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Adhesion properties of UV crosslinked polystyrene-*block*-polybutadiene-*block*-polystyrene copolymer and tackifier mixture

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Abstract

The peel and tack properties of mixtures of polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) and a tackifier were investigated after these were crosslinked by ultraviolet (UV) irradiation at various amounts of benzophenone (BP) as a photoinitiator and trimethylolpropane mercaptopropionate (TRIS) as a crosslinking agent.

The degree of crosslinking of polybutadiene (PB) block in the SBS mixture was qualitatively estimated from the amount of gel fraction as well as the change in the glass transition temperature of the PB block. The crosslinking of the PB block was done within 3 min after UV irradiation and the peel strength of crosslinked specimens was as low as 45% of specimens without crosslinking. Nano-tack and bulk tack properties as well as the surface tension of mixtures were measured depending upon amounts of BP and TRIS. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Pressure-sensitive adhesive; SBS block copolymer; Ultraviolet curing

1. Introduction

Pressure-sensitive adhesives (PSA) consisting of elastomers, tackifiers, and various additives have been widely used as tapes in stationery and for electric and medical purposes [1]. Although acrylics based elastomers are widely used, an additional crosslinking should be done to increase the cohesive strength. Polydiene-based triblock copolymers (for instance, polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) and polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS)) have been used as elastomers due to higher cohesive strength resulting from the physical network of polystyrene (PS) blocks.

Recently, some PSAs have been developed for semiconductor [2] and medical tapes [3]. In those cases, PSAs have high tack properties during the application of PSA to the substrate. However, during removal from the substrate, PSAs are easily detached without damaging silicone wafer or skin. Since the tack (or peel) strength is related to the viscoelastic properties of PSA, a rapid change in adhesion properties can be achieved by the irradiation with ultraviolet (UV) wavelength. Bonye et al. [4] showed that acrylic polymer with pendent methacrylate can be crosslinked by UV or light irradiation. Mateo et al. [5] investigated the crosslinking mechanism of polybutadiene block (PB) in SBS by using two photoinitiators (benzophenone (BP) and 2,2-dimethoxy-2-phenylacetophenone). However, the crosslinking of PB block estimated from the swelling ratio took place very slowly (irradiation time of 30–120 min). To reduce the crosslinking time for the PB block in SBS, Decker and coworkers [6–8] used a crosslinking agent of trimethylolpropane mercaptopropionate (TRIS) together with a photoinitiator, and showed that the crosslinking reaction was completed within 3 s.

In this paper, we investigated the adhesion properties of SBS mixtures and a tackifier after the PB block was crosslinked with TRIS and BP with the aid of UV irradiation. Emphasis was placed upon the effect of amounts of TRIS and BP on the peel strength of mixtures. Finally, nano-tack and bulk tack properties were measured and compared with the peel strength.

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2. Experimental

2.1. Materials

SBS triblock copolymer was a commercial grade of Kraton D1102 (Shell Chem. Co.) which has molecular weight (10,000 PS–50,000 PB–10,000 PS) and polydispersity of 1.145 for triblock copolymer. However, this SBS has ~20 wt% of uncoupled diblock copolymer, and once this diblock copolymer was considered, the polydispersity was increased to 1.2. Since SBS itself does not show good tack properties, in this study we employed a partially hydrogenated C-9 hydrocarbon resin (HM-100: Kolon Petrochemical Co., Korea) as a tackifier. Since the hydrogenation degree of HM-100 was 0.7–0.85, this showed a good miscibility with the PB block in SBS [9]. The crosslinking agent was trimethylolpropane mercaptopropionate (TRIS: Aldrich Chemical Co.), which can crosslink the PB block in SBS due to three S–H groups in TRIS, and the photo-initiator was benzophenone (BP) (Jenssion Chem., Japan).

2.2. Sample preparation

Various PSA mixtures of SBS and HM100 were prepared by solution casting of toluene in solid content of 33 wt%. After stirring this mixture for 24 h, we added TRIS and BP to the above solution and mixed them for 24 h in dark environment to prevent to exposure to light. The mixture was bar-coated onto the poly(ethylene terephthalate) (PET) film with 56 μm as a back tape. After coating, toluene was removed by using a vacuum oven at room temperature. The final thickness of PSA was 20–23 μm. Then this PSA was attached to a stainless steel (SUS 304) by using a roller with 2 kg.

