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Nano- and bulk-tack adhesive properties of 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

Nano-tack (measured using AFM) and bulk-tack adhesive forces of blends of C_{60} and either polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) or polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) triblock copolymer pressure sensitive adhesives were measured after exposure to white light irradiation. The nano-tack adhesive forces in C_{60}–SIS/SBS were found to decrease with increasing C_{60} concentration and exposure time, approaching the value for 100% polystyrene, providing an indication that significant surface hardening and crosslinking of the soft isoprene and butadiene phases occurs in the presence of C_{60}. Films produced during the study were smooth, having low RMS surface roughness, and showed nanoscale phase separation between the soft (diene) and hard (styrene) segments. This phase separation disappeared after addition of C_{60} sensitizer and white light irradiation. Bulk adhesive measurements (tack and peel strength) showed a similar trend with C_{60} concentration and exposure time, and in irradiated systems containing as little as 0.2 wt% C_{60}, a significant decrease in adhesion was observed. Estimated T_g (measured using DMA, shear mode) of the soft-block shifts to higher temperatures (increasing by 30–40 °C), and high gel fractions were obtained, indicating the presence of chemically crosslinked networks.

Keywords: Pressure sensitive adhesive; Fullerene; Photochemistry

1. Introduction

Pressure sensitive adhesives (PSAs) are widely utilized in tape and label manufacturing – for home, office, electronic and medical purposes – and are available in a wide variety of chemical compositions, such as acrylic, methacrylic, silicones, and rubber-based [1]. Rubber-based systems are typically highly flexible and elastic, and polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) and polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymers are examples of commonly applied thermoplastic elastomer-based PSAs [2]. These block copolymers have high cohesive strength due to the high glass transition temperature of the polystyrene blocks external to the rubbery portions derived from the unsaturated polybutadiene and polyisoprene center blocks. A microphase separated morphology between the hard and the soft-block segments in the films – yielding physically crosslinked networks of polystyrene – contributes to the high cohesive strength [3].

Recently, SBS PSAs having "easy-release" properties have been designed. In these systems a rapid and permanent change in the adhesion is induced, switching the polymer from a tacky

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"on" state to an un-tacky "off" state using a variety of crosslinking agents and UV-irradiation. Releasable adhesives have application in numerous markets, such as the semi-conductor and medical dressings industries. Using a combination of benzophenone photoinitiator and trimethylolpropane crosslinking agent, Kim et al. [4] reported the dramatic reduction in adhesive properties of SBS and mixtures of tackifiers when irradiated under UV light and nitrogen environment. Crosslinking of the polybutadiene (PB) block was achieved after 3 min of irradiation to produce systems with peel strengths 45% of the uncrosslinked films.

Although not for easy-release applications, several other examples of photo-crosslinked SBS and SIS exist where chemical crosslinks are introduced, resulting in an insoluble material. Decker et al. [5–7] applied a combination of photoinitators, trimethylolpropane mercaptopropionate (TRIS) as the crosslinking agent, and a UV radiation source in air to quickly produce photo-crosslinked SBS and SIS films having increased solvent and heat resistance over non-crosslinked films, making them more suitable for the higher temperature requirements of flexographic applications. This increased thermal stability was also demonstrated in the UV-crosslinked SIS/SBS blends of Lim et al. [8], where samples were prepared using hot-melt techniques and crosslinked using thiolene reactions. Mateo and coworkers [9] studied the diffusion of organic solvents through photo-crosslinked SBS films, which were prepared using two photoinitiators, benzophenone and 2,2-dimethoxy-2-phenylacetophenone, respectively. However, in this latter system, the crosslinking was found to proceed slowly. These examples indicated that the chemical and physical properties of SBS and SIS thermoplastic elastomers can be altered significantly through modification of the butadiene and isoprene elastomeric segments via photochemically initiated reactions.

Our group's research interests lie in discovering the unique properties of polymer–nanocomposite structures containing nanomaterials such as fullerenes, nanotubes, and metal nanoparticles. 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 [10]. In this current work, we report the preliminary findings concerning the nano- and bulk-tack adhesive properties of blends of C_{60} fullerene and SIS and SBS copolymers (Fig. 1) when irradiated with white light. Nano- and bulk-scale adhesion forces are monitored along with peel strength and mechanical properties of the resulting nanocomposite films. C_{60} – in the presence of visible light and molecular oxygen – generates singlet oxygen [11–16], which is likely responsible for the rapid and irreversible oxidative crosslinking of SIS and SBS polymers and subsequent loss in adhesion. During this work, the detection of an interesting thermal response in the films as well as the photoinitiated chemical reaction has prompted us to initiate a detailed investigation into the mechanisms surrounding this transformation and is reported separately.

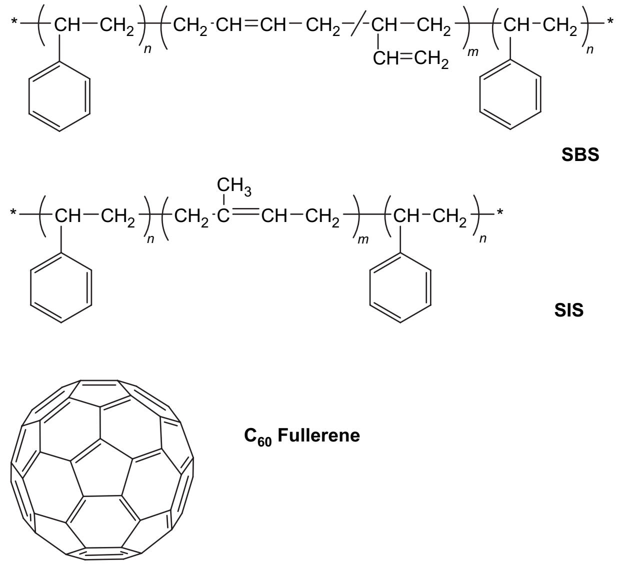

Fig. 1. Chemical structures of SBS, SIS and C_{60} fullerene.

