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Preparation of SIS/SBS-based UV-cross-linkable pressure-sensitive adhesives using the thiol-ene reaction

DONG-HYUK LIM¹, HYUN-SUNG DO¹, HYUN-JOONG KIM^{1,*},
JUNG-SUK BANG² and GOAN-HEE YOON²

¹ *Laboratory of Adhesion and Bio-Composites, Program in Environmental Materials Science, Seoul National University, Seoul 151-921, South Korea*

² *Vixxol A&C Co., Inc., Ansan 425-110, South Korea*

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Abstract—Hot-melt pressure-sensitive adhesives (HMPSAs) usually contain styrene-isoprene-styrene (SIS) or styrene-butadiene-styrene (SBS) block copolymers, tackifier, plasticizer and other additives. However, these PSAs cannot be used in high-temperature applications or where solvent and chemical resistance properties are required. We, therefore, developed UV-cross-linkable HMPSAs by the thiol-ene reaction with the aim to increase adhesion properties at elevated temperature. For effective UV cross-linking, the selection of photoinitiator and photo-cross-linker is very important for thermal stability and fast curing. Adhesion properties, such as probe tack, peel strength and shear adhesion failure temperature (SAFT), were evaluated to measure PSA performance as a function of photoinitiator type.

Keywords: Hot-melt; PSA; UV curing; photoinitiator.

1. INTRODUCTION

Pressure-sensitive adhesives (PSAs) are semi-solid materials with viscoelastic properties, which possess many advantages such as quick stick, easy bond and removability. Especially, hot-melt PSAs (HMPSAs) have high tack and peel strength, good bonding to rough surfaces, fast manufacturing and require only small manufacturing factory. However, the maximum service temperature of HMPSAs is not high compared to solvent-type PSAs. In HMPSAs, styrenic block copolymers such as SIS (styrene-isoprene-styrene), SBS (styrene-butadiene-styrene) and SEBS (styrene-ethylene-butylene-styrene), which show high cohesion and good PSA performance at ambient temperature, were used. This cohesion is acquired by

*To whom correspondence should be addressed. Tel.: (+82-) 2-880-4784; Fax: (+82-) 2-873-2318; e-mail: hjokim@snu.ac.kr

physical cross-linking of the styrene endblock due to immiscibility between the styrene and rubbery phase. The physical network, however, is collapsed at elevated temperatures, so if the application temperature is high, an SBS-based PSA cannot be used. One of the solutions to overcome poor heat resistance of SBS-based PSAs is a combination of the hot-melt with UV-curing systems to induce chemical cross-linking.

Chemical cross-linking was induced in HMPSAs by photo induced addition of a thiol (RSH) onto the olefinic double bond of the base polymer [1–4]. The reaction between thiol and polyene proceeds by a step growth addition reaction by sulfenyl radical ($\cdot\text{RS}$) through an efficient chain transfer process. The thiol-ene reaction has the advantage in manufacturing a UV-cross-linkable HMPSA product. Special facilities such as equipment for nitrogen gas purging are not needed in manufacturing UV-cross-linkable HMPSAs, so UV-cross-linked HMPSAs can be manufactured using existing facilities. UV cross-linking by the thiol-ene reaction can be effectively accomplished in the presence of air, because peroxy radicals formed by the O_2 scavenging of alkyl radicals are also capable of abstracting hydrogen atoms from the thiol [3].

The PSA in this study was obtained by blending SIS and SBS copolymers. The SBS has reactive vinyl groups which are able to cross-link by UV radiation. In general, SBS-based PSA is more rigid than SIS-based PSA, and therefore shows lower tack property. SIS addition can increase the tack property of SBS-based PSA. In this study, various types of photoinitiators for UV-curable HMPSAs were examined as effective photoinitiators in HMPSAs. The thermal stability of the photoinitiators and the photo-cross-linker was evaluated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the UV curing rate was studied by measuring pendulum hardness. Finally, UV-cross-linkable HMPSAs were prepared based on the measured thermal stability of the photoinitiator and photoinitiator types.

2. EXPERIMENTAL

2.1. Preparation of PSA specimens

The PSA was prepared by hot-melt blending of SIS and SBS block copolymers, tackifier, photoinitiator, photo-cross-linker and plasticizer. SIS copolymer was Vector4111 (diblock content < 1%, styrene content: 18%) and the SBS copolymer was D KX-405-CP (Kraton Polymers, Japan). The tackifier used was Hikorez A 1100 (Kolon, South Korea) and the plasticizer was Plastol 542 (ExxonMobil, USA). Photoinitiators were Micure BK-6 (Miwon Commercial, South Korea), Irgacure 970, Irgacure 819, and Darocur TPO (all from Ciba Chemical). Information on the photoinitiators is presented in Table 1. To enhance UV cross-linking, trimethylolpropane mercaptopropionate (TRIS, Aldrich) was used as the photo-cross-linker.

Table 1.

Specifications of the four photoinitiators used

	Chemical composition	Melting point ¹ (°C)
Micure BK-6	Benzil dimethyl ketal	66
Irgacure 907	α -aminoalkylphenones	74.8
Irgacure 819	Bis-acylphosphine oxides	133
Darocur TPO	Mono-acylphosphine oxides	93.5

¹ Measured by DSC.

