

Singlet Oxygen Generation and Adhesive Loss in Stimuli-Responsive, Fullerene-Polymer Blends, Containing Polystyrene-Block-Polybutadiene-Block-Polystyrene and Polystyrene-Block-Polyisoprene-Block-Polystyrene Rubber-Based Adhesives

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ABSTRACT: The adhesive properties, as measured by bulk tack and peel strength analysis, were found to decrease in polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) and polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) PSA films containing common singlet oxygen generators, acridine, rose bengal, and C₆₀ fullerene, when irradiated with a tungsten halogen light in air. The addition of the singlet oxygen quencher, β -carotene, to the C₆₀ fullerene samples was found to significantly deter the rate of adhesive loss in the fullerene-SBS and -SIS PSA nanocomposites. The presence of oxygen was essential to the mechanism of adhesive loss and, in combination with the effects of singlet oxygen generators and a singlet oxygen

scavenger, strongly supports a singlet-oxygen mediated process. FTIR investigations of fullerene-SBS and -SIS systems suggest the initial formation of peroxides which, upon further irradiation, lead to the generation of carbonyl-containing compounds of a ketonic type after cross-linking. Rates of SBS and SIS C-H abstraction were comparable and found to decrease when the high-pressure, mercury xenon irradiation source was filtered to allow only light of $\lambda > 390$ nm. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2895–2904, 2008

Key words: adhesives; blends; fullerenes; irradiation; photochemistry

INTRODUCTION

The solution chemistry of C₆₀ fullerene is well-documented^{1,2}—particularly the ability to generate singlet oxygen in the presence of molecular oxygen and light^{3–7}—and there is practical interest in designing blends of fullerene materials and polymers for use in photovoltaic cells,^{8–10} nonlinear optical devices,^{11–15} and as oxygen sensors.¹⁶ Considering fullerenes as polymer constituents, a recent review exists, which provides an overview of the synthesis and properties of these often elegant and complex structures.¹⁷ Our group is interested in probing changes in the chemical, mechanical, and adhesive properties of rubber-based, pressure sensitive adhesives (PSAs) when

blended with fullerene sensitizers to produce stimuli-responsive nanocomposites.

The chemical and physical properties of common polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) and polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) rubber-based adhesives can be altered significantly through modification of the butadiene and isoprene elastomeric segments via photochemically initiated reactions. This was demonstrated most recently in studies by Decker and coworkers,^{18–21} where SBS was efficiently crosslinked under UV light in air using a trifunctional thiol and an acyl phosphine oxide photoinitiator to produce polymer networks having increased thermal stability for high-temperature applications. This increased thermal stability was also demonstrated in the UV-*cross*-linked SIS/SBS blends of Lim et al.,²² where samples were prepared using hot-melt techniques and crosslinked using thiol-ene reactions. Mateo and coworkers²³ produced polymer crosslinked networks under nitrogen atmosphere, having significantly altered sorption and diffusion of organic solvents and using a combination of SBS, common photoinitiators, and UV light. Finally, Kim et al.²⁴ found the adhesive properties of various blends of SBS and tackifiers to be

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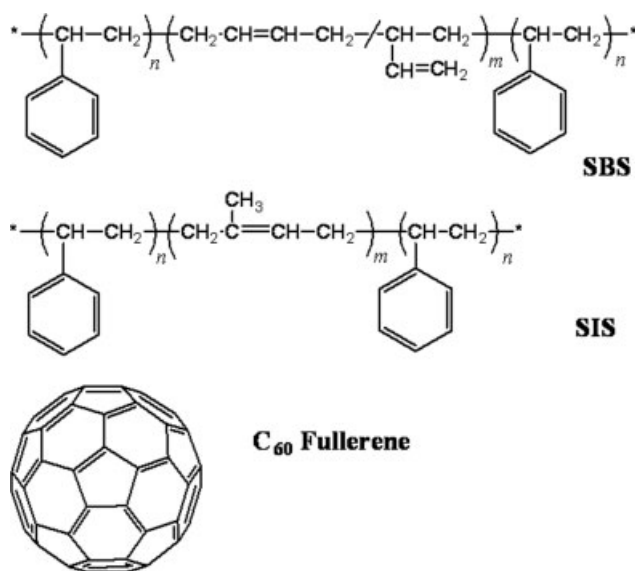


Figure 1 Chem structures of SBS, SIS and C₆₀ fullerene.

significantly reduced when irradiated under nitrogen atmosphere with benzophenone photoinitiator and trimethylolpropane mercaptopropionate (TRIS) crosslinking agent.

In mechanistically related work, Tajima et al.^{25–27} report that the fullerene-sensitized, photo-oxidation-induced crosslinking of furan-substituted polyimides produces a thermally stable material suitable for lithography applications. Tajima has identified the reactive species in these studies to be the singlet-oxygen generated furan endoperoxide—formed during irradiation of the polymer in the presence of C₆₀ fullerene—and has found the photocuring kinetics to be sensitive to the reactions oxygen partial pressure.²⁸ We recently found²⁹ that the nano-tack (measured by AFM) and bulk-tack adhesive forces in blends of C₆₀ and either SBS or SIS polymer (Fig. 1) can also be dramatically altered on demand when exposed to white light irradiation in air, and this current work represents an investigation into the mechanistic details of the chemical transformations leading to the observed loss of adhesive properties. We found the mechanism of adhesive loss to be dependent on the presence of C₆₀, light, and air, and therefore tentatively assigned a singlet-oxygen mediated process. To further probe the mechanistic details of the potentially singlet-oxygen mediated process, we have systematically incorporated alternative singlet oxygen generators (rose bengal and acridine) and a quencher (β -carotene) and monitored adhesive loss as a function of reagent concentrations and light exposure time.

