

Viscoelastic and Adhesive Properties of Single-Component Thermo-Resistant Acrylic Pressure Sensitive Adhesives

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ABSTRACT: Poly(butyl acrylate-vinyl acetate-acrylic acid) based acrylic pressure sensitive adhesives (PSAs) were synthesized by solution polymerization for the fabrication of high performance pressure sensitive adhesive tapes. The synthesized PSAs have high shear strength and can be peeled off substrate without residues on the substrate at temperature up to 150°C. The PSAs synthesized in the present work are single-component crosslinked and they can be used directly once synthesized, which is convenient for real applications compared to commercial multi-component adhesives. The results demonstrated that the viscosity of the PSAs remained stable during prolonged storage. The effects of the preparation conditions such as initiator concentration, cross-linker amount, organosiloxane monomer amount and tackifier resin on the polymer properties, such as glass transition temperature (T_g), molecular weight (M_w), surface energy and shear modulus, were studied, and the dependence of the adhesive properties on the polymer properties were also investigated. Crosslinking reactions showed a great improvement in the shear strength at high temperature. The addition of tackifier resin made peel strength increase compared to original PSAs because of the improvement of the adhesion strength. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40086.

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INTRODUCTION

Pressure sensitive adhesives (PSAs) are special viscoelastic materials that can bond to various surfaces by a small contact pressure without being heated up, and can be removed easily without any residue.¹ Acrylic polymers have been most widely used as PSAs in commercial products, such as tapes, labels, and protective films because of the low-cost, nontoxicity, transparency, and good resistance to weathering.^{2–4} Most conventional PSAs are designed for applications at room temperature and with multiple-components. However, the demand for single-component acrylic PSAs with high adhesive properties applicable at elevated temperature increases rapidly in recent years.

It is well-known that tack (the ability of PSAs to be quickly adhered to an objective surface at a slight pressure), peel strength (the ability of PSAs to resist interface separation by peeling), and shear strength (the ability of PSAs to resist creep when shear force is applied up on) are the major parameters that define the end-use properties of PSAs. The values of these parameters are associated with and can be adjusted by intrinsic viscosity, glass transition temperature (T_g), molecular weight (M_w), and crosslinking density.^{5–7} Generally, modulating the crosslinking density is the most effective method to improve

adhesive properties, especially for heat and chemical resistance.^{8–10} PSAs can be classified to two categories: single-component adhesives and multi-component adhesives. Single-component adhesives can be stored and sold in an integrated system containing a built-in cross-linker and they can be used anytime conveniently. However, for multi-component adhesives, the major adhesives and the cross-linker must be stored and sold separately and the adhesives need to be made on the application site by mixing the major adhesive component with the cross-linker, repeatedly according to the application speed, which may lead to unstable properties issues. The acrylic PSAs currently used are mostly multi-component^{11–14} and the synthesis of single-component acrylic PSAs have seldom been investigated, besides, the researches on developing adhesives that resist elevated temperature and consist of a single-component are even less.¹⁵ Czech and Wojciechowicz¹⁶ studied the crosslinking reaction of acrylic PSAs using chelating metal acetylacetonates and it was proposed that addition of isopropanol prolonged the pot-life of the single-component adhesive; however, the shear strength at a temperature higher than 120°C was not excellent. Zhang¹⁷ filed a patent, in which a single-component acrylic PSA was modified by MQ silicon resin for the purpose of improving the thermo-resistance of the adhesives, however, the shear

resistance time that is the indicator of the shear strength at 150°C was less than 1 h due to the lack of crosslinking structure.

The viscoelasticity of PSAs connects the macroscopic adhesion properties and microscopic polymer structures. The bonding and debonding behaviors are reflected by the adhesion energy and viscoelastic energy dissipation (VED) characterized by storage modulus (G') and loss modulus (G''). Dahlquist¹⁸ firstly found that when a PSA's storage modulus was above 3.3×10^5 Pa, it lost its tack property. Chang¹⁹ developed the concept of viscoelastic window for guiding PSAs products development. PSAs with different adhesive properties were divided into five types according to their shear modulus at bonding and debonding frequency. It was reported that^{20–24} the increase in the M_w , T_g and crosslinking density led to improvement of shear modulus, while the increase in the entanglement molecular weight (Me), tackifier resin and plasticizer content had a reverse effect. For example, Tobing and Klein²⁵ studied dynamic mechanical behaviors in tackified acrylic emulsion PSA and found that rubbery plateau modulus decreased with the addition of tackifier resin.

The key in developing single-component adhesives with superior thermo-resistance is to understand the adhesion mechanism behind and to develop proper cross-linkers. This study aimed at finding a solution that can inhibit the crosslinking reaction during storage, and achieve superior thermo-resistance adhesion property, simultaneously. Associated with this study, this paper presented the synthesis of our specially designed adhesives and discussed the dependence of end-use properties of the adhesives on the polymer properties, such as T_g , M_w , surface energy, and shear modulus.

EXPERIMENTAL

Materials

Butyl acrylate (BA), vinyl acetate (VAc), and acrylic acid (AA) were supplied by HuaYi Acrylic Co. Ltd., Shanghai, China. Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were purchased from YiDe Co. Ltd., Zhenjiang, China. 3-Methacryloxypropyl trimethoxy silane (TMSPMA) was supplied by Dow Corning