The PSA was formed by blending in an internal mixer at about 150°C for about 40 min. The SIS/SBS, tackifier and plasticizer were initially introduced in the internal mixer. After a homogeneous mixture was obtained, the photoinitiator and photo-cross-linker were added to protect against thermal degradation during mixing. The PSA was coated onto a polyester (PET) film (thickness: 25 μm , SKC, South Korea) by melt coating with an average thickness of 20 μm at 150°C. The prepared samples were cured in a conveyor belt-type UV curing machine equipped with a medium-pressure mercury lamp (100 W/cm², main wavelength 365 nm) in the presence of air. Due to the heat sensitivity, a cold mirror was used as a reflector as it is partially transparent to IR, while most of the UV and visible radiation is reflected. The UV doses were 0, 200, 600, 1000, 1400 and 1800 mJ/cm². The UV doses were measured with an IL 390C Light Bug UV radiometer (International Light, USA).

2.2. Thermogravimetric analysis (TGA)

The TGA provides information on the thermal degradation characteristics of the material. The TGA measurements were carried out using a thermogravimetric analyzer (Rheometric Scientific TG1000). The TGA samples comprised 4–5 mg each of the photoinitiator and photo-cross-linker. The TGA measurements were conducted at a heating rate of 10°C/min in a N₂ atmosphere in order to avoid unwanted oxidation.

An isothermal test is a method for measuring the mass change of a sample under constant temperature (170°C) as a function of time.

2.3. Differential scanning calorimetry (DSC)

DSC is a technique for measuring the difference between the heat flux into a sample and that into a reference as a function of temperature, while the samples are subjected to a controlled temperature profile. Only a small sample size is required and the measurement time is very short, while relatively good reproducibility is obtained. DSC analysis was carried out using a TA Instruments DSC Q1000 equipment (at NICEM, Seoul National University) with 5–8 mg of photoinitiator. The sample was scanned as the temperature was raised from 25 to 250°C at a heating rate of 10°C under a N₂ atmosphere.

2.4. Gel content

The gel content provides information on the degree of cross-linking. The gel content was determined by soaking the sample in toluene for one day at room/temperature (RT). The insoluble polymer was recovered by filtration and dried at 70°C to a constant weight. The gel fraction of the samples was calculated by the following equation:

$$\text{Gel fraction (\%)} = \frac{W_t}{W_0} \times 100,$$

where W_t and W_0 are the PSA weights after and before soaking, respectively.

2.5. Pendulum hardness

Hardness measurement is a simple technique for determining the extent of cure of a sample. The hardness of a material depends on the extent to which the material has cured, and since hardness is also related to the modulus of the material, a hardness value gives an indication of the degree of cross-linking. Among the various hardness measurement methods, the pendulum hardness test (König Pendulum Hardness Tester, Sheen Instruments, UK) was used to monitor the SBS surface hardness during UV curing. SBS film samples were prepared. The pendulum hardness test is based on the principle that the harder a measured surface, the longer the oscillation time of pendulum.

2.6. PSA performance

The probe tack was measured using a Texture Analyzer (TA-XT2i, Micro Stable Systems, UK) with a 5 mm diameter, stainless steel cylindrical probe. The probe is brought in contact with the PSA surface at the pre-test speed which has to be low enough to affect the tack value. Next, the probe stops for a short time (generally 1 s) under a low pressure. Finally the probe is separated from the PSA surface. The measurements were carried out at a separation rate of 1–10 mm/s under a constant pressure (100 g) and dwell time (1 s).

To prepare the the 180° peel strength samples, the PSA films were bonded to the stainless steel substrate which had been cleaned with acetone. The PSA specimen was pressed onto the stainless steel substrate using 2 passes of a 2-kg rubber roller and stored at RT for over 12 h. The peel rate was 300 mm/min at RT. The average force in the debonding process was taken as the peel strength.

The shear adhesion failure temperature (SAFT) indicates the heat resistance under a constant shear load at an elevated temperature. The PSA specimen was pressed onto a stainless steel substrate by a 2-kg rubber roller. The load attached to the specimen was 1 kg and the heating rate was 0.4°C/min. The SAFT value is the measured temperature where a constant load is applied to induce a shear stress, and the temperature is raised until the PSA specimen fails.

3. RESULTS AND DISCUSSION

3.1. Thermal stability of photoinitiators and photo-cross-linker

The use of combined hot-melt coating and UV curing contributes to improved PSA properties including fast coating, non-VOC emission and high heat resistance due to chemical cross-linking. However, the difficulty of manufacturing UV-cross-linkable HMPSAs is that many components such as base polymer, tackifier, plasticizer, photoinitiator and photo-cross-linker must be optimized.

