Effect of crosslinking density on adhesion performance and flexibility properties of acrylic pressure sensitive adhesives for flexible display applications

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ABSTRACT

The use of acrylic pressure sensitive adhesives (PSAs) in flexible displays involves their attachment to each layered device. Due to the high industrial demand of flexible displays, acrylic PSAs must necessarily exhibit high flexibility. In this study, the effect of the crosslinking density of acrylic PSAs on their adhesion and flexibility properties has been investigated by incorporating a diisocyanate crosslinking agent into the PSA structure. As the content of the crosslinking agent increased, the measured peel strength and tack of the synthesized PSAs decreased, while the maximum value of the lap shear stress increased. In addition, the maximum stress and shear strain determined for the crosslinked PSA specimens decreased with an increase in the crosslinking agent concentration (although, the stress measured at low strain values was initially increasing until the crosslinking agent content reached 1 phr). The results of stress relaxation testing showed a stress increase at specified strain levels with an increase in the crosslinking agent content up to 0.5 phr, while the results of creep testing revealed that the measured strain was inversely proportional to the degree of elastic recovery. The obtained data indicate that crosslinking generally improves the PSA properties related to their use in flexible display applications; however, very high crosslinking densities produce mostly a negative effect on the PSA flexibility and adhesion characteristics.

1. Introduction

Pressure sensitive adhesives (PSAs) represent a class of materials that possess the ability to bond to various substrates under light pressure and be subsequently removed without leaving any residue [1] (in other words, their main purpose is to ensure prompt adhesion after the application of light pressure [2]). Different PSA types can be classified as acrylic, rubber, and silicone. Among these groups, acrylic PSAs are widely used in various industrial applications, such as splicing tapes, protective foils, graphic films, and medical products, due to the existence of a large variety of acrylic monomers [3]. Typically, acrylic PSAs contain 3–10 wt.% of acrylic acid and 90–97 wt% of a soft alkyl acrylate body, which is comprised of butyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, and isooctyl acrylate or decyl acrylate components. Various copolymers, which include acrylic acid and butyl acrylate, are generally used for the synthesis of acrylic PSAs [4,5]. Since PSAs are frequently used as adhesives for layered devices in flexible display applications, they must possess sufficient flexibility or the ability to endure stress under bending. According to the results of previous studies, PSAs can be generally characterized as flexible materials with high viscoelasticity. However, their ability to sustain stress in flexible display applications has not been investigated in sufficient detail.

Crosslinking is one of the most important techniques for improving the mechanical properties of PSAs (such as creep resistance and cohesive strength). Generally, this method is based on the chemical reaction that occurs between the crosslinking agent and the main PSA chain [6,7]. However, a high crosslinking density causes gelation, which deteriorates the tack properties of crosslinked PSAs [7].

In our previous study, the flexibility properties of neat and crosslinked PSAs (including stress relaxation and creep resistance) were estimated via dynamic mechanical analysis (DMA). According to the obtained stress relaxation and creep testing results, the magnitudes of initial stress and degree of recovery increased after PSA crosslinking, while the strain values obtained for the crosslinked acrylic PSAs were

lower than that of the neat PSA. Therefore, crosslinking of acrylic PSA can produce a significant effect on its flexibility properties [8].

In this work, solvent-based acrylic PSAs have been synthesized from reactive monomers, and their basic mechanical properties analyzed. Following synthesis the acrylic PSAs were crosslinked with various contents of a polyisocyanate crosslinking agent. The adhesion performance of the crosslinked acrylic PSAs was investigated via peel, tack, and lap shear tests, which were conducted using a texture analyzer. In addition, stress relaxation and creep tests were performed via DMA to evaluate the PSA flexibility properties and to determine their suitability for flexible display applications.

2. Experimental

2.1. Materials

Acrylic monomers, including 2-ethylhexyl acrylate (2-EHA, 99.0% purity, Samchun Pure Chemical, Republic of Korea), isobutyl acrylate (IBA, 99.0% purity, Samchun Pure Chemical), glycidyl methacrylate (GMA, 99.0% purity, Samchun Pure Chemical), and 2-hydroxyethyl acrylate (2-HEA, 99.0% purity, Samchun Pure Chemical) were used as received without further purification. Ethyl acetate (EAc, 99.0% purity, Samchun Pure Chemical) was used as a solvent. 2,2'-azobisisobutyr-onitrile (AIBN, Junsei Chemical, Japan) was used as a thermal initiator. AK-75 diisocyanate compound (Aekyung Chemical Corp. Ltd., Republic of Korea) with an NCO content between 12.5% and 13.5% was used as a crosslinking agent.

2.2. Synthesis of acrylic PSAs

The acrylic monomers (2-EHA, IBA, GMA, and 2-HEA) were mixed with an AIBN solution in EAc inside a 500-mL four-neck flask and heated to a temperature of 80 °C under continuous mechanical stirring (the formulations of the synthesized acrylic PSAs are listed in Table 1). During polymerization, the reaction system was purged with N_2 gas to prevent the inhibition of the polymerization process via oxidation. As the polymer viscosity increased, a specified amount of EAc was added to the remaining thermal initiator. Fig. 1 shows the ideal schematic diagram of the PSA synthesis procedure (the PSAs obtained in this work corresponded to random copolymers).

