



Effect of propyleneimine external cross-linker on the properties of acrylate latex pressure sensitive adhesives

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ABSTRACT

Acrylate pressure sensitive adhesive (PSA) latexes were synthesized via a starved monomer seeded semi-batch emulsion polymerization process with butyl acrylate (BA), methyl methacrylate (MMA), acrylic acid (AA) and 2-hydroxyethyl acrylate (HEA). These PSA polymers were then cross-linked with trifunctional propyleneimine external cross-linker (SAC-100) to study the cross-linking reaction between carboxylic group of the polymer chain and cross-linking agent. It was found that cross-linking provided a significant influence on the film formation process based on the result of SEM analysis. In addition, with the increase of SAC-100 content, the gel content of the polymer increased significantly, while molecular weight between cross-link points (M_c) and the sol molecular weight (M_w , M_n) of the polymer decreased remarkably. The TGA result showed that the addition of the external cross-linker can enhance the thermal stability of the latex film. Moreover, for the cross-linked adhesive film, the shear strength was improved greatly while at the sacrifice of loop tack and peel strength, when compared with the uncross-linked counterparts. Besides, dynamic mechanical analysis (DMA) was also used to evaluate the viscoelastic properties of the acrylate emulsion PSA film.

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1. Introduction

Pressure sensitive adhesives (PSAs) are viscoelastic materials with permanent stickiness, and can adhere strongly to solid surfaces upon application of slight contact pressure under a relatively short contact time [1]. The adhesion properties of the PSA are characterized by three basic applicative properties: tack (the property that enables an adhesive to form a bond of measurable strength with a surface of another material upon brief contact under light pressure), peel strength (the force required to remove a standard PSA strip from a specified test surface under a standard test angle (90° or 180°) under standard conditions), and shear strength (the length of time it takes for a standard strip of PSA to fall from a test panel after application of a load) [2].

Acrylic ester monomers are widely used to synthesize pressure sensitive adhesives (PSAs) through solution or emulsion polymerization. Their saturated nature makes them transparent, colorless, and resistant to yellowing from sunlight or oxidation [3]. However, as these synthesized acrylic PSAs consist of linear molecules that are held together by physical cross-linking, van der Waals forces, or hydrogen bonding, they have insufficient thermo-mechanical stability. On the other hand, the environmental disadvantage and high cost have

promoted the replacement of many solvent-borne acrylic PSAs with emulsion counterparts. Nevertheless, the solvent-borne acrylic PSAs have been preferred over the emulsion PSAs in high performance applications which require a high shear holding power together with high peel and tack. It is known that solvent-borne acrylic PSA films have a much higher shear-holding power than that of their emulsion counterparts [4]. This is mainly due to the continuous network morphology formed by the chain entanglements in the solvent-borne adhesive when the solvent has evaporated [5]. In contrast, microgels were produced during the process of emulsion polymerization and retain their discrete morphology in the adhesive film [4]. This morphology decreases the shear resistance of the emulsion adhesive because of the poor interconnections between the microgels and the linear polymers in the film.

Cross-linking is one of the key techniques controlling the balance between cohesive and adhesive strength of the PSA polymer. Typical cross-linking methods are based on the chemical reaction that takes place between the cross-linking agents and the main chain of the PSA copolymers [6]. With the aid of cross-linking agents, an increase in cohesion may be accomplished during the drying stage of the PSA film. As expected, the adhesion properties of the PSA film, such as tack and peel adhesion, decrease with the increment in cross-linker concentration (Fig. 1). The cross-linking of PSAs based on acrylates has been discussed in many industrial papers [7–10]. The physico-chemical and mechanical properties of cross-linked PSAs are determined to a large extent by the type and

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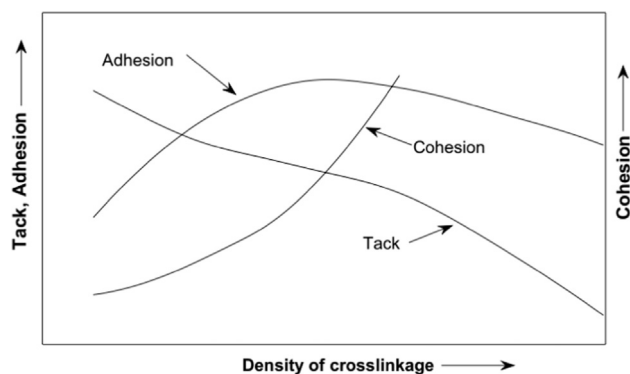


Fig. 1. General effects of cross-linking to the PSA performances [13].