The final film was irradiated by using a UV generator (Hg Arc Lamp) with an intensity of 800 W under nitrogen environment. The wavelength of 254–365 nm was selected by using a glass filter. The irradiation intensity onto a specimen measured by a photometer was 11.2 mW/cm^2. After irradiation, we carried out 180° peel test using a Texture Analyzer (Stable Micro System TA-XT2*i*) with the speed of 5 mm/s at room temperature.

Bulk tack was also measured by the same Texture Analyzer at the adhesion test mode with crosshead speed of 10 mm/s, contact time of 1 s, and loading force of 100 g/cm^2. On the other hand, nano-tack was measured by an atomic force microscope (AFM: Autoprobe CP. Park Scientific Instruments) with tip force of 5 nN and tip radius of 30 nm. The nano-tack was defined as the force during the debonding of the tip from the PSA film. We prepared this film by spin coating at 5000 rpm of mixtures from toluene (7 wt% in solid content) onto a silicone wafer.

In the meantime, the glass transition (T_g) of the PSA films with various UV exposure times was obtained at a maximum in the tan δ measured by a dynamic mechanical analyzer (DMA: TA Instruments) using a tension mode with a heating rate of 3 °C/min and a frequency of 1 Hz. The PSA film for T_g measurement was prepared by coating PSA with final thickness of ~20 μm onto the Teflon film as a back tape. Then, to mimic the peel test where a PET film was directly attached to the PSA, a PET film was placed at a distance of 1 cm from the PSA surface. Note that the PET film should not be attached to the PSA surface due to the good adhesion between two. Once the PSA surface was directly contacted to the PET film, the PSA film itself for DMA experiment was not prepared because it could not be detached from the PET film. After the UV irradiation under the nitrogen environment followed by quenching the specimen into liquid nitrogen, the PSA film itself was easily detached from the Teflon back.

The gel fraction of the film after UV irradiation was obtained after it was dissolved into toluene for 24 h. Finally, films for contact angle measurement were prepared by the same method used for peel strength. Then, PSA was attached to a wafer and irradiated by UV. After the specimen was quenched into liquid nitrogen, the film was detached from the wafer. Using water and di-iodomethane, we measured the contact angle for the wafer-side film by using a surface tensiometer (SEO-300 Plus: Surface-Electric Optics Co.).

3. Results and discussion

Fig. 1 shows the peel strength change with UV exposure time for 80/20 (wt/wt) SBS/HM100 mixture as a function of BP content at two different amounts (1 and 2 wt%) of TRIS. With increasing UV exposure time, peel strength decreased rapidly within 1 min, and then slowly decreased before leveling off at 3 min. The relative peel strength (RPS), defined as the peel strength after UV exposure divided by the peel strength before UV exposure, was 0.7–0.9 for 1 wt% of TRIS, but this decreased to 0.45–0.55 for 2 wt% of TRIS. Once the amount of crosslinking agent is increased, more crosslinking of PB block is expected, which results in an increased modulus (or decreased peel strength). Thus, one expects that RPS would be increased further at higher amounts of TRIS. However, we could not obtain the peel strength of PSA with TRIS larger than 3 wt%, because interfacial (or cohesive) failure occurs due to poor adhesion between PSA film and PET substrate.

It is also seen that with increasing amount of BP, the initial peel strength (namely, without UV exposure) of PSA slightly decreased. This is attributed to the fact that excess amounts of BP play the role of impurities near interface; thus the wettability between PSA film and substrate became worse. In addition with increasing amount of BP, more peroxide radicals from BP can be generated during a long solution mixing (24 h), even though the specimen was not exposed to light due to dark condition. These peroxides can crosslink TRIS, which causes low peel strength. In order to