2. Experimental

2.1. Materials and methods

Triblock polymers SBS and SIS were provided by Kraton Polymers, Inc. (Belpre, Ohio) 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. Piccotac™ 8095 hydrocarbon resin was provided by Eastman Chemical Co. C_{60} and C_{70} were purchased from MER Corporation (Tucson, AZ). Piccotac, C_{60}, and C_{70} were used as received. Solutions were prepared by dissolving PSAs in toluene solution containing C_{60} fullerene and stirring ~24 h in the dark to prevent early exposure to light. Calculated C_{60} weight percents are relative to PSA polymer. Films were prepared 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 purchased from Paul N. Gardner Company, Inc. (Pompano Beach, FL). Poly(ethylene terephthalate) (PET) 2-mil films were purchased from Polymershapes and used as received. Specimen and silicon wafer chips were obtained from Ted Pella (Redding, CA), and the silicon wafers were cleaned before use with 35 wt% aqueous hydrogen peroxide solution. Samples were irradiated using a 150 W tungsten/halogen visible light source and at a distance of 6 inches from sample surface to source. The radiation intensity at the sample was measured (30 s at 22 °C) with a "power puck" photometer to give 0.004 W/cm^2 visible, no measurable UV-A, UV-B, or UV-C.

2.2. 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. C_{60} fullerene concentration varied from 0 to 1.0 wt%, and irradiation time varied from 0 to 4 h. Peel strength samples were prepared similarly except samples were drawn on 2-mil thick PET films, and the fullerene concentration varied from 0 to 2.0 wt%. To test the impact of sample warming during irradiation, dark and reduced-oxygen control samples were analyzed. 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.

Bulk-tack studies were conducted on the TA.XTplus Texture Analyser (Godelming, Surrey, UK). An applied force (35 g for SIS and 42 g for SBS) on the 1-inch round probe tip (57R stainless steel) and a probe insertion speed of 0.1 mm/s gave an insertion depth of 10% film thickness. To perform the tack test experiment, the probe tip was brought in contact with the PSA surface at a pre-test speed of 0.1 mm/s, held at the applied force for 10 s, and then withdrawn at a 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 was cleaned with solvent and dried after each experiment. The peak force was found to decrease linearly with increasing rate of separation over the range of 0.1–1.0 mm/s and to change very little over the range of 1.0–10.0 mm/s. Since the tack forces we are measuring are small, a 0.1 mm/s rate of separation was chosen and used for all samples. Force curves generated during bulk-tack experiments are related to the nature of the bonding within the adhesive as well as the adhesive and substrate. 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 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-inch strips, and a weighted roller was used to adhere the strips to the 3″ × 6″ Q-panel. The strip was mechanically pulled from the coupon at a 180° angle, room temperature, and at a speed of 0.5 mm/sec. 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).

2.3. AFM sample preparation and analysis

AFM polymer nanocomposite adhesive samples were spin cast (EC101D Digital Photo Resist Spinner; Headway Research Inc., Texas) on Si from 7 wt% solid solution in toluene. A 10 µL solution aliquot was applied to the silicon wafer chip and spun at 5000 rpm, 30 s, followed by drying under reduced pressure overnight. Ellipsometry measurements were performed on a Gaertner Scientific LSE-Stokes ellipsometer with an incidence angle of 70° using a 632.8 nm He–Ne laser and Gaertner GEMP software. The average thickness for spin-coated films was 140 nm. C_{60} fullerene concentration varied from 0 to 0.8 wt%, and irradiation time varied from 0 to 4 h using a150 W tungsten/halogen irradiation source.

AFM studies were conducted on a multimode scanning probe microscope from Digital Instruments (Santa Barbara, CA). A standard RTESP silicon tip with 125 µm silicon cantilever (VEECO Industries, CA) was used for tapping mode evaluations. A triangular silicon nitride (Si_3N_4) probe, with a nominal cantilever spring constant of 0.58 N/m, was used for relative surface adhesion (nano-tack) measurements. Both tapping and contact mode evaluations were performed in air at room temperature. Crosslinked as well as control surfaces were imaged at several locations throughout the surface. Surface roughness analysis was performed using Nanoscope version 5.30 r2 image analysis software and root mean square (RMS) roughness reported. The same tip was used during all the measurements in a specific mode in order to minimize error which might arise due to use of different tips. Force distance curves were obtained at various deflection set points in order to obtain statistical data for nano-tack analysis. Each measurement was repeated twice and the median reported. Error bars displayed on the plot represent the range of the values measured, which in all cases was very small (±1–3 nN). In AFM contact mode, the probe remains in close contact with the surface and is subjected to a downward force as the scanning proceeds. This force has two components, an adhesive force (F_a) between the polymer surface and the tip, and the loading force (F_l), which is applied on the cantilever. These forces are calculated by the cantilever deflection and normal spring constant (k) of the spring. The total normal downward force (F_N) is the algebraic sum of these two forces. The nano-tack force was defined as the force during the debonding of the tip from the PSA film. It should be noted that a relative nano-tack measurement is reported, based on a nominal spring constant and using the same probe for all samples. The probe was imaged after measurements to ensure that there was no contamination or damage to the tip [11–13].

