

UV Exposure Effects on Photoinitiator-Grafted Styrene-Butadiene-Styrene Triblock Copolymer

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ABSTRACT: The grafted copolymer (SBS-g-MBP) with different grafting ratio, synthesized by our laboratory, was irradiated by ultraviolet (UV) radiation with different time. The structure of SBS-g-MBP before and after UV exposure was characterized by Fourier transform infrared spectrometer, and the results confirmed that the UV-crosslinked structure was formed. The gel fraction before and after UV exposure was discussed, and the results indicated that the gel fraction increased with both exposure time and grafting ratio, and it also indicated the gel fraction was affected mainly by the exposure time. Further-

more, the results of scanning electron microscopy showed that the mode of fracture surfaces transmitted gradually from tough fracture to brittle fracture. The differential scanning calorimetry and thermal gravimetric analyzer indicated that the crosslinking has taken place in the polybutadiene block, and the thermal property was improved after UV exposure. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2627–2631, 2011

Key words: SBS; UV exposure; grafted polymer; crosslinking

INTRODUCTION

Thermoplastic elastomer (TPE), a polymer category of attractive elastic properties and convenience in processing and recycling, is widely used in industries.¹ The styrene-block-butadiene-block-styrene (SBS) triblock copolymer is one of the most productive and important TPE widely used in various applications, such as footwear, impact modifiers in engineering plastics, and adhesives, because of its good balance of mechanical properties along with favorable processability and recyclability.^{2–7}

However, SBS contains plentiful carbon–carbon double bond, and the glass transition temperature of polystyrene (PS) blocks is $\sim 100^\circ\text{C}$. So, it can not be used at high temperature or where solvent resistance and chemical resistance are required. Therefore, many researchers used technology of ultraviolet (UV) exposure to improve property of SBS. Yang et al.^{8,9} researched the graft copolymerisation of dimethyl amino ethyl methacrylate with SBS and found that the degree of grafting was related to the irradiation time, dimethyl amino ethyl methacrylate concentration, and temperature. And the grafted

polymer could be used as biomedical material. Kennedy et al.¹⁰ have successfully grafted SBS with acrylic acid via UV polymerization techniques for use as a potential biomedical material and in doing so; they proved that the glass transition values for each of the grafted copolymers increased in the butadiene domain, thus proving that grafting had occurred. Geever et al.^{11,12} investigated the spectral, thermal, and surface characteristics of a random styrene butadiene rubber with monomeric graft(s) of acrylic acid, *N*-vinyl-2-pyrrolidinone, or Nisopropylacrylamide synthesized using UV polymerization. And they have evaluated the potential use of UV polymerized SBS-g-Nisopropylacrylamide copolymers for biomedical applications.¹³ Besides UV grafting, UV crosslinking was one of more familiar methods to get high property's SBS. Decker et al.^{14–16} applied a combination of photoinitiators and trimethylolpropane mercaptopropionate (TRIS) as the crosslinking agent. By means of a UV radiation source in air, photo-crosslinked SBS and SIS films were quickly produced, which increased solvent and heat resistance over noncrosslinked films, and made them more suitable for the higher temperature requirements of flexographic applications. Lim et al.¹⁷ used thiolene reactions to prepare the UV-crosslinked polystyrene–isoprene–polystyrene (SIS)/SBS blends, which were used for hot-melt techniques, and its thermal stability also increased. Mateo and coworkers¹⁸ used two photoinitiators

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(benzophenone and 2,2-dimethoxy-2-phenylacetophenone) to prepare the photo-crosslinked SBS films, and studied the diffusion of organic solvents through them. Kim et al.¹⁹ reported that crosslinking of the polybutadiene (PB) block was achieved after 3 min of irradiation of UV light under nitrogen environment. These examples indicated that the chemical and physical properties of SBS TPE could be altered significantly through modification of the butadiene elastomeric segment via crosslinking. In our previous study,²⁰ we presented a new generation of UV crosslinking solvent-based pressure-sensitive adhesive (PSA) based on photoinitiator-grafted polystyrene-block-polybutadiene-block-polystyrene (SBS-g-MBP). This PSA would be suited specially to use as medical PSA because of photoinitiator grafted onto rubber: no influence about the crosslinking reaction by oxygen; no poisonous and harmful cleavage products; no migration of excess photoinitiator.

