UV-curing behavior and adhesion performance of polymeric photoinitiators blended with hydrogenated rosin epoxy methacrylate for UV-crosslinkable acrylic pressure sensitive adhesives

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ARTICLE INFO

ABSTRACT

UV-crosslinkable polyacrylates were synthesized for use as pressure sensitive adhesives (PSAs). These polyacrylates acted as polymeric photoinitiators due to the benzophenone incorporated into their backbones. Hydrogenated rosin epoxy methacrylate (HREM; based on hydrogenated rosin and glycidyl methacrylate) was also synthesized as a tackifier, and blended at different levels with the synthesized, UV-crosslinkable polyacrylates for use as PSAs. The effect of the new tackifier, HREM, on the properties of the UV-crosslinkable PSAs was examined in comparison with the properties exhibited by PSA/hydrogenated rosin blends. The characteristics of these PSA/tackifier blends were examined by Fourier-transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) and an advanced rheometric expansion system (ARES). In addition, the adhesion performance of the PSA blends was investigated using probe tack tests. DSC and ARES revealed all the PSA blends with HREM or hydrogenated rosin to be miscible at the molecular level. The glass transition temperature (T_g) of HREM was $-25.6\ ^\circ\text{C}$, which is lower than that of other commercially available rosin tackifiers. FTIR revealed changes in the relative concentration of benzophenone groups in the PSAs at 1580 cm^{-1}, which demonstrated that the crosslinking efficiency is proportional to the benzophenone content and UV dose, but decreases with increasing hydrogenated rosin content. However, the reduced crosslinking reaction efficiency was improved in the PSA/HREM blends due to the low T_g of HREM which only slightly increased the T_g of the PSA blends. Moreover, the relative initial decrease in the probe tack of the PSA/HREM blends was lower than that of the PSA/hydrogenated rosin blends after UV irradiation.

1. Introduction

UV-curing of multifunctional monomers produces highly crosslinked networks with high thermal stability, mechanical strength, and resistance to solvent absorption. The polymeric networks produced have many industrial applications, particularly as coatings for flooring and furniture, dental restorative materials, optical fiber coatings, hard and soft contact lenses, and photolithography [1–3]. Multifunctional acrylates and methacrylates are the monomers used most widely for photo-polymerization [4–10]. The photo-polymerization of various acrylates has been studied using differential scanning calorimetry (DSC), dilatometry, dynamic mechanical testing, and real-time infrared spectroscopy [4,8,11,12].

Acrylic ester monomers are widely used to synthesize pressure sensitive adhesives (PSAs) through solution or emulsion polymerization. These synthesized acrylic PSAs have excellent properties. Their saturated nature makes

them transparent, colorless, and resistant to yellowing from sunlight or oxidation [13]. However, as these synthesized acrylic PSAs consist of linear molecules that are held together by physical crosslinking, van der Waals forces, or by hydrogen bonding, they have limited mechanical and thermal properties. A variety of UV-curing techniques have been used to crosslink these acrylic PSAs in an attempt to improve their dimensional stability [13–15].

In general, acrylic PSAs had not previously been formulated with tackifier resins because their adhesion properties can be adjusted by varying their monomer composition. However, recent studies have described the blending of acrylic PSAs and tackifier resins for efficient modification of their adhesion properties [16–18]. Tackifiers improve the tack property of the base polymers by altering both their surface and viscoelastic properties [19]. However, because most tackifiers do not have a UV reactive site, they act as non-crosslinkable species during UV-curing, and retard the UV-curing rate of PSAs. In addition, the miscibility between acrylic PSAs and the tackifier needs to be considered. Moreover, there is a limitation in the blending ratio because most tackifiers have a high glass transition temperature (T_g) [16,20–22].

In this study, a mono-functional hydrogenated rosin epoxy methacrylate (HREM) was synthesized from a hydrogenated rosin and glycidyl methacrylate (GMA), as a new tackifier, in an attempt to overcome the common problems of tackifiers in a UV-crosslinking PSA system. This HREM was then blended at different levels with the synthesized UV-crosslinkable acrylic PSAs. The UV-curing behavior and characteristics of these PSA blends were examined by comparing the Fourier-transform infrared (FTIR) spectroscopy, DSC, and advanced rheometric expansion system (ARES) data with those of the acrylic PSA/hydrogenated rosin blends. In addition, the adhesion performance of the PSA blends was evaluated through probe tack measurements.

2. Experimental

2.1. Materials

The 2-ethylhexyl acrylate (2-EHA), butyl acrylate (BA), vinyl acetate (VAc), and acrylic acid (AA) used to synthesize the acrylic PSAs were purchased from Junsei Chemicals Co., Ltd. (Japan). The 2-(acryloyoxy)ethyl 4-(4-chlorobenzoyl) benzoate (P-36) used as the polymerizable photoinitiator was obtained from SK Cytec Co., Ltd. (South Korea). Ethyl acetate (analytical grade, Junsei Chemicals Co., Ltd., Japan) and 2,2′-azobisisobutyronitrile (AIBN, Daejung Chemicals & Metals Co., South Korea) were used as the solvent and initiator for synthesizing the acrylic PSAs, respectively.

Hydrogenated rosin (Foral AX-E, Eastman Chemical Co., Ltd., Netherlands) and GMA (Junsei Chemical Co., Ltd., Japan) were used to synthesize the HREM in methyl ethyl ketone (MEK, Samchun Pure Chemical Co., Ltd., Korea). Hydroquinone (HQ, Sigma–Aldrich) and tetramethylammonium bromide (TMAB, Sigma–Aldrich) were used the inhibitor and catalyst, respectively.

2.2. Synthesis of UV-crosslinkable polymeric photoinitiators and HREM

The UV-crosslinkable polymeric photoinitiators were synthesized using 2-EHA, BA, VAc, AA, and P-36 through solution polymerization initiated by 1.5 wt% AIBN in ethyl acetate at 40 wt% solids. The polymerization was performed in a 500-ml, four-necked, round-bottomed flask equipped with a thermometer, condenser, dropping funnel, and mechanical stirrer. The typical synthetic method was as follows. The flask was charged with 50% of a monomer and solvent mixture, and then polymerization was started at 80 °C in a heating mantle for 2 h. After polymerization, the remaining 50% of the monomer and solvent mixture was added over 1 h, and the flask was kept at 80 °C for 3 h [23]. Table 1 shows the composition of polymeric photoinitiators used without purification in the synthesized, UV-crosslinkable, acrylic PSAs.

HREM was synthesized from hydrogenated rosin and GMA in MEK. An equimolar mixture of hydrogenated rosin and GMA with 1 wt% TMAB and 0.2 wt% HQ dissolved in MEK as 50% solid was charged into a 500 ml, three-necked, round-bottomed flask. The synthesis was carried out at 80 °C for 24 h. The solution was evaporated to remove the MEK. The residue was washed with a 5% sodium hydroxide solution to remove the HQ and dried in a vacuum oven at 40 °C for 72 h. The final product was used as HREM. Fig. 1 shows the procedure for the formation of HREM [24].

Each hydrogenated rosin and HREM as a tackifier was blended with the synthesized polymeric photoinitiators at levels ranging from 0 to 30 wt% (on a non-volume basis).