2.4. Mechanical analysis and gel fractions

Glass transition temperatures (T_g) of the soft-block were measured on a TA Instruments #2980 Dynamic Mechanical Analyzer (DMA). Samples were prepared as in prior tack and peel tests, except that films were drawn on silicone coated release paper. This process produced ~30 µm thick films, which were peeled from the release paper after irradiation

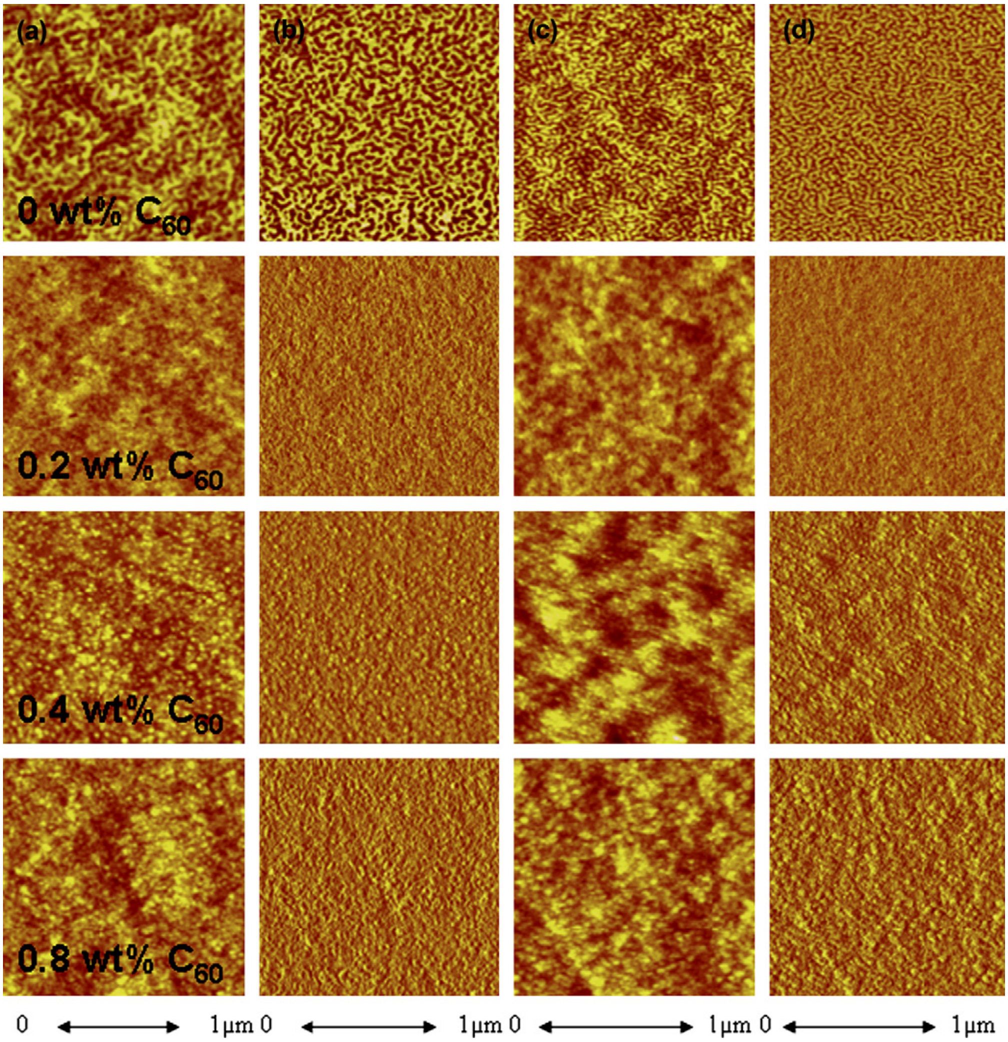

Fig. 2. AFM analysis of C_{60}–PSA blends illustrating height and phase changes with increasing C_{60} concentration (columns from left to right: (a) height-SIS; (b) phase-SIS; (c) height-SBS; and (d) phase-SBS with increasing C_{60} concentration from 0 to 0.8 wt%). Data scale is 5 nm for height and 12° for phase images.

and just prior to mechanical testing. Samples were analyzed in shear mode, 3 μm amplitude, and 2 °C/min temperature ramp rate. Finally, gel fractions of the irradiated films were obtained by dissolving a known mass of film in toluene for 24 h at room temperature and recovering the insoluble mass fraction via membrane filtration and solvent evaporation under reduced pressure. HPLC analysis was performed on extracting solvents using a Beckman HPLC #110 B pump coupled to a Lab Alliance #500 UV/Vis detector. Analysis conditions included 1.0 mL/min toluene mobile phase, 4.6 × 250 mm analytical PYE column (Phenomenex), and a 360 nm UV interrogation wavelength.