Changes in adhesive properties may be monitored using common adhesive testing procedures, which measure tack force and peel strength as a function of composition, reaction condition, and irradiation

time. Reaction chemical kinetics are investigated using FTIR analysis techniques. FTIR is a commonly applied technique to investigate the oxidation of polyolefins leading to crosslinked polymer networks. Uhniat et al.³⁰ and Gugumus^{31,32} offer detailed FTIR analysis of the oxidative crosslinking of LDPE in the presence of peroxides. In these published studies, the initial formation of hydroperoxides is followed immediately by the formation of carbonyl groups. In an elegant study by Cataldo,^{33,34} the author followed the thermally initiated crosslinking of *cis*-1,4-polyisoprene in blends with C₆₀ fullerene in nitrogen and air using TGA, FTIR, and UV-vis spectroscopy. At 190°C under nitrogen, C₆₀ fullerene initiates the crosslinking of *cis*-1,4-polyisoprene to form a three-dimensional network. Similarly in our work, *in situ* FTIR studies are intended to probe the chemical transformations occurring during irradiation in fullerene-SBS and SIS adhesive systems, and where possible obtain reaction rate and chemical functional-group information. Evidence provided by quenching using a traditional singlet oxygen scavenger suggests that the primary mechanism for crosslinking proceeds via a singlet oxygen intermediate followed by a subsequent series of reactions.

EXPERIMENTAL

Materials and methods

Triblock polymers SBS and SIS were provided by Kraton Polymers (Belpre, OH) and used as received. SBS (Kraton D1102) was comprised of ~30 wt % polystyrene and sold stabilized with 0.14 wt % BHT antioxidant. SIS (Kraton D1161) was comprised of ~15 wt % polystyrene and stabilized with 0.14 wt % Irganox 565 antioxidant. GPC analysis of commercial SBS in THF gave M_w fractions of 154,500 (70%) and 61,500 (30%) with polydispersities of 1.06 and 1.22, respectively. M_w fractions of 315,800 (64%) and 102,500 (36%) and polydispersities of 1.08 and 2.45 were obtained for commercial SIS. Toluene (Aldrich, >99.9% HPLC grade) was used without further purification. PiccotacTM 8095 hydrocarbon resin was provided by Eastman Chemical. C₆₀ and C₇₀ were purchased from MER (Tucson, AZ). Piccotac, C₆₀, and C₇₀ were used as received. Solutions were prepared by dissolving PSAs in toluene solution containing C₆₀ fullerene and stirring ~24 h in the dark to prevent early exposure to light. Calculated C₆₀ weight percents are relative to PSA polymer. β -carotene (Fluka, >97%), acridine (Sigma-Aldrich, 97%), and rose bengal (Aldrich, 93%) were also used as received. Films were prepared from solution according to the specific testing method used. The Damon variable wet film applicator, eight-path wet film applicator, and Q-panel brand test panels were pur-

chased from Paul N. Gardner Company, (Pompano Beach, FL). Poly(ethylene terephthalate) (PET) 2-mil films were purchased from Polymershapes and used as received. Unless otherwise indicated, samples were irradiated using a 150 W tungsten/halogen white light source. The radiation intensity was measured at the sample (30 s at 22°C) with a "power puck" photometer to give 0.004 W/cm² visible, no measurable UV-A, UV-B, or UV-C.

Bulk tack and peel strength sample preparation and testing

Using an eight-path wet film applicator, bulk tack samples were drawn on Q-panel brand test panels from 20 wt % solid solutions in toluene, followed by solvent evaporation in a dark hood overnight. The prepared films averaged 25–30 μm thickness and were visually uniform. C₆₀, acridine, rose bengal, and β-carotene concentrations varied from 0 to 1.0 wt % (0.014 mmol/g polymer), and irradiation time varied from 0 to 4 h. For reduced-oxygen experiments, the samples were placed in an air-tight aluminum case (equipped with gas purge valves and a quartz window) and purged with high purity nitrogen for 15 min prior to irradiation. Peel strength samples were prepared similarly except samples were drawn on 2-mil thick PET films.

Bulk tack studies were conducted on the TA.XT-plus Texture Analyser (Godelming, Surrey, UK). An applied force (35 g for SIS and 42 g for SBS) on the 1-in. round probe tip (57R stainless steel) and a probe insertion speed of 0.1 mm/s gave an insertion depth of 10% film thickness. In the tack test, the applied force was held for 10 s, and then the probe tip was withdrawn at a constant rate of 0.1 mm/s. The force required to remove the probe tip from the film was obtained in grams per unit time, and the highest point was recorded as the peak force. The probe tip is cleaned with toluene solvent and dried after each tack experiment. Force curves generated during bulk tack experiments are related to the bonding of the adhesive and substrate, as well as within the adhesive itself. Defining the peak force as the primary separation point of the probe tip from the PSA, bulk tack analysis allows the early and late forces (before and after the peak force) to be considered, and the ratio (after : before) of these two quantities can further describe the nature of the bonding in the PSA. Very tacky films to the touch tend to hang on to the probe tip after primary separation has occurred and possess a high ratio and therefore lower cohesiveness component to the adhesive bond.

For peel strength tests, the exposed SIS and SBS films were cut into 1-in. strips, and a weighted roller was used to adhere the strips to the 3 in. × 6 in. Q-panel. The strip was mechanically pulled from the

coupon at a 180° angle, room temperature, and at a speed of 0.5 mm/s. The force per unit time required to remove the strip was recorded. The test protocols employed in the tack and peel experiments were designed from standard test procedures provided by the commercial instrument supplier (<http://www.stablemicrosystems.com>).