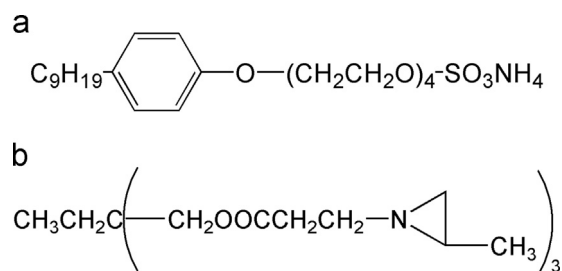
amount of cross-linking agents added to the copolymer. For example, Tobing and Klein [11] synthesized acrylic emulsion PSAs with different functional groups, using isobutoxy methyl acrylamide (IBMA) and AA comonomers. Their research showed that cross-linking reactions between reactive groups in the adhesive film at an elevated temperature resulted in high shear resistance without significant loss in peel and tack properties. Czech [12] discussed the influence of some kinds of cross-linking agents (internal and external cross-linkers) and their contents on the important properties of acrylic based PSA dispersions such as tack, adhesion and cohesion.

Multifunctional propyleneimines have proved to be versatile and highly effective external cross-linking agents or curing agents for acrylic PSAs (which contain acrylic acid in the polymer chain) and other adhesive types containing carboxylic groups [8]. In the present study, a series of emulsion acrylic pressure sensitive adhesives have been synthesized and cross-linked with trifunctional propyleneimine external cross-linker (SAC-100) at contents of 0.0–0.8 wt%. The effects of curing agent contents on the gel content, molecular weight between cross-links (M_c), soluble molecular weight (M_w , M_n) and its distribution (M_w/M_n) and adhesive properties of the PSA copolymers were investigated. In addition, IR, TGA, SEM and DMA were used to characterize the latex film before and after cross-linking.

2. Experimental

2.1. Materials

Butyl Acrylate (BA; technical grade, Shanghai Huayi Acrylic, China), Methyl Methacrylate (MMA; Reagent grade, Shanghai Lingfeng Chemical, China), Acrylic Acid (AA; reagent grade, Shanghai Lingfeng Chemical, China), 2-Hydroxy ethyl Acrylate (HEA, technical grade, Shanghai Huayi Acrylic, China), Ammonium persulfate (APS; technical grade, Shanghai Aijian Modern Reagent Factory, China) and Sodium Bicarbonate (NaHCO_3 ; reagent grade, Shanghai Lingfeng Chemical, China) were used as the initiator and the buffer agent. All these materials were used without further purification. The emulsifier used in this work was CO-458 (58–60 wt%), which was supplied by Shanghai Honesty Fine Chemical (China), and it was used as received. Distilled deionized water ($\text{DI-H}_2\text{O}$) was used throughout the study. Ammonia (25 wt% in H_2O) was obtained from Nanjing Chemical Reagent Co. All solvents used in the polymer characterization such as tetrahydrofuran (THF, HPLC grade, Shanghai Lingfeng Chemical) and toluene (reagent grade, Nanjing Chemical Reagent Co.), were also used as supplied by the manufacturer. PTFE porous membranes with pore size of 0.22 μm for use in gel content and M_c measurements, were purchased from Science, China. Trimethylolpropane-tris-(N-methylaziridinyl)-propionate was used as the propyleneimine external cross-linking agent obtained from Shanghai



Scheme 1. The molecular structures of (a) CO-458 and (b) SAC-100.

UN Chemical, China, and the product model was SAC-100. The molecular structures of CO-458 and SAC-100 are shown in Scheme 1.

2.2. Preparation of pre-emulsion and initiator solution

The 75 g $\text{DI-H}_2\text{O}$ and 6.0 g surfactant were added to a 1 L four-neck round-bottom flask and were stirred rapidly to make the emulsifier dissolved sufficiently, then the monomer mixture, which contains 258.93 g BA, 14.07 g MMA, along with 3 g AA and 6 g HEA, was slowly added into the water-emulsifier mixture through a constant pressure funnel over 20 min. After that, the pre-emulsion was stirred for further 30 min.

Then, the initiator stock solution was prepared by adding 1.05 g APS into 75 g $\text{DI-H}_2\text{O}$ and continuously stirred to become homogeneous solution.

2.3. Polymerization procedure

The latex was prepared by the monomer seeded semi-batch emulsion polymerization process, which was carried out in a 1 L four-neck round-bottom flask equipped with an electromotive stirrer, thermometer, two separated addition funnel, and reflux condenser. The theoretical solid content in the formulation was 50 wt%. The stirring speed was maintained at 230 rpm throughout the experiments. First, a homogeneous aqueous solution containing 150 g $\text{DI-H}_2\text{O}$, 0.3 g CO-458, and 0.6 g NaHCO_3 was charged into the reactor. When the temperature reached 70 $^\circ\text{C}$, an initiator solution containing 0.45 g APS and 15 g water and a monomer mixture containing 17.07 g BA and 0.93 g MMA were charged into the reactor to form the seed latex. The temperature was then raised to 83 ± 2 $^\circ\text{C}$ and the seed polymerization was continued for an additional 30 min. Subsequently, the pre-emulsion and initiator stock solutions were added slowly to the reactor using two separate constant pressure funnels. The feeding times for the pre-emulsion and the initiator solution were 3.5 and 4.0 h, respectively. After the feed was completed, the reaction was allowed to proceed for an additional 1 h to increase monomer conversion. The latex was then cooled to room temperature and ammonia was added to adjust the pH to 7–8.