From the earlier point of view, technology of UV is an effective way to improve the property of SBS. Photoinitiator grafted SBS will draw more attention in the future. Especially, it would be attractive for biomedical materials applications such as medical PSA. However, no research was reported about UV exposure effects on SBS-g-MBP. Therefore, in this article, the effect of UV exposure on SBS-g-MBP was investigated. Emphasis was placed on the effects of UV exposure on the structure, gel fraction, morphology, and thermal property, and some good results were obtained.

EXPERIMENTAL

Materials

SBS-g-MBP was synthesized in our laboratory.²⁰ Figure 1 shows the structure formula of SBS-g-MBP. Toluene, of analytical grade, was supplied by Shanghai Chemical Reagent Co., China.

Preparation of UV-crosslinked SBS-g-MBP samples

Weighted SBS-g-MBP was dissolved in toluene, and then the mixture was poured into a petri dish. To enhance the speed of UV crosslinking, TRIS was used as the crosslinking agent, which could crosslink the PB block in SBS due to three S-H groups in TRIS.^{14–16} It was added to a toluene solution of SBS-g-MBP at a concentration 2 wt% of SBS-g-MBP. The prepared samples were casted in a self-made vessel, and then samples were exposed to the radiation of an 80 W/cm medium pressure mercury lamp, in the presence of air, at a passing speed of 60 m/min, which corresponds to exposure duration of 0.1 s per pass. The maximum light intensity at the sample position was measured by radiometry to be 600 mW cm⁻² in the

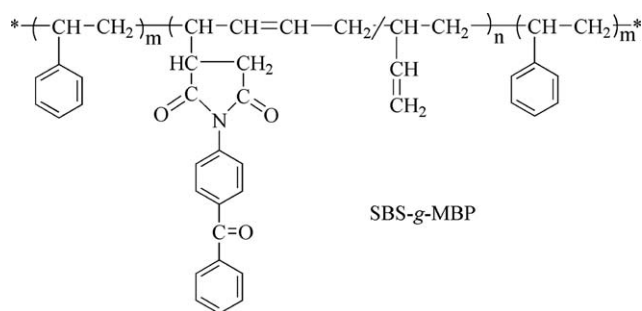


Figure 1 Structure formula of the SBS-g-MBP.

UV range. The resultant homogeneous crosslinked SBS was dried in a vacuum oven at 80°C, and the thickness of the crosslinked SBS was 0.120 ± 0.001 mm. The gel content provides information on the degree of crosslinking. Gel content of the irradiated polymer was determined by extracting the sample in boiling toluene for 48 h. The insoluble polymer was vacuum-dried at 100°C to constant weight. The gel fraction (*w*) was obtained by Eq. (1), as follow:

$$W = \frac{M_2 - M_1}{M_0} \times 100\% \quad (1)$$

where M_0 is weight of the sample before extraction, M_1 is weight of the filter paper after extraction, and M_2 is the total weight of the sample and filter paper after extraction.

Analytical instruments

Fourier transform infrared spectrometer (FTIR) analysis was performed on a WQF-410 Fourier transform infrared spectrometer (Beijing, China) between 4000 and 400 cm⁻¹ in the form of KBr pellets. Quantitative analyses were made by the peak area ratio of the C=C stretching region (1645 cm⁻¹). The ring breathing stretching region (1493 cm⁻¹) of styrene units was used as the internal standard peak, which was seen to be invariant during UV exposed and thermal treatment.²¹ The thermal stability of the samples (~ 7 mg) was investigated with a thermal gravimetric analyzer (TGA, a Netzsch STA 449C) under nitrogen from room temperature (~ 30°C) to 800°C at a heating rate of 10°C/min. The morphological modifications produced on the SBS-g-MBP fracture surfaces were analyzed using a scanning electron microscopy (SEM, JEOL-6700). The grafting samples were gold-coated before analysis. Glass transition temperature (T_g) of the sample was determined by differential scanning calorimetry (DSC-822e, Mettler-Toledo Corp., Swiss). The sample was scanned from -110 to 0°C at a programmed rate of 10°C/min, using indium to calibrate the temperature and heat flow of the DSC device.