FTIR sample preparation and testing

FTIR samples were spin cast (EC101D Digital Photo Resist Spinner; Headway Research, TX) on sodium chloride salt plates from 20 wt % solids solution in toluene to yield ~10 μm thick films. A 100-μL solution aliquot was applied to the salt plates and spun at 1000 RPM, 60 s, followed by drying overnight in a vacuum desiccator under reduced pressure. C₆₀ fullerene concentration varied from 0 to 0.5 wt %, and irradiation time spanned 0–4 h with and without a 390-nm, cutoff filter. FTIR measurements were taken before and after irradiation with a tungsten halogen light source. *In situ* FTIR spectra were recorded on a modified Bruker 88 spectrometer. UV light from an Oriel lamp system equipped with a 200 W, high-pressure mercury-xenon bulb was channeled through an electric shutter and fiber-optic cable into the sample chamber. Light intensity measurements were made with an IL-1400 calibrated radiometer from International Light. Infrared absorption spectra were recorded at various time intervals during irradiation. The unfiltered light intensity at full arc was 187 mW/cm².

Transmission electron microscopy

Representative C₆₀/SBS films were embedded into Spurr's Low Viscosity embedding mixture and cured at 70°C for 36 h. Ultrathin cuts were obtained by a Sorvall, Porter Blum ultra-microtome with glass knives and applied to copper grids. The thickness of the sections was ~10 μm. Glass knives were prepared from ultra glass knife strips purchased from Electron Microscopy Sciences and cut using a LKB Knifemaker Type 7801 B. TEM images were taken on a Zeiss High-Resolution Electron Microscope EM 10C/CR operated at 50 kV and at a magnification of 20 k.

RESULTS AND DISCUSSION

In an effort to support a singlet oxygen mediated crosslinking reaction leading to the dramatic loss of adhesive properties in C₆₀-SBS/SIS nanocomposite films, the systematic incorporation of alternative singlet oxygen generators in addition to C₆₀ fullerene in polymer blends was performed. Figure 2(a,b) describes the change in bulk tack of SIS and SBS

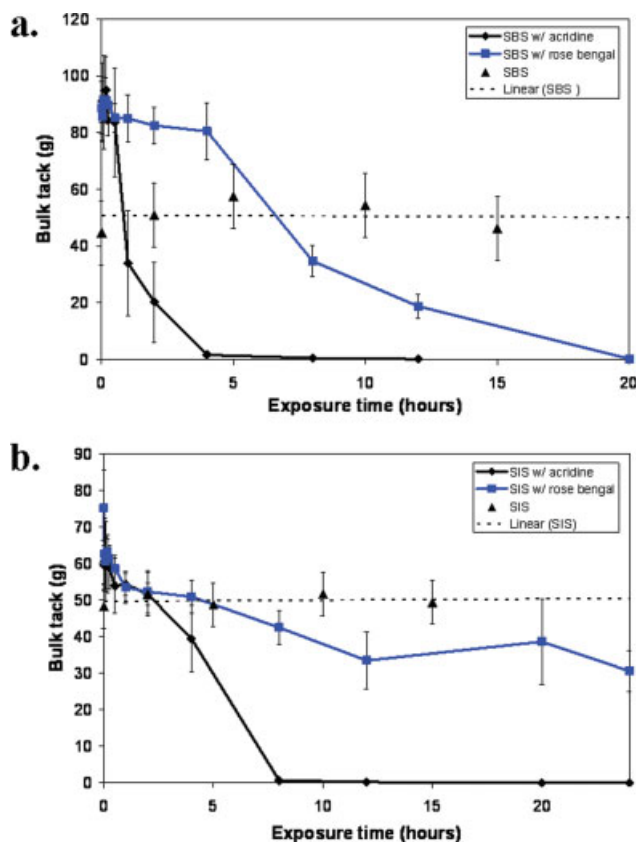


Figure 2 (a,b) Effects of common singlet oxygen generators on the bulk tack force of (a) SBS and (b) SIS adhesives (concentrations of additives were adjusted to yield samples with the same molar equivalent as 1 or 0.1 wt% C_{60} samples, [acridine]/gram polymer = 0.014 mmol/g, [rose bengal]/gram polymer = 0.0014 mmol/g). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

films when blended with the common singlet oxygen generators, acridine and rose bengal, and exposed to irradiation from a tungsten-halogen source. Concentrations of rose bengal and acridine additives were adjusted to yield film samples having the same molar equivalent of additive as 0.1 to 1 wt % C_{60} samples ([acridine]/g polymer = 0.014 mmol/g, [rose bengal]/g polymer = 0.0014 mmol/g). The lim-

ited solubility of rose bengal in the toluene/polymer casting solution governed the concentration range employed. Bulk adhesive forces of the prepared SIS and SBS control films remain relatively unchanged as a function of exposure time; however, after extended light exposure, the SIS and SBS films incorporating the singlet oxygen generators, acridine and rose bengal, lose most of their adhesive tack force. In both SBS and SIS polymer systems, the acridine additive was more efficient at reducing the tack forces. In addition to bulk tack adhesive forces, peel strengths in SBS/SIS adhesive blends were monitored as a function of additive and white light exposure time. Due to the lower peel strength of SBS polymer, peel test samples of SBS were formulated with 10 wt % tackifier. Table I provides the peel strength loss—listed as a % loss relative to initial peel strength values—in blends of SBS and SIS PSAs and common singlet oxygen generators, acridine and rose bengal. After 60-min exposure, SBS films containing acridine lost all (100%) peel strength, and in films containing rose bengal, >60% of peel strength was lost. A more dramatic peel strength loss was observed in formulations containing SIS PSA with comparable exposure time, and >90% peel strength loss was observed at 60-min exposure with either acridine or rose bengal.