2.4. Characterization

2.4.1. IR spectrographic analysis

Infrared (IR) spectra of the latex films were recorded with a Bruker VERTEX80 IR spectrometer (Germany) in the range 4000–400 cm^{-1} .

2.4.2. Gel content and M_c determination

The gel content of the acrylic PSA polymers was measured via the solvent-extraction method. Three samples (around 0.2 g) of the dried latex film were weighed and sealed in the PTFE coated membrane pouch. Then the membrane pouch was put in a Soxhlet extractor with tetrahydrofuran (THF), refluxing for 24 h. After the extraction process, the membrane pouch was removed and first dried in a fume hood for 3 h and then in a vacuum oven at 70 $^\circ\text{C}$

until it reached a constant weight. The weight of the remaining dry gel was taken and the gel content was calculated using

$$\text{Gel content} = \frac{\text{mass of the dry gel}}{\text{mass of the initial dry polymer}} \quad (1)$$

The dry gel polymer was then immersed in toluene at 25 °C to measure swelling. The Flory–Rehner equation was used to calculate the average molecular weight between cross-link points (M_c) [14]

$$M_c = \frac{V_1 \rho_p [\phi^{1/3} - \phi/2]}{-[\ln(1 - \phi) + \phi + \chi \phi^2]} \quad (2)$$

where V_1 is the molar volume of toluene (106.3 cm³/mol [4]) and ρ_p is the density of polymer (1.06 g/cm³ and 1.19 g/cm³ for PBA and PMMA, respectively [15], 1.067 g/cm³ for the BA/MMA (95/5 by weight) copolymer). ϕ is the volume fraction of the gel polymer in the swollen gel and can be calculated as follows:

$$\phi = \frac{W_p \rho_s}{W_p \rho_s + W_s \rho_p} \quad (3)$$

where W_p and W_s are the weight fractions of the gel polymer and solvent (toluene) in the swollen gel, respectively. ρ_s and ρ_p are the densities of solvent (0.8669 g/cm³) and polymer, respectively. χ is the polymer and solvent interaction parameter, and can be calculated as

$$\chi = 0.34 + \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (4)$$

where δ_1 is the solubility parameter of the polymer. As the solubility parameter value of PBA is 8.9 (cal/cm³)^{1/2} [4], that of PMMA is 9.2 (cal/cm³)^{1/2} [15], δ_1 should be 8.915 (cal/cm³)^{1/2} for BA/MMA (95/5 by weight) copolymer, and δ_2 is the solubility parameter of toluene, 8.9 (cal/cm³)^{1/2} [4].

2.4.3. Molecular weight determination

The molecular weight, number average molecular weight (M_n) and weight average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the soluble fraction of polymer were determined by using Agilent HPLC 1200 Infinity Series. The THF solution remaining from the gel content test was concentrated and analyzed for sol molecular weight. THF was used as the eluent and the flow rate was set at 1 mL/min. The internal temperature was set at 30 °C. Narrow polystyrene standards having molecular weight range from 400 to 1 × 10⁶ were used for calibration.

2.4.4. Thermal gravimetric analysis (TGA)

TGA was carried out to demonstrate the thermal stability of the latex PSA polymers using SHIMADZU DTG-60AH, Japan. The polymer films (around 5–10 mg) were heated from ambient temperature to 600 °C at the rate of 10 °C/min under 100 mL/min nitrogen flow.

2.4.5. SEM analysis

The surface morphology of the latex films was characterized by scanning electron microscopy (SEM) using a JSM-7600F.

2.4.6. Dynamic mechanical analysis (DMA)

The viscoelastic properties of the PSA were characterized via a model Q800 (TA Instruments) dynamic mechanical analyzer in shear sandwich mode. The sample with typical dimensions of 10 × 10 × 2 mm³ was prepared. The DMA measurements were done by heating the sample from −100 °C to 100 °C at a rate of 3 °C/min and under a shear frequency of 1 Hz. The glass transition temperature (T_g) was obtained from the maximum of the tan δ curve.

2.4.7. PSA testing

Different amounts of cross-linker were added into the latex. Then the latex was coated with RK (Manchester, UK) KHC.10.5 wire-rod coater onto 30 μm thickness, 25 mm width poly(ethylene terephthalate) strip to give a film with a dry thickness of 20 μm and dried in a vacuum oven at 105 °C for 3 min. The PET strips with adhesive coated on its one side were stuck on release paper for further tests. Before tests, the PET strips were conditioned for 24 h at standard conditions of temperature and humidity (23 ± 2 °C and 50 ± 5% Relative Humidity). A universal BLD-100S electronic stripping tester was used to evaluate loop tack and peel strength.