The manufacturing process of UV-cross-linkable HMPSAs is so hot that photoinitiator and photo-cross-linker which are essential components for fast curing must have high heat resistance. An SIS- or SBS-based PSA usually was produced by hot-melt technology with a very high process temperature of over 150°C at which the base polymer has low viscosity. If a photoinitiator with poor heat stability is used, fast and effective curing is impossible. The thermal stability of the photoinitiator and photo-cross-linker was evaluated by TGA and DSC. TGA can measure changes in sample mass with temperature, and the degradation temperature of the photoinitiator and photo-cross-linker can be evaluated by TGA. The thermal stability of three kinds of photoinitiators is shown in Fig. 1. Irgacure 819 and Darocur TPO were more stable than Irgacure 907 during the hot-melt process. The 1% mass loss temperature is assigned as the decomposition temperature of the photoinitiator, and it was 145°C for Irgacure 907, 202°C for Irgacure 819 and 200°C for Darocur TPO. The mass loss of Irgacure 907 at 150°C at which temperature PSA was formed and coated was 0.11% and at 170°C it increased to 4.29%. A previous study suggested that the photoinitiator can maintain a high thermal stability through the introduction of an aromatic ring or fluoro substituents [6]. For example, titanocenes are thermally unstable with a decomposition temperature of -30°C; however, the

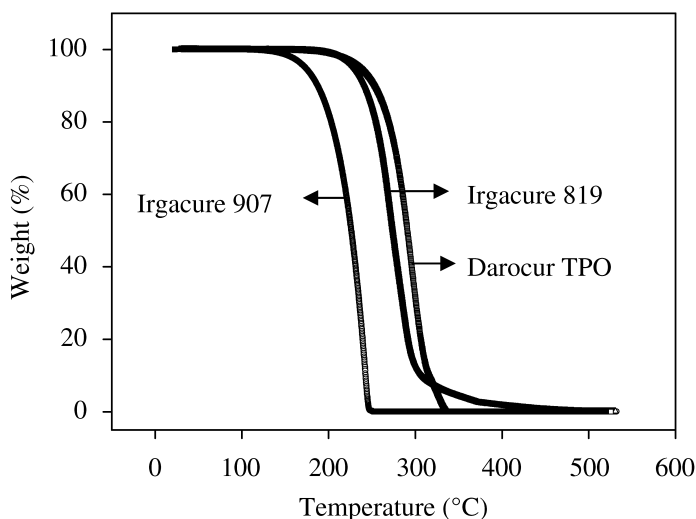


Figure 1. TGA thermograms of the three photoinitiators.

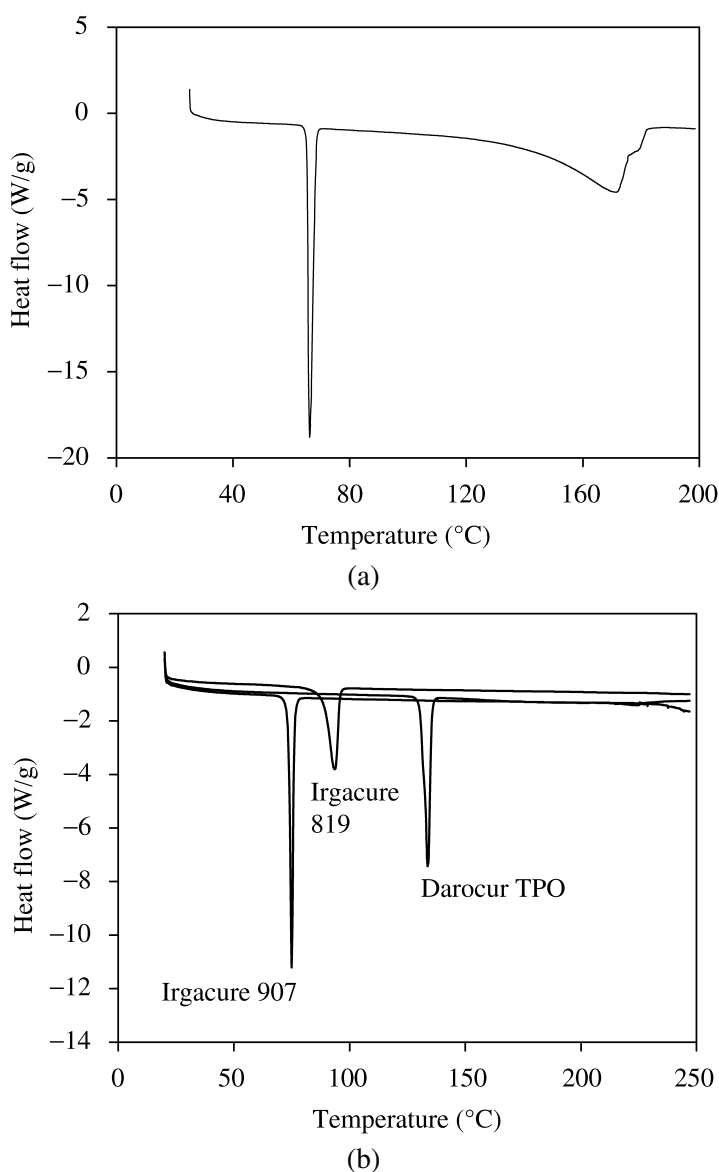


Figure 2. DSC diagrams of (a) Micure BK-6 and (b) Irgacure 907, Irgacure 819 and Darocur TPO photoinitiators.

introduction of an aromatic substituent increases the stability to a decomposition temperature of 146°C without affecting the photochemical reactivity.