Table 1
PSA characteristics

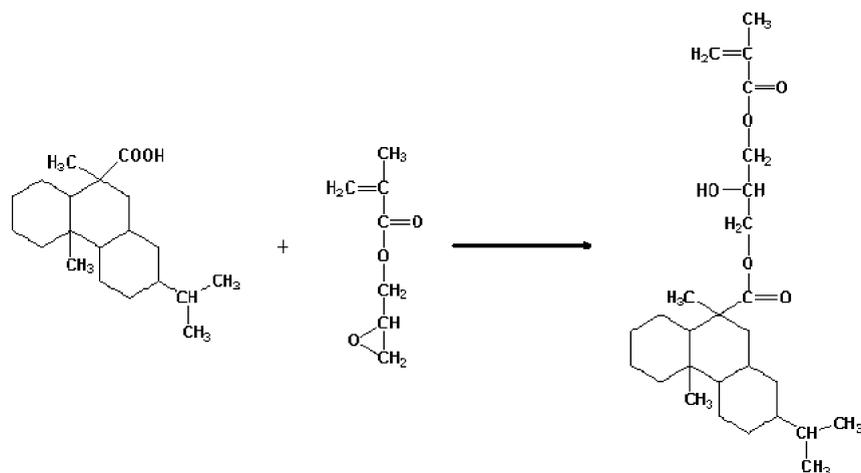| Sample	Solvent	PSA composition (wt%)					M_w ($\times 10^5$)	PDI	T_g
		2-EHA	BA	VAc	AA	P-36			
P01	Ethyl acetate	65	20	10	5	0.1	6.6	3.1	−48.7
P03	Ethyl acetate	65	20	10	5	0.3	6.4	2.5	−50.6
P06	Ethyl acetate	65	20	10	5	0.6	6.3	2.4	−47.9
P09	Ethyl acetate	65	20	10	5	0.9	6.5	2.8	−53.1
P12	Ethyl acetate	65	20	10	5	1.2	6.1	2.1	−51.2
P010[a]	Methanol	65	20	10	5	0.1	–	–	–

[a] Gel formed during polymerization.

Fig. 1. Synthesis of the hydrogenated rosin epoxy methacrylate (HREM).

2.3. Preparation of PSA samples and UV-curing

The PSA samples were prepared by coating the PSA blends onto the corona-treated, polyethylene terephthalate (SKC Co., Ltd., South Korea) at 20 μm using a bar coater (No. 22), followed by drying in an oven at 70 °C for 10 min. These dried PSA samples were maintained at 22 ± 2 °C and 60 ± 5% RH for 24 h before testing, and were cured using a conveyer belt-type, UV-curing machine equipped with a high-pressure mercury lamp (100 W/cm, main wavelength: 340 nm). A cold mirror was used as a reflector to avoid the heating effect of the mercury lamp. The UV doses applied were 0, 200, 600, 1000, 1400, 1800, and 2200 mJ/cm^2, as determined using an IL 390C Light Bug UV radiometer (International Light Inc., USA).

2.4. Measurements

The T_g was measured using a DSC unit (TA, Q-1000). The samples were first cooled to −85 °C and then heated to 60 °C at 10 °C/min for the first scan. They were then quenched immediately to −85 °C and maintained at this temperature for 3 min. The samples were reheated to 200 °C at 10 °C/min during the second scan. The T_g values were obtained using the second scans to ensure thermogram reproducibility and freedom from thermal history effects.

The viscoelastic properties (G', $\tan\delta$) of the PSA blends were determined using an ARES unit (Advanced Rheometrics Expansion System, Rheometric Scientific Inc.) in 8 mm parallel plate mode. A typical scan covered the range from −80 to 200 °C at 5 °C/min with a frequency of 6.3 rad/s.

The infrared reflectance spectra were measured using an FTIR spectrometer (JASCO FTIR-6300) with a Mylar beam splitter. The spectra were collected for 32 scans to reduce the noise at a resolution of 8 cm^{-1} between 650 and 4000 cm^{-1}. During UV-curing of the PSA blends, the benzophenone groups were copolymerized, which involved a loss of conjugation between their carbonyl groups and the aromatic rings, and a reduction of the absorption at *ca.*

1580 cm^{-1} [25,26]. Therefore, the conversion was analyzed by observing the characteristic absorption band at approximately 1580 cm^{-1} and the relative benzophenone concentration was estimated [8,25]. The C=O stretching vibration at about 1732 cm^{-1} of acrylic monomer was adopted as an internal standard band for calculation in order to compensate an effect of difference in thickness existing in PSA samples. The relative benzophenone concentration as a function of the UV dose and photoinitiator concentration of the PSA samples was calculated using the following equation:

Relative concentration of UV-cured group (%)

$$= \frac{[A]_{P_{UV}}/[A]_{C_{UV}}}{[A]_{P_0}/[A]_{C_0}} \times 100$$

where $[A]_{P_{UV}}$ is the peak area of the absorbance at approximately 1580 cm^{-1} in the normalized spectrum of the UV-cured sample, $[A]_{C_{UV}}$ is the peak area intensity of the C=O group in the normalized spectrum of the UV-cured sample, $[A]_{P_0}$ is the peak area of absorbance at approximately 1580 cm^{-1} in the normalized spectrum of the sample before UV-curing, and $[A]_{C_0}$ is the peak area intensity of the C=O group in the normalized spectrum of the sample before UV-curing.

The cured PSA samples were weighed and immersed in toluene for 4 days at 50 °C, and then screened and dried at 80 °C to a constant weight. The gel fraction of the samples was calculated using the following equation:

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

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

The tack measurements of the PSA samples on glass plates were carried out with a TA-XTi Texture Analyzer (Texture Technologies Co., UK) at 20 °C using a probe tack consisting of a polished stainless steel (type 304), 5 mm-diameter, cylinder probe. The measurements were conducted at a debonding speed of 0.5 mm/s under a constant pressure of 100 g/cm^2 and a swell time of 1 s.

3. Results and discussion

3.1. Miscibility of PSA blends by DSC and T_g measurements

The phase structure of each blend was assessed by the number of T_g transitions observed in the thermograms; two transitions are a clear indication of phase separation. Miscibility was indicated by a single glass transition located at a temperature intermediate between those of the pure components [27]. Tackifying a PSA is limited by its miscibility, which highlights the need for miscibility measurements [21]. Fig. 2(a) shows the T_g of hydrogenated rosin and a P01/30 wt% hydrogenated rosin blend. The T_g of the hydrogenated rosin was approximately 132.1 °C. However, the T_g curve disappeared after blending with PSA. In addition, all PSAs blended with hydrogenated rosin were transparent. Each of the blends with varying hydrogenated rosin contents showed a single T_g curve, as shown in Fig. 2(b). The T_g of P01 was approximately −47.8 °C, which increased gradually with increasing hydrogenated rosin content to −41.3, −37.1, and −33.2 °C at 10 and 20–30 wt% hydrogenated rosin, respectively. The existence of a single composition-dependent T_g is evidence that PSA is miscible with hydrogenated rosin at the molecular level.
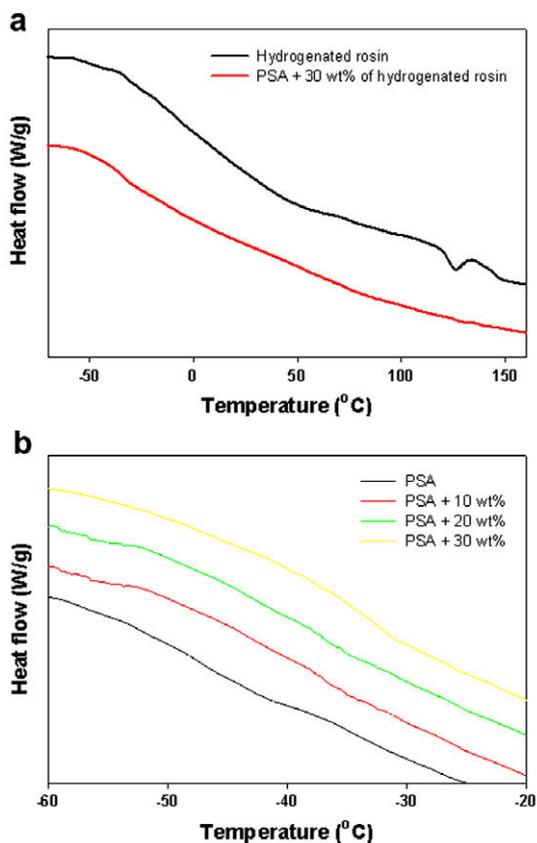
Fig. 3(a) shows the DSC result for HREM. The T_g of HREM was approximately −25.6 °C, and an exothermic reaction was observed at 146.4 °C. HREM was cured thermally at this temperature because it has an acrylate group, even though it does not have a thermal initiator.