For the loop tack test, the strip was formed into a loop with the adhesive side facing outward. Approximately 25 mm at both ends of the strip was inserted into the upper grip. The instrument moved the upper grip downward at a speed of 300 mm/min until an area of 25 mm² came into contact with the stainless steel substrate mounted into the lower grip. Next, the tester moved the upper grip upwards at the same speed while recording the force needed to detach the loop from the substrate. The maximum force of detachment was reported as loop tack.

For the 180° peel test, strips of the adhesive-coated films were laminated against the stainless steel substrate using a 2 kg rubber roller. The rubber roller was passed through the PET strip front to back three times. After 20 min dwell, 180° peel of the substrate was done at 300 mm/min. The average force per 25 mm required to peel the strip from the substrate was recorded and reported as 180° peel strength.

For shear holding power, the strips were laminated against stainless steel using 2 kg rubber roller to make contact areas of 25 mm². After 20 min dwell, the sample was fixed in the tester vertically with a 1 kg load suspended in the other hand. Automatic timers were placed below the weights to count the time of failure. The shear holding power was the time that elapsed between the application of the load and the completed separation of the strip from stainless steel.

Every result was an average of five parallel measurements.

3. Results and discussion

3.1. Cross-linking mechanism

The cross-linking of carboxylated pressure sensitive adhesives with multifunctional propyleneimines is mainly based on the carboxyl groups offered by the carboxylic acids within the polymer chain. The oxygen of the nucleophilic carboxyl group causes the opening of the strained propyleneimine rings while the hydrogen atoms accompanying the carboxyl groups protonate the tertiary nitrogen atoms [9]. The cross-linking mechanism is outlined in Fig. 2.

3.2. IR spectrographic analysis

Fig. 3 shows the IR spectra for carboxylated PSA films without and with trifunctional propyleneimines cross-linker SAC-100. Both curves showed characteristic stretchings for the methyl and methylene groups at 2958 cm^{−1}, 2933 cm^{−1}, 2872 cm^{−1} and 1452 cm^{−1}, 1394 cm^{−1}, 1378 cm^{−1}, the carbonyl group at 1728 cm^{−1}, the C–O–C stretching at 1241 cm^{−1} and 1158 cm^{−1}, the characteristic absorption peaks for poly(butyl acrylate) at 1063 cm^{−1} and 941 cm^{−1}. However, for the PSA film cross-linked with SAC-100, it would be expected that the intensity of the OH stretching vibration peak at 3285 cm^{−1} would be reduced and even disappeared (curve b), when compared with uncross-linked adhesive (curve a), indicating the reaction between the curing agent SAC-100 with carboxylated PSA, as shown in Fig. 2.

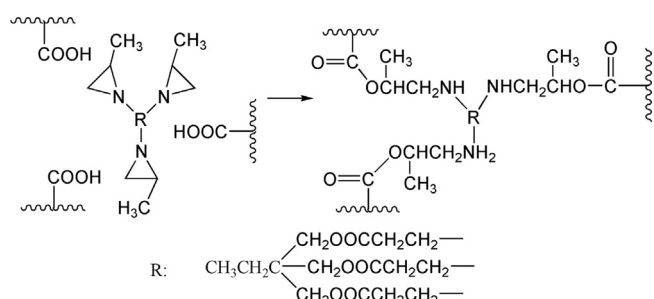


Fig. 2. Curing reaction between trifunctional propyleneimine cross-linker (SAC-100) with carboxylated PSA.

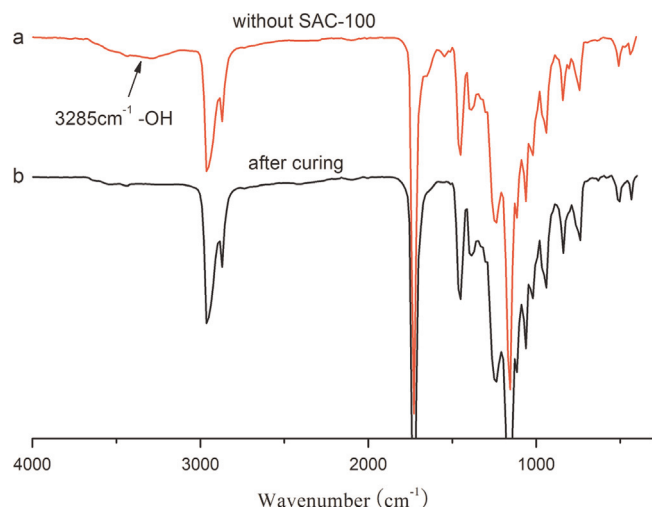


Fig. 3. IR spectra of (a) acrylate latex film without SAC-100 and (b) acrylate latex film after curing.

Table 1
Effect of curing agent content on molecular weight of the acrylate latex PSA.