The DSC diagrams of the photoinitiators are presented in Fig. 2. Figure 2a is an example of the sample with a lower heat resistance (Micure BK-6). Figure 2b shows the DSC diagrams of the three photoinitiators used in this study. The photoinitiator with poor heat stability shows two peaks in the diagram, one at

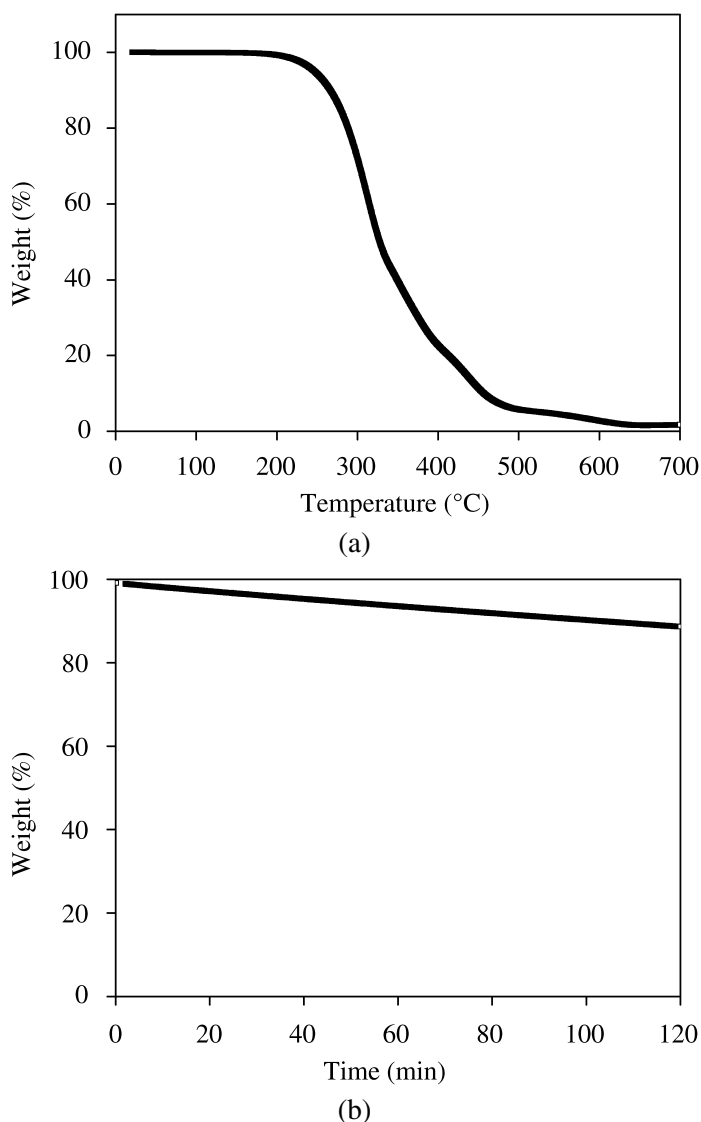


Figure 3. (a) TGA thermogram of photo-cross-linker and (b) weight loss of photo-cross-linker TRIS at 170°C.

65°C being the melting point and the other representing the chemical change of the sample. However, the photoinitiators with good heat stability show only one peak related to melting. Irgacure 907, Irgacure 819 and Darocur TPO all demonstrated sufficient heat stability in the hot-melt process.

For an effective UV cross-linking, a photo-cross-linker with three thiol functional groups was used. The heat stability of the photo-cross-linker was also determined by TGA. Figure 3a shows a TGA diagram of the photo-cross-linker. The photo-cross-linker with three thiol functional groups showed adequate heat stability in

melt process conditions. The decomposition temperature of the photo-cross-linker was 208°C and 10% mass loss was shown at 266°C. In addition to the temperature sweep test, the heating time also required investigation, because the components of the UV-cross-linkable HMPSAs had been heated for a long time. Figure 3b shows an isothermal diagram of the photo-cross-linker. The mass loss was checked at 170°C for 2 h. In Figure 3a, the photo-cross-linker shows stable behavior at 170°C, but the mass of the photo-cross-linker decreased at a steady rate with time. The photo-cross-linker was thermally decomposed at 0.09%/min. Due to the short mixing time of the photo-cross-linker, the mass loss minimized the heat-induced damage. Therefore, in the blend process of UV curing HMPSAs, components like SIS or SBS copolymer, tackifier and oil were mixed first, after which a photoinitiator and a photo-cross-linker were added when the hot-melt component almost showed a homogeneous phase.

3.2. UV cross-link density of SBS

The degree of cross-link density induced by UV radiation can be estimated by gel content and pendulum hardness. The gel content of the SBS with vinyl group is shown in Fig. 4 [7]. In the case of only SBS, there was no residue before and after the UV curing process (Fig. 4a), whereas upon photoinitiator addition to the SBS, the SBS gel content gradually increased up to 60% at 2200 mJ/cm², and the residues were fiber-like and fragile (Fig. 4b). When SBS was cross-