3. Results and discussion

Figs. 2–5 illustrate changes in nano- and bulk-tack adhesive forces as a function of C_{60} concentration and visible exposure time in fullerene–PSA composite films containing SBS and SIS rubber-based adhesives. AFM analysis of the SBS and SIS/C_{60} nanocomposite adhesive samples yields measurements of surface morphology and relative nanoscale adhesive forces (nano-tack), and several examples of this approach exist [17–20]. Morphology studies indicate that the adhesive films produced in this study are smooth with an average of 0.4 nm (±0.1) RMS roughness, and no trends in surface roughness were observed with C_{60} concentration or lamp exposure time, see Table 1. Because of the chemical incompatibility of the polystyrene end-block and the polydiene mid-block, phase separation occurs on the nanoscale, and discrete hard and soft zones are observed in the phase plot, Fig. 2. However, these discrete phases are lost upon white light exposure in the presence of C_{60}.

The effects of irradiation time (Fig. 3a) and C_{60} concentration (Fig. 3b) on the change in nano-tack are evaluated for both SBS and SIS adhesives. Fig. 3a illustrates the effects of lamp exposure time on nano-tack in 0.2 wt% C_{60}/SBS and SIS nanocomposite adhesives. At longer irradiation times, nano-tack measurements approach a constant value of 60 nN, indicating hardening of the surface as a function of exposure time and crosslinking. The final constant nano-tack value is similar to that measured for pure (100%) polystyrene. As shown in Fig. 3a and at a constant irradiation time of 2 h,

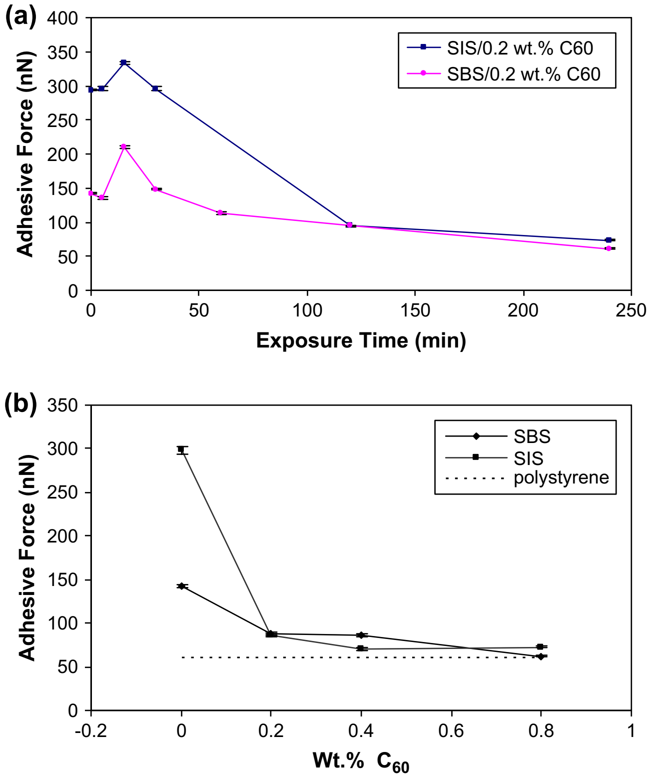

Fig. 3. (a) Adhesive force (nano-tack) as a function of visible light exposure time; irradiation times shown from 0 to 250 min using a 150 W tungsten/halogen visible light source and C_{60} concentration constant at 0.2 wt% of polymer; (b) adhesive force as a function of C_{60} wt% showing convergence of nano-tack measurement of fullerene–PSA to that of 100% polystyrene control. Each point represents the median of two measurements, error bars represent the range of values measured. Irradiation time was constant at 120 min using a 150 W tungsten/halogen light source, and C_{60} concentration varied from 0 to 0.8 wt% of polymer.

nano-tack decreases with increasing C_{60} concentration, again approaching a constant value of approximately 60 nN. Under these conditions the butadiene and isoprene components dominate the adhesive forces at low C_{60} loadings; however, after significant photochemical reaction has occurred, the resulting photochemically altered butadiene and isoprene exhibit more glassy behavior and tack is reduced. Optimization of the extent of photochemical reaction is possible by balancing C_{60} and lamp exposure time. An interesting phenomenon is observed at short irradiation times, where an increase in the nano-tack occurs briefly at ~15 min exposure time before decaying. This brief increase in adhesive force is also observed in data from the bulk tack and peel tests. Although first attributed solely to the ballooning of the more hydrophobic soft-block segments to the surface with heating, these observations have prompted a separate study into the chemical reactions surrounding this work, and a second manuscript is in preparation concerning the kinetics and mechanisms of the photoinduced transformations leading to changes in the adhesive properties.