2.3. Thermal crosslinking of acrylic PSAs

2.3.1. Preparation of crosslinked acrylic PSAs
Crosslinked PSAs were prepared by blending 100 wt% of the obtained PSAs with 0.1, 0.2, 0.5, 1, or 2 parts per hundred resin (phr) of the crosslinking agent. Both the as-synthesized and crosslinked PSAs were coated onto the surface of 75 μm thick corona-treated polyethylene terephthalate (PET) films and then dried at a temperature of 80 °C for 10 min followed by thermal crosslinking at 120 °C for 2 min and at 60 °C for 12 h.

2.3.2. Gel content
The gel content in the synthesized polymers depends on the solubility of the utilized solvent. The gel fractions of the acrylic PSAs blended with the crosslinking agent were determined by soaking and shaking the resulting samples (with weights of approximately 5 g) in toluene at room temperature for 1 d. Afterwards, the soluble part of the obtained mixture was removed via filtration, while the remaining solid was dried at a temperature of 80 °C to a constant weight. The gel fraction in the produced polymer was calculated using the following equation:

$$\text{Gel fraction}(\%) = (W1/W0) \times 100$$

where W_o and W_1 were the sample weights before and after filtration, respectively.

2.4. Characterization of acrylic PSAs

2.4.1. Gel permeation chromatography measurements
Molecular weights and polydispersity indices for the synthesized PSAs (see Table 2) were measured using an Agillant 110 instrument equipped with a pump and a refractive index detector. Tetrahydrofuran was used as an eluent, and the flow rate was equal to 1 mL/min.

2.4.2. Differential scanning calorimetry studies
Glass transition temperatures for the synthesized acrylic PSAs were determined by differential scanning calorimetry (DSC; Q-200, TA Instrument, USA). The samples were first scanned from room temperature to 150 °C at a heating rate of 5 °C/min, after which they were rapidly cooled to −80 °C and then scanned again to 0 °C at the same heating rate. During the analysis, glass transition temperatures of the acrylic PSAs were measured in the region between −80 °C and 0 °C after annealing to higher temperatures to exclude possible thermal history effects (the obtained values are listed in Table 2).

2.5. Transmittance

Visible light transmittances for the crosslinked acrylic PSAs were measured in the wavelength range from 800 to 400 nm using a UV−vis spectrophotometer (Cary 100, Agilent Technologies, USA). The thicknesses of all acrylic PSA films deposited on transparent PET substrates were 50 μm.

2.6. Adhesion performance

2.6.1. Peel strength
The peel strengths of the crosslinked PSA specimens with widths of 25 mm were measured using a texture analyzer (TA-T2i, Micro Stable Systems, UK). The specimens were pressed onto stainless steel (SUS) substrates by two passes of a 2-kg rubber roller and then stored at room temperature for 24 h. The peel strength magnitude (defined as the average force applied to a PSA specimen during debonding) was determined in accordance with the ASTM D3330 standard at an angle of 180° crosshead rate of 300 mm/min, and temperature of 20 °C. The applied force was recorded for six different runs with an average value of N/25 mm.

2.6.2. Probe tack testing
Probe tack testing was conducted at a temperature of 20 °C in accordance with the ASTM D2979 standard using the texture analyzer equipped with a 5-mm SUS cylinder probe. The utilized standard probe tack testing procedure consisted of the following three stages: approaching the PSA surface, touching the PSA surface, and detaching from the PSA surface. The probe rate was 0.5 mm/s, the separation rate was 10 mm/s, and the contact time with the PSA surface was 1 s at a constant force of 100 g/cm². During debonding, the measured tack values corresponded to the maximum debonding forces.

2.6.3. Lap shear testing
Lap shear testing was conducted using the texture analyzer. The tested specimens were cut into smaller pieces with widths of 25 mm.
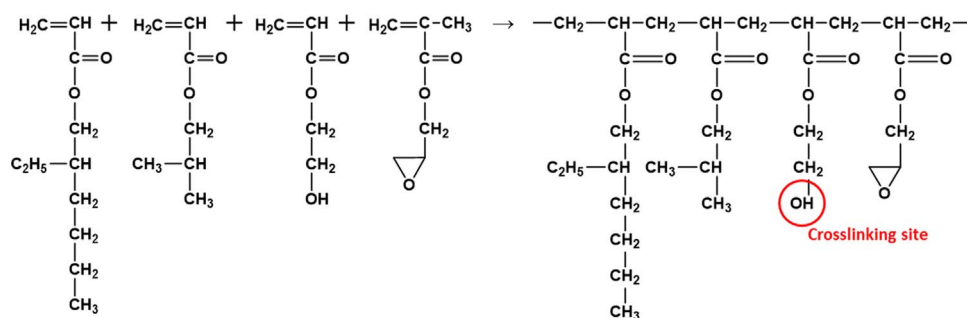
Table 1
Formulations of the acrylic PSA samples.