Fig. 3(b) shows that the T_g curve of HREM had disappeared after blending with P01, and the blends showed a single T_g below the T_g of HREM. Furthermore, all PSA/HREM blends were transparent. The T_g of P01, −47.8 °C, increased slightly with increasing the HREM content to −46.1, −43.1, and −42.2 °C at 10, 20, and 30 wt% HREM, respectively. The existence of a single T_g indicates that HREM is also miscible with PSA at the molecular level. Its rate of width increase was very small compared with that of the PSA/hydrogenated rosin blends, which was attributed to the low T_g of HREM. As the T_g of hydrogenated rosin decreased drastically from 132.1 to −25.6 °C after reacting with GMA, the T_g increase of the PSA/HREM blends with increasing HREM content in PSA was small.

3.2. Viscoelastic properties of PSA blends

The viscoelastic properties of the PSA blends were determined using ARES measurements. A compatible blend will show a single broad transition, which is the weight average of the individual transitions [27]. The influence
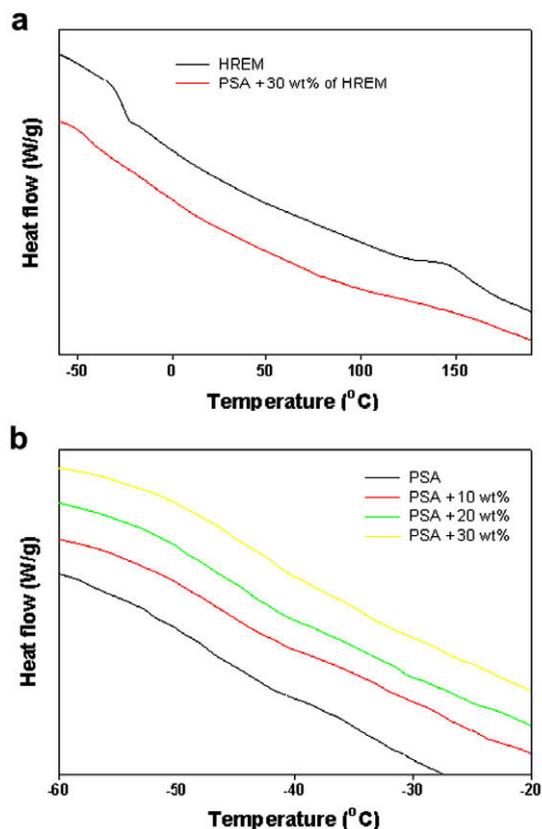

Fig. 2. DSC thermograms of (a) hydrogenated rosin and PSA(P01)/30 wt% hydrogenated rosin blend, and (b) PSA(P01)/hydrogenated rosin blends with increasing hydrogenated rosin content.

Fig. 3. DSC thermograms of (a) HREM and PSA(P01)/30 wt% HREM blend, and of (b) PSA(P01)/HREM blends with increasing HREM content.

of a tackifier on the modulus is another index of compatibility. A decrease in the elasticity of a polymer matrix can be achieved by mixing with viscous compounds. Generally, tackification decreases G' and increases $\tan\delta$ [13,28].

Fig. 4(a) shows the changes in G' of the P01 blends at different hydrogenated rosin contents. G' decreased continuously with increasing content of hydrogenated rosin blended into the PSA. A lower G' favors bonding by increasing the efficiency of contact between PSA and the substrate [29]. The tack is related to the tackifier concentration because the tackifier alters the viscoelastic properties of the PSAs [30]. PSA should deform easily in the short time required to make intimate contact with substrates with a high tack value [31]. Therefore, viscous flow is essential for the quick deformability of PSAs. A probe tack test also includes the process of detaching PSA from the surface. The measured tack results indicate the resistance to detachment. Therefore, a higher G' value is also desired. However, G' cannot increase indefinitely while maintaining good tack because good wetting of the surface would be prevented if G' is too high [13].

Fig. 4(b) shows the changes in the T_g of the blends (temperature at peak $\tan\delta$) in the ARES test, as the hydrogenated rosin was mixed with an acrylic PSA. The T_g of all blends increased with increasing hydrogenated

rosin content, which is in accordance with the DSC results. In addition, only one glass transition range was detected for all PSA blends, indicating that the synthesized acrylic PSAs were miscible with the hydrogenated rosin. As mentioned previously, formulating a PSA with a tackifier usually decreases the modulus and increases the T_g, but a high tackifier loading increases the modulus. A lower modulus always promotes bond formation, while an increased T_g causes bond rupture [19,32].

Fig. 5(a) shows that the G' of the P01/HREM blends decreased with increasing HREM content. Compared with Fig. 4, the hydrogenated rosin with high T_g and the HREM with low T_g, both tackifiers lowered G' but the low T_g HREM showed a more significant decrease in G'. Fig. 5(b) shows the changes in T_g (temperature at peak $\tan\delta$) as HREM was blended into the acrylic PSA, P01. While the T_g of the PSA/hydrogenated rosin blends increased with increasing hydrogenated rosin content, the PSA/HREM blends showed a similar T_g: -20.4, -19.6, and $-19.7\,^\circ C$ for PSA blends containing 0, 10, and 30 wt% of HREM, respectively. These results were in accordance with the DSC results shown in Fig. 3, i.e. the T_g values increased slightly with increasing HREM content. In addition, only one glass transition point was detected for all PSA blends, indicating that the synthesized acrylic PSAs are miscible with HREM.
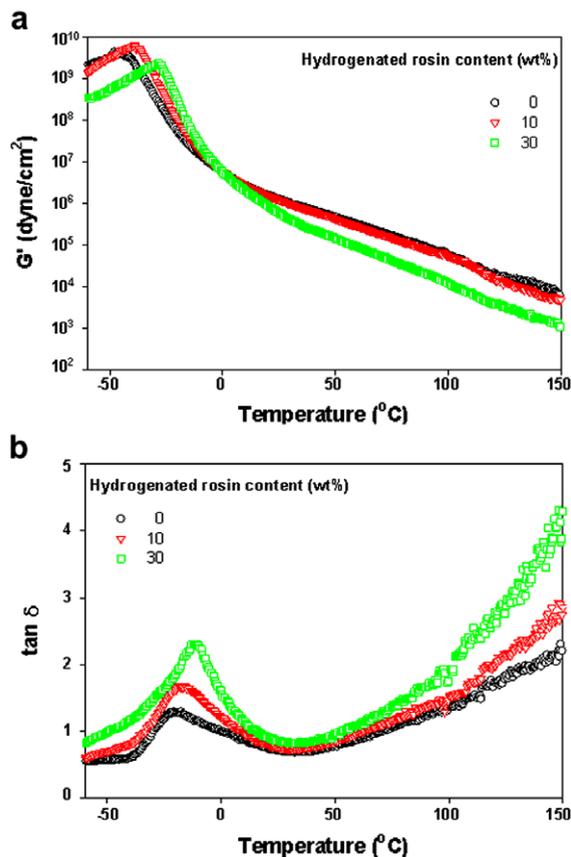

