90 min) (90/10) blend is 49.6 kJ/m², is higher than that of PA6/ozonized SEBS602 (90 min) (90/10) blend, which is only 21.3 kJ/m². The impact strength of PA6/ozonized SEBS503 (90 min) (80/20) blend is 68.7 kJ/m², is still higher than that of PA6/ozonized SEBS602 (90 min) (80/20) blend, which is 60.2 kJ/m². © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1281–1287, 2008

Key words: SEBS; PA6; ozone treatment; functionalization; toughness

INTRODUCTION

Polyamide 6 (PA6) is one of the most useful polymers for engineering applications because of its high melting temperature, high strength, and good chemical resistance. However, PA6 suffers from high moisture absorption and high impact notch sensitivity. For improving its toughness, PA6 is usually blended with various elastomers such as ethylene-propylene-diene monomer rubber, ethylene-propylene rubber, and styrene-*b*-(ethylene-*co*-1-butene)-*b*-styrene triblock copolymer (SEBS).^{1,2}

SEBS is one of commercially important thermoplastic elastomers. It is widely used as plastics, coatings, adhesives, sealants, footwear, and impact modifiers in engineering plastics.³ Because of the nonpolar nature of SEBS elastomer, the compatibility and adhesion between SEBS and polar materials are poor. Blends of polyamides and unfunctionalized SEBS tend to have low impact toughness because SEBS particles formed during melt blending are rela-

tively large, and the interfacial interaction between polyamide and SEBS is weak. For improving the polarity of hydrophobic polymer such as SEBS, some methods have been investigated, including chemical methods and irradiation techniques.

For the conventional chemical approach, some polar monomers like maleic anhydride are usually grafted onto the molecular chains of SEBS elastomer.^{4–11} These functional groups could react with the amine groups of PA6, leading to both a finer dispersion of SEBS elastomers and a better adhesion between SEBS elastomers and PA6 matrix. Consequently, the elastomers act as stress concentrators favoring the dissipation of impact energy. However, chemical grafting techniques are complex, cause environmental pollutions, and damage the apparatus. Furthermore, grafting monomer residues affect thermal, electrical, and mechanical properties of the materials.

Irradiation technologies, involve exposure of the polymer surface to ultraviolet light, electron beam, or gamma ray. The irradiation in air causes oxidation of polymer. The chemical or physical changes occur mainly in the polymer surface without affecting the bulk properties seriously.^{12–22} The irradiation methods are efficient, require no solvent and chemicals.

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Ozone, the isotope of oxygen, has been applied to the grafting and oxidation of polymers.^{23–29} Compared with conventional chemical grafting methods and irradiation modification techniques, functionalization through ozone treatment has many advantages such as simple equipment, low operation cost, and absence of various noxious chemical additives. Ozone treatment is suggested as an alternative to the traditional chemical methods to modify the molecular structure of polymers, and is paid more and more attentions.

In this study, two types of SEBS were functionalized through ozone treatment. Some oxygen-containing groups (mainly carbonyl group) were introduced onto the molecular chains of SEBS copolymer, which led to the improvement of the interfacial interaction of PA6 and ozonized SEBS. The impact strength of PA6/ozonized SEBS blend was thus improved. The effect of ozone treatment on molecular structure of two kinds of SEBS and the toughness of their blends with PA6 were also compared in this article.

EXPERIMENTAL

Materials

The SEBS used in this work was SEBS YH-503, which is linear molecule structure, containing 33% styrene and SEBS YH-602, which is star molecule structure, containing 35% styrene. Both of these SEBS were obtained from Balin Petrochemical Company of China. PA6 M52800, with a melt index of 6.16 g/10 min and a relative viscosity of 2.8, was obtained from Xihuimeida-DSM Nylon Chips Corp. of China.

The ozone treatment of SEBS

The home-made apparatus for ozone treatment is shown in Figure 1. The ozone treatment of SEBS was performed at 80°C for different times, the ozone concentration was 55 mg/L and the gas flux was 0.1 m³/h.