SAC-100 concentration (wt%)	$M_c (\times 10^{-3})$ (g/mol)	$M_w (\times 10^{-3})$ (g/mol)	$M_n (\times 10^{-3})$ (g/mol)	M_w/M_n
0.0	–	204.6	36.9	5.54
0.2	79.3	50.4	18.5	2.73
0.4	30.0	33.3	18.1	1.84
0.6	20.7	24.3	13.8	1.76
0.8	14.2	5.38	0.82	6.56

3.3. Effect of curing agent content on polymer latex properties

Table 1 and Fig. 4 showed the effect of curing agent content on molecular weight and gel content of the acrylate latex PSA, respectively. It can be seen that the gel content increased significantly with SAC-100 concentration, while the M_c of the gel polymers and the M_w of the sol polymers decreased remarkably. This phenomenon is well known for the emulsion polymerization of BA and BA-dominated comonomer systems [16]. When cross-linker was not used, gel was formed by either intermolecular or intramolecular chain transfer to polymer via backbiting, plus termination by combination [17,18]. In this case, gel content was very low, and the formed gel had many branches and very few cross-linking points, which indicated that the actual M_c was very large. On the other hand, when cross-linker was used, gel formed via another mechanism, the formation of a denser gel network in the film after the cross-linking reaction between SAC-100 with the carboxyl functionality existed in the polymer chain, thus increasing the gel content and decreasing the M_c of the gel polymers. Based on Tobing and Klein's research [11], network morphology

plays a significant role in influencing the shear-holding power and its balance with peel and loop tack properties in acrylate PSA, which will be further discussed later in our paper.

In the meantime, the reduction in sol molecular weight (M_w , M_n) of the polymer with cross-linker concentration was mainly due to the transformation of sol polymer to gel parts. Besides, the molecular weight distributions (M_w/M_n) of the soluble polymer become narrower with the increase in SAC-100 concentration. It should be noted here that when the concentration of cross-linker reach 0.8 wt%, the sol molecular weight become extremely low ($M_w=5380$ g/mol, $M_n=820$ g/mol), but with a broad M_w/M_n (6.56), which was clearly shown in Fig. 5.

3.4. SEM analysis

The surface morphology of the carboxylated PSA films without and with multifunctional propyleneimines cross-linker SAC-100 was examined by SEM and shown in Fig. 6. It is well known that latex film formation involved three primary physical stages [19,20]: (1) water evaporation and particle ordering; (2) particle deformation; and (3) polymer interdiffusion across particle–particle boundaries. It can be seen obviously from Fig. 6 that cracks appeared on the surface of the uncross-linked latex film (image a) which was mainly due to a too fast drying procedure in the wet state [19].

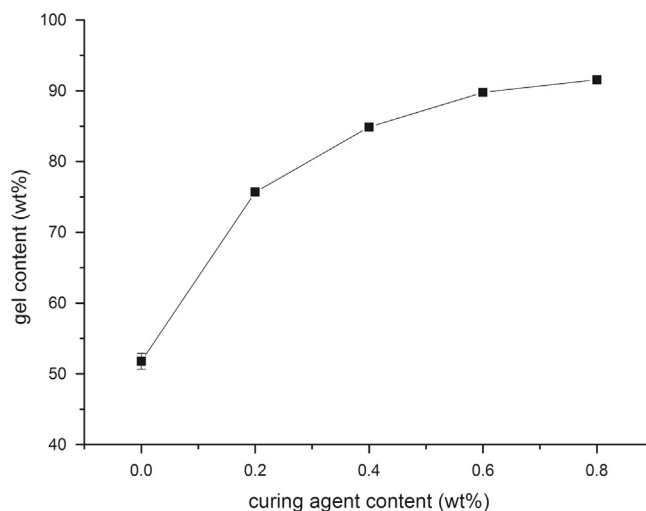


Fig. 4. Effect of curing agent content on gel content of the acrylate latex PSA.

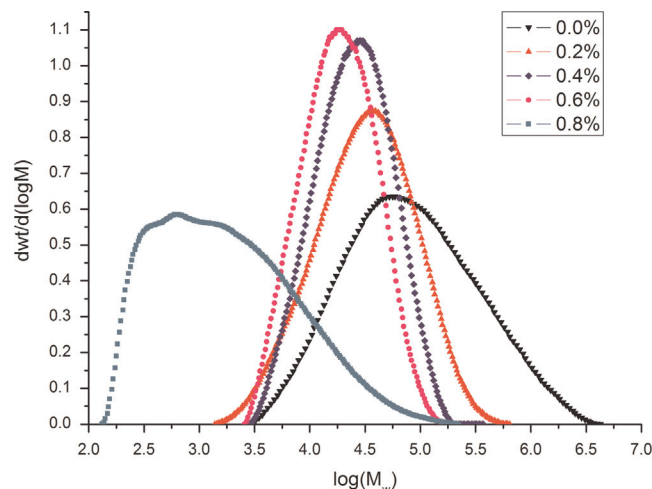


Fig. 5. The curves of molecular weight distributions of the soluble polymer with different curing agent contents.