Fig. 4. Viscoelastic curves of the P01/hydrogenated rosin blends as a function of the hydrogenated rosin content: (a) G' and (b) $\tan\delta$.
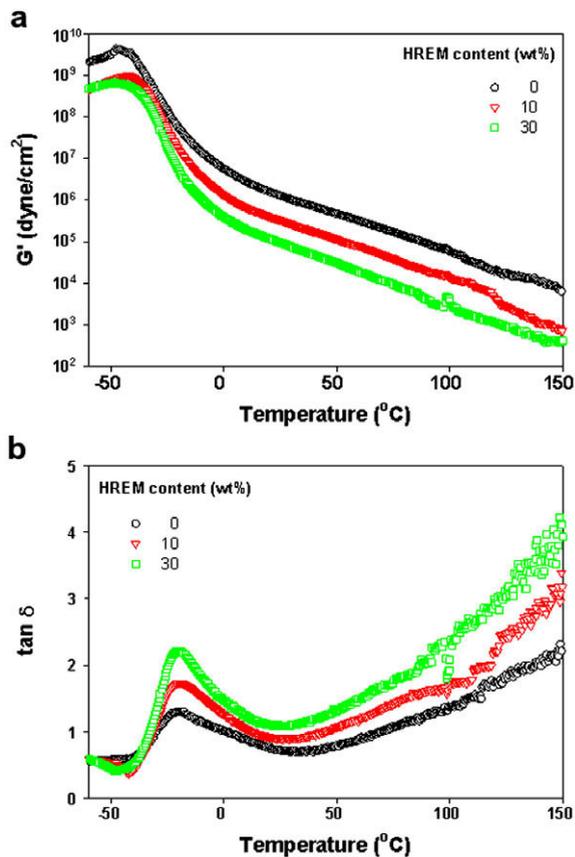

Fig. 5. Viscoelastic curves of the P01/HREM blends as a function of HREM content: (a) G' and (b) $\tan\delta$.

3.3. UV-curing behavior

3.3.1. FTIR spectroscopy

The synthesized PSAs with benzophenone as the pendant groups in the polymer backbone were polymeric photoinitiator compounds. After UV irradiation, the PSAs were crosslinked without the need for further addition of photoinitiators, functional monomers and oligomers [14]. During UV-curing of the PSA blends, the copolymerized benzophenone groups were converted. The resonance in the benzene ring showed strong stretching vibrations at approximately 1500 cm^{-1}. However, a band at approximately 1580 cm^{-1} could be observed when these groups were conjugated to the C=O, such as benzophenone [33]. When exposed to UV, the C=O in the benzophenone was excited to a triplet state through a singlet state, which then abstracted hydrogen from a suitable hydrogen donating group. Therefore, the characteristic absorption bands at approximately 1580 cm^{-1} decreased in intensity due to the loss of conjugation between the C=O and resonance in the aromatic ring due to the conversion of the C=O group [14,26,34]. Fig. 6 shows the changes in the relative concentration of benzophenone groups in the PSA/hydrogenated rosin blends at approximately 1580 cm^{-1} with

increasing UV dose and hydrogenated rosin content. Before blending with the hydrogenated rosin, the benzophenone concentration decreased gradually with increasing UV dose (Fig. 6(a)). However, in the case of the P01/20 and 30 wt% hydrogenated rosin blends, the benzophenone concentration remained relatively unchanged with increasing UV dose, which was similar to that of the P03 blends. In contrast, the benzophenone concentration of P03 without hydrogenated rosin showed a sharp decrease from 100% to approximately 35%. In the case of the P06, P09, and P12 blends with 20 and 30 wt% hydrogenated rosin, the benzophenone concentration began to decrease with increasing UV dose. At a UV dose of 2200 mJ/cm^2, the benzophenone concentration in the P06 blends containing 0–30 wt% of hydrogenated rosin decreased considerably compared to the ones at a UV dose of 200 mJ/cm^2. In the PSA blends containing the higher hydrogenated rosin content, the benzophenone concentration still remained at a high value despite the high UV dose. Although the benzophenone concentration of these P09 and P12 blends had decreased to 20%, 22%, 40%, and 60%, and to 15%, 18%, 25%, and 35% at a UV dose of 2200 mJ/cm^2, respectively, the concentration of benzophenone remained high in the PSA blends containing the higher hydrogenated rosin content.

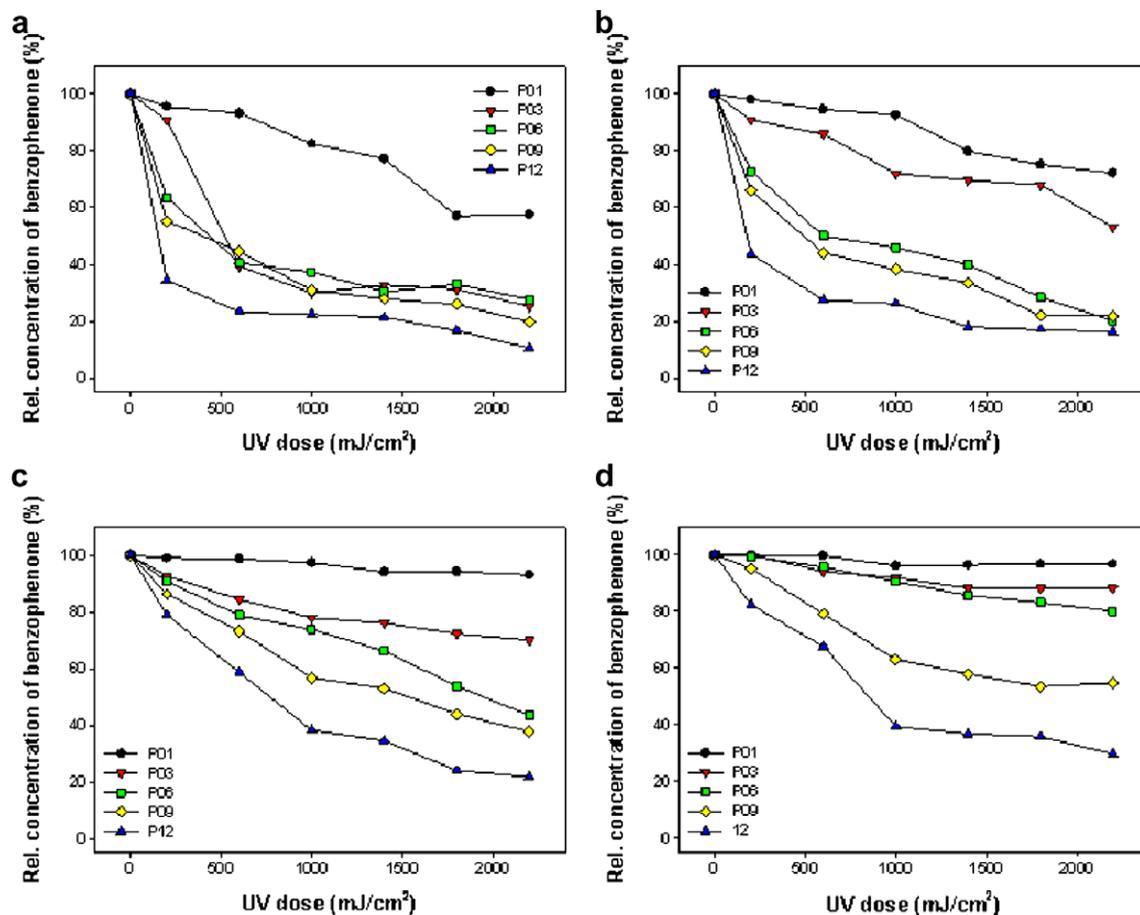**Fig. 6.** Changes in the relative concentration of benzophenone groups in the PSAs at 1580 cm^{-1} with different UV doses, benzophenone content, and hydrogenated rosin content: (a) 0, (b) 10, (c) 20, and (d) 30 wt% hydrogenated rosin in PSA.