	#1	#2	#3	#4	#5	#6
Base resin (2-EHA: 70 wt%, IBA: 10 wt%, GMA: 10 wt%, 2-HEA: 10 wt%)						
'Crosslinking agent	0	0.1	0.2	0.5	1.0	2.0

Fig. 1. An ideal schematic diagram of the acrylic PSA synthesis, which shows a crosslinking site.

Table 2
Parameters of the acrylic PSAs utilized in this study.

	M_n (g/mol)*	M_w (g/mol)*	PDI	T_g (°C)**
Acrylic PSA	46,528	723,380	15.6	−31

Molecular weight was measured by GPC*, T_g was measured by DSC**.
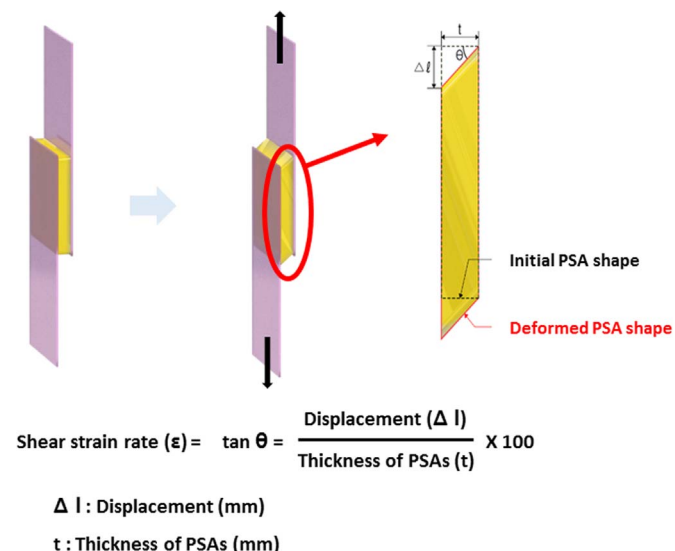
Fig. 2. A schematic of the lap shear testing procedure, which contains a formula for calculating the shear strain rate [8].

After being removed from a silicone release film, each PSA film was

attached to another PET substrate (the adhesion cross-sectional area was equal to 25×25 mm², and a 2-kg rubber roller was passed over the film surface three times). Lap shear tests were performed at a cross-head rate of 5 mm/min (the corresponding diagram containing a formula for calculating the shear strain rate is shown in Fig. 2). Shear strain rate values were calculated using the following equation:

$$\text{Shear strain rate}(\%) = \Delta L/t \times 100$$

where ΔL was the moving distance, and t was the thickness of the PSA film [7].

PSA-containing flexible displays are usually subjected to different values of shear strain depending on their structure and radius of curvature. Therefore, studying the relationship between the shear strain rate and the thickness of the obtained PSA films is important for their future use in flexible display applications.

2.7. Flexibility characteristics of acrylic PSAs

2.7.1. Stress relaxation testing

Stress relaxation testing was conducted using a DMA apparatus (Q-800 TA Instruments, USA). The goal of this experiment was to determine PSA characteristics and their suitability for flexible display applications by measuring the correlation between the deformation and stress with time. During the initial testing period, the studied PSA samples were stabilized for 1 min at a stress of 0.001 N followed by the application of a 400% strain for 10 min. Afterwards, the studied specimens were recovered at 0.001 N for 5 min. Degrees of elastic recovery and residual creep strain values were measured for the PSA samples as a function of time at different applied strain magnitudes. Initial stress, final stress, and relaxation ratio values were determined from the obtained stress/time graphs (see Fig. 3).
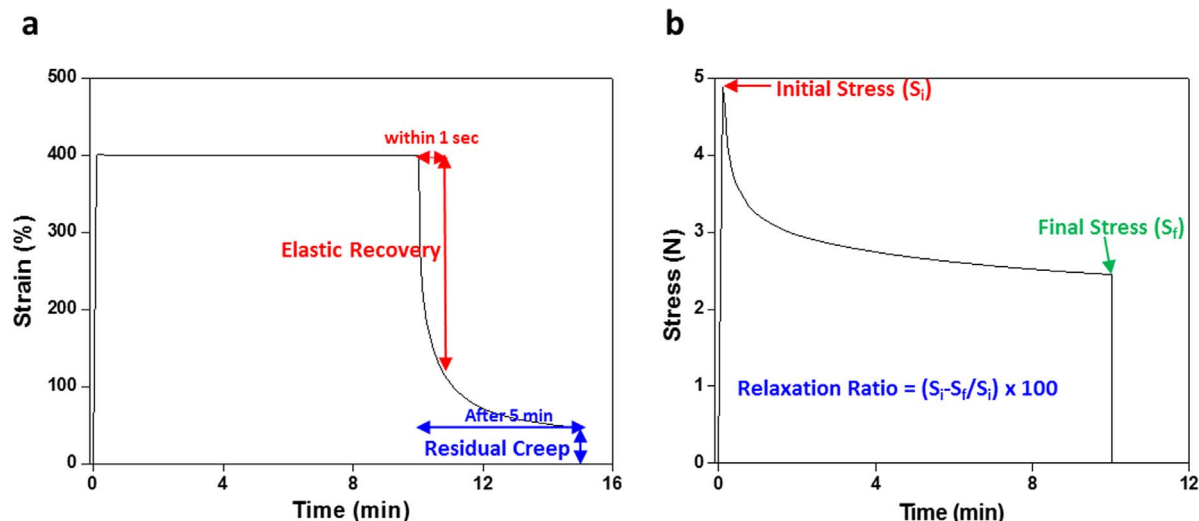