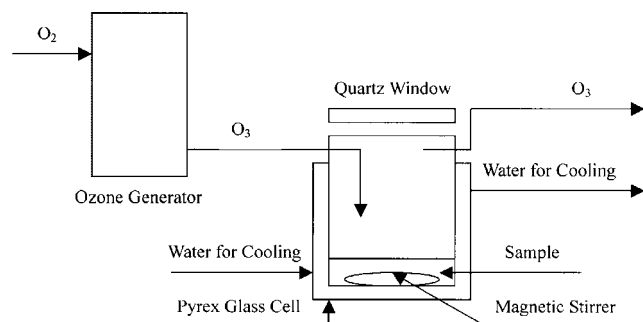


Figure 1 The schematic diagram of apparatus for ozone treatment.

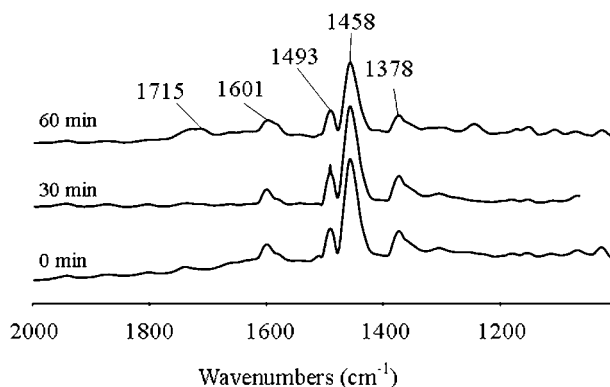


Figure 2 FTIR spectra of SEBS503 ozonized at different time.

Sample preparation and mechanical properties testing

SEBS or ozonized SEBS was blended with PA6 with a twin screw extruder, then injection molded to the specimens for mechanical properties measurement. Tensile tests were performed using an Instron tensile tester 4302 (Instron Corp., USA) under a crosshead speed of 50 mm/min at 23°C according to ISO 527-1993E. At least five specimens of each composition were tested and the average values were reported. Notched Izod Impact tests were conducted with XJ40-A impact tester (Wuzhong Test Instrument Plant, China) according to ISO 180-1993. Seven specimens were tested and the average values reported.

Fourier transform infrared spectroscopy

FTIR spectra were recorded on a Nicolet-560 FTIR spectrometer (Nicolet Corp., USA). SEBS samples were first dissolved in chloroform. The solutions were coated on KBr crystal surface to form a thin film, and solvent was evaporated under infrared lamp. Carbonyl group (C=O) contents were evaluated by $A_{C=O}/A_{CH_3}$ ratios, where the $A_{C=O}$, and A_{CH_3} are areas of absorption peaks at 1715 cm⁻¹ and 1378 cm⁻¹ in the FTIR spectra, respectively.

GPC analysis

Gel permeation chromatography (GPC) analyses were performed using an Agilent1100 GPC instrument (Agilent Corp., USA) (solvent of mobile phase: tetrahydrofuran, temperature: 25°C, velocity of flow: 1 mL/min).

Gel content measurement

Gel content was determined with a Soxhlet extractor. The samples were exposed to refluxing chloroform

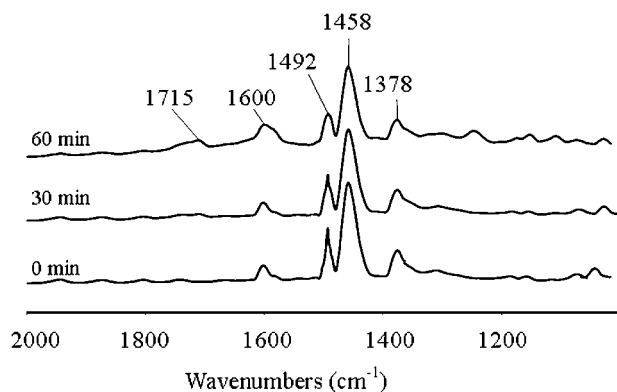


Figure 3 FTIR spectra of SEBS602 ozonized at different time.

for 72 h. The insoluble residual gel was weighed after drying.

Static contact angle measurement

Static contact angle of SEBS with distilled water and liquid paraffin was measured with Erma G-1 contact angle tester at room temperature.