These results were attributed to the ability of the tackifiers to act as UV-curing retardants. The mixed hydrogenated rosin expanded the distance of the PSA polymers but reduced the PSA polymer mobility by increasing T_g.

Fig. 7(b) shows the changes in the relative concentrations of benzophenone in the PSA/10 wt% HREM blends with increasing UV dose. At a UV dose of 200 mJ/cm^2, the rate of benzophenone loss in these PSA blends increased rapidly with increasing benzophenone content, and it increased gradually at a UV dose > 600 mJ/cm^2 except for the P01 blends. At a UV dose of 2200 mJ/cm^2, the relative benzophenone concentration in the P01, P03, P06, P09, and P12 blends with 10 wt% HREM was 87.9%, 43.1%, 17.2%, 13.8%, and 9.2%, respectively. These values were lower than those of the PSA/10 wt% hydrogenated rosin blends with the exception of the P01 blends, which were 72.1%, 53.1%, 20.2%, 21.8%, and 16.2%, respectively, at this UV dose. This result indicated that the mobility of the PSA polymer increased when the T_g of the blended HREM was sufficiently lower (−25.6 °C) than that of the hydrogenated rosin. Hydrogenated rosin increased the stiffness of the PSA polymers because its high T_g (132.1 °C) increased the T_g of the PSA blends. This reduced UV-crosslinking rate increased the concentration of the remaining benzophe-

none. The T_g is related to the PSA chain flexibility in that chain flexibility decreases with increasing T_g of the PSA blends. In general, the conversion at the maximum rate of polymerization increases as the chain flexibility increases, i.e. T_g decreases. The reason for the increased conversion at the maximum rate is the delayed gel effect [10]. As the mobility of the system was enhanced in the PSA blends containing HREM compared to those containing the hydrogenated rosin, the gel effect was delayed and the level of crosslinking was maximized. Fig. 7(c) shows the changes in the relative benzophenone concentration in PSA/20 wt% HREM blend with increasing UV dose. As shown in Fig. 7(b), the rate of benzophenone loss in the PSA blends increased rapidly with increasing benzophenone content at a UV dose of 200 mJ/cm^2. Even though this loss rate in the PSA/20 wt% HREM blend decreased somewhat compared with that of the PSA/10 wt% HREM blend, the relative concentration of benzophenone in PSA/20 wt% HREM was lower than the values of the PSA/20 wt% hydrogenated rosin blends. These variations were caused by the lower T_g of HREM compared to that of the hydrogenated rosin. For the same reason, these blends showed a lower benzophenone concentration at a UV dose of 2200 mJ/cm^2 than that of the PSA/20 wt% hydrogenated
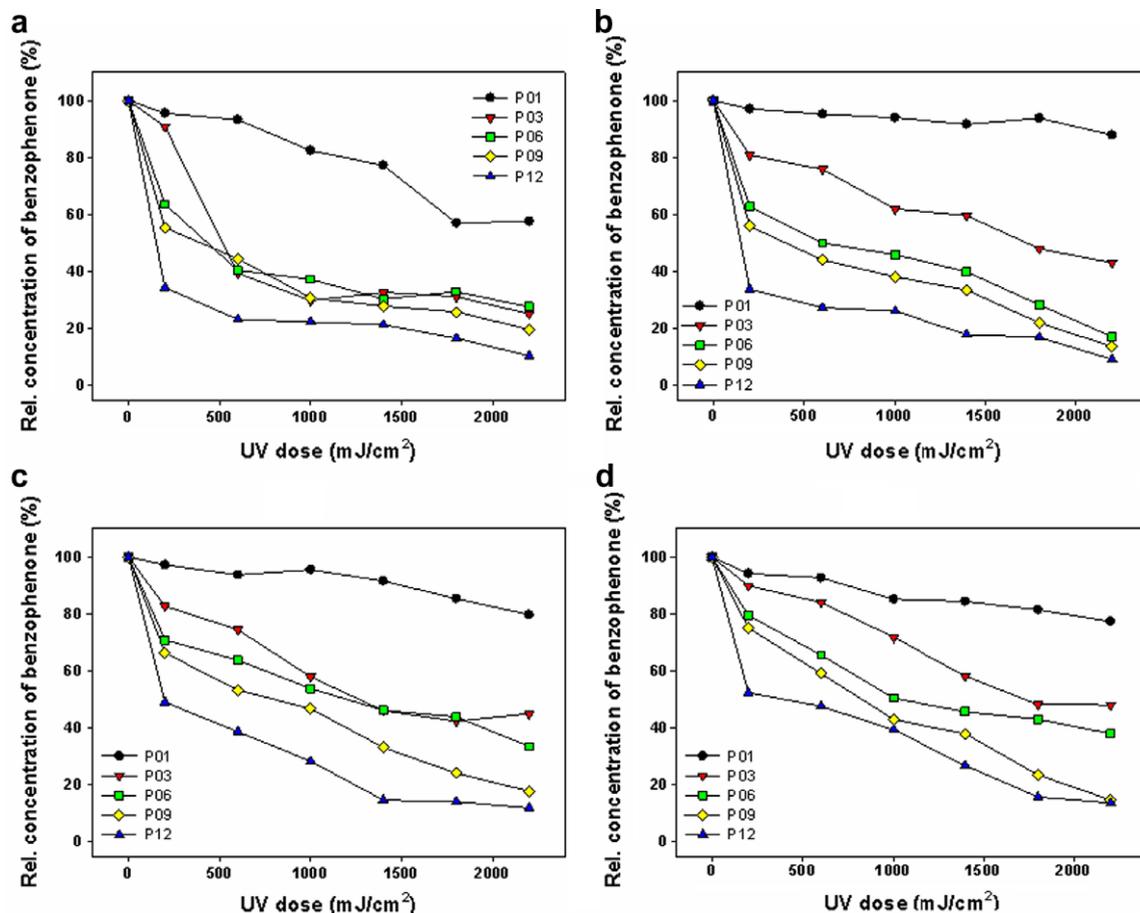

Fig. 7. Changes in the relative concentrations of benzophenone groups in the PSAs at 1580 cm^{-1} at different UV doses, benzophenone contents, and HREM content: (a) 0, (b) 10, (c) 20, and (d) 30 wt% HREM in PSA.

rosin blends. Fig. 7(d) shows the changes in the relative benzophenone concentration in PSA/30 wt% HREM blends with increasing UV doses. These blends showed a similar tendency to the previous results in that the relative concentration of benzophenone remaining decreased with increasing benzophenone content at a UV dose of 200 mJ/cm^2. Moreover, these values were lower than those of the PSA/30 wt% hydrogenated rosin blends, as shown in Fig. 6.