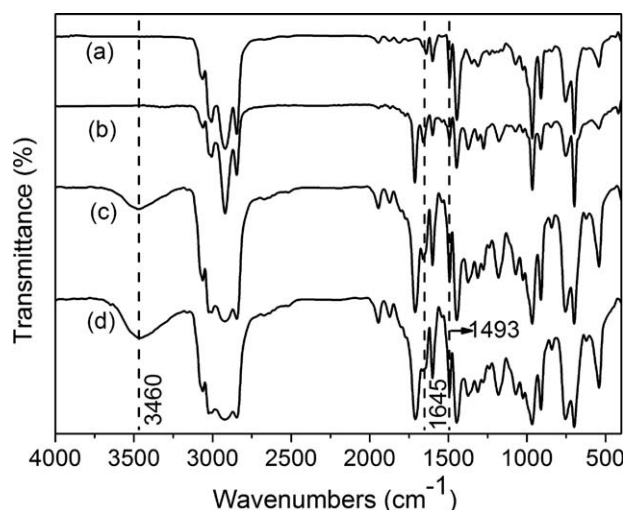


Figure 2 FT-IR spectra of (a) pure SBS, (b) SBS-g-MBP, (c) UV-crosslinked SBS-g-MBP (graft yield = 7.4%, and exposure time = 2 min), and (d) UV-crosslinked SBS-g-MBP (graft yield = 7.4%, and exposure time = 3 min).

RESULTS AND DISCUSSION

Indication of UV radiation

The chemical groups of the SBS, SBS-g-MBP, and SBS-g-MBP after UV exposure are investigated by FTIR spectra shown in Figure 2. As shown in Figure 2, when compared with pure SBS and SBS-g-MBP, we can see that an absorption band at 3460 cm^{-1} corresponding to hydroxyl group of initiator (Fig. 3) in the IR spectra of UV crosslinked SBS; it indicates that the crosslinking has occurred, which is because MBP is a type of photoinitiator with capturing hydrogen, and this kind of photoinitiator is often used in the thiolene photopolymerization.¹⁴ The benzoyl radical produced by the photocleavage reaction is also capable to abstract a hydrogen atom from the thiol to generate the propagating thiol radical.²² The mechanism of the crosslinking reaction is depicted in Figure 3. Furthermore, Table I shows the relationship between the exposure time and the content of the C=C. The Table shows that the content of the C=C are decreased with an increase of exposure

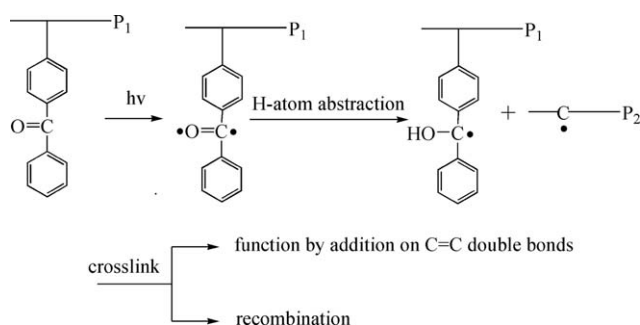


Figure 3 The mechanism of the crosslinking reaction.

TABLE I
Influence of the Exposure Time on the Content of the C=C

Samples	The time of UV exposure (min)	Area ratio of $A_{C=C}^a/A_0^b$
SBS-g-MBP	0	1.11
SBS-g-MBP (7.2 wt%)	2	0.83
SBS-g-MBP (7.2 wt%)	3	0.78

^a The peak area of C=C.

^b The peak area of interior label peak.

time, which indicates again that the photoinduced crosslinking has been carried out.

Gel fraction of different exposure time

Figure 4 shows the insolubilization profiles obtained on UV exposure of SBS-g-MBP samples containing various amounts of 4-MBP, between 4 and 8 wt%. The gel fraction is evaluated by the Eq. (1). It is quite remarkable that the gel fraction of crosslinked SBS-g-MBP increases with increase of grafting ratio and exposure time. It shows clearly that the crosslinking reaction accelerates from the 60 s, and the gel fraction almost keeps constant after 150 s. After 180 s exposure, the gel fraction values of 20.5 and 49.8 wt% were measured at grafting ratio of 4 and 8 wt%, respectively. Furthermore, it can be seen from the Figure 4 that the gel fraction was affected mainly by the exposure time. This means that the gel fraction can be facily controlled by grafting ratio and exposure time.