Fig. 3. Determination of the (a) strain deformation and (b) stress deformation with the corresponding stress relaxation ratio for the obtained PSA specimens [8].
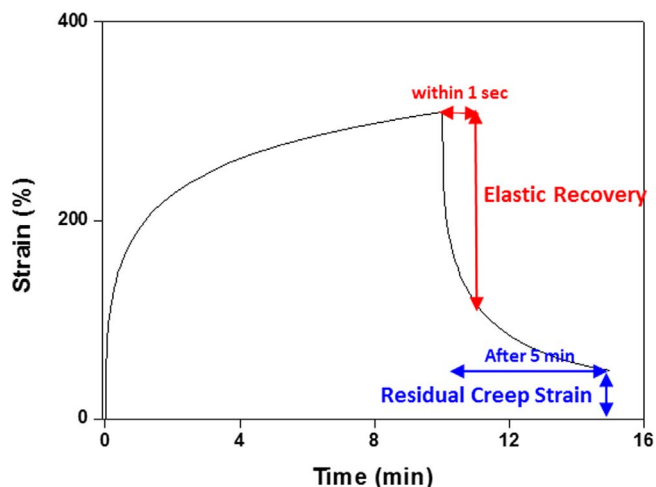
Fig. 4. Determination of the strain deformation for the obtained PSA specimens using the results of the creep test [8].

2.7.2. Creep testing

Creep testing was conducted using the DMA apparatus. During the initial testing period, the PSA samples were stabilized for 1 min at a stress of 0.001 N, after which a stress of 1 N was applied for 10 min followed by a recovery at 0.001 N for 5 min. Degrees of elastic recovery and residual creep strain values were obtained from the strain measured for the tested PSA specimens as a function of time (see Fig. 4).

3. Results and discussion

3.1. Gel content

The crosslinking density for the obtained PSA samples can be measured indirectly by calculating their corresponding gel contents from the polymer insoluble fractions [9]. Fig. 5 shows the gel fraction of the acrylic PSAs plotted as a function of the crosslinking agent concentration. Thus, the gel fraction obtained for the neat acrylic PSA was 0%, while after crosslinking its magnitude increased from 58% to 87% with an increase in the crosslinking agent content.

3.2. Transmittance

The transmittance of the acrylic PSAs is a very important parameter, which affects the possibility of their usage in display applica-
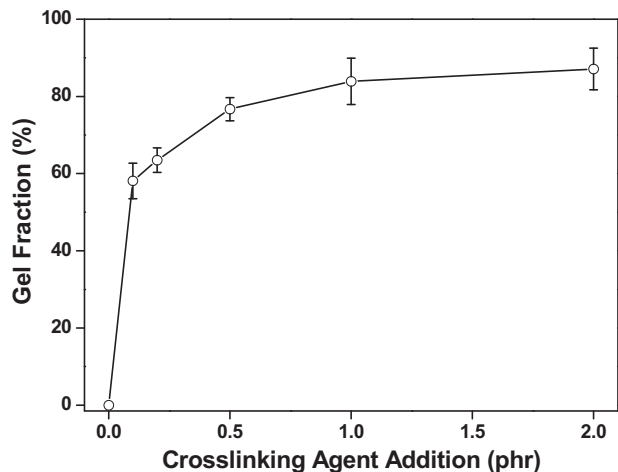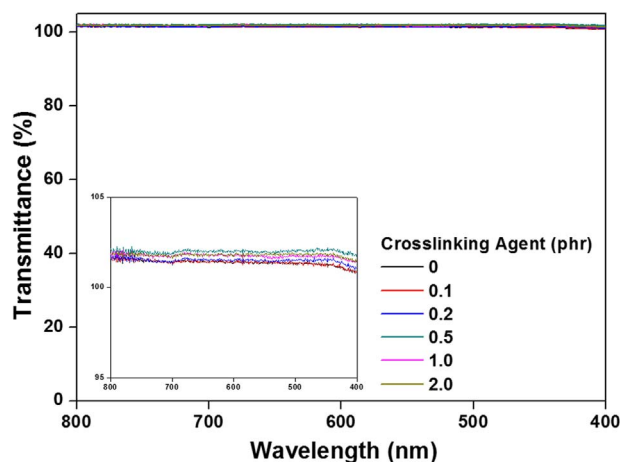

Fig. 6. Visible light transmittance of the acrylic PSAs as a function of the crosslinking agent addition.

tions. Fig. 6 shows the transmittance spectra recorded for the acrylic PSAs in the visible light region (the utilized baseline corresponded to the transmittance of the neat 75 μm PET film, which was assumed to be equal to 100%). The measured transmittances of the acrylic PSAs were above 100%, indicating that the acrylic PSA-coated PET films exhibited better transparency than that of the neat PET support [10]. In addition, no haze was detected for any of the studied PSA specimens.