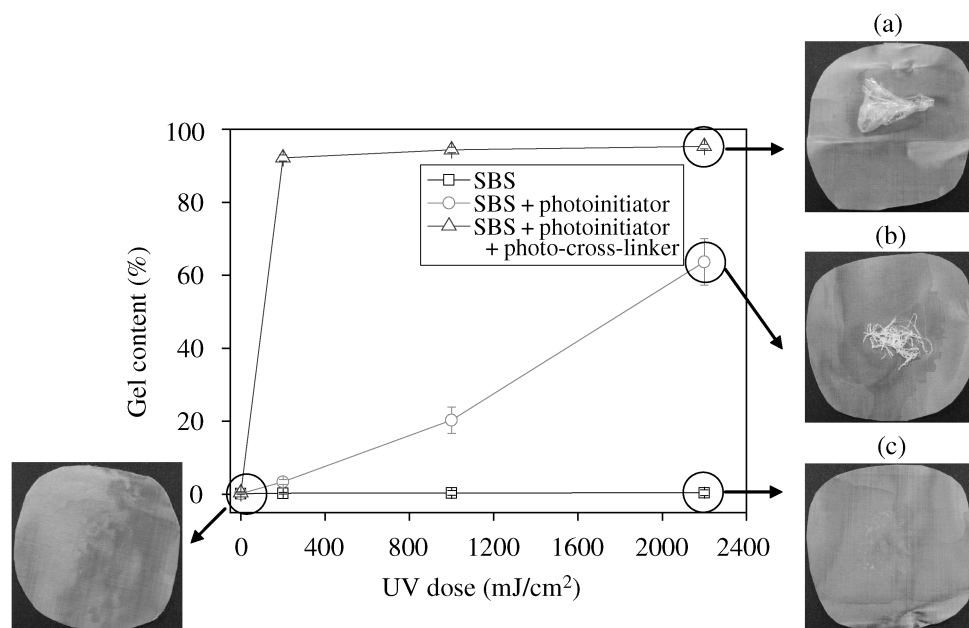


Figure 4. Gel content of UV-cured SBS films and photographs of insoluble residues after filtration (photoinitiator, Micure BK-6).

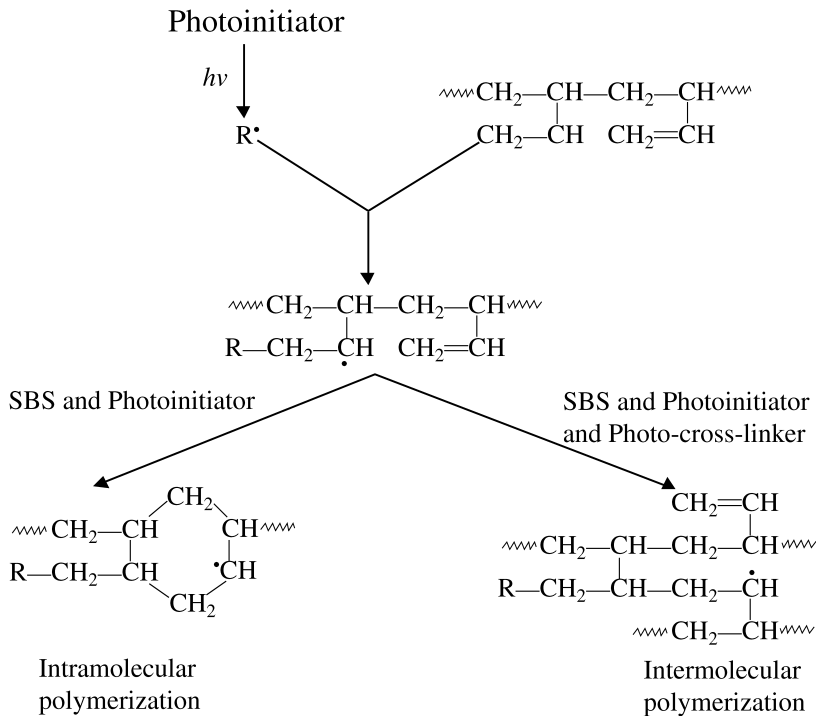


Figure 5. Schematic diagram of intermolecular and intramolecular polymerizations of SBS [3].

linked with both a photoinitiator and a photo-cross-linker, SBS showed a fast UV-curing rate and high cross-link density. The insoluble residue in Fig. 4c is a cured film which was necessary to achieve a three-dimensional network in the internal structure able to improve the PSA cohesion through intermolecular polymerization. To effectively form a three-dimensional network, SBS requires a large number of reaction sites of carbon double bonds. In the case of photoinitiator only, there is an insufficient number of reactive sites to form a three-dimensional network, so intramolecular polymerization is additionally used besides the vinyl double bond of polybutadiene [3]. It converts the cyclic structure into polybutadiene chains and leads to fragile residues comparable to UV-cured SBS residues with a photoinitiator and a photo-cross-linker. The intermolecular and intramolecular SBS polymerizations are shown in Fig. 5.