SEM observation

The fractured surfaces of specimens after frozen with liquid nitrogen and the impact fractured surfaces were observed with X-650 Scanning Electron Microanalyzer (Hitachi Corp., Japan). The fractured surfaces of specimens frozen with liquid nitrogen were etched with chloroform so as to remove SEBS particles on the surface.

RESULTS AND DISCUSSION

FTIR analysis

SEBS is a hydrophobic thermoplastic elastomer. Through ozone treatment, oxygen-containing groups (mainly carbonyl groups, situated at 1715 cm^{-1} in FTIR spectra) are introduced onto the molecular chains of SEBS (Figs. 2 and 3). With the increase of ozonization time, the peak of carbonyl group increases, indicating that the content of carbonyl groups increases. Carbonyl group (C=O) contents were evaluated by $A_{\text{C=O}}/A_{\text{CH}_3}$ ratio, where the $A_{\text{C=O}}$, and A_{CH_3} are the areas of absorption peaks at

TABLE I
FTIR Analysis of Ozonized SEBS

| Ozonization time (min) | $A_{\text{C=O}}/A_{\text{CH}_3}$ | |
|------------------------|----------------------------------|---------|
| | SEBS503 | SEBS602 |
| 60 | 0.90 | 0.71 |

TABLE II
Average Molecular Weight and its Distribution and Gel Content of Ozonized SEBS503

| Ozonization time (min) | $\bar{M}_w (\times 10^5)$ | $\bar{M}_n (\times 10^5)$ | \bar{M}_w/\bar{M}_n | Gel (%) |
|------------------------|---------------------------|---------------------------|-----------------------|---------|
| 0 | 2.91 | 2.67 | 1.09 | 0 |
| 10 | 2.65 | 1.87 | 1.72 | 0 |
| 30 | 2.13 | 0.94 | 2.26 | 0 |
| 60 | 1.89 | 0.35 | 5.37 | 0 |

\bar{M}_w , weight average molecular weight; \bar{M}_n , number average molecular weight.

1715 cm^{-1} and 1378 cm^{-1} in the FTIR spectra, respectively. Compared with ozonized SEBS602, which is star molecule structure, the $A_{\text{C=O}}/A_{\text{CH}_3}$ ratio of ozonized SEBS503, which is linear molecule structure, is higher (Table I), indicating that SEBS503 is more susceptible to ozone oxidation.

GPC and gel content analysis

The average molecular weight and distribution of SEBS503 and SEBS602 ozonized at different time were studied by GPC as shown in Tables II and III. The gel contents of the samples were also measured. After ozone treatment, the average molecular weight of SEBS decreases, its distribution becomes wider and no gel is formed, which indicates that the ozone treatment causes the oxidation degradation of SEBS. While ozonization time is 60 min, compared with SEBS602, SEBS503 is degraded more seriously (Tables II and III).

Static contact angle measurement

The static contact angle measurement of a substrate with water is an effective method of evaluating the hydrophilic or hydrophobic nature of the substrate surface. SEBS is a hydrophobic polymer. Through ozone treatment, oxygen-containing groups (mainly carbonyl groups) are introduced onto the molecular chains of SEBS (Figs. 2 and 3). With the increase of ozonization time, the static contact angle of SEBS with water becomes smaller, and the static contact angle with liquid paraffin increases (Table IV), indicating that the polarity of SEBS increases. While

TABLE III
Average Molecular Weight and its Distribution and Gel Content of Ozonized SEBS602

| Ozonization time (min) | $\bar{M}_w (\times 10^5)$ | $\bar{M}_n (\times 10^5)$ | \bar{M}_w/\bar{M}_n | Gel (%) |
|------------------------|---------------------------|---------------------------|-----------------------|---------|
| 0 | 2.48 | 1.74 | 1.43 | 0 |
| 60 | 1.88 | 0.65 | 2.89 | 0 |