Films containing 1.0 wt % C_{60} demonstrate a significant loss of tack with exposure time, reaching 0 g tack force by a 60-min exposure. A common singlet oxygen quencher, β -carotene, was employed in fullerene-adhesive systems, and Figure 3(a,b) describes the change in bulk tack of SIS and SBS films as a function of irradiation time at an equal molar C_{60} and singlet oxygen quencher concentration. The bulk tack of SIS and SBS films are relatively constant during irradiation when blended with β -carotene. Conversely, the bulk tack of SIS and SBS films decreased to 0 g in 1 h when formulated with only 1 wt % C_{60} . The incorporation of equal molar quantities of β -carotene in the SIS and SBS films including 1 wt % C_{60} has a significant retarding effect on the loss of bulk tack ([β -carotene]/g

TABLE I
Effect of Common Singlet Oxygen Generators on the Percentage of Peel Strength Loss in SBS and SIS PSAs

Exposure time ^a	SIS w/acridine (% loss) ^b	SBS w/acridine (% loss) ^c	SIS w/rose Bengal (% loss)	SBS w/rose Bengal (% loss)
15 min	74 (11) ^d	39 (6)	72 (11)	21 (3)
30 min	82 (12)	53 (8)	75 (11)	36 (5)
60 min	94 (14)	100 (15)	90 (14)	61 (9)
120 min	93 (14)	100 (15)	92 (14)	56 (8)

^a 150 W tungsten halogen.

^b Concentrations of additives were adjusted to yield samples with the same molar equivalent as 1 or 0.1 wt % C_{60} samples, [acridine]/gram polymer = 0.014 mmol/g, [rose bengal]/gram polymer = 0.0014 mmol/g.

^c SBS samples were formulated with 10 wt % piccotac resin.

^d Error was estimated at (15%) from multiple trials.

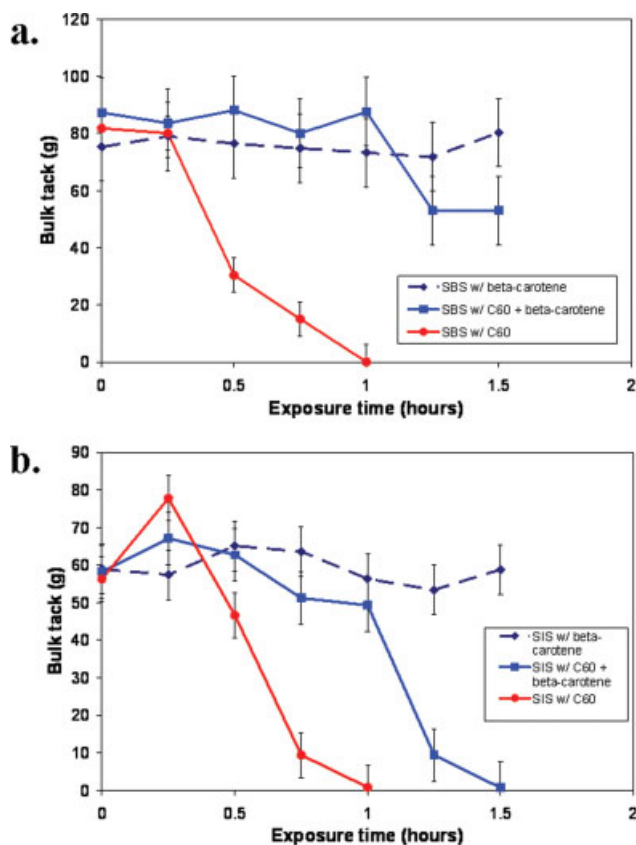


Figure 3 (a,b) Effects of β -carotene on the bulk tack force of (a) fullerene-SBS and (b) fullerene-SIS adhesives ([β -carotene]/gram polymer = [C_{60}]/gram polymer = 0.014 mmol/g). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymer = [C_{60}]/g polymer = 0.014 mmol/g). The photochemical efficiency of a photosensitizer to generate singlet oxygen is the singlet oxygen quantum yield, Φ_{Δ} , and is reported to be high (0.8–1) for acridine, rose bengal, and C_{60} fullerene in common solvents at visible wavelengths.^{3–7,35} Solubility variations, knowledge of singlet oxygen quantum yields and wavelength dependent absorption extinction coefficients as solid film constituents in SIS and SBS composites limits detailed direct comparisons. However, these findings support the premise that singlet oxygen generators other than C_{60} also produce a significant loss in adhesion in SBS/SIS adhesive blends, and at comparable molar concentrations, C_{60} fullerene is more efficient in this process. Concomitantly, the resulting singlet oxygen mediated photochemical crosslinking reactions are apparently retarded by the incorporation of the singlet oxygen quencher, β -carotene.

Bulk tack measurements allow for further inspection of the adhesive bonding in the fullerene-PSA films. Defining the peak force as the primary separation of the probe tip with the substrate, the areas before and after the peak separation (shaded/

unshaded areas) can be used to describe the stringiness or cohesive strength of the sample [Fig. 4(a) insert]. The results in Figure 4(a,b) describes the changes in bonding ratio in SBS and SIS PSA films containing equal molar (0.014 mmol additive/g polymer) amounts of both C_{60} and β -carotene as a function of irradiation time with the tungsten-halogen lamp. The bonding ratio of SBS remains relatively constant with exposure time at ~ 1 and is independent of additive effects. SIS typically has a much higher bonding ratio at $t = 0$, and therefore SIS feels more “tacky” to the touch. An interesting observation was made while following the bonding ratio or stringiness of fullerene-SIS PSAs containing β -carotene [Fig. 4(b)]. The bonding ratio of SIS containing β -carotene appears to stay constant or increase slightly with irradiation time, while the bonding ratio of SIS containing C_{60} sensitizer quickly decreases to that of SBS in the initial 2 min of irradiation. The addition of β -carotene to SIS films containing 1 wt %