The gel content is an estimation of the chemical properties of the cured film, while the surface hardness is a method to estimate the degree of cross-linking and the surface physical properties of cured film. The surface hardness of SBS with photoinitiators is shown in Fig. 6. The pendulum hardness is measured in terms of pendulum oscillation time on the SBS film surface and represents the elastic properties of the SBS surface. The pendulum hardness is not a general measure of hardness but is proportional to the reciprocal of the damping capacity or mechanical loss [8]. The SBS samples were prepared using three kinds

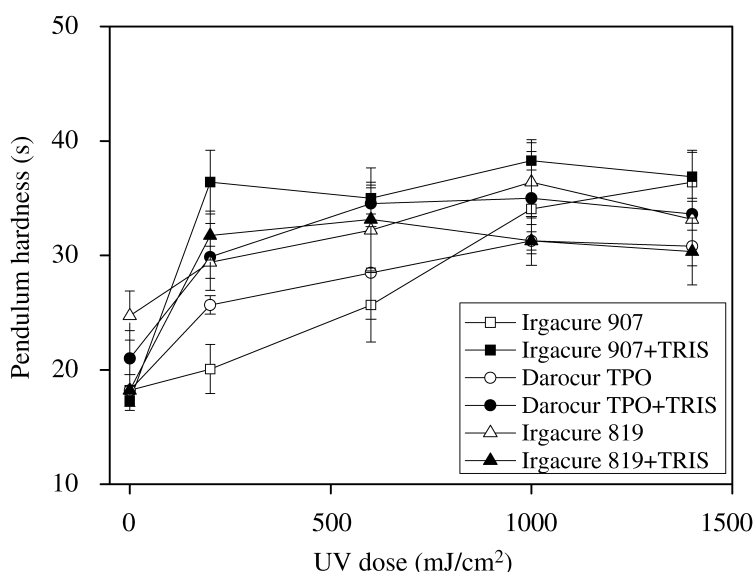


Figure 6. Pendulum hardness results for SBS films as a function of photoinitiator and photo-cross-linker.

of photoinitiator: Irgacure 907, Irgacure 819 and Darocur TPO. Irgacure 907 is composed of α -aminoalkylphenones and Irgacure 819 and Darocur TPO are acylphosphine oxides. The SBS film surface becomes harder as cross-linking proceeds by UV irradiation due to the chemical reaction between thiol functional group and vinyl side group in SBS. In the absence of a photo-cross-linkable, the surface hardness increased at a slow rate (Irgacure 907 < Darocur TPO < Irgacure 819), but with a photo-cross-linker it sharply increased at the initial stage for all samples. In particular, Irgacure 907 showed the highest cross-link density among the three photoinitiators. α -Aminoalkylphenone derivatives are the most recent type of α -cleavage photoinitiators that are commercially available, and they are good for raising curing performance, improving storage stability and maintaining thick layer curing [9]. A previous study investigating the influence of the radical photoinitiator showed that phosphine oxide initiator had better curing efficiency than benzoin derivatives and hydroxycyclophenylketone [3].

The addition of thiol material as a photo-cross-linker contributes to fast cross-linking in UV curing. Without a photo-cross-linker, the radiation-excited photoinitiator attacks directly the C=C double bonds, and increases the PSA cross-link density. With thiol functional compounds as the photo-cross-linker, the radiation-excited photoinitiator attacks not only the C=C double bonds but also the thiol functional group, and thereby generates thiyl free radicals [4]. The thiyl free radicals can initiate polymerization of the butadiene. The combination of photoinitiator and photo-cross-linker was found to increase the reaction rate, as well as enhance the cross-link density.

3.3. Adhesion properties of UV-cross-linkable HMPSAs

In the previous section, the thermal stability of the photoinitiator was studied by TGA and DSC. To evaluate the effect of the photoinitiator's thermal stability on adhesion properties, UV-cross-linkable HMPSAs were made with two types of photoinitiators: Irgacure 819 and Micure BK-6, where the former is thermally more stable than the latter. UV-cross-linkable HMPSAs were prepared from SIS, SBS, tackifier, two types of photoinitiators and photo-cross-linker.

Figure 7 shows the probe tack, peel strength and SAFT values as three measures of PSA performance for UV-cross-linkable HMPSAs with Irgacure 819 (Fig. 7a) and Micure BK-6 (Fig. 7b). Irgacure 819 has good thermal stability, but Micure BK-6 has poor thermal stability. Since UV radiation can change the viscoelastic properties of a PSA, the three measures of PSA performance showed different behaviors with the degree of curing.

In Fig. 7a, probe tack does not show a large change, and after an initial increase it decreases slightly. However, peel strength and SAFT are strongly affected by increasing UV dose. Peel strength is sharply decreased at the initial stage, and then maintains a low level of about 1000 g. In the peel process, peel strength is the sum of the energy required to break the bond and to deform the backing and PSA. UV radiation elevates the PSA modulus, so the PSA elongation ability is reduced after UV curing. Therefore, UV-cured HMPSAs show a low peel strength of around 500–1000 g. As the UV-cross-linkable acrylic PSA shows a low peel strength, so it is used as a dicing tape in semiconductor manufacture. In contrast, the UV-cross-linkable HMPSA in this study was a HMPSA with a tackifier. The small tackifier molecules give some mobility to PSA, which allows peel strength to be sustained after UV curing. In the SAFT results, UV-cured HMPSAs show high cohesive strength and high heat resistance, because the UV radiation produces chemical cross-links in the PSA. Generally, SIS- and SBS-based PSAs have a poor cohesive property at elevated temperatures. SIS and SBS are copolymers composed of styrenic and rubbery blocks. The entanglement of styrenic block is disentangled above the glass-transition temperature (T_g). However, UV-cross-linkable HMPSAs have chemically-induced cross-linking, which provides good heat resistance. In contrast to Fig. 7a, Fig. 7b does not show large changes in the three measures of PSA performance. In high-temperature processes like melt blending and hot coating, the photoinitiator can evaporate as a gas, or is so decomposed that it cannot generate free radicals in the UV-curing process. These results indicate that the thermal stability of the photoinitiator controls the efficiency of UV curing.