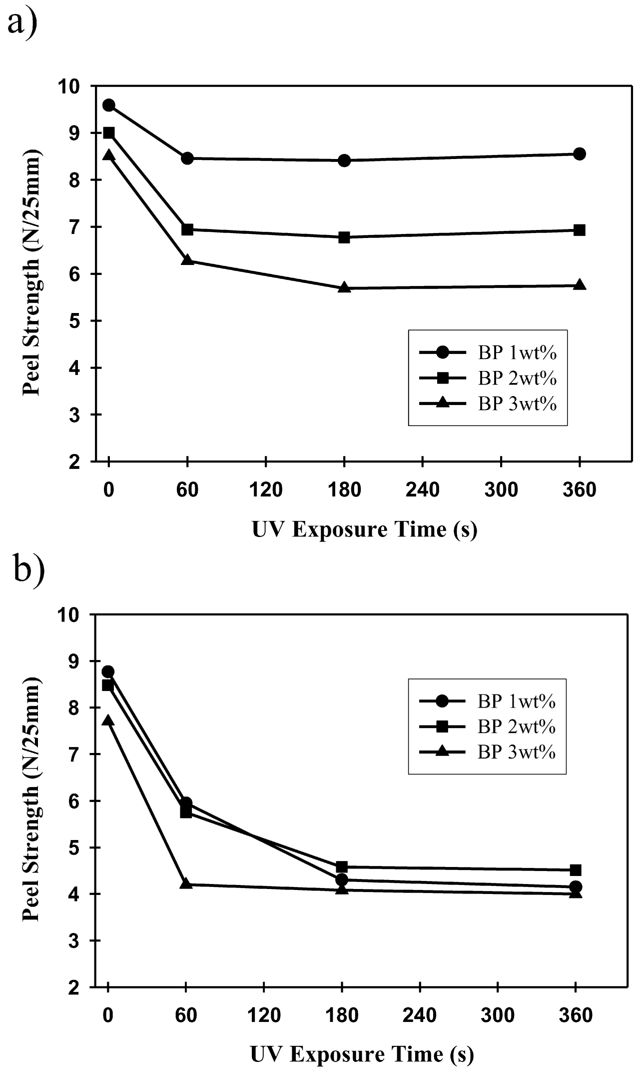

Fig. 1. Peel strength change with UV exposure time as function of BP contents for 80/20 (wt/wt) SBS/HM100 mixtures. The amount of TRIS was (a) 1 wt% and (b) 2 wt%.

test the effect of generated radicals from BP on the peel strength during the sample preparation, we prepared other specimens consisting of 80/20 (wt/wt) SBS/HM100 and 2 wt% of TRIS with 1–3 wt% 2-hydroxy diphenyl methane (HDM) ($C_6H_5-CH_2-C_6H_4(OH)$) instead of BP ($C_6H_5-C(O)-C_6H_5$), by using the same procedure as the preparation of specimens with BP. It is known that HDM has almost the same molecular weight as BP, but this cannot generate peroxide radicals. We found that when the amount of HDM is increased from 1 to 3 wt%, the peel strength was decreased from 9.2 to 8.0 N/25 mm. Thus, we can consider that the initial decrease in peel strength is mainly due to the impurities effect of BP rather than a possible crosslinking reaction during the sample preparation.

The change in peel strength with UV exposure time is also corroborated with the gel fraction of PSA as well as the glass transition (T_g) of PB block, as shown in Fig. 2. It is seen that with increasing UV exposure time, the gel fraction and T_g of PB block increased rapidly at short times and slowly reached steady values. Since HM100 cannot be crosslinked, the maximum gel fraction of SBS in 80/20 (wt/wt) SBS/HM100 would be 0.8. We found that for 95/5 (wt/wt) SBS/HM100 mixture, the maximum gel fraction of SBS was 0.95. Thus, we considered that all PB blocks are crosslinked.