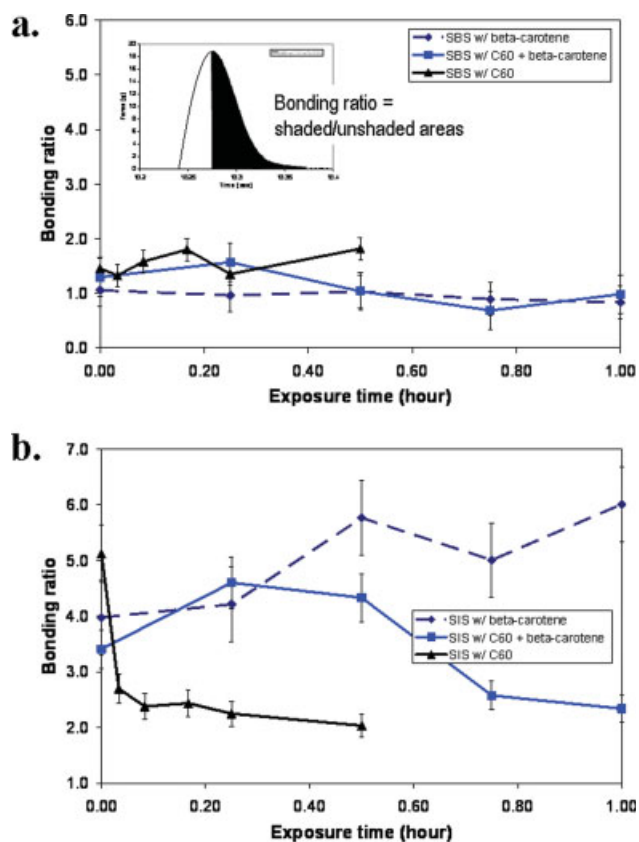


Figure 4 (a,b) (a) a representative bonding profile of the tack measurement in SBS; peak force = primary separation between the substrate and probe tip, and the bonding ratio = area of the shaded/unshaded portions of the curve (insert); effect of β -carotene on the bonding ratio in fullerene-SBS and (b) fullerene-SIS PSA system containing [β -carotene]/gram polymer = [C_{60}]/gram polymer = 0.014 mmol/g. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Time Required to Reduce Peel Strength by 90% in β -Carotene-Doped Fullerene-PSAs

Concentration of C_{60} and β -carotene ^a	90% Peel strength loss in fullerene-SIS	90% Peel strength loss in fullerene-SBS ^b
1 wt % C_{60} (0.014 mmol/g)	60 min	15 min
1 wt% C_{60} and 1 eq of β -carotene (0.014 mmol/g)	120 min	90 min
1 eq of β -carotene (0.014 mmol/g)	>12 h	>12 h

^a Concentrations of additives were adjusted to yield samples with the same molar equivalent as 1 wt % C_{60} samples: [β -carotene]/gram polymer = [C_{60}]/gram = 0.014 mmol/g.

^b SBS was formulated with 10 wt % piccotac resin.

C_{60} has the effect of preserving the stringiness and low cohesive strength of the sample.

As found for acridine and rose bengal in Table I, corresponding results in Table II illustrate the peel strength loss in SBS and SIS PSAs containing C_{60} sensitizer. In Table II, the data is presented as the time required to reduce the adhesive peel strength to 10% of the initial value or a 90% peel strength loss. The addition of 0.014 mmol β -carotene/g polymer in the SIS and SBS films including 1 wt % C_{60} (0.014 mmol C_{60} /g polymer) significantly retards the rate of peel strength loss. The peel strength results, when combined with the tack force data, provide compelling evidence for a singlet-oxygen-mediated process.

The effect of purge gas (air or nitrogen) on bulk tack force was investigated in SBS and SIS films containing 1 wt % C_{60} and irradiated for 1 h (Table III). The bulk tack of fullerene-SBS and -SIS films decreased to 0 g after 1-h exposure in air; however, in films irradiated in a reduced oxygen environment, the bulk tack was found to remain relatively stable. The dramatic effect of purge gas environment adds further support to the key role that oxygen must play during the adhesive loss process.

FTIR analysis of SBS and SIS films as a function of C_{60} additive and irradiation wavelength selection was next investigated. Films were spin cast directly onto salt plates at an average thickness of 10 μ m and stored in the dark until use. This *in situ* IR technique allows for accurate monitoring of IR band intensities,

TABLE III
Effect of Purge Gas on Bulk Tack Force

Exposure time (h)	Polymer; 1 wt % C_{60}	Purge gas ^a	Bulk tack (g) ^b
0	SBS		38 (12)
1	SBS	N_2	43 (5)
1	SBS	Air	0.3 (0.1)
0	SIS		55 (3)
1	SIS	N_2	73 (7)
1	SIS	Air	0.3 (0.2)

^a A gas-tight aluminum case with a quartz window was employed; samples were purged for >15 min with purge gas prior to irradiation.

^b Average error from five measurements.

since the analysis is performed on the same sample in exactly the same spot at various irradiation times. Film exposure was performed using a high-pressure, mercury-xenon UV source at full-arc and with a 390-nm, cut-off filter to differentiate UV and vis contributions to the photochemical reactions observed. IR spectra were also obtained for samples exposed externally to the tungsten-halogen light source for comparison.

SBS films both with and without 0.5 wt % C_{60} additive (0.007 mmol C_{60} /g polymer) were irradiated

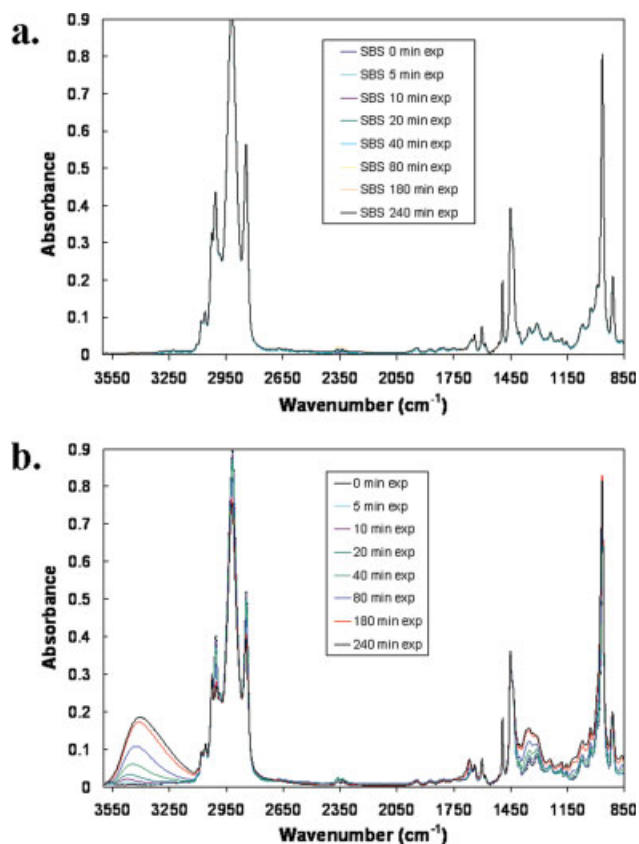


Figure 5 (a,b) Real-time FTIR analysis of SBS films from 0–4 h irradiation by high-pressure, mercury-xenon source equipped with 390 nm cut-off filter; plots of films shown without (a) and with (b) 0.5 wt % C_{60} . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