3.3.2. Gel fraction

Fig. 8 shows that the gel fraction of P01 without the hydrogenated rosin gradually increased with increasing UV dose up to approximately 40% of the gel fraction at a UV dose of 2200 mJ/cm^2. However, the gel fraction in the P01 blends containing the hydrogenated rosin was relatively constant regardless of the UV dose. These results changed with increasing benzophenone content in the PSA blends i.e. the gel fraction in the PSA/hydrogenated rosin blends increased with increasing UV dose. The gel fraction in the P03/hydrogenated rosin blends gradually increased with increasing UV dose, but was relatively low in the P03 blends containing a higher hydrogenated rosin content. These results indicated that the hydrogenated rosin acted as a UV-curing retardant. Furthermore, these results corresponded to the FTIR results in that the rate of the decrease in the relative benzophenone concentration

decreased with increasing hydrogenated rosin content in the PSA blends.

Fig. 9(b) shows the changes in the gel fraction in the PSA/10 wt% HREM blend with increasing UV doses at various benzophenone contents. The gel fractions in all PSA/HREM blends increased gradually with increasing UV dose but the trend differed to that with the hydrogenated rosin blends. At a UV dose of 200 mJ/cm^2, the gel fraction in the P01, P03, P06, P09, and P12 blends with 10 wt% HREM was 2.5%, 22.5%, 58.6%, 75.5%, and 84.4%, respectively, while that of the PSA/hydrogenated rosin blends was 3.1%, 9.8%, 26.9%, 39.3%, and 40.8%, respectively. As the T_g of HREM is very low, none of the PSA blends exhibited significant increase in T_g after being blended with HREM, which indicated that the blended HREM did not stiffen the PSA polymer. Adding a tackifier can alter the intermolecular forces and packing density between polymers and decrease the PSA modulus, which usually improves its adhesion properties. However, because the T_g of the tackifiers generally used in the PSA formulation is higher than 60 °C, they gradually reduce the PSA polymer mobility as their content in PSA increases [19]. These phenomena were also observed in these PSA blends because the T_g of hydrogenated rosin was 132.1 °C. Blending stiffens the PSA polymer, and reduces the UV-crosslinking rate of the PSA blends. Therefore, the gel fraction decreased after the hydrogenated
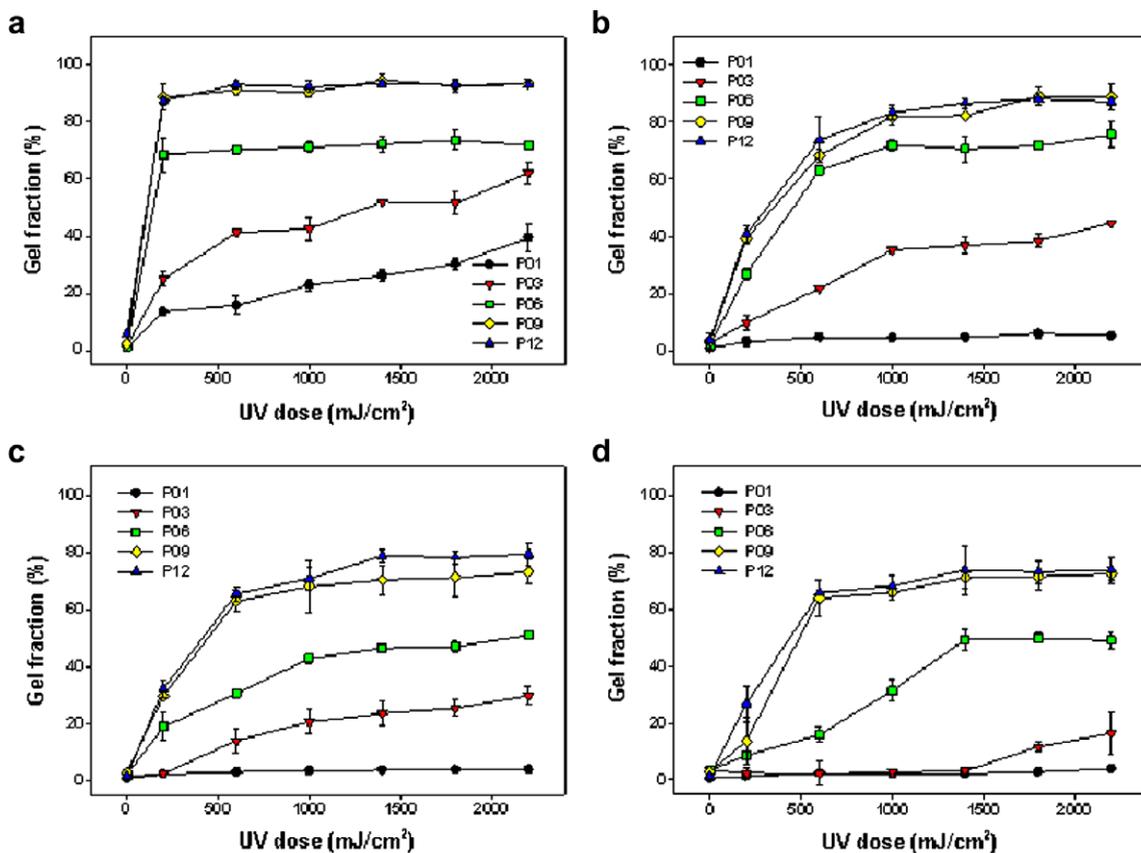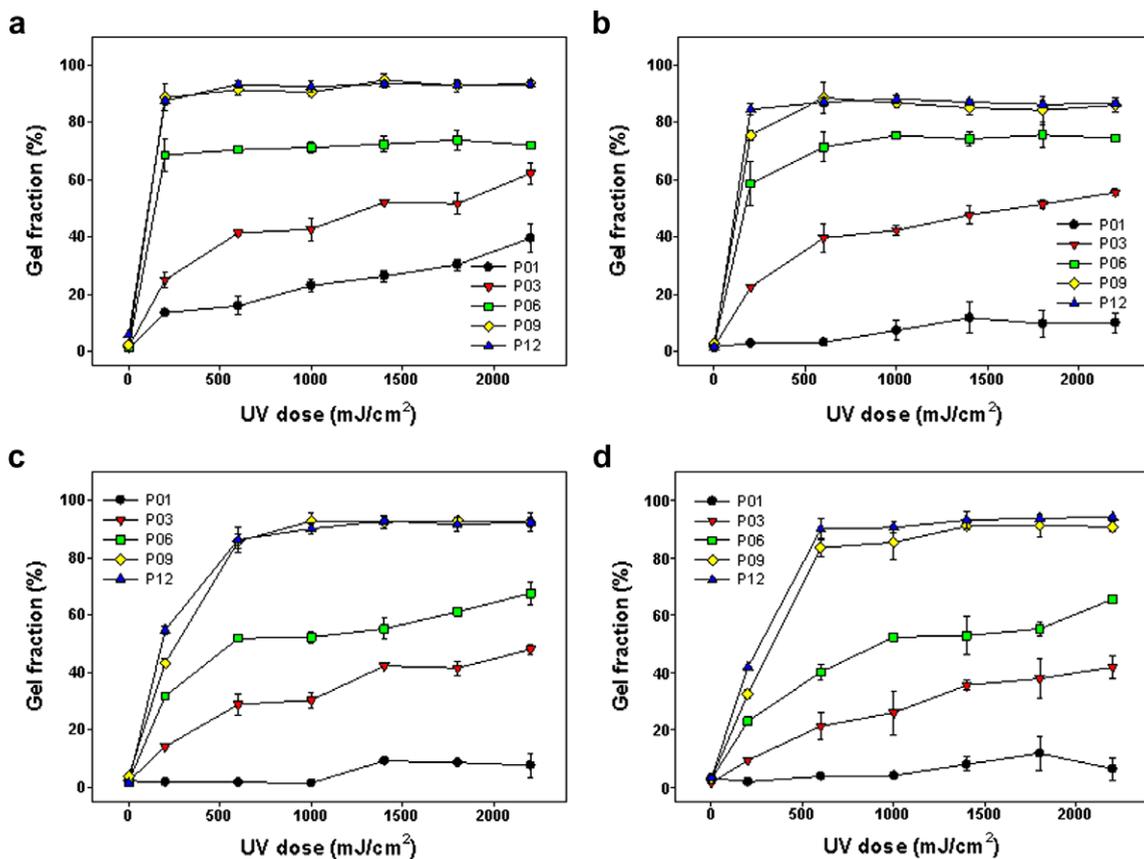