To estimate the influence of photoinitiator type, PSAs were produced with 3 types of photoinitiator: Irgacure 907, Irgacure 819 and Darocur TPO. In Fig. 6, the curing kinetics of SBS was studied as a function of photoinitiator type and thiol-based photo-cross-linker. The curing rate was dependent on the photoinitiator type.

Figure 8 shows the effect of photoinitiator type on the probe tack. UV radiation generates free radicals using the photoinitiator, and causes radical polymerization in PSA. By introducing chemical cross-linking, the PSA became rigid and the probe

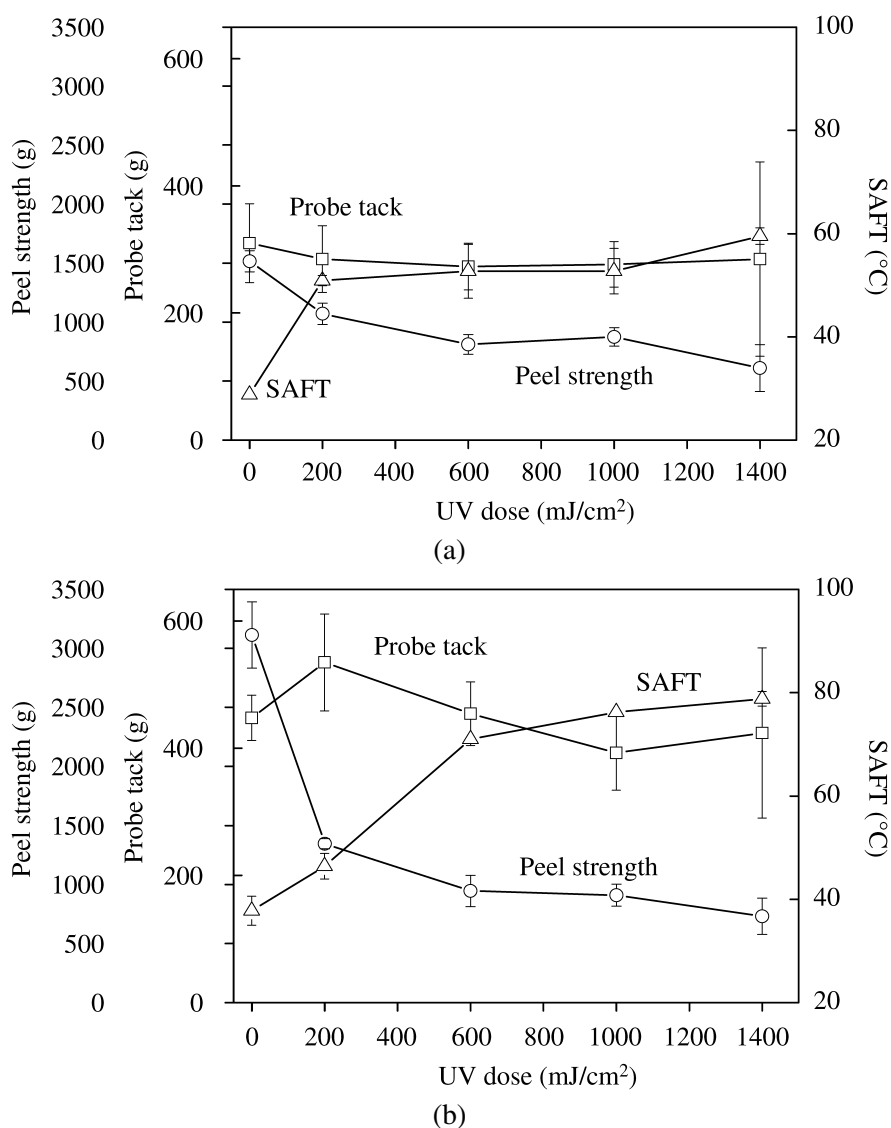


Figure 7. Probe tack, peel strength and SAFT of PSAs with (a) low thermal stability photoinitiator (Micure BK-6) and (b) high thermal stability photoinitiator (Irgacure 819).

tack decreased with increasing UV dose. The photoinitiator type barely affected the PSA probe tack in Fig. 8. Figure 9 shows the peel strength. The peel strength was sharply reduced in the initial curing process and a nearly constant peel strength was maintained up to UV dose of 1400 mJ/cm². Figure 10 presents the SAFT results which represent the cohesive property, as well as heat resistance of PSA. With no curing, PSA has a very low SAFT, about 40°C. With chemical cross-linking induced by UV radiation, SAFT shows a dramatic increase up to 80°C. This confirms that UV curing is an effective method to control the SAFT of a PSA.

