Ultraviolet-Initiated Photografting of Glycidyl Methacrylate onto Styrene–Butadiene Rubber

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ABSTRACT: Photografting reaction onto styrene-butadiene rubber (SBR) as a function of monomer concentration, grafting method, irradiation time, and the carbon black content has been studied using ultraviolet (UV). Glycidyl methacrylate and benzophenone are used as monomer and initiator, respectively. The occurrence of graft reaction onto SBR surface is identified by infrared attenuated total reflection (IR-ATR) analysis. The degree of monomer graft increases with monomer concentration and tends to level off at high monomer concentration (>8.3M/L). Graft ratio also increases with UV irradiation time. Carbon black content is found as one of important factors that determine the monomer graft efficiency. The amount of monomer graft onto SBR decreases with increasing carbon black content and it is attributed to the reduction of irradiation absorbance due to the presence of carbon black. The occurrence of reaction between glycidyl methacrylate grafted SBR and nylon-6 via melt phase reaction is also identified using IR-ATR analysis. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1733–1739, 1999

Key words: surface modification; UV photografting; styrene–butadiene rubber; glycidyl methacrylate

INTRODUCTION

Surface modification of polymers has been received a great deal of attention to improve a specific surface property, such as wettability, adhesion, and biocompatibility, without affecting the bulk properties of the polymer.^{1–5} Recently, surface modification technique is used for recycling scrap rubber^{6,7} This approach consists of modifying the exterior surface of scrap rubber that has been finely ground. Ground rubber particles are surface-modified in order to facilitate combination with other types of polymers.⁸ McInnis et al. chlorinated rubber particles by a gas-solid reaction with chlorine containing gas⁶ and Bagheri et al. used surface-modified rubber particles for toughening epoxy polymers.⁷ The redox method and grafting by gamma irradiation were also used to reuse waste rubber.⁹ Technical and commercial feasibility of using treated rubber particles as a filler with polymer have been demonstrated by many applications, such as roofing material and shoe soles.

In general, photografting is performed by irradiating the polymer in the presence of a solvent containing monomer. The energy sources commonly used are high-energy electrons, X-rays, UV, and visible light. Radiation in the near UV is not absorbed by most hydrocarbon polymers but is well absorbed by UV initiators. So the photoinitiator, e.g., benzophenone and its derivatives,

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Trade Name	Material	Source
		Kumho
Kosyn 1502	SBR	Petrochemical Co.
SRF	Carbon black	POSCO Chem.
_	Benzophenone	Fluka
_	Glycidyl methacrylate	Fluka

 Table I
 Materials Used in This Study

has been used to initiate the reaction. When photoinitiator is excited by the UV irradiation, it abstracts hydrogens from the polymer matrix and forms a polymer radical. This reactive site then initiates a monomer graft. The general photografting mechanism is described in earlier publications.^{10,11}

Photografting has been extensively used to improve specific surface properties and its efficiency depends on many factors such as monomer, polymer substrate, type of reaction phase, solvent, photoinitiator, and others.^{2,10–13} Carbon black has been widely used in polymer industry, especially in the rubber industry. For example, carbon black is an essential ingredient for automobile tire industry. Thus, even though the study for the effect of carbon black on the photografting reaction is necessary to modify the surface properties of carbon black filled polymeric materials, little information has been reported about this.

In the present paper, the photografting of glycidyl methacrylate (GMA) onto vulcanized styrene-butadiene rubber (SBR), which is a major component of tires, is studied as a function of monomer concentration, UV irradiation time, reaction method, and carbon black content. Nylon-6 is reacted with GMA-grafted SBR to investigate the possible use of GMA-grafted SBR powder as a filler or extender for nylon-6. The aim of this work is to investigate the factors affecting the graft efficiency of GMA onto SBR, especially in the presence of high carbon black content, and find out a reaction between nylon-6 and GMA grafted SBR.

EXPERIMENTAL

Materials

Table I summarized the sources and some pertinent characteristic information about the materials used in this study. The composition of SBR was 23.5 wt % styrene and 76.5 wt % butadiene. The amount of 3 phr ZnO and 1.5 phr sulfur were added to prepare a vulcanized SBR sheet. To investigate the effect of carbon black in the graft reaction, 10-50 wt % carbon black filled SBR compounds were prepared using roll mixer. GMA is an unsaturated monomer that has double bond at one chain end and also contains an epoxy group at the other end, which is reactive with specific groups such as amine. Benzophenone (BP) was used as a photoinitiator. Monomer and initiator were used as received from producer.

Photografting Procedure

SBR sheets were immersed in a distilled water ultrasonic bath for 30 min to clean their surfaces and then vacuum dried for 3 h before grafting experiment. Grafting was performed by two different ways. One was vapor phase grafting and the other was direct grafting. Vapor phase grafting was performed in a small reactor with a quartz window as previous works used.^{1,2,10} In the reactor a SBR sheet was placed together with a beaker containing a solution of benzophenone (1.8 g) and preweighed monomer with 36 mL acetone as solvent (Fig. 1).