Fig. 8. Changes in the gel fraction of the PSA blends at different UV doses and benzophenone and hydrogenated rosin content: (a) 0, (b) 10, (c) 20, and (d) 30 wt% hydrogenated rosin/PSA blends.

Fig. 9. Changes in the gel fractions of the PSA blends at different UV doses and benzophenone and HREM content: (a) 0, (b) 10, (c) 20, and (d) 30% HREM/PSA blends.

rosin had been blended at each UV dose compared with PSA alone. However, as the T_g of HREM was −25.6 °C, the PSA/HREM blends were less stiff. Hence, the gel fraction reached higher values after UV irradiation. The gel fraction of the PSA/10 wt% HREM blend reached more than 75% after a UV dose of 600 mJ/cm^2, with the exception of the P01 and P03 blends. In particular, the P09 and P12 blends with HREM contained gel fractions > 85%. Fig. 9(c) shows the changes in the gel fraction of the PSA/20 wt% HREM blends with various benzophenone contents and with increasing UV dose. All PSA/20 wt% HREM blends also showed gradually increased gel fractions with increasing UV dose. The P09 and P12 blends with 20 wt% HREM showed gel fractions > 90% at a UV dose of 2200 mJ/cm^2. In the case of the PSA/30 wt% HREM blends, as shown in Fig. 9(d), the gel fractions of the P09 and P12 blends also reached > 90% at a UV dose of 2200 mJ/cm^2. At a UV dose of 2200 mJ/cm^2, the gel fraction of the P12 blends containing 10, 20, and 30 wt% HREM was 90.4%, 92.4%, and 94.2%, respectively, i.e. the gel fractions increased with increasing HREM content. These phenomena were explained by the fact that the viscosity of the P12/HREM blend decreased with increasing HREM content due to the reduced modulus. Therefore, the reduced viscosity of the PSA/HREM blends increased the molecular mobility and UV-reactivity, and thereby increased the gel fraction of the blends.

3.4. Adhesion performance

The probe tack increased with increasing hydrogenated rosin content before UV irradiation. Although P01 with no hydrogenated rosin showed slightly decreased probe tack with increasing UV dose, the probe tack of the P01 blends with hydrogenated rosin remained constant regardless of the UV dose (Fig. 10). As shown in Fig. 4, the modulus decreased with increasing hydrogenated rosin content, which decreased the viscosity of the PSA/hydrogenated rosin blends and hence decreased the bonding viscosity and increased the wettability of the blends to the probe, which thereby increased the probe tack. However, in spite of the increased probe tack, a fibrillation phenomenon occurred during the debonding process regardless of the UV dose, with the exception of P01 which contained no hydrogenated rosin. This phenomenon arose because the blended hydrogenated rosin acted as a UV-curing retardant and reduced the cohesive strength between the polymer chains. The probe tack of the P09 blends containing 0, 10, 20, and 30 wt% of hydrogenated rosin before UV irradiation was 243, 258, 271, and 293 g, respectively, which was similar to that of the P01, P03, and P06 blends. However, these values decreased at UV doses > 200 mJ/cm^2 due to the higher cross-link density caused by UV exposure. In particular, PSAs
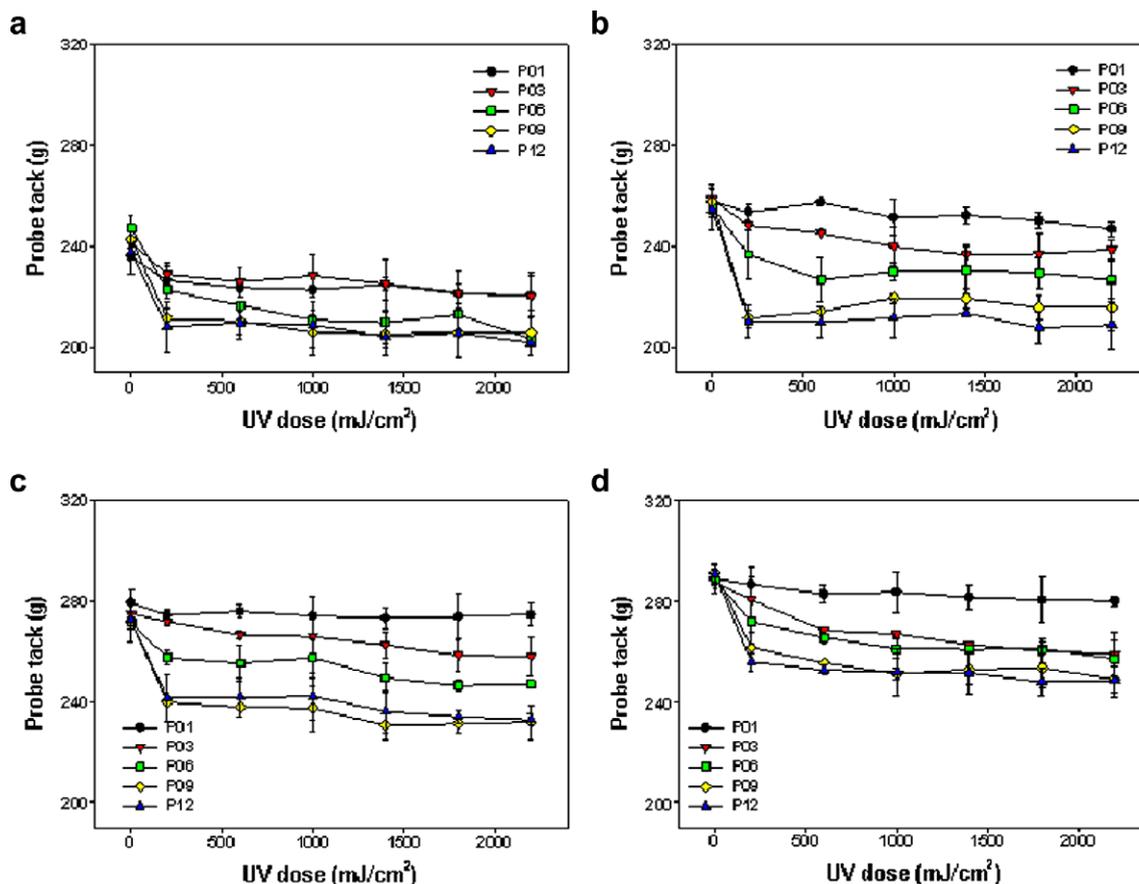
Fig. 10. Changes in the probe tack of the PSA blends at different UV doses and benzophenone and hydrogenated rosin content: (a) 0, (b) 10, (c) 20, and (d) 30 wt% hydrogenated rosin/PSA blends.

containing more than 0.9 phr of photoinitiator (P09 and P12) showed a considerably decreased probe tack at a low UV dose due to the decreased PSA chain mobility resulting from the crosslinking of PSA with increasing UV dose, which decreased the ability of the PSA to wet the probe during the bonding process of the probe tack test [35]. These results corresponded to the FTIR results in that the probe tack decreased because of the increased consumption of benzophenone groups with increasing UV dose.