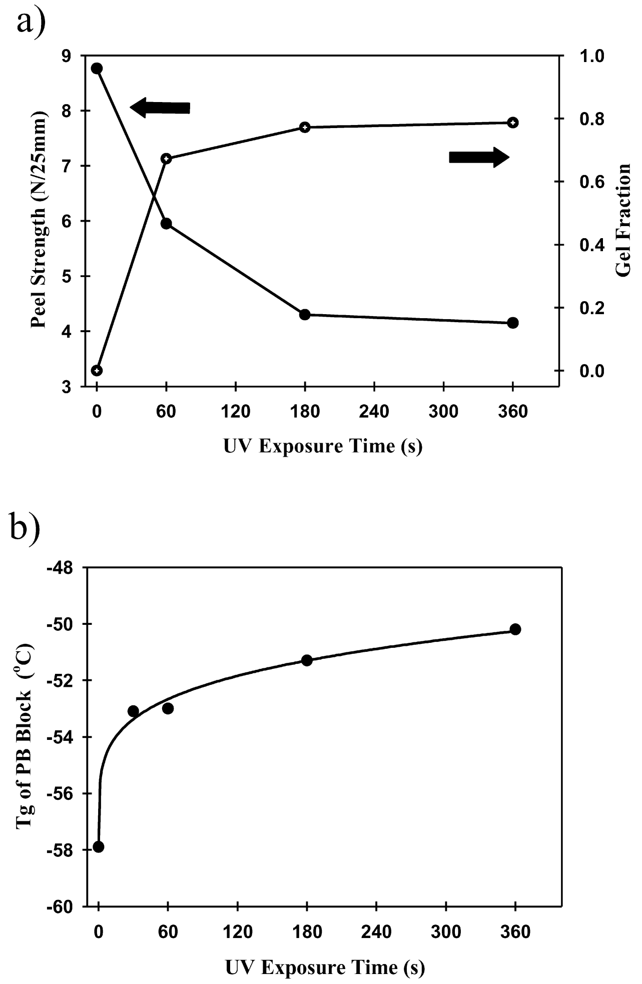

Fig. 2. Changes of (a) peel strength (filled symbols) and gel fraction (open symbols) as well as (b) the glass transition of the PB block with UV exposure time for 80/20 (wt/wt) SBS/HM100 mixtures with 2 wt% of TRIS and 1 wt% of BP.

Fig. 3 shows the RPS change with the amount of BP for 80/20 (wt/wt) SBS/HM100 blend with 2 wt% of TRIS, from which the minimum RPS was observed at 0.5–1 wt of BP. An initial decrease in RPS at lower amounts of BP is due to more crosslinking reactions due to larger amounts of BP. The increase in RPS at higher amounts of BP might be due to the excess termination reaction. According to Ref. [10], BP and TRIS attack the double bond in PB block and thus generate the radical of $R'-S^{\cdot}$. However, at higher amounts of BP, although larger amounts of radical are generated, termination reaction between the radicals ($2\ R'-S^{\cdot} \rightarrow R'-S-S-R'$) is also accelerated; thus an optimum amount of BP gives the minimum peel strength.

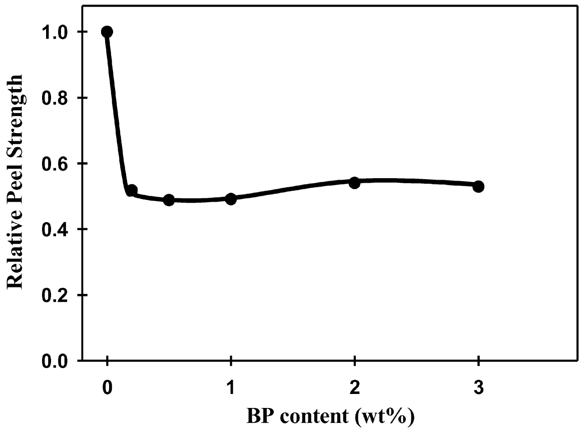

Fig. 3. Effect of BP content on RPS for 80/20 (wt/wt) SBS/HM100 mixtures with 2 wt% of TRIS. The UV exposure time was 180 s.

Since RPS can be proportional to the relative amount of PB block in PSA, we studied the effect of composition of SBS/HM100 blend on the peel strength. The results are shown in Fig. 4. Here, the amounts of BP and TRIS are 1 and 2 wt%, respectively. As expected, with decreasing amount of double bond in PSA, RPS increases. However, it is noted that when the amount of HM100 is less than 5 wt%, initial peel strength was ~4 N/25 mm, which is half of that for specimen with 20 wt% of HM100.

Note that the effect of photo-crosslinking condition on the peel strength, as shown in Figs. 1–4, was explained mainly by changing bulk viscoelastic properties, for instance, T_g and gel fraction. However, measured peel strength (or adhesion energy) (G_c) is the sum of the intrinsic work of adhesion and bulk viscoelastic energy, although the latter is much more important [11]