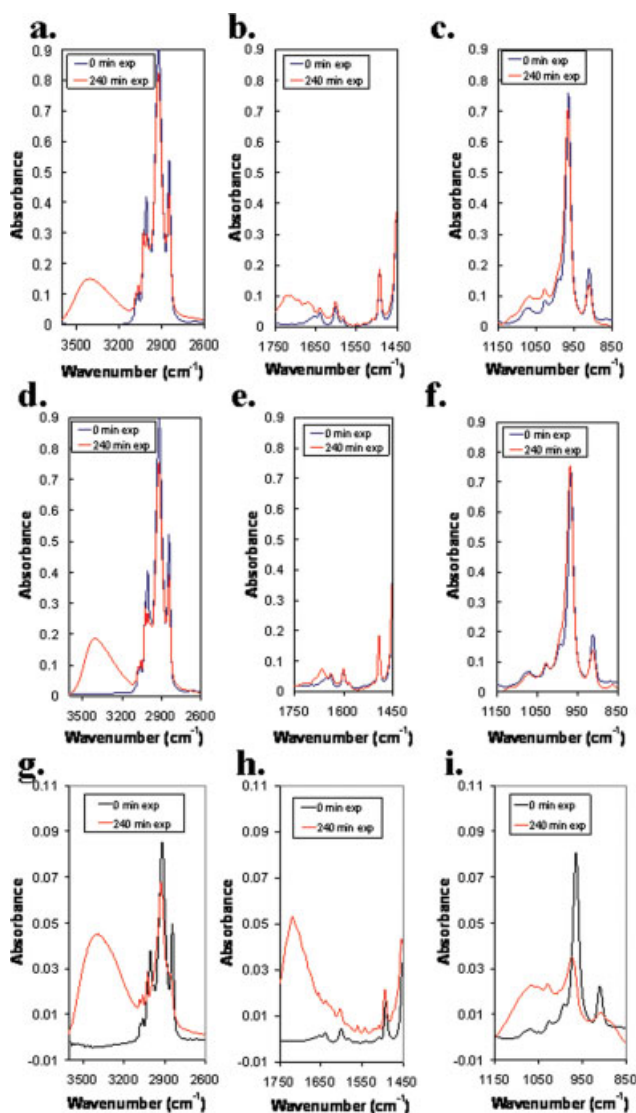


Figure 6 (a–i) IR spectra of SBS films with and without 0.5 wt % C_{60} additive and 0- to 4-h irradiation using a high-pressure, mercury-xenon source (a–c); same source equipped with a 390 nm cut-off filter (d–f); and films containing 0.2 wt % C_{60} and 0- to 4-h irradiation using a 150 W tungsten halogen source (g–i). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ated from 0 to 4 h using the 390-nm, cut-off filter or full arc. In the absence of C_{60} additive, SBS films remain unchanged after 4 h of irradiation at $\lambda > 390$ nm [Fig. 5(a)]. A small baseline increase is observed in the SBS samples irradiated at full arc for 4 h (not shown), particularly in the areas assigned to the OH stretch of film alkyl peroxides; however, when compared to the photochemical processes observed in C_{60} containing films [Fig. 5(b)], these changes are considered negligible.

SBS films containing 0.5 wt % (0.007 mmol/g) C_{60} are dramatically transformed during irradiation, and the significant areas of chemical change are high-

lighted in Figure 6(a–i). Within minutes of irradiation, a strong band at 3388 cm^{-1} appears, which is assigned to the valence vibrations of the hydroperoxide group. A simultaneous decrease in the aliphatic stretching bands of 3004 , 2917 , and 2842 cm^{-1} is observed. Assuming pseudo first order kinetics for the reaction of the aliphatic C–H groups with the oxygen radicals produced ($\ln A = \ln A_0 - kt$), the slopes of the plots of $\ln(A_0/A)$ versus irradiation time will be a measure of the reactivity of the peroxy radicals toward the SBS C–H. Figure 7(a) indicates that a rate increase is observed for light using the 390-nm filter ($2 \times 10^{-5}\text{ s}^{-1}$) to full arc ($1 \times 10^{-4}\text{ s}^{-1}$) due to the enhanced peroxide generation and decomposition under UV full-arc.

New peaks in the 1650 – 1750 cm^{-1} range appear that are associated with C=O containing compounds, resulting from the reaction of peroxides with the internal and vinyl double bonds of the butadiene. The out-of-plane deformations of the *trans*-internal C=C–H (967 cm^{-1}) and terminal vinyl C=CH₂ (910 cm^{-1}) were monitored and found to decrease with time. The styrene/butadiene ratio in