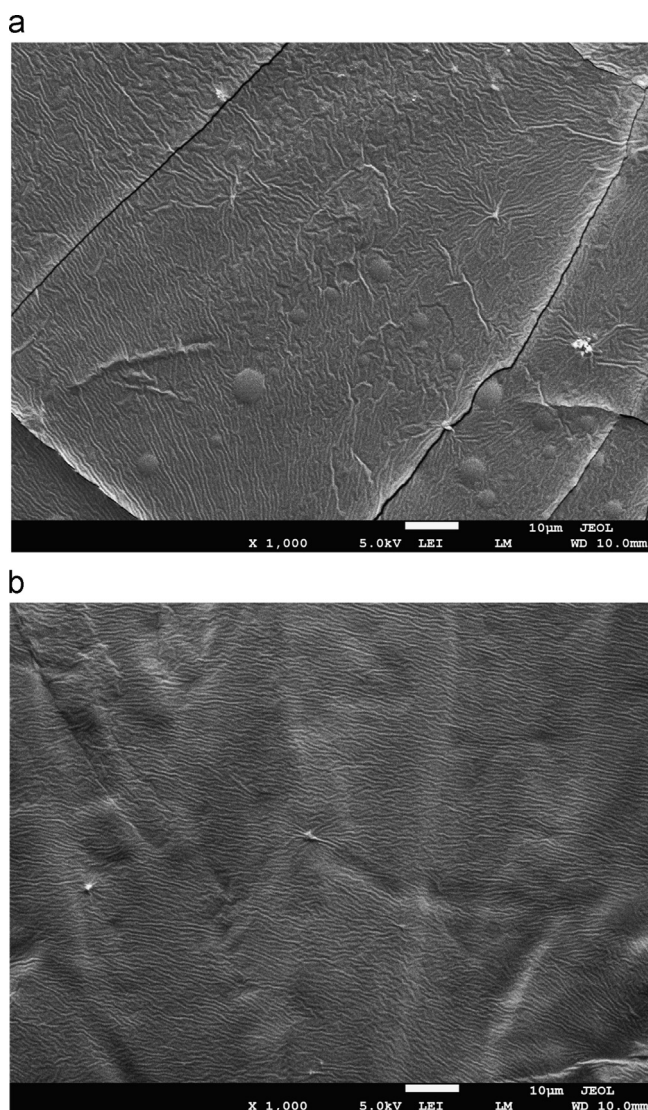


Fig. 6. The SEM micrographs of the latex PSA films.

3.5. TGA analysis

Some thermal resistance parameters of the carboxylated PSA films before and after cross-linking are summarized in Table 2. As can be seen, the initial degradation temperature of the carboxylated PSA film was elevated obviously with the addition of the propyleneimines external cross-linker SAC-100, which was expected. This is probably because polymer degradation at high temperature is associated with the initiation of random scission [21]. And the initiation of this random process may be slow after the addition of SAC-100 due to the dense cross-linking network formed in the film. Nevertheless, the final decomposition temperatures of the PSAs were nearly the same, this might be because both the PSAs have the identical molecular structures, once the temperature was high enough to destroy the cross-linking networks, the residual part will be decomposed in a short time. In conclusion, the polymers cured with SAC-100 are more thermally stable than the uncross-linked polymers. This is in good agreement with the works of Mukhopadhyay [22].

3.6. Dynamic mechanical analysis (DMA)

The performance of a PSA is related to the viscoelastic response of the bulk adhesive. The storage modulus (G') is determined by the elasticity property of the PSA, while the loss modulus (G'') is

Table 2

Thermal resistance parameters of the PSA films.

SAC-100 concentration (wt%)	T_i (°C)	T_f (°C)	T_{max} (°C)
0.0	347.05	421.63	400.25
0.6	358.37	423.11	408.19

T_i : Initial decomposition temperature; T_f : final decomposition temperature; T_{max} : maximum weight loss% temperature.

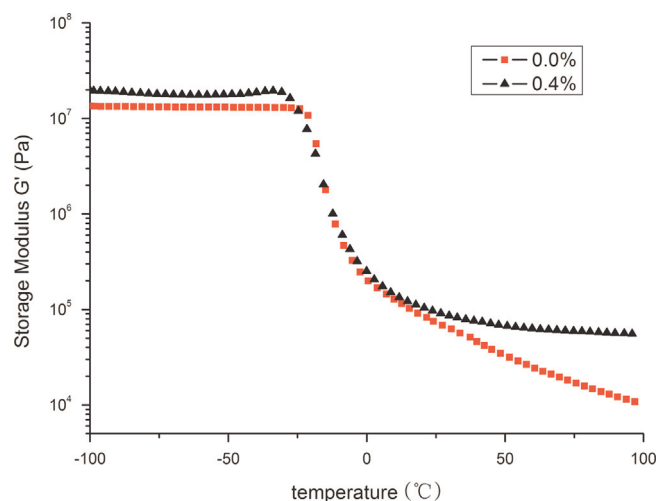


Fig. 7. Effect of curing agent on storage modulus (G') of the PSA films.