Morphology of UV-crosslinked SBS-g-MBP

The SEM of the pure SBS and its UV-crosslinked sample (graft yield = 7.4%, and radiation time = 2

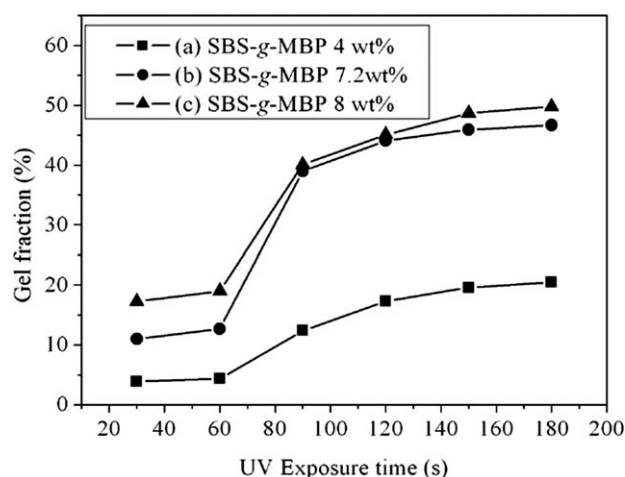


Figure 4 Influence of the exposure time on the insolubilization of the SBS-g-MBP system upon different grafting ratio.

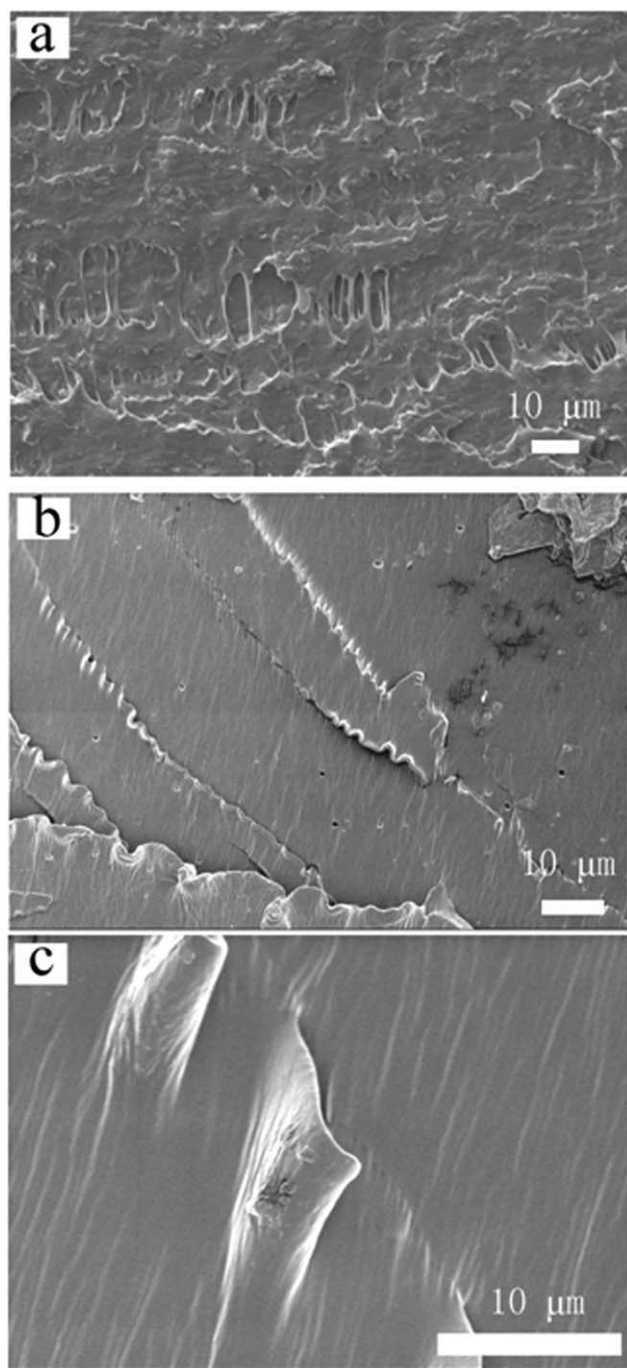


Figure 5 SEM photos of the fracture surfaces of the pure SBS (a) and its UV-crosslinked sample (graft yield = 7.4%, and radiation time = 2 min) (b and c).

min) are shown in Figure 5. Examination of the fracture surfaces of the samples by SEM gives information about how the UV exposure affects the morphology of the crosslinked sample. A distinction can be made between the pure SBS whose fracture surface is very rough with many fibrous glitches (Fig. 5a) and that of crosslinked sample is relative smooth compared with SBS (Fig. 5b). As depicted in Figure 5, when the photo is amplified to 5 μm

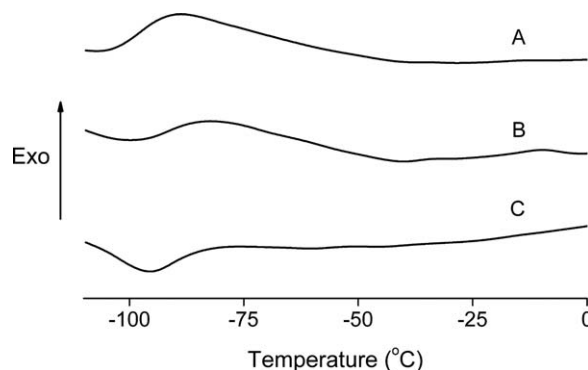


Figure 6 The DSC curves of the pure SBS (A) and UV-cured SBS-g-MBP with different exposure time (B) 2 min and (C) 3 min.