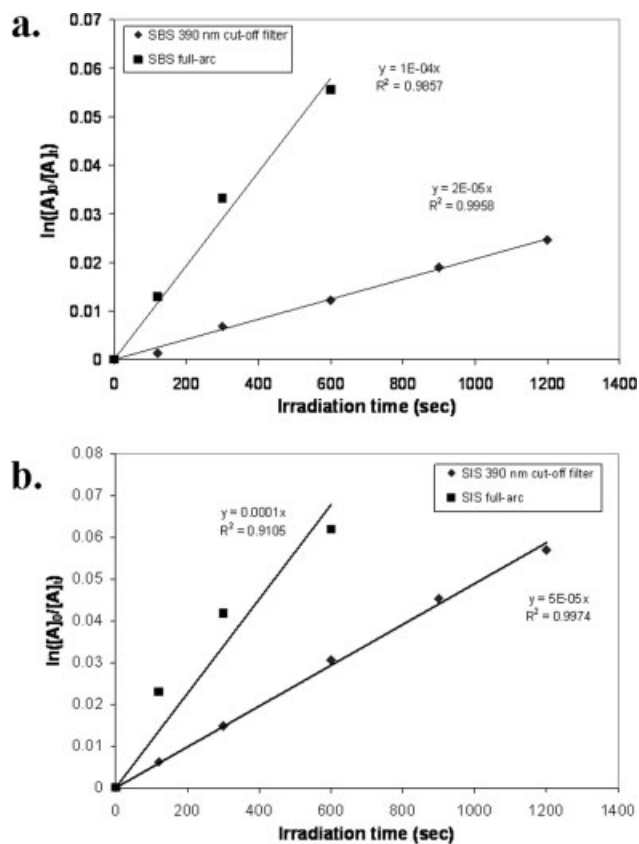


Figure 7 (a,b) Decrease of the IR absorbances, (A)—corresponding to the dominant aliphatic carbon-hydrogen stretches at. (a) 2917 cm^{-1} in SBS and. (b) 2925 cm^{-1} in SIS polymer adhesive blends, containing 0.5 wt % C_{60} —as a function of irradiation time using a high-pressure, mercury-xenon source with and without 390-nm, cut-off filter.

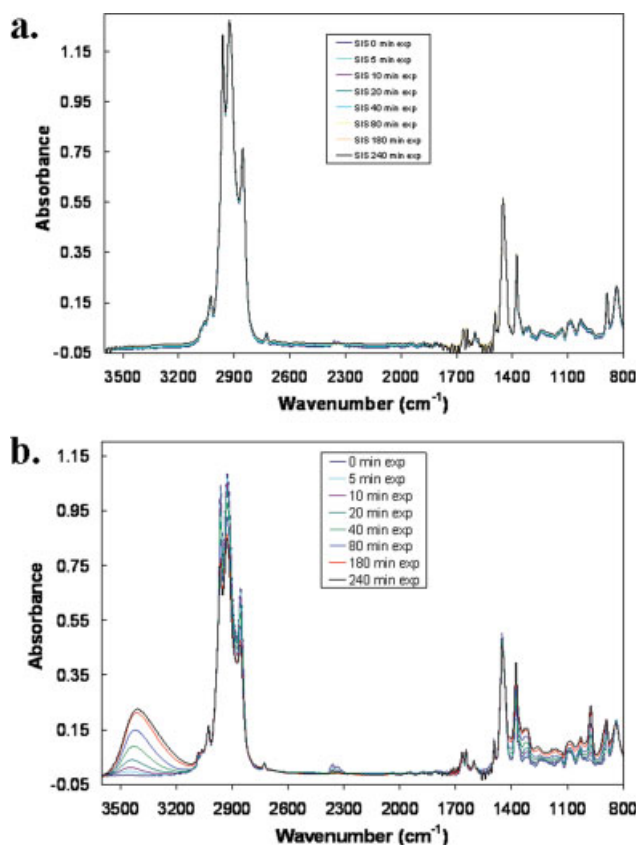


Figure 8 (a,b) Real-time FTIR analysis of SIS films from 0 to 4 h irradiation by high-pressure, mercury-xenon source equipped with a 390 nm cut-off filter; plots of films shown without (a) and with (b) 0.5 wt % C_{60} . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the commercial SBS (Kraton D1102) used in this study was 30/70 (wt/wt), and the butadiene composition consists of a mixture of internal (88%) and vinyl (12%) double bond content. Relative percents of internal to external double bonds were estimated in the commercial sample using 1H NMR.

The most dramatic change in the IR analysis of SBS films resulted from the static IR measurements obtained after irradiation using the tungsten-halogen light source [Fig. 6(g-i)]. In these samples an almost complete conversion of the double bonds of butadiene is observed, as demonstrated by the loss of $C=C$ and increase in the absorbance of the $C=O$ vibrations. The tungsten-halogen source output has a higher contribution from longer wavelengths, which may lead to complementary enhancing of the thermal decomposition of the peroxides produced. The conversion of the elastic portions of SBS results in the production of a new material, having very different chemical composition, and the PSA properties are lost.

FTIR analysis was also performed on *in situ* exposed SIS films as a function of irradiation source

wavelength selection, irradiation time, and presence of C_{60} fullerene. Representative spectra are provided in Figure 8, with the most significant changes highlighted in Figure 9(a-i). Like SBS, SIS in the absence of C_{60} additive remains unchanged after 4 h of irradiation at $\lambda > 390$ nm. A small baseline increase is observed when irradiated at full arc over time, but is again considered negligible when compared to the photochemical reactions initiated by the presence of fullerene sensitizers. Within minutes of irradiation, strong bands at 3392 and 972 cm^{-1} appear, assigned