determined by the viscosity property. The damping factor ($\tan \delta$) is equal to G''/G' , reflecting the proportion of viscous component. In Fig. 7, it can be observed that the cross-linked adhesive film showed a higher storage modulus, when compared with the uncross-linked adhesive, through the whole temperature range. This was mainly due to the higher gel content related to the presence of external cross-linker SAC-100. On the other hand, through DMA testing in shear mode, Fig. 8 provides the relationship between $\tan \delta$ and temperature for the PSA copolymer without and with external cross-linker SAC-100. It was clearly seen from Fig. 8 that only one single T_g peak (temperature at peak $\tan \delta$) occurred for both curves, indicating that the copolymers are of uniform composition. The value of the T_g measured by DMA were around -13°C for both polymers, and no significant increase in T_g was observed with the addition of trace amount of SAC-100 (0.4 wt%). In addition, the shape of the G' and $\tan \delta$ curves stayed almost unchanged.

Table 3 listed some viscoelastic parameters for the PSA films without and with external cross-linker SAC-100 at temperature of 25°C . From Table 3, we can see that with the addition of curing agent, the storage modulus of the PSA film increased significantly. Correspondingly, the polymer will have high cohesive strength and therefore good shear property. Nevertheless, the uncross-linked adhesive will have higher $\tan \delta$ value. These DMA data will be very useful for us to further analyze the adhesive properties of the PSA polymer at room temperature in our discussion below.

3.7. Adhesive properties

The results of experimental measurements of loop tack, peel strength, and shear strength of cross-linked acrylic latex PSAs are presented in Figs. 9, 10 and Table 4, respectively. It is well known that the strength of an adhesive bond is determined by the thermodynamic contributions to the interfacial energy (van der Waals interactions, electrostatic forces, and hydrogen bonding) and the rheological contributions due to the viscoelastic dissipation during

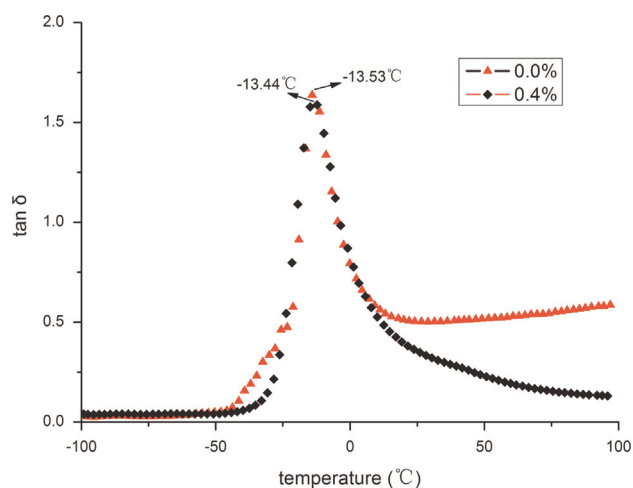


Fig. 8. Effect of curing agent on damping factor ($\tan \delta$) of the PSA films.

Table 3

Some viscoelastic parameters for the PSA film at temperature of 25 °C.

SAC-100 concentration (wt%)	G' (KPa)	$\tan \delta$
0.0	72.8	0.5047
0.4	94.4	0.3541

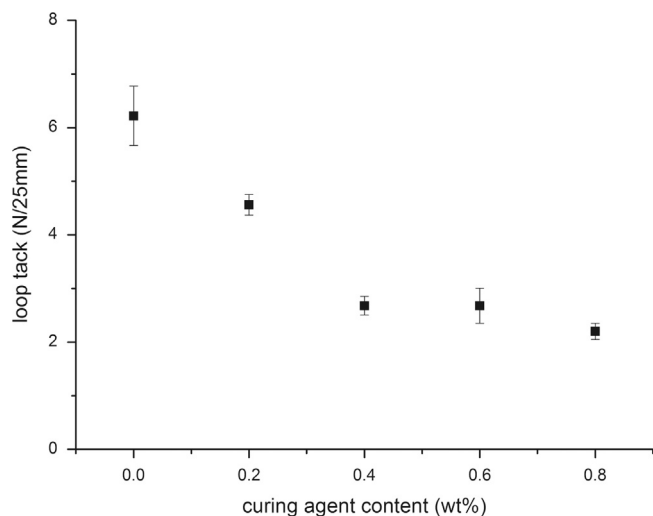


Fig. 9. Effect of curing agent content on loop tack of latex PSA film.