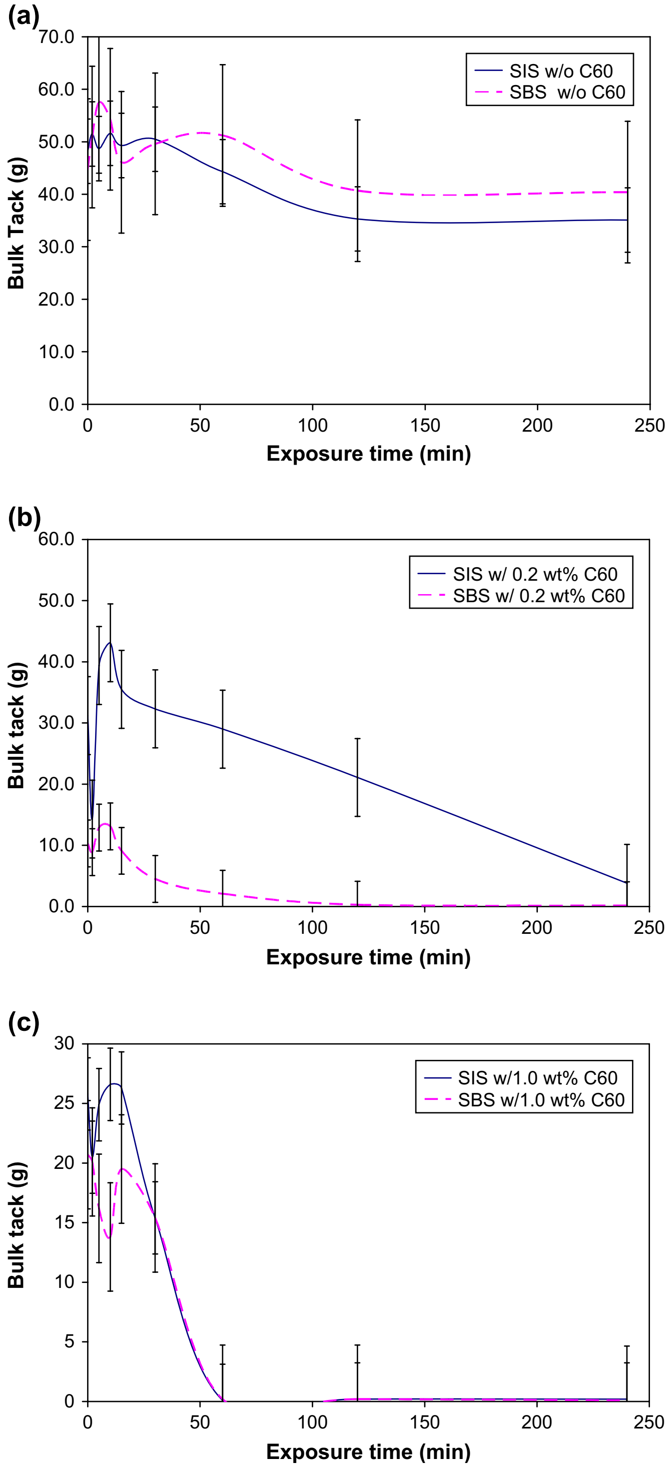

Fig. 4. Change in bulk tack of SIS and SBS films as a function of C_{60} concentration and visible irradiation exposure time; (a) films prepared from SIS and SBS without C_{60} sensitizer; (b) films containing 0.2 wt% C_{60} sensitizer; and (c) 1.0 wt% C_{60} sensitizer; irradiation time varies from 0 to 4 h using a 150 W tungsten/halogen light source in air. Each data point represents the average of the peak force of five individual tack measurements.

Fig. 4a–c describes the average change in bulk tack of SIS and SBS films as a function of C_{60} concentration and white light irradiation exposure time, and selected individual tack plots are provided in Fig. 5a–d. Although the bulk adhesion evaluations involve measurement of thick films and the nano-tack studies probe only the thin film regime within several nanometers of the surface, similar trends in measured tack

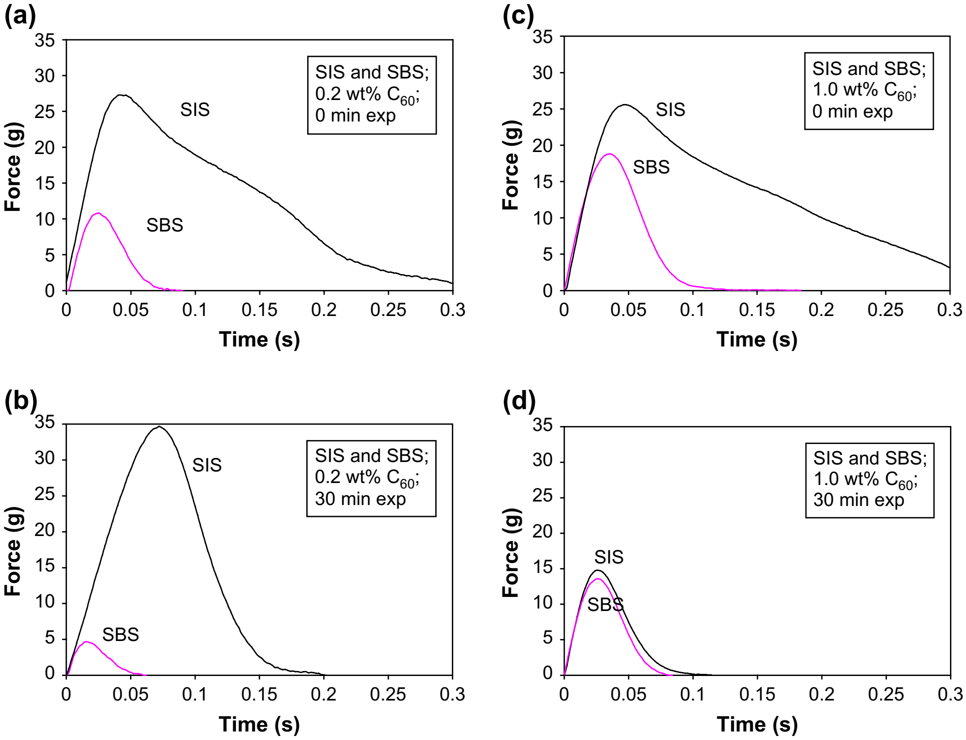

Fig. 5. Selected individual tack plots for SIS and SBS films as a function of C_{60} concentration and visible irradiation exposure time; films prepared from SIS and SBS with 0.2 wt% C_{60} sensitizer at (a) $t = 0$ min; (b) $t = 30$ min; and 1.0 wt% C_{60} sensitizer at (c) $t = 0$ min; (d) $t = 30$ min irradiation time, using a 150 W tungsten/halogen light source in air.