TABLE IV
Static Contact Angle of Ozonized SEBS

| Ozonization time (min) | SEBS503 | | SEBS602 | |
|------------------------|------------------------------|---|------------------------------|---|
| | Contact angle with water (°) | Contact angle with liquid paraffine (°) | Contact angle with water (°) | Contact angle with liquid paraffine (°) |
| 0 | 88 | 20 | 92 | 18 |
| 10 | 82 | 23 | 86 | 20 |
| 30 | 73 | 30 | 77 | 27 |
| 60 | 65 | 45 | 71 | 40 |

ozonization time is the same, compared with ozonized SEBS602, the static contact angle with water of SEBS503 is smaller, and the static contact angle with liquid paraffin is larger, which means that the polarity of ozonized SEBS503 is higher than that of ozonized SEBS602. These results further prove that some polar groups are introduced onto the molecular chains of SEBS, and agree with the FTIR analysis.

Mechanical properties of PA6/ozonized SEBS blend

Owing to weak interfacial interaction between PA6 and SEBS and poor dispersion of SEBS in PA6 matrix, the notched Izod impact strength of PA6/SEBS blend is lower. Compared with PA6, the impact strength of PA6/SEBS503 (80/20) and PA6/SEBS602 (80/20) blend is increased from 8.8 to 21.5 and 16.4 kJ/m², respectively (Fig. 4).

When ozonization time is 60 min, compared with PA6/SEBS602 blend, the impact strength of PA6/ozonized SEBS602 (60 min) blend increases slightly.

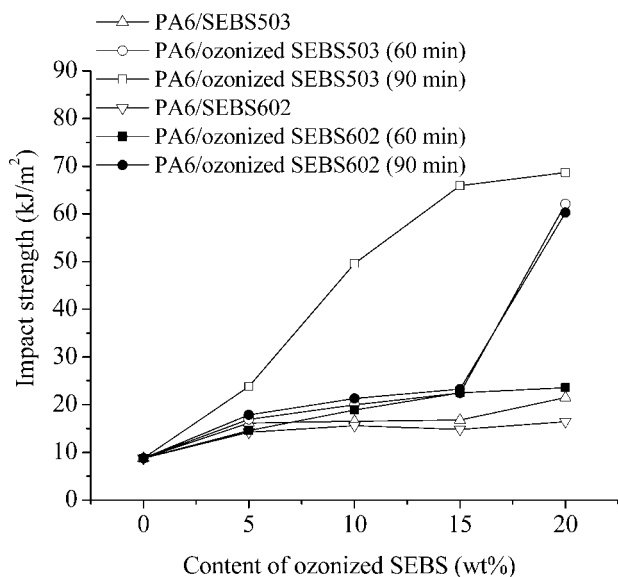


Figure 4 Notched Izod impact strength of PA6/ozonized SEBS blend vs. content of ozonized SEBS.

The impact strength of PA6/ozonized SEBS602 (60 min) (80/20) blend is only 23.5 kJ/m². However, for SEBS503 of linear molecule structure, when the content of ozonized SEBS503 (60 min) beyond 15 wt %, the impact strength of PA6/ozonized SEBS503 (60 min) blend increases greatly. When the content of ozonized SEBS503 (60 min) is 20 wt %, the impact strength of PA6/ozonized SEBS503 blend is 62.1 kJ/m² (Fig. 4).

After SEBS was ozone treated for 90 min, the impact strength of PA6/ozonized SEBS (90 min) blend increases obviously (Fig. 4). For PA6/ozonized SEBS602 (90 min) blend, its impact strength increases slowly while the content of ozonized SEBS602 (90 min) is less than 15%. When the content of ozonized SEBS602 (90 min) exceeds 15%, the impact strength increases greatly. For the blend of PA6/ozonized SEBS602 (90 min) (80/20), its impact strength is 60.2 kJ/m². With the increase of ozonized SEBS503 (90 min) content, the impact strength of PA6/ozonized SEBS503 (90 min) blend increases greatly. For PA6/ozonized SEBS503 (90 min) (90/10) blend, its impact strength is 49.6 kJ/m², is higher than that of PA6/ozonized SEBS602 (90 min) (90/10) blend, which is only 21.3 kJ/m². When the content of ozonized SEBS503 (90 min) is 20 wt %, the impact strength of PA6/ozonized SEBS503 (80/20) blend is 68.7 kJ/m², which is still higher than that of PA6/ozonized SEBS602 (90 min) (80/20) blend.