3.3. Adhesion performance

The adhesion performance of the acrylic PSAs, which was determined via peel strength, probe tack, and lap shear testing, was clearly affected by the content of the added crosslinking agent (it should be noted that crosslinking density is an important parameter for controlling adhesion performance of a material [11]).

According to the results presented in Fig. 7, varying the concentration of the added crosslinking agent significantly affected the adhesion performance of the studied PSA specimens (here the peel strength corresponded to the sum of the bond breaking and deformation energies during PSA peeling). The peel strength of the acrylic PSAs decreased considerably with an increase in the crosslinking agent concentration, except for the sample containing 0.1 phr of the crosslinking agent. In particular, in the region between 0 and 0.1 phr, cohesive failure occurred after the acrylic PSA sample was detached from the SUS surface. On the other hand, at crosslinking agent concentrations between 0.2 to 2 phr, the acrylic PSA specimens did
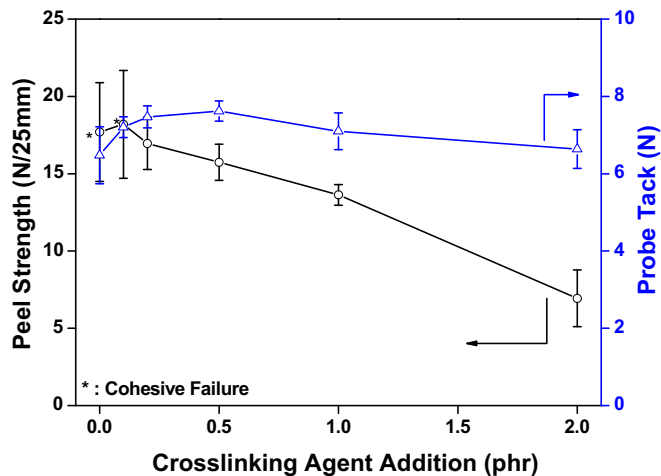

Fig. 5. Gel fraction measured for the acrylic PSAs as a function of the crosslinking agent addition.

Fig. 7. Peel strength and probe tack of the acrylic PSAs as a function of the crosslinking agent addition.

not exhibit any cohesive failure, and their peel strengths decreased consistently with increasing crosslinking agent content. According to the results obtained in a previous study, crosslinking density enhances the modulus of the acrylic PSAs; hence, the PSA elongation was reduced after crosslinking [12] due to the decreasing wettability of adhesives attached to SUS surfaces, which in turn can be attributed to the decreasing mobility of polymer chains caused by crosslinking.

Fig. 7 also shows the results of probe tack testing conducted at different crosslinking densities. The probe tack of the acrylic PSAs decreased with an increase in the crosslinking agent concentration. However, in the region between 0.1 and 0.5 phr, the tack magnitude slightly increased, while at higher contents of crosslinking agent it decreased again. The relative decrease in probe tack (D) measured as a function of crosslinking density can be estimated using the following equation:

$$D\ (\%) = (1 - tack_0/tack_\chi) \times 100$$

The values of D obtained at crosslinking agent concentrations of 0.1, 0.2, 0.5, 1, and 2 phr were equal to 10.1, 13.3, 15.0, 8.8, and 2.4, respectively. The observed trend can be attributed to the stronger interaction between polymer chains after crosslinking, which enhances PSA cohesion. However, the tack magnitude dramatically decreased on increasing the crosslinking agent content above 0.5 phr due to a reduction in the molecular mobility of acrylic PSA chains.

Fig. 8 shows the results of lap shear testing conducted at various PSA crosslinking densities. In general, non-crosslinked acrylates do not exhibit satisfactory PSA performance. In this study, the lap shear characteristics obtained for all crosslinked PSA specimens were better than those of the neat PSA. The observed improvement of the lap shear properties was related to the steady increase in the cohesive strength of the utilized adhesive at higher crosslinking agent concentrations [13]. However, the magnitudes of the maximum stress and strain decreased with increasing crosslinking agent content (Fig. 9), which could be explained by the stiffening of acrylic PSA species at very small elongations and the inability to endure shear stress.