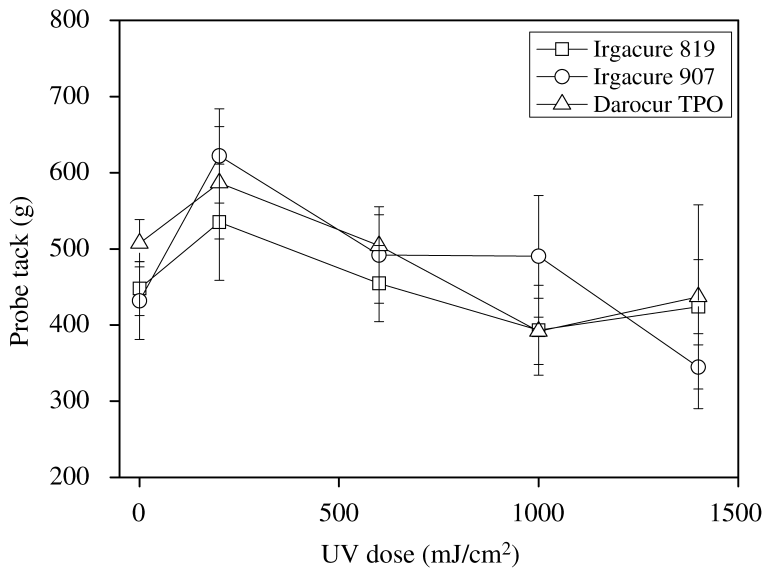


Figure 8. Probe tack of PSAs with the three photoinitiators.

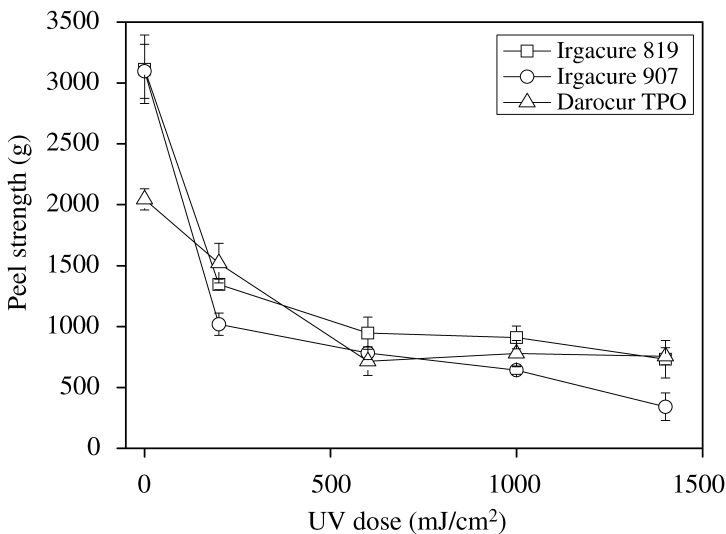


Figure 9. Peel strength of PSAs with the three photoinitiators.

4. CONCLUSIONS

An essential prerequisite for the manufacture of UV-cross-linkable HMPSAs is to ensure the thermal stability of the photoinitiator and photo-cross-linker. The thermal stability of the photoinitiator and photo-cross-linker was evaluated by TGA and DSC. Irgacure 907, Irgacure 819 and Darocur TPO demonstrated sufficient thermal stability in both hot-melt blending and coating. The SBS surface hardness, which

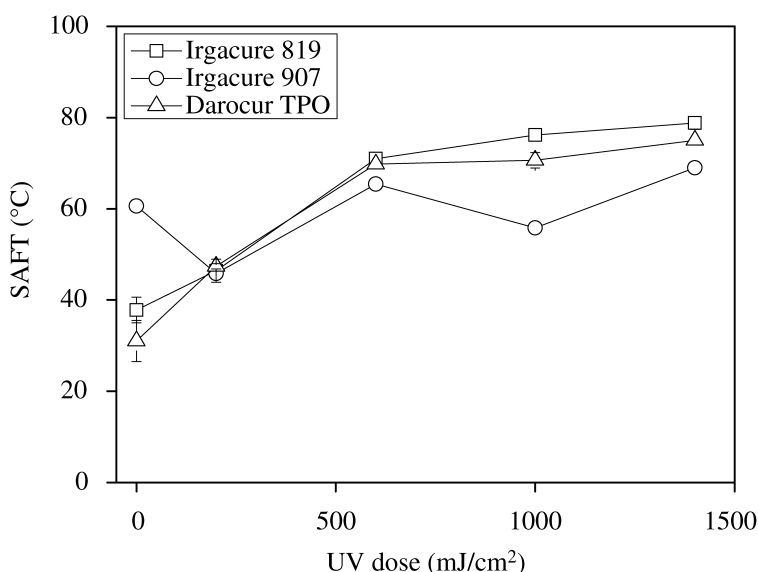


Figure 10. SAFT of PSAs with the three photoinitiators.

is an indication of the degree of cross-linking, increased at a slow rate (Irgacure 907 < Darocur TPO < Irgacure 819), but with photo-cross-linker addition the surface hardness sharply increased at the initial stage for all samples and sustained a similar hardness level. The thiol functional group increases the cross-link density in UV-cross-linkable HMPSA. To estimate the effect of photoinitiator thermal stability on PSA performance, PSA samples were prepared with two types of photoinitiators: low thermal stability and high thermal stability. For the former, the PSA performance showed no change, indicating that the thermal stability of the photoinitiator and photo-cross-linker is an essential prerequisite for effective UV curing. The three photoinitiator types showed similar PSA performance in this system.

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