Fig. 11(b) shows the probe tack of the PSA/10 wt% HREM blends at different UV doses. The probe tack in the P01, P03, P06, P09, and P12 blends with 10 wt% HREM was 318, 305, 318, 314, and 307 g, respectively, which was higher than that of the PSA/10 wt% hydrogenated rosin blends at 258, 258, 255, 257, and 255 g, respectively, before UV irradiation. The differences between the HREM blends and the hydrogenated rosin blends are reflected by the T_g value. Tack is a function of T_g, and the T_g of general PSAs results from the combination of a low T_g base elastomer and a high T_g tackifier [20]. Therefore, the T_g of HREM influences the probe tack before UV irradiation. As shown in Fig. 3, the T_g of the PSA/HREM blends was −47.8, −46.1, −43.1, and −42.2 °C for PSA blends containing 0, 10, 20, and 30 wt% HREM, respectively. These lower T_g values of

the PSA/HREM blends raised the probe tack of these blends above that of the PSA/hydrogenated rosin blends. Furthermore, because the PSA/HREM blends provided a lower storage modulus than the PSA/hydrogenated rosin blends before UV irradiation, they exhibited a high probe tack due to their better wettability. After UV irradiation at 200 mJ/cm², the relative percentage initial decrease in the probe tack of the PSA/10 wt% HREM blends for P01, P03, P06, P09, and P12 was 1.3%, 2.8%, 5.2%, 11.2%, and 11.5%, respectively. These values were lower than those of the PSA/10 wt% hydrogenated rosin blends at 1.7%, 4%, 7.3%, 17%, and 17.4%, respectively. At this UV dose, fibrillation did not occur during the debonding process because there was sufficient crosslinking to enhance the cohesive strength between the polymers. Fig. 11(c) and (d) shows the probe tack of the PSA/20 and 30wt% HREM blends at different UV doses, respectively. The probe tacks were higher than those of the PSA/20 and 30 wt% hydrogenated rosin blends before UV irradiation, and the relative initial decrease in the probe tack of the PSA/20 and 30 wt% HREM blends was lower than that of the PSA/20 and 30 wt% hydrogenated rosin blends after UV irradiation. With decreasing T_g of the tackifier, the tackifier concentration at which the T_g of the PSA blends exceeds room temperature increased, as did the tackifier concentration
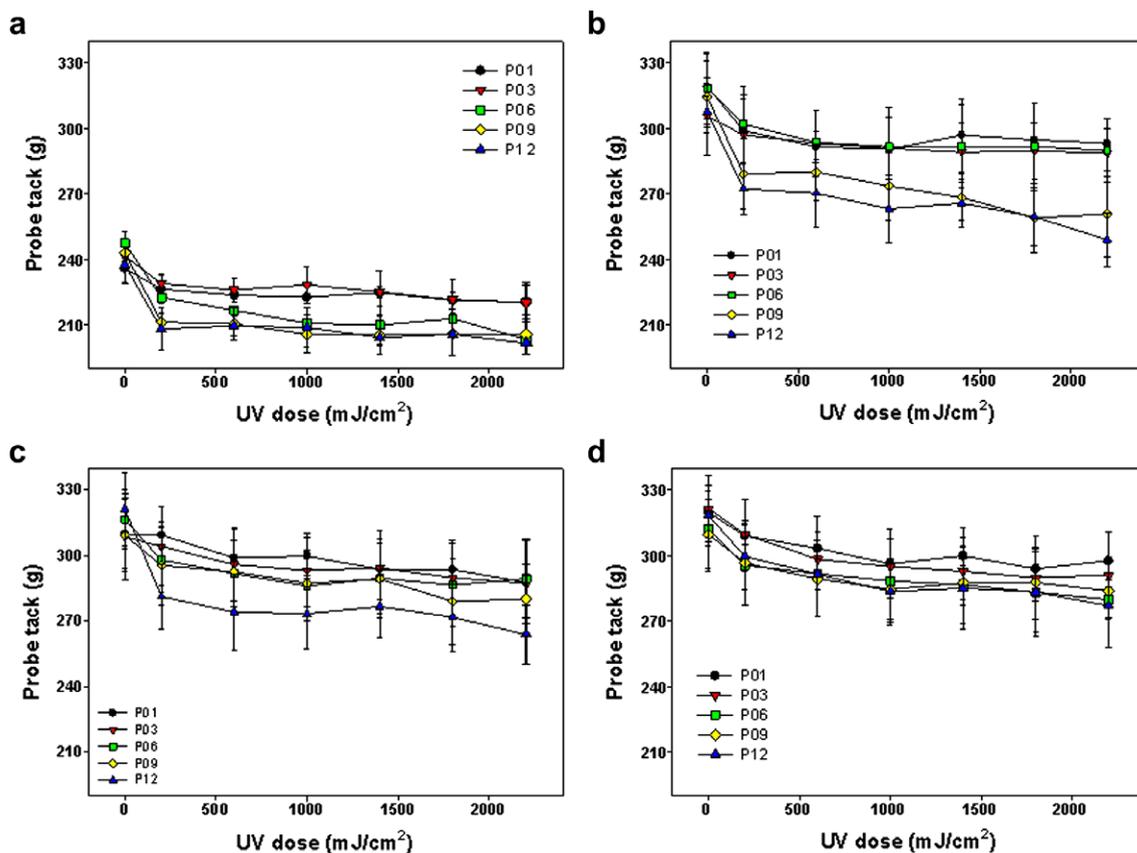
Fig. 11. Changes in the probe tack of the PSA blends at different UV doses and benzophenone and HREM content: (a) 0, (b) 10, (c) 20, and (d) 30% HREM/PSA blends.

at the maximum probe tack. On the other hand, a lower tack was obtained with a high T_g tackifier because it stiffened the PSA blends and prevented good wetting of the probe surface. Although the HREM content in the PSAs increased their T_g, it did not exceed room temperature because the T_g of HREM is in the sub-zero temperature range. To summarize, our results indicated that the probe tack increases with increasing HREM content without any limitation on the T_g.

4. Conclusion

Hydrogenated rosin and HREM were miscible with acrylic PSAs, as confirmed by DSC and ARES results. The T_g of the tackifier influenced the UV-curing behavior of the PSA/tackifier blends. In the case of the PSA/hydrogenated rosin blends, the high T_g of the hydrogenated rosin retarded the UV reaction. However, as the T_g of HREM and the modulus of the PSA/HREM blends were sufficiently low, the PSA molecular mobility and its crosslinking efficiency increased after blending with HREM. As the PSA/HREM blends maintained their T_g in the sub-zero temperature range with high wettability, the properties and probe tack of the PSAs increased remarkably with increasing HREM content compared with the PSA/hydrogenated rosin blends.

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