3.4. Stress relaxation testing

The stress relaxation parameters of a polymer can be controlled by varying its crosslinking density. Fig. 10 depicts the strain deformation characteristics obtained during stress relaxation testing of the acrylic PSA specimens at different crosslinking densities. The degree of elastic recovery measured for the crosslinked acrylic PSAs increased with an increase in the crosslinking agent content. In particular, the elastic recovery measured at a crosslinking agent content of 1.0 phr exhibited
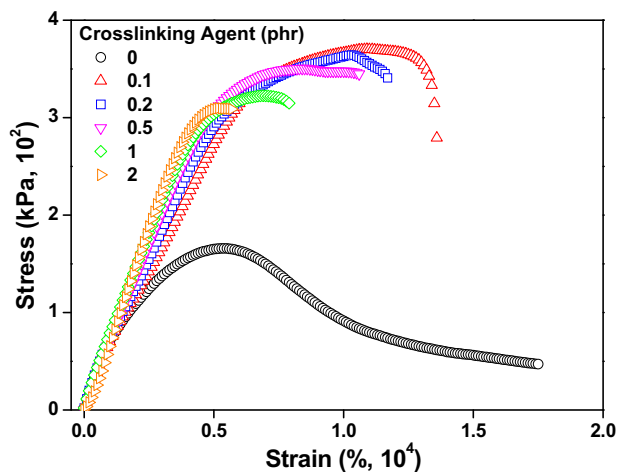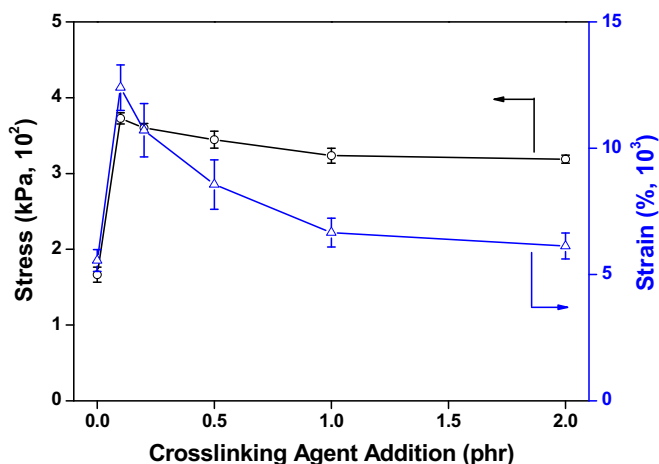

Fig. 9. Maximum stress and strain values obtained at the maximum lap shear stress for the acrylic PSAs as functions of the crosslinking agent addition.

the highest value. The residual creep strain magnitude first decreased after the crosslinking agent addition; however, it increased again at crosslinking agent contents above 0.5 phr. Both the degree of elastic recovery and residual creep strain are important parameters for flexible display applications. Since crosslinking can enhance the flexibility of PSAs, the optimum content of crosslinking density must be determined in the related studies.

As shown in Fig. 11, the initial stress obtained at a strain of 400% increased significantly with an increase in PSA crosslinking density, indicating that the crosslinking process hardened the internal PSA structure. The observed decrease in the initial stress over time results from the PSA structural changes. In particular, the relaxation ratio decreased as the crosslinking agent content increased from 0.1 to 1 phr due to internal structural changes caused by the increase in the PSA crosslinking density. However, the acrylic PSA specimen containing 2.0 phr of the crosslinking agent exhibited the lowest final stress and the highest relaxation ratio, which made it unsuitable for flexible display applications.

3.5. Creep testing

Fig. 12 shows the results of the creep tests conducted at different crosslinking densities of the PSA specimens. The strain measured for the neat acrylic PSA increased substantially at a stress of 1 N. On the other hand, the strain obtained for the crosslinked PSAs was reduced in several stages. The PSA specimens with different crosslinking densities exhibited different strains at specified stress levels. As the PSA crosslinking density increased, its degree of elastic recovery increased, while the residual creep strain measured after the detachment of the PSA coating decreased. Thus, the results obtained during creep testing can be used when selecting PSAs for different applications.

4. Conclusions

In this study, acrylic PSAs with various molecular weights have been synthesized and then mixed with crosslinking agent to prepare crosslinked acrylic PSAs, while their adhesion, stress relaxation and creep parameters were examined to investigate the effect of crosslinking density on the suitability of acrylic PSAs for flexible display applications.

1) Based on the observed gel fraction increase with crosslinking density, the synthesized acrylic PSAs were thoroughly crosslinked through the addition of the crosslinking agent, while their transmittance values were greater than 100% due to the higher transparency of the PSA-coated PET films as compared to that of neat
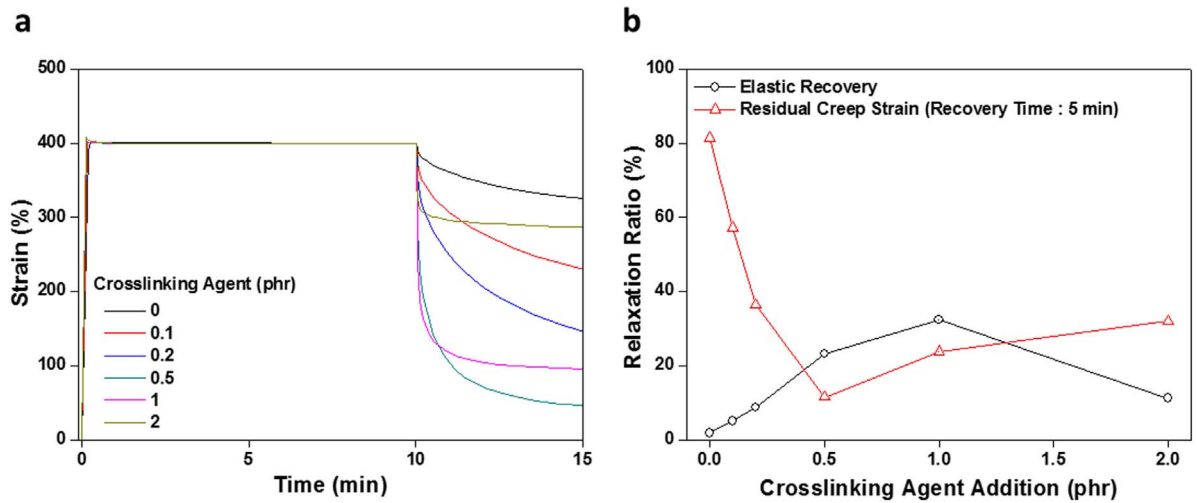

Fig. 8. A stress-strain curve obtained during lap shear testing of the acrylic PSAs at different crosslinking agent addition.