$$G_c = G_0 + \Psi \tag{1}$$

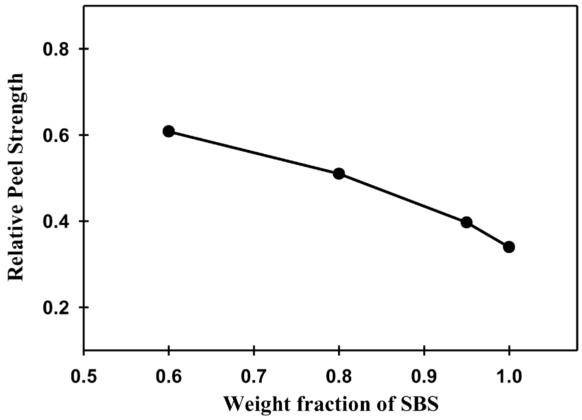

Fig. 4. The change of RPS with the amount of SBS in SBS/HM100 mixtures. The amounts of TRIS and BP are 2 and 1 wt%, respectively, and the UV exposure time was 180 s.

$$\Psi = G_0 f(\dot{a}, T, \varepsilon) \tag{2}$$

where G_0 is the intrinsic work of adhesion which is independent of peel speed, and Ψ is the energy loss due to the viscoelastic properties, which depends upon crack growth rate ($\dot{a}$), temperature (T) and strain level (ε). In order to test whether or not the surface properties of PSA are changed depending upon PSA compositions as well as UV exposure time, we measured contact angles (θ) using two liquids, water and di-iodomethane. The surface energy (γ_S) is calculated from contact angles and known values of dispersive and polar components of surface tension γ_{lv}^{D} and γ_{lv}^{P} of water (22.0 and 50. 2 mJ/m^2) and di-iodomethane (DIM) 48.5 and 2.3 mJ/m^2 [11].

$$1 + \cos\theta_i = \frac{2(\gamma_S^D)^{1/2}\left(\gamma_{lv,i}^D\right)^{1/2}}{\gamma_{lv,i}} + \frac{2(\gamma_S^P)^{1/2}(\gamma_{lv}^P)^{1/2}}{\gamma_{lv,i}} \tag{3}$$

Table 1
Contact angles and surface energy for various PSAs

PSA specimens		Contact angle and surface energy (mJ/m^2)	UV exposure time (s)			
SBS/HM100 (wt/wt)	TRIS/BP (wt/wt)		0	30	60	180
80/20	1/1	W	69.6	71.0	69.1	71.5
		DIM	31.9	32.0	30.4	30.5
		γ_S	45.7	45.2	46.4	45.6
80/20	2/2	W	73.1	72.4	72.6	73.0
		DIM	36.8	35.5	33.0	34.0
		γ_S	43.0	43.6	44.5	44.0
80/20	2/1	W	73.1	72.0	72.7	73.7
		DIM	34.4	35.0	33.3	34.0
		γ_S	43.8	43.9	44.3	44.1
95/5	2/1	W	69.8	70.3	70.4	69.4
		DIM	33.7	33.0	33.1	34.3
		γ_S	45.0	45.1	45.1	44.9
100/0	2/1	W	70.2	69.7	68.9	69.2
		DIM	31.8	31.5	33.6	33.9
		γ_S	45.5	45.8	45.3	45.1

W: water; DIM: di-iodomethane.

$$\gamma_{lv,i} = \gamma^{\mathrm{D}}_{lv,i} + \gamma^{\mathrm{P}}_{lv,i} \qquad (i = \text{water or DIM}) \tag{4}$$

$$\gamma_S = \gamma^{\mathrm{D}}_S + \gamma^{\mathrm{P}}_S \tag{5}$$

As shown in Table 1, the contact angles, thus surface energy of PSA, changed very little, if at all, with various compositions in PSA as well as UV exposure times. A little change in surface energy might be due to either smaller change in the work of adhesion or little sensitivity measured by contact angles. It is generally considered that PB block is covered at the surface of PSA specimens because of lower surface tension compared with PS block. This indicates that even though PB block is further crosslinked after UV exposure, the surface tension of PB block changes very little, if at all, with crosslinking degree. In order to find in detail the effect of crosslinking degree near the surface on adhesion properties, we performed a nano-tack test.