To prepare the sample for direct grafting experiment, an SBR sheet was soaked into a solution of monomer, BP, and acetone for 12 h and vacuum dried for 2 h at ambient temperature to remove acetone. Only a dried SBR sheet was placed in a reactor for direct grafting experiment.

All grafting experiments were done under nitrogen atmosphere at 60°C. A SBR sheet was irradiated at a distance of 12 cm through the quartz window with an Hanovia 400 W high pressure mercury lamp (>300 nm).



Figure 1 Schematic diagram of surface photografting reactor.

Analysis

Infrared analysis (FT-IR 2000, Perkin Elmer) was carried with the attenuated total reflection technique (ATR) to identify the surface composition of modified SBR sheet. IR-ATR analysis has been widely used to characterize the surface composition.^{10,14} KRS-5 crystal was used and incident angle was 45°. Eighty scans were made of each spectrum to improve the signal-to-noise ratio. All UV-treated samples were soxhlet extracted with acetone for 12 h to remove the residual monomers and homopolymers from the surface of SBR sheet. Any variations of characteristic IR peak intensity of GMA were not observed at the surface of sheet for further extraction.

RESULTS AND DISCUSSION

The IR-ATR spectra of SBR, GMA, and GMA grafted SBR (SBR-g-GMA) are shown in Figure 2. Spectra (a) and (b) are essentially identical to SBR and GMA, respectively.¹⁵ Spectrum (a) shows the characteristic peak of the phenyl group at 700 cm⁻¹ and carbonyl peak at 1735 cm⁻¹ is observed for GMA in spectrum (b). Both phenyl and carbonyl peaks are observed in spectrum (c) and it indicates the graft of GMA onto the surface of SBR sheet. Because it is difficult to measure the absolute amount of GMA graft, the relative graft ratio of GMA onto SBR surface is determined using relative absorbance of the carbonyl peak at 1735 cm⁻¹ against phenyl peak at 700 cm^{-1} as internal standard.^{2,4} The disappearance of peak at about 1550 cm⁻¹ in spectrum (c) is related to the loss of ingredient from SBR due to 12 h acetone extraction. More than three different



Figure 2 IR-ATR spectra of (a) SBR, (b) GMA, and (c) SBR-g-GMA.

samples were used to obtain a graft ratio data and those were quite reproducible.

Effect of Monomer Concentration

Figure 3 shows the effect of monomer concentration on the graft ratio for vulcanized SBR without carbon black under vapor phase reaction condition. Monomer concentration means the concen-



Figure 3 Relative graft ratio versus monomer concentration in the vapor phase reaction.



Figure 4 Relative graft ratio versus monomer concentration in the direct reaction.

tration of GMA in 1000 mL acetone solution. UV irradiation time is 30 min. The graft ratio of unextracted samples increases with monomer concentration, while that of extracted samples tends to level off at high monomer concentration (>8.3M/L). Unextracted samples always show a higher graft ratio than that of extracted samples, and it can be attributed to the residual unreacted monomers and/or homopolymers attached on the reacted surface of SBR sheet. It is found that the deviation of graft ratio between extracted and unextracted samples increases with monomer concentration, and it indicates that homopolymerization dominates the reaction at high monomer concentration and also optimum monomer concentration exists for GMA photografting.

Graft ratios in the direct reaction are shown in Figure 4. It increases with monomer concentration, the same as in the vapor phase reaction. As observed in the vapor phase reaction, extracted samples show a lower graft ratio than that of unextracted samples. In addition, the amount of extraction increases with monomer concentration. Comparison of graft ratios between vapor phase reaction and direct reaction is shown in Figure 5. It is clear that direct reaction is a more efficient grafting method than the vapor phase reaction, especially in the high monomer concentration region, and the change of graft ratio against monomer concentration shows a somewhat different trend. Zhang et al. also reported that the presoaking method played an important role for the high monomer graft in the photografting reaction. 11,12

In the vapor phase reaction, acetone probably carries monomer and initiator from the beaker solution.² Allmer et al.² measured the actual concentration of glycidyl acrylate and benzophenone in the vapor phase during the photografting reaction, and found that monomer and initiator concentrations in the vapor phase were significantly low compared to the concentration of beaker solution. Through gas chromatograph analysis, the glycidyl acrylate and benzophenone concentration in the vapor phase were found to be 5 μM and 50 mM, respectively, while monomer and initiator concentration in solution was 2 and 0.2M. On the other hand, monomer and initiator concentration on the surface of SBR sheet in direct reaction can be more or less same as solution concentration. Thus, one of the reasons for low graft ratio in the vapor phase reaction is due to low monomer concentration in the vapor phase.

In Figure 5, it is found that the relative graft ratio levels off in the vapor phase method at an apparent vapor concentration well below the concentrations in the direct method. These different trends can be attributed to the ratio of homopolymerization and monomer/SBR graft reaction for different reaction methods. In the direct reaction, uniform distribution of monomers and initiators



Figure 5 Comparison of relative graft ratio between vapor phase reaction and direct reaction.