(Fig. 5c), the smooth structure is more obvious without any crazes and sheared zones. So with the crosslinking, the mode of fracture surfaces transmits gradually from tough fracture to brittle fracture. Because of crosslinking via the UV radiation, the size of dispersive phase (polystyrene) minishes, and there is no fibrous glitches under the function of force, which are the character of the tough fracture.²³ In this situation, the properties of the crosslinked sample are mainly determined by the type of the polymer phase. The sample with this phase morphology has good thermal property, which is supported by the following results.

DSC of pure SBS and UV-cured SBS-g-MBP samples

Figure 6 shows DSC thermograms of the pure SBS and UV-cured SBS-g-MBP samples with different exposure time. In all the DSC curves, there is a glass transition signal (T_g of PB) at about -90°C . From the Figure 6, it can be seen that the T_g of PB block shifted to higher temperatures with increasing exposure time. All the corresponding data of the T_g are summarized in Table II. It suggests that mobility

TABLE II
Thermal Stability of the Pure SBS and UV-Cured SBS-g-MBP Samples

Samples	Onset degradation temperature ($^\circ\text{C}$) ^a	Maximum degradation temperature ($^\circ\text{C}$)	Elastic T_g ($^\circ\text{C}$)
SBS	365	445	-98.5
SBS-g-MBP (7.2 wt% 2 min)	378	451	-91.3
SBS-g-MBP (7.2 wt% 3 min)	382	453	-88.0

^a The onset degradation temperature is denoted as the 5% weight loss temperature.

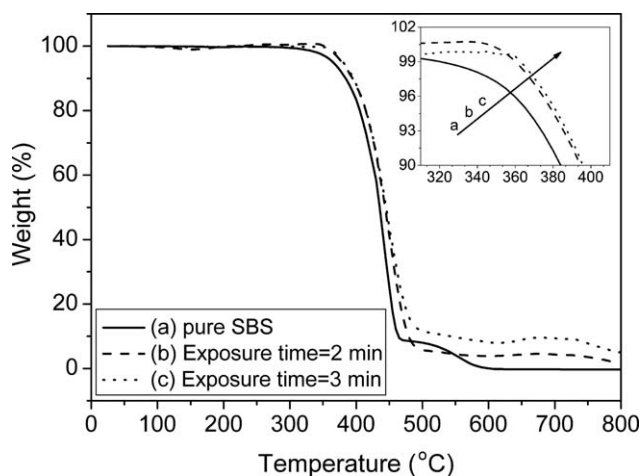


Figure 7 TGA traces obtained from the pure SBS and UV-cured SBS-g-MBP samples. The inset shows picture of the part, which is from 90 to 102% for y axis.

of the PB chain may decrease owing to increased crosslinking degree of the PB block.

Thermal analysis of pure SBS and UV-cured SBS-g-MBP samples

The TGA curves of the pure SBS and UV-cured SBS-g-MBP samples are presented in Figure 7. The Figure shows that there is a considerable change in the thermal behavior of SBS upon UV exposure. The onset degradation temperature and maximum degradation temperature of UV-cured are considerably higher than those of pure SBS, the values of which are given in Table II.

CONCLUSIONS

The SBS-g-MBP copolymer was irradiated by the UV radiation. The crosslinking density of SBS-g-MBP could be facily controlled by grafting ratio and exposure time. On the basis of the FTIR spectra analysis, it is concluded that the structure of UV crosslinking was formed. SEM showed that the mode of fracture surfaces transmitted gradually from tough fracture to brittle fracture. TGA data showed that the thermal stability of UV-cured SBS-g-MBP was

improved $\sim 17^\circ\text{C}$. Furthermore, DSC testing indicated that the glass transition temperature (T_g) of UV-cured SBS-g-MBP was higher than that of SBS. Therefore, it is concluded that UV exposure effects on thermal properties and morphology of the SBS-g-MBP obviously.

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