Through ozone treatment, oxygen-containing groups (mainly carbonyl groups) are introduced onto the molecular chains of SEBS. These carbonyl groups could interact with the polar amino groups on the molecular chains of PA6, the interfacial interaction between PA6 and SEBS is thus strengthened. Because of the improvement of interfacial interaction, the SEBS particles act as stress concentrators, and the interfacial phase can transmit the stress to PA6 matrix, then make the matrix absorb energy by plastic yield or deformation, the impact strength of PA6/ozonized SEBS blend is thus improved. Compared with ozonized SEBS602, ozonized SEBS503 is more effective to toughen PA6.

For the same content of ozonized SEBS in PA6 matrix, with increasing ozonization time, the tensile

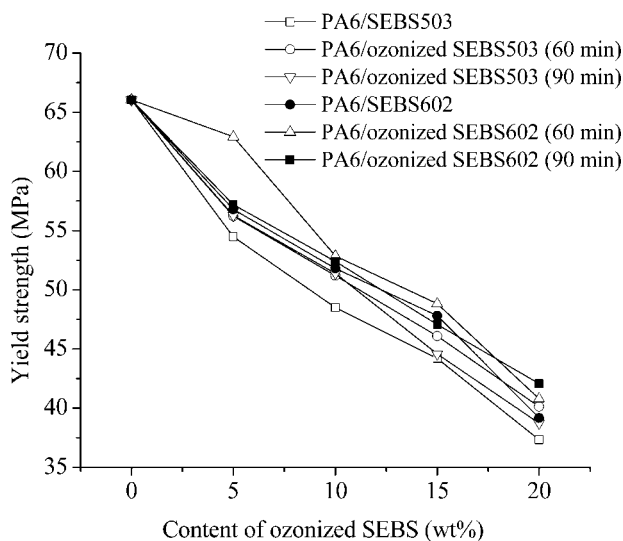


Figure 5 Yield strength of PA6/ozonized SEBS blend vs. content of ozonized SEBS.

yield strength of PA6/ozonized SEBS changes slightly (Fig. 5). With the increase of ozonized SEBS content, the tensile yield strength of PA6/ozonized SEBS is decreased gradually. When the content of ozonized SEBS is same, the yield strength of PA6/ozonized SEBS602 blend is slightly higher than that of PA6/ozonized SEBS503 blend.

With the increase of ozonized SEBS content, the elongation at break of PA6/ozonized SEBS increases (Fig. 6). For the same content of ozonized SEBS, the elongation at break of PA6/ozonized SEBS blend is improved with the increase of ozonization time of SEBS. This is due to that SEBS particles disperse more evenly and the interfacial interaction between SEBS and PA6 matrix is strengthened with the increase of ozonization time of SEBS. For the same content of SEBS, the elongation at break of PA6/SEBS503 and PA6/SEBS602 blend is almost same. Moreover, when ozonization time is 60 min, the elongation at break of PA6/ozonized SEBS503 and PA6/ozonized SEBS602 blend is also almost same.

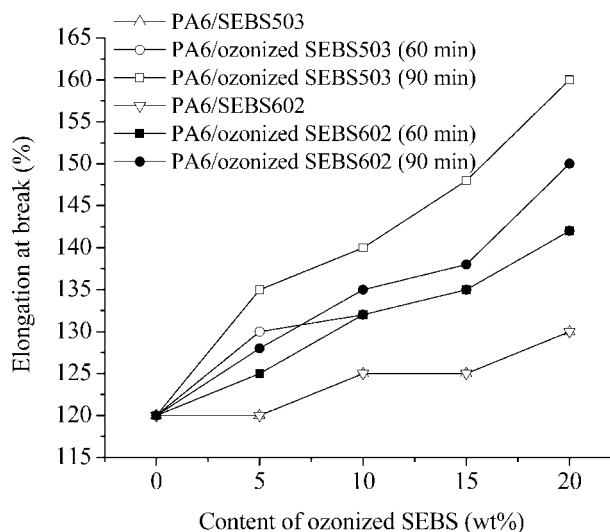


Figure 6 Elongation at break of PA6/ozonized SEBS blend vs. content of ozonized SEBS.