Fig. 10. Stress relaxation testing of the acrylic PSAs. (a) strain change and (b) degrees of elastic recovery and residual creep strain values measured as functions of the crosslinking agent addition.
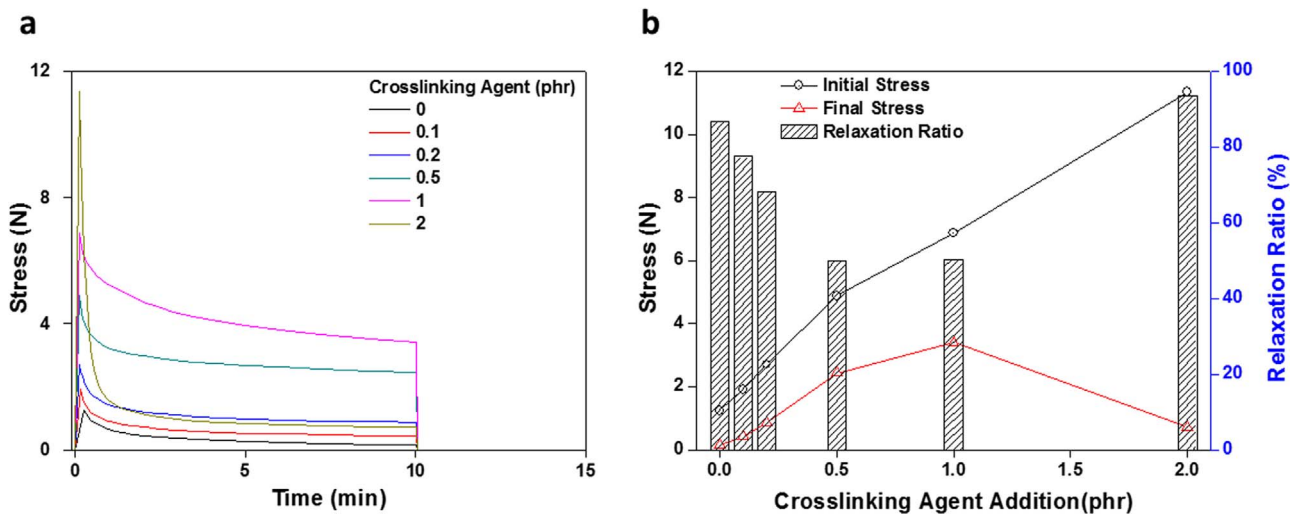

Fig. 11. Stress relaxation testing of the acrylic PSAs. (a) stress change and (b) initial/final stress and relaxation ratio values measured as functions of the crosslinking agent addition.
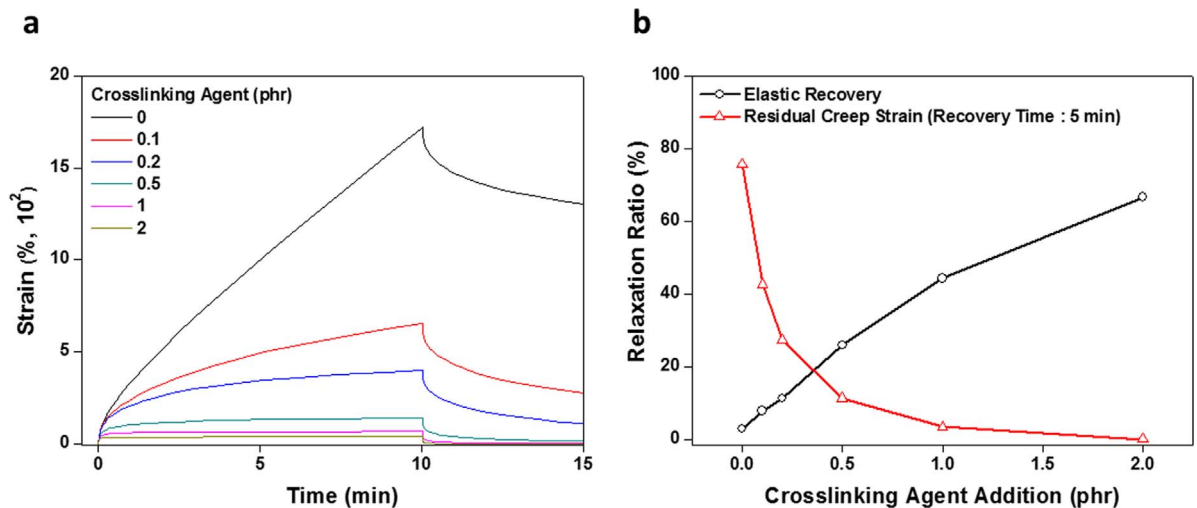

Fig. 12. Creep results of the acrylic PSAs (a) strain change and (b) degrees of elastic recovery and residual creep strain values measured as functions of the crosslinking agent addition.