Figure 6 Effect of irradiation time on the relative graft ratio in the vapor phase reaction.

on the SBR surface can be obtained before UV irradiation and it will result in more or less competitive reaction between monomer/SBR graft reaction and homopolymerization even at high monomer concentration. For the vapor phase method, however, large portion of monomers and initiators still remains in the vapor phase during irradiation and it can provide more chance for homopolymerization rather than monomer/SBR graft reaction especially at high monomer concentration.

Effect of Irradiation Time

Figure 6 shows the graft ratio in the vapor phase reaction as a function of irradiation time. As shown in Figure 6, the graft ratio increases with irradiation time, as in previous works.^{2,3} After 30 min irradiation time, the graft ratio of unextracted sample shows a significant rise. The deviation of graft ratio by the extraction is not significant until 30 min irradiation. Allmer et al.¹⁶ showed a similar behavior in acrylic acid graft reaction on low-density polyethylene. The surface of the SBR sheet starts to initiate a crack for more than 40 min irradiation.

Effect of Carbon Black

Graft ratios with different carbon black contents are shown in Figure 7 as a function of monomer concentration. Graft reaction is carried out by the vapor phase reaction method and carbon black was compounded with SBR up to 50 wt %. The trend of graft ratio against monomer concentration for carbon black filled SBR is the same as SBR without carbon black. The graft ratio increases with monomer concentration and tends to level off at high monomer concentration for the same carbon black content sample. As shown in Figure 7, however, the presence of carbon black affects the degree of monomer graft significantly. Graft ratio decreases with increasing carbon black content. Especially for 50% carbon black content, little variation of graft ratio is observed even at high monomer concentration.

This can be explained by the reduction of absorbance of irradiation at the SBR surface due to carbon black. The presence of carbon black probably reduces the absorbance of irradiation and its influence becomes significant with increasing carbon black content. Geuskens et al.¹⁷ reported that rate of any photochemical reaction is proportional to the absorbed intensity that is a function of the incident intensity and of the absorbance of the sample. Incident intensity is dependent on the irradiation distance if other conditions are the same and absorbance of the sample depends on the presence of additives and/or fillers, such as carbon black.



Figure 7 Effect of carbon black content on the relative graft ratio in the vapor phase reaction



Figure 8 IR-ATR spectra of (a) SBR-g-GMA, (b) nylon-6, and (c) formic acid extracted SBR-g-GMA/nylon-6.

Reaction Between SBR-g-GMA and Nylon-6

Nylon/epoxide functionalized polymer blends have been reported by several workers.^{18–20} Nylon blends with EPDM-g-GMA have been described by Oliver and showed improved notched izod impact strength.¹⁸ Mussig et al. formed a high-impact nylon blend with styrene/methyl methacrylate/GMA.¹⁹ Allmer et al.² also reported that the epoxidized polyethylene surface reacted with amine in ethanol solution.

SBR-g-GMA is used for further reactions with nylon-6 (KN 111, Kolon, Inc.). Thin nylon-6 film was prepared using a hot press. Nylon-6 film was placed on the SBR-g-GMA sheet and pressed with the hot press at 250°C for 3 min to induce a reaction between the nylon film and the surface of SBR-g-GMA. Nylon-6 was extracted with formic acid from the reacted nylon-6/SBR-g-GMA sheet to identify the surface composition of the reacted SBR-g-GMA sheet.²¹Figure 8 shows the IR-ATR spectra of SBR-g-GMA, nylon-6, and formic acid extracted nylon-6/SBR-g-GMA sheet. Nylon-6 shows the prominent C=O peak at 1638 $\rm cm^{-1}$. From formic acid extracted SBR-g-GMA/nylon-6 (spectrum c), a prominent peak at 1638 cm^{-1} is also observed, and this indicates that nylon-6 exists on the SBR-g-GMA surface.

Though it is difficult to measure the degree of interfacial reaction between SBR-g-GMA and nylon-6 quantitatively, the occurrence of reaction at SBR-g-GMA surface is identified qualitatively from spectrum (c). The presence of nylon-6 on the SBR-g-GMA surface indicates the occurrence of reaction between nylon-6 and SBR-g-GMA and this can be done through the reaction between the epoxy group of GMA and amine group in nylon-6. This result can give a clue that GMA grafted rubber powder can be used as a filler for nylon-6 via reactive compounding. The authors find there can be improvements of some mechanical properties, e.g., tensile elongation, in the GMA-grafted rubber powder/nylon-6 compound, and intensive work is being carried out now.

CONCLUSIONS

The photografting reaction of glycidyl methacrylate onto styrene-butadiene rubber with benzophenone is investigated as a function of reaction method, monomer concentration, irradiation time, and carbon black content. Relative graft ratio increases with glycidyl methacrylate concentration and irradiation time. Homopolymerization occurs during graft reaction, and its effect becomes significant at high glycidyl methacrylate concentration and irradiation time, especially in the vapor phase reaction. It is found that direct reaction is a more efficient method than the vapor phase reaction for GMA photografting onto SBR. Carbon black content is one of the important factors that determines the monomer graft efficiency. Graft ratio decreases with increasing carbon black content, and it is attributed to the reduction of irradiation absorbance due to the presence of carbon black. It is observed that glycidyl methacrylate grafted SBR reacts with nylon-6.

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