When the ozonization time is increased to 90 min, the elongation at break of PA6/ozonized SEBS503 (90 min) blend is higher than that of PA6/ozonized SEBS602 (90 min) blend.

SEM observation of PA6/ozonized SEBS blend

The dispersion of SEBS in PA6 matrix and the interfacial adhesion between PA6 and SEBS could be observed from SEM photos of the impact fractured surfaces of the specimen. For PA6/SEBS blend, SEBS particles expose on the surface and disperse unevenly, and some holes are formed by desquamation of SEBS particles during the impact process [Figs. 7(a) and Fig 8(a)], indicating the poor dispersion of SEBS particles in PA6 matrix and the weak interfacial adhesion between SEBS and PA6 matrix. The ozonized SEBS particles in PA6/ozonized SEBS blend become smaller and are wrapped by PA6 matrix [Figs. 7(b) and 8(b)], indicating that both the

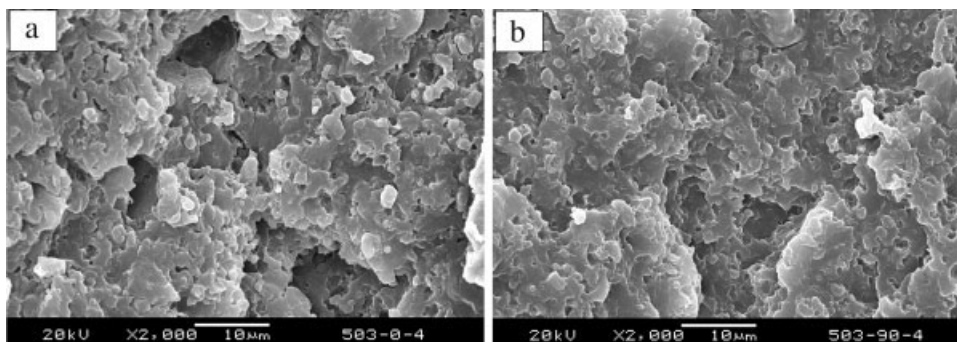


Figure 7 SEM of impact fractured surface of PA6/ozonized SEBS503 blend ($\times 2000$). (a) PA6/SEBS503 (80/20), (b) PA6/ozonized SEBS503 (90 min) (80/20).

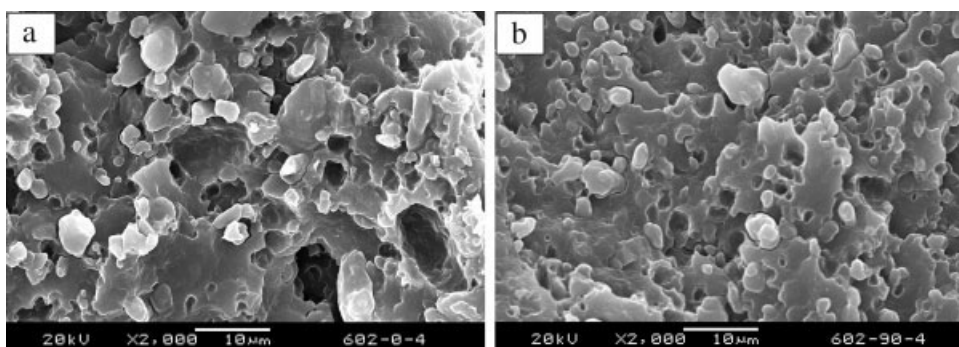


Figure 8 SEM of impact fractured surface of PA6/ozonized SEBS602 blend ($\times 2000$). (a) PA6/SEBS602 (80/20), (b) PA6/ozonized SEBS602 (90 min) (80/20).

dispersion and interfacial adhesion are improved because of ozone treatment of SEBS.