PET.
2) The peel strength of the crosslinked acrylic PSAs decreased considerably with an increase in the crosslinking agent content.

However, at a crosslinking agent concentration of 0.1 phr, the PSA peel strength slightly increased, and cohesive failure occurred due to the decreased wettability of the adhesive species caused by the

decreasing mobility of polymer chains. The measured tack values also decreased with an increase in the PSA crosslinking density. However, the tack magnitude slightly increased when the crosslinking agent content was within the range between 0.1 and 0.5 phr, which could be attributed to the interactions between polymer chains via a crosslinking reaction, which enhanced the PSA cohesion. The maximum stress and the corresponding strain measured for the PSA specimens decreased with crosslinking density due to their very small elongations.

3) The flexibility properties of the synthesized acrylic PSAs were investigated using the stress relaxation and creep testing techniques. According to the results of the stress relaxation tests, the measured degree of elastic recovery increased, while the residual creep strain decreased with an increase in the PSA crosslinking density (similarly, the loaded stress measured at a strain of 400% increased considerably, and the calculated relaxation ratio decreased at higher concentrations of the added crosslinking agent). Importantly, the crosslinking agent concentration can be optimized to make the resulting crosslinked PSA material suitable for flexible display applications. During creep testing, the strain of the crosslinked PSAs decreased, while the strain of the neat acrylic PSA increased.

Hence, the obtained results revealed that crosslinking of acrylic PSAs represented a very effective method for controlling their adhesion and flexibility properties, while the stress relaxation and creep testing techniques could be used to determine the suitability of acrylic PSAs for flexible display applications.

Acknowledgements

References

[1] Satas D. Handbook of pressure-sensitive adhesive technology, 3rd ed.. New York: Van Nostrand-Reinhold; 1999.

[2] Czech Z, Pelech R. The thermal degradation of acrylic pressure-sensitive adhesives based on butyl acrylate and acrylic acid. Progress Org Coat 2009;65(1):84–7.

[3] Ishikawa N, Furutani M, Arimitsu K. Pressure-sensitive adhesive utilizing molecular interactions between thymine and adenine. J Polym Sci Part A-Polym Chem 2016;54(10):1332–8.

[4] Czech Z. Vernetzung von haftklebstoffen auf polyacrylatbasis. German: Wydawn. Uczelniane Politechniki Szczecinskiej; 1999.

[5] Lee S-W, Park J-W, Park C-H, Kwon Y-E, Kim H-J, Kim E-A, Woo H-S, Schwartz S, Rafailovich M, Sokolov J. Optical properties and UV-curing behaviors of optically clear PSA-TiO2 nano-composites. Int J Adhes Adhes 2013;44:200–8.

[6] Czech Z. Solvent-based pressure-sensitive adhesives for removable products. Int J Adhes Adhes 2006;26(6):414–8.

[7] Zhang X, Ding Y, Zhang G, Li L, Yan Y. Preparation and rheological studies on the solvent based acrylic pressure sensitive adhesives with different crosslinking density. Int J Adhes Adhes 2011;31(7):760–6.

[8] Lee J-H, Lee T-H, Shim K-S, Park J-W, Kim H-J, Kim Y, Jung S. Molecular weight and crosslinking on the adhesion performance and flexibility of acrylic PSAs. J Adhes Sci Technol 2016;30(21):2316–28.

[9] Joo H-S, Park Y-J, Do H-S, Kim H-J, Song S-Y, Choi K-Y. The curing performance of UV-curable semi-interpenetrating polymer network structured acrylic pressure-sensitive adhesives. J Adhes Sci Technol 2007;21(7):575–88.

[10] Park C-H, Lee S-J, Lee T-H, Kim H-J. Characterization of an acrylic polymer under hygrothermal aging as an optically clear adhesive for touch screen panels. Int J Adhes Adhes 2015;63:137–44.

[11] Nakamura Y, Imamura K, Yamamura K, Fujii S, Urahama Y. Influence of cross-linking and peeling rate on tack properties of polyacrylic pressure-sensitive adhesives. J Adhes Sci Technol 2013;27(17):1951–65.

[12] Lim D-H, Do H-S, Kim H-J, Bang J-S, Yoon G-H. Preparation of SIS/SBS-based UV-cross-linkable pressure-sensitive adhesives using the thiol-ene reaction. J Adhes Sci Technol 2007;21(7):589–603.

[13] Poh BT, Suid NH. Dependence of adhesion properties of cross-linked epoxidized natural rubber (ENR25)-based pressure-sensitive adhesives on benzoyl peroxide loading in the presence of gum rosin and petroresin tackifiers. J Adhes 2014;90(11):899–911.