Fig. 5 shows changes of nano-tack and bulk tack properties with UV exposure time for two different PSAs (80/20 (wt/wt) SBS/HM100 and SBS itself) with 2 wt% of TRIS and 1 wt% of BP. Even though nano-tack was measured by AFM with a tip of 30 nm diameter and 5 nN force, this value was much increased when 20 wt% of the tackifier was added. This is due to the increased wettability in the presence of the tackifier. However, nano-tack for both specimens decreased by ~20% after UV exposure due to the increase of the chain stiffness of PB blocks. Therefore, we consider that nano-tack test would be important for the case where the contact angle measurement does not measure a subtle difference. Finally, we measured bulk tack properties of two PSAs, 80/20 and 60/40 (wt/wt) SBA/HM100 with 2 wt% of TRIS and 1 wt% of BP. But, we did not obtain bulk tack properties of SBS itself, and 95/5 (wt/wt) SBS/HM100 PSA due to too low tack values. Interestingly, compared with nano-tack change with UV exposure, the bulk tack values decreased significantly (60–70%) with UV exposure, which is the same level of decrease in peel strength as shown in Fig. 1. This is because bulk tack is mainly due to viscoelastic properties, whereas nano-tack properties exclude most of bulk properties. Thus, even though the adhesion at the surface is small, this can affect the total peel strength significantly. On the basis of these results, we consider that for specimens after UV exposure, the deformation zone is sharply reduced because of the increased modulus of PSA incurred by the crosslinking. At the same time, the intrinsic adhesion between rigid substrate (SUS 304 in this study) and PSA can be decreased. Both effects give more decrease in the peel strength of PSA after UV exposure.

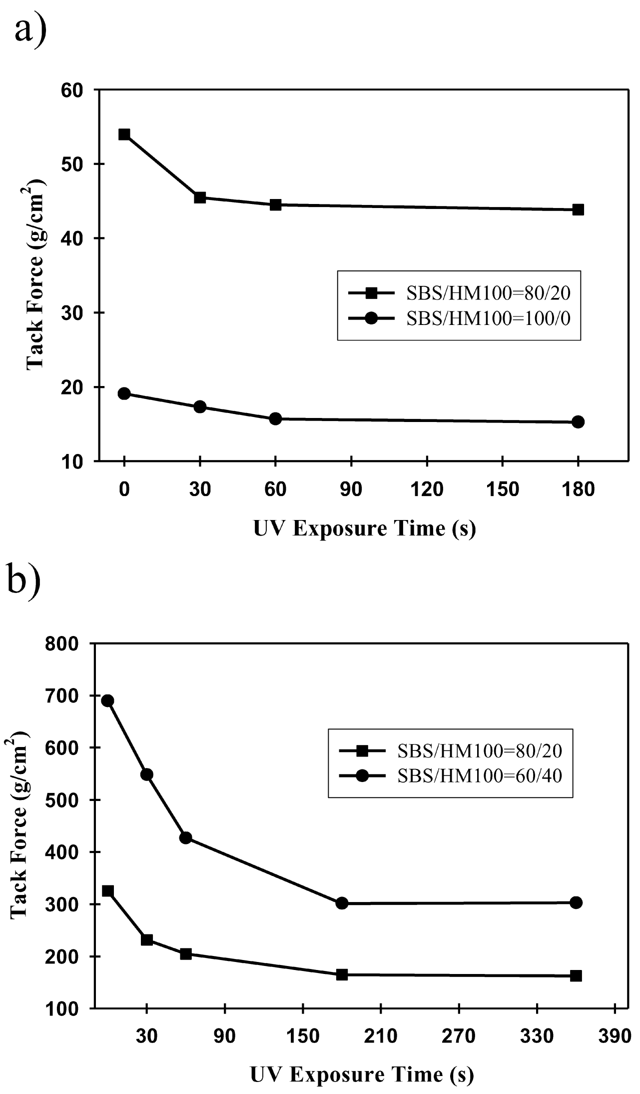

Fig. 5. Changes of (a) nano-tack force and (b) bulk tack force with UV exposure time for two different mixtures of SBS/HM100.

4. Conclusions

In this study, we investigated the effect of UV exposure on the peel and tack properties of PSA with crosslinking agent of TRIS and photoinitiator of BP. The crosslinking reaction completed within 3 min even if small amounts of TRIS and BP were used. The peel strength of crosslinked specimens was as low as 45% of specimens without crosslinking. However, we found that the contact angle for PSA after UV exposure did not change, whereas nano-tack properties changed with UV exposure. Therefore, the adhesion properties changes near the surface cannot be easily determined by contact angle measurement itself. The PSA employed would be used in tapes for silicon wafers as well as for medical purposes.

Acknowledgments

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