Compared with SEBS602 particles in PA6/SEBS602 blend [Fig. 8(a)], SEBS503 particles in PA6/SEBS503 blend [Fig. 7(a)] are smaller and are wrapped by PA6 matrix much better. After ozone treatment of SEBS, this difference is much more obvious. For PA6/ozonized SEBS503 blend [Fig. 7(b)], the ozonized SEBS503 particles are much smaller and almost all are wrapped by PA6 matrix. On the contrary, in PA6/ozonized SEBS602 blend [Fig. 8(b)], there are still more ozonized SEBS602 particles exposed on the surface of impact fractured specimen and the ozonized SEBS602 particles are relatively larger. This result is further approved by SEM photos of liquid nitrogen frozen fractured surface of PA6/ozonized SEBS blend (Fig. 9). The fractured surface of the specimen after frozen with liquid nitrogen was etched with chloroform so as to remove SEBS particles on the surface. Compared with PA6/ozonized SEBS602 blend [Fig. 9(b)], the particles of ozonized SEBS503 are smaller and disperse more evenly in PA6 matrix [Fig. 9(a)].

SEM observations indicate that the dispersion of ozonized SEBS503 in PA6 matrix and interfacial

adhesion between PA6 and ozonized SEBS503 are both better than those of ozonized SEBS602, respectively.

CONCLUSIONS

Through ozone treatment, some oxygen-containing groups (mainly carbonyl groups) are introduced onto the molecular chains of SEBS. The polarity of SEBS is thus improved. Ozone treatment causes the degradation of SEBS. Its average molecular weight is decreased and distribution becomes wider. Compared with SEBS602, which is star molecule structure, SEBS503 which is linear molecule structure is more susceptible to ozone oxidation. The polarity of ozonized SEBS503 is higher than that of ozonized SEBS602. Through ozone treatment, both the dispersion of ozonized SEBS in PA6 matrix and interfacial adhesion between PA6 and ozonized SEBS are improved, the mechanical properties of PA6/ozonized SEBS are thus improved. Compared with that of PA6/ozonized SEBS602 blend, the size of dispersed phase in PA6/ozonized SEBS503 blend is smaller, and the interfacial adhesion is stronger. The impact strength of PA6/ozonized SEBS503 (90 min)

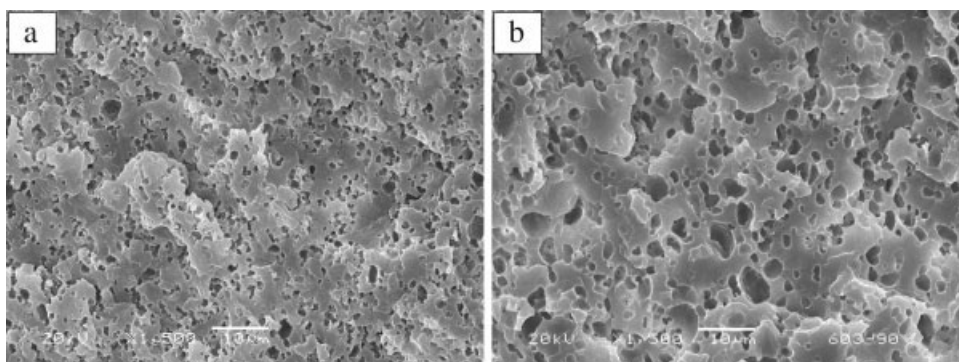


Figure 9 SEM of liquid nitrogen frozen fractured surface of PA6/ozonized SEBS blend ($\times 1500$). (a) PA6/ozonized SEBS503 (90 min) (80/20), (b) PA6/ozonized SEBS602 (90 min) (80/20).

(90/10) blend is 49.6 kJ/m^2 , is higher than that of PA6/ozonized SEBS602 (90 min) (90/10) blend, which is only 21.3 kJ/m^2 . The impact strength of PA6/ozonized SEBS503 (90 min) (80/20) blend is 68.7 kJ/m^2 , is still higher than that of PA6/ozonized SEBS602 (90 min) (80/20) blend, which is 60.2 kJ/m^2 . These results indicate that ozonized SEBS503 is more effective to toughen PA6 than ozonized SEBS602. With increasing ozonization time of SEBS, the tensile yield strength of PA6/ozonized SEBS blend changes slightly and the elongation at break of the blend increases.

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