Table 1
AFM RMS roughness measurement

Sample	RMS Roughness (nm)
SIS	0.54
SIS + 0.2 wt% C_{60}	0.25
SIS + 0.4 wt% C_{60}	0.29
SIS + 0.8 wt% C_{60}	0.41
SBS	0.55
SBS + 0.2 wt% C_{60}	0.27
SBS + 0.4 wt% C_{60}	0.39
SBS + 0.8 wt% C_{60}	0.38

were observed in the two test methods. Bulk adhesive forces of the prepared SIS and SBS control films (0 wt% C_{60}) remain relatively unchanged as a function of exposure time; however, films containing as little as 0.2 wt% C_{60} show a significant loss of tack with exposure time. This tack loss is even more dramatic in films containing $\geq$1.0 wt% C_{60} sensitizer, and at high concentrations, the transformation occurs too quickly to obtain significant data using current analytical methods. The styrene/butadiene ratio in the commercial SBS (Kraton D1102) used in this study was 30/70 (wt/wt), and the butadiene composition consists of a mixture of 1,4- (88%) and 1,2-microstructure (12%) double bond content. Relative percents of internal to pendant double bonds were estimated using ^{1}H NMR. SIS (Kraton D1161) was comprised of ~15 wt% polystyrene (15/85 styrene/rubber ratio) and has no vinyl C=C bonds. The residual vinyl double bonds of SBS polybutadiene have been shown to have higher reactivity in chemical crosslinking reactions than internal C=C of SBS and SIS. Decker and Viet [6] found that SIS (15/85) does not gel easily in the presence of photoinitiator and UV light, under conditions which would readily crosslink SBS (30/70). Despite its slower reactivity relative to SBS, researchers were able to eventually crosslink SIS using TRIS (2 wt%), photoinitiator (1 wt%), and UV-irradiation. In our work, a comparable response was observed in SIS systems relative to SBS fullerene–PSA composites under white light irradiation in the presence of C_{60} fullerene.

Bulk-tack measurements allow for further inspection of the adhesive properties 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 can be used to describe the cohesive strength of the sample, Fig. 6a. SIS clings more to the probe tip after the primary debonding event has occurred, and as a result, SIS samples also feel more "sticky" to the touch. The presence of residual sample on the tip after testing could not be visually confirmed; however, it should be noted that cleaning the probe tip between each tack analysis was required to obtain reproducible results, supporting some degree of cohesive failure within non-irradiated SIS samples. Fig. 6b describes the changes in bonding ratio (after and before the primary separation of the probe tip from the film – shaded/unshaded areas) as a function of white light irradiation time. SIS has a much higher bonding ratio at $t = 0$, while SBS has a bonding ratio of ~1: the experiment with 1 wt% C_{60} is shown in Fig. 6b. The bonding ratio of SIS quickly decreases to that of SBS in the initial 2 min of

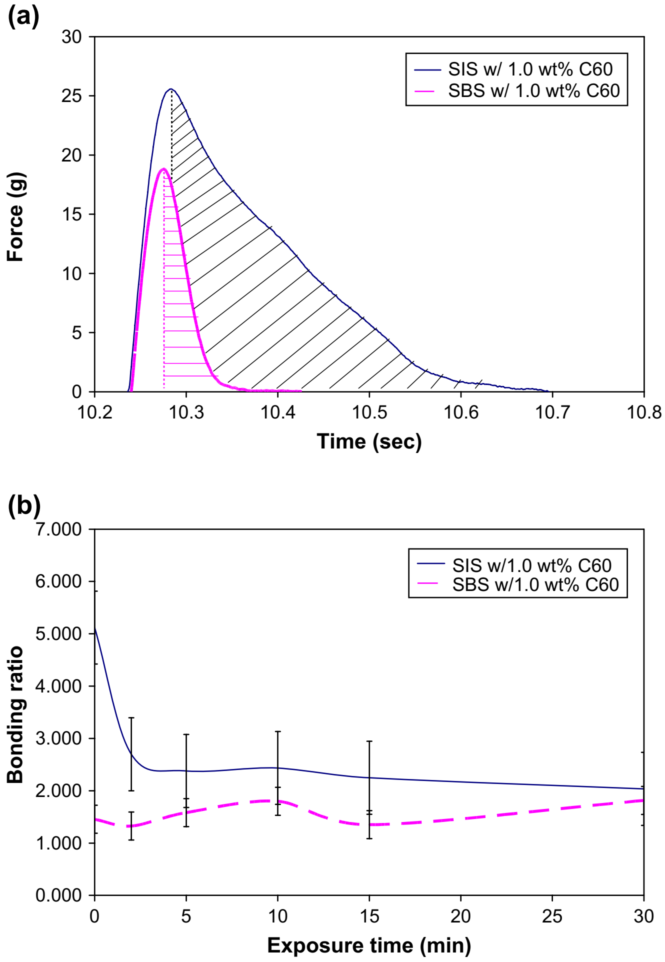

Fig. 6. (a) Bonding profile of tack measurements in fullerene–PSA systems containing 1 wt% C_{60} prior to irradiation; (b) changes in the bonding ratio (after and before the primary separation of the probe tip from the film – shaded/unshaded areas) as a function of visible irradiation time.

irradiation, corresponding to a change in initial tack values of 25.8 g at $t = 0$ to 20.5 g at $t = 2$ min. After the initial drop, tack values increase over several minutes before showing another dramatic drop to 0 gf; however, during this time the bonding ratio remains relatively constant at 1. This behavior is observed in both tack and peel tests of SIS and SBS fullerene–PSAs.