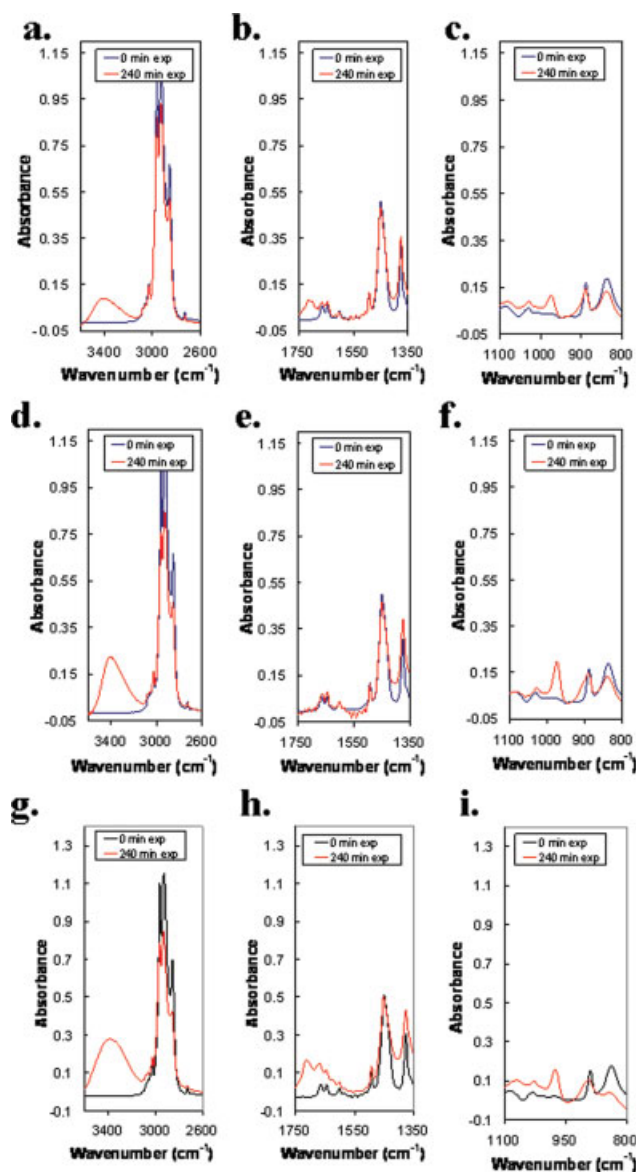


Figure 9 (a-i) IR spectra of SIS films with and without 0.5 wt % C_{60} additive and 0- to 4-h irradiation using a high-pressure, mercury-xenon source (a-c); same source equipped with a 390 nm cut-off filter (d-f); and films containing 0.2 wt % C_{60} and 0- to 4-h irradiation using a 150-W tungsten halogen source (g-i). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

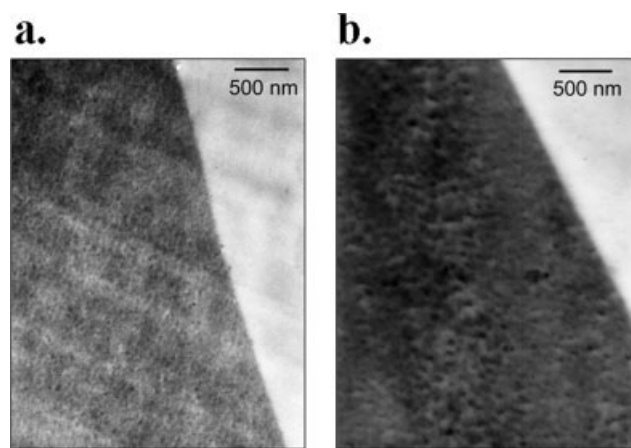


Figure 10 (a,b). TEM images of C_{60} -SBS samples prior to irradiation, containing (a) 0.2 wt % and (b) 1.0 wt % C_{60} relative to SBS adhesive polymer. Samples were imaged at 20,000 \times magnification.

to the hydroperoxide group and accompanying C—O stretch, respectively. Simultaneous decreases in the aliphatic stretching bands of 2962, 2925, and 2854 cm^{-1} and internal C=C—H out-of-plane bending vibration at 835 cm^{-1} are observed. In the kinetic treatment [Fig. 7(b)], the rate of reaction of SIS C—H toward reactive oxygen species was found to be comparable to SBS C—H and also increase when the source was switched from the mercury lamp with the 390-nm filter ($5 \times 10^{-5} \text{ s}^{-1}$) to full arc ($9 \times 10^{-5} \text{ s}^{-1}$). New broad peaks between 1650 and 1750 cm^{-1} appear and are contributed to C=O containing compounds resulting from oxidation of the olefin units. Commercial SIS (Kraton D1161) was comprised of ~ 15 wt % polystyrene (15/85 styrene/rubber ratio) and has no pendent vinyl C=C bonds. Similar to SBS, the chemical conversion of the SIS elastic isoprene portions results in the production of a new material, having very different chemical composition, and the PSA properties are lost.

TEM analysis was performed on select compositions to optically interrogate the distribution of C_{60} within fullerene-doped films, Figure 10. Samples were prepared and microtomed for testing using standard techniques. The 0.2 and 1.0 wt % loading of C_{60} in SBS were chosen as representative samples and imaged prior to irradiation. At the higher concentration (1.0 wt % C_{60} relative to SBS polymer) larger fullerene aggregates can be seen distributed throughout the sample, suggesting that the sample is not entirely homogeneous in nature although initial tack values are comparable.

CONCLUSIONS

The bulk tack and peel strength of polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) and polysty-

rene-*block*-polyisoprene-*block*-polystyrene (SIS) pressure-sensitive adhesive systems (PSA), containing common singlet oxygen generators, were found to decrease when irradiated with a tungsten-halogen light source in air. The addition of the singlet oxygen quencher, β -carotene, was found to significantly deter the rate of adhesive loss in the fullerene-SBS and -SIS PSA nanocomposites. Purge gas experiments confirmed that the presence of oxygen was essential to the mechanism of adhesive loss, and in combination with the effects of singlet oxygen generators and scavenger support a singlet-oxygen mediated process. FTIR analysis shows the initial generation of hydroperoxides, which upon further irradiation decompose leading to the rapid conversion of butadiene and isoprene components to ketone containing species after crosslinking. The rates of C—H abstraction were approximated assuming a first-order process and found to be comparable in SBS and SIS and decrease when the high-pressure mercury xenon irradiation source was filtered to all only light of $\lambda > 390$ nm. Regardless of irradiation source, the same mechanism governs the chemical transformations, and FTIR analysis provides some characterization of the new species formed during irradiation. As a result of the drastic change in chemical composition of the films after irradiation, the adhesive properties of the films are lost.

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