deformation of the polymer chains in the adhesive layer itself [23]. As can be seen in Figs. 9 and 10, the loop tack and peel strength are considerably reduced by the increase of SAC-100 concentration. There may be two reasons for this: (1) when the external cross-linker SAC-100 was introduced, dense cross-linking network was formed in the PSA latex film and the gel content was increased. Thus the resulting lower deformability and flow ability of the PSA weakened the bonding between the PSA and substrate, causing lower tack and peel strength [24]. (2) Yang and Chang [25] reported that adhesion properties of the PSA copolymer have a strong dependence on the loss factor $\tan \delta$. For the PSA film, the larger the $\tan \delta$, the more capable of deforming and wetting the adherent surface, thus increasing the loop tack and peel strength. According to the DMA data aforementioned, the value of $\tan \delta$ of the PSA film cured with external cross-linker SAC-100 become lower, when compared with the uncross-linked PSA, resulting in lower adhesion properties. The result is consistent with the work of Czech [9], who found that the

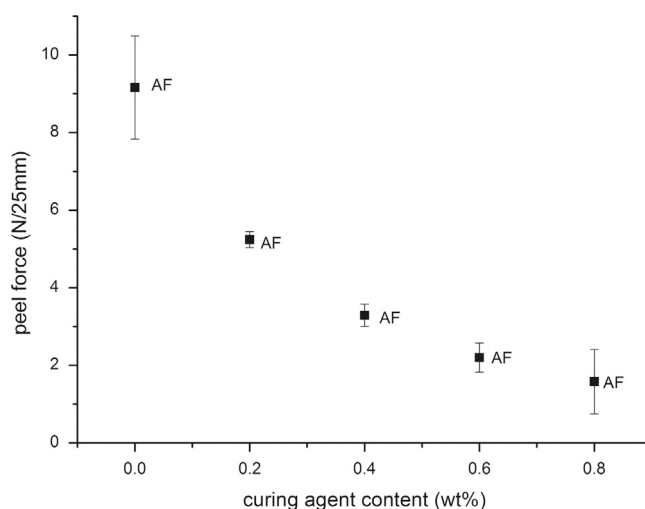


Fig. 10. Effect of curing agent content on peel strength of latex PSA film.

increase of propyleneimine content affects negatively the adhesiveness and positively the cohesion of the PSA.

From Table 4, it can be seen that the cohesive strength of the PSA film without SAC-100 was very weak, only 2–3 h for holding power with cohesive failure occurred. Nevertheless, after cross-linking, the cohesive strength of the latex film increased significantly, more than 72 h for holding power with adhesive failure happened. This is mainly because that the significant increase in gel content (as shown in Fig. 4) led to higher cohesive strength and a larger shear strength. This result was in good agreement with the work of Qie [26], who found that with the increase in gel content, tack and peel strength decreased, while shear strength increased. Moreover, for weakly cross-linked adhesive, failure occurs by creep while for highly cross-linked adhesive failure is caused by fracture [27].

It should be noted here that the test results of the adhesive properties for the cross-linked PSA were totally consistent with the DMA data aforementioned. After cross-linking with SAC-100, the PSA film exhibited high values of G' in the terminal region, corresponding to a higher shear strength. On the other hand, the cross-linked adhesive gave lower value of $\tan \delta$ compared to uncross-linked counterpart, corresponding to the decrease in loop tack and peel strength.

4. Conclusions

In this paper, acrylate pressure sensitive adhesive (PSA) latexes were produced via a starved monomer semi-batch emulsion polymerization process with butyl acrylate (BA), methyl methacrylate (MMA), acrylic acid (AA) and 2-hydroxyethyl acrylate (HEA). These synthesized PSA polymers were subsequently cross-linked with trifunctional propyleneimine external cross-linker (SAC-100), which was commonly used in the solvent-based acrylic PSA, to modify the polymer comprehensive properties. The main conclusions derived were as follows:

1. With the increase of the external cross-linker (SAC-100) content, the gel content of the acrylate PSA polymer increased significantly, while molecular weight between cross-link points (M_c) and the sol molecular weight (M_w , M_n) of the polymer decreased remarkably as expected. Besides, the molecular weight distributions (M_w/M_n) of the soluble polymer first become narrower and then broader with the increase in SAC-100 concentration.
2. The cracks observed by SEM in the uncross-linked latex film are due to a too fast drying procedure in the wet state. Besides, the

Table 4

Effect of curing agent content on the shear strength of latex PSA film.

SAC-100 concentration (wt%)	0.0	0.2	0.4	0.6	0.8
Shear resistance (min)	158 ± 3 (CF)	> 4320 (AF)	> 4320 (AF)	> 4320 (AF)	> 4320 (AF)

CF: Cohesive failure; AF: adhesive failure.

thermal stability of the PSA polymer was improved after cross-linked with SAC-100.

- The cross-linked adhesive film showed a higher storage modulus (G'), when compared with the uncross-linked counterparts, through the whole temperature range. Nevertheless, the uncross-linked adhesive have higher $\tan \delta$ value. The DMA data at temperature of 25 °C are very useful for us to further analysis the adhesive properties of the PSA polymer at room temperature.
- The external cross-linker has significant effects on the adhesive properties of the acrylic latex PSA films. The loop tack and peel strength of the PSAs are considerably reduced by the increase of SAC-100 concentration, while the cohesive strength of the latex film increased significantly.

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