Table 2 provides peel test data in the form of the irradiation exposure time required for the sample to lose 90% of its initial peel strength value. Tabular data is presented as a function of PSA chemical composition and weight percent of C_{60} loading in the sample. At higher C_{60} concentration, the exposure time required to reduce the peel strength is significantly less, and SIS maintains adhesive properties longer under comparable conditions to SBS polymer. Due to the low peel strength of SBS polymer, peel test samples were formulated with 10 wt% tackifier (Piccotac™ 8095) to increase initial peel strength values. Similar to the study performed by Kim et al. [4], our lab found the addition of 10–20 wt% of a tackifier to significantly increase SBS polymer adhesion.

The temperature of tack coupons was found to increase approximately 20 °C over the first 30 min of irradiation to 42 °C and remain constant thereafter. Control samples were prepared to test if the loss in bulk tack was accelerated by the increase in temperature of the sample during irradiation. Bulk-tack force was evaluated in SBS and SIS films containing 1 wt% C_{60}. In both dark controls and in films irradiated for 1 h in a reduced-oxygen environment at thermal equilibrium, the bulk tack was found to increase slightly in SBS samples by 10% and more significantly by 30% in SIS samples. As in the case of nano-tack experiments, some increase in tack is attributed to the ballooning of the soft-block to the surface upon heating.

Table 2
180° Peel strength loss with C_{60} concentration and visible irradiation in SIS and SBS fullerene–PSAs

Concentration of C_{60} (wt %)	90% Peel strength loss in fullerene–SIS	90% Peel strength loss in fullerene–SBS[a]
0 wt%	> 12 h	>12 h
0.5 wt%	120 min	30 min
1.0 wt%	60 min	15 min
2.0 wt%	30 min	10 min

[a] SBS formulated with 10 wt% piccotac resin.

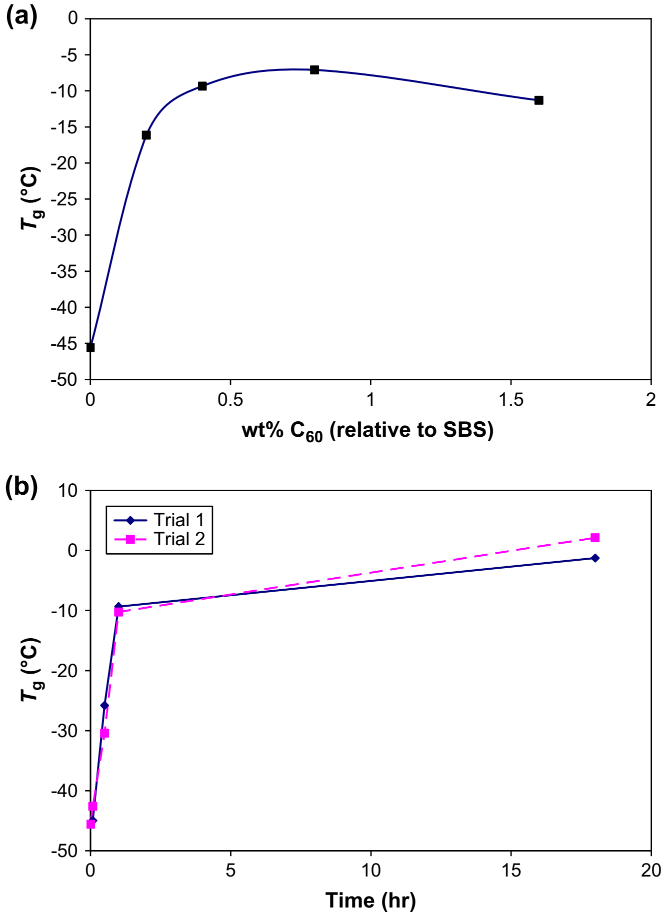

Fig. 7. Effect of (a) C_{60} wt% at a constant irradiation time of 12 h and (b) light exposure time on soft-block T_g in fullerene–PSA blends with SBS; solution drawn (20 wt% in toluene) 30 μm films on release paper; shear mode; 3 μm amplitude; 2 °C/min ramp rate; 0–18 h using a 150 W tungsten/halogen irradiation source.

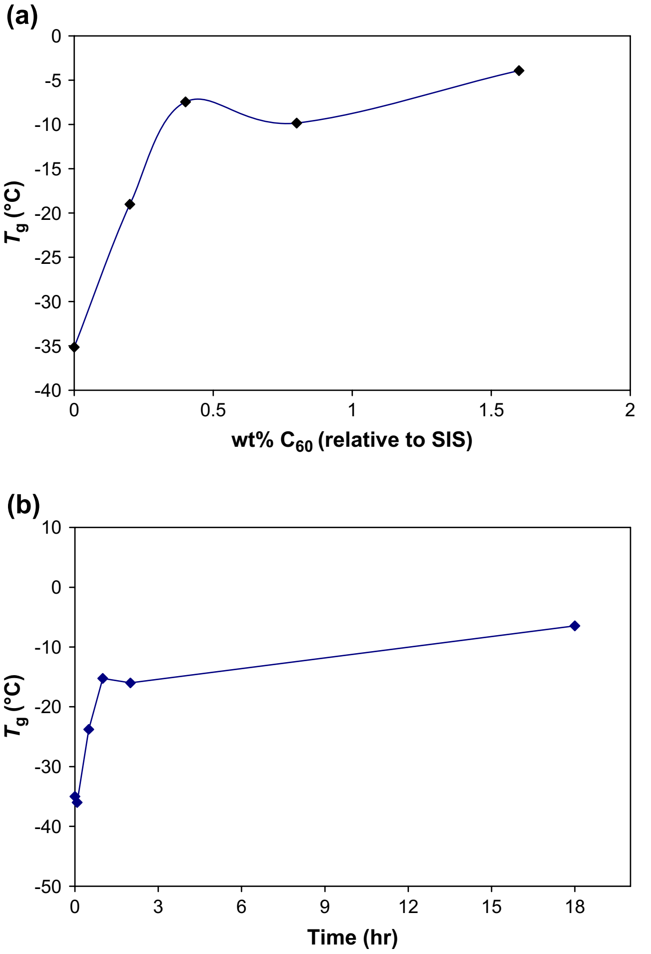

Fig. 8. Effect of (a) C_{60} wt% at constant irradiation time of 12 h and (b) light exposure time on soft-block T_g in fullerene–PSA blends with SIS; solution drawn (20 wt% in toluene) 30 μm films on release paper; shear mode; 3 μm amplitude; 2 °C/min ramp rate; 0–18 h exposure using a 150 W tungsten/halogen irradiation source.

Mechanical tests to monitor T_g (tan δ) of the butadiene and isoprene soft-blocks were performed via DMA, and the results are presented in Figs. 7 and 8 (SBS and SIS). In these experiments, effects of C_{60} wt% and light exposure time on soft-block T_g in fullerene–PSA blends were explored. Prepared films on release paper were irradiated and removed from the release paper just prior to testing. A dramatic shift in the T_g to higher temperatures is observed with increasing C_{60} concentration and irradiation time. Gel fractions were obtained on DMA samples of fullerene–SBS composite films, and the insoluble fraction was found to increase to >80% at 2 h irradiation and 0.2 wt% C_{60}. A high value of 94.5% for the gel fraction of photo-crosslinked SBS was obtained at 18 h of exposure, Table 3. The amount of C_{60} extracted from the film per mass unit relative to the initial value present in the film was determined by HPLC analysis of the extracting solvent. The changes in T_g and the observance of significant gel fractions with increasing C_{60} concentration and irradiation exposure time support the formation of extensive chemical networks in the fullerene–PSA adhesive composites. In many cases low C_{60} extractables were obtained, indicating a significant incorporation of C_{60} fullerene into the matrix under optimized conditions. Although the chemical crosslinks may be extensive in the sample due to the peroxides formed from the in situ generation of singlet oxygen, the most significant changes in chemical and physical properties are observed in the soft-block segments as demonstrated by the AFM nano-tack and DMA results. A homopolymer of polystyrene was prepared according to the same protocol, containing 2.0 wt% C_{60}, and the T_g was found to be constant over the 1 h testing period.

Table 3
Representative gel fractions of SBS fullerene–PSAs

Concentration of C_{60} (wt %)	Irradiation time (h)	Gel fraction%[a]	% of C_{60} extracted[b]
0	12	7 (0.6)	0
0.2	12	86 (8)	1.5 (0.2)
0.4	12	79 (8)	1.8 (0.2)
0.8	12	87 (8)	2.8 (0.3)
1.6	12	87 (9)	32.0 (3)
0.2	0.08	52 (5)	24.3 (2)
0.2	0.5	57 (6)	5.5 (0.5)
0.2	1	76 (8)	4.1 (0.4)
0.2	2	82 (8)	1.9 (0.2)
0.2	18	95 (9)	1.3 (0.1)

[a] Error percents were estimated from the average analysis of multiple samples.

[b] C_{60} wt% extracted from films was determined by HPLC analysis of extracting solvent and is relative to initial C_{60} concentration present in films.

4. Conclusions

Nanoscale (nano-tack, measured by AFM) and bulk-scale (tack and peel) adhesive forces of mixtures of polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) and polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS)/C_{60} nanocomposite adhesive systems were found to decrease with increasing C_{60} concentration and white light exposure time. Although the absolute values of adhesive force measured via the two methods differed, similar trends were observed in both nanoscale and bulk-scale measurements. Reduced nano-tack forces in both SIS and SBS studies approached the value for 100% polystyrene, indicating surface hardening and crosslinking of the soft-blocks. Films produced during the study were smooth, having low RMS surface roughness, and showed nanoscale phase separation between the soft (diene) and hard (styrene) segments. This phase separation was lost after addition of C_{60} sensitizer and white light irradiation. Estimated T_g of the soft-block shifts to higher temperatures (increasing by 30–40 °C) and high gel fractions were obtained, indicating the presence of chemically crosslinked networks. In irradiated systems containing as little as 0.2 wt% C_{60}, a significant decrease in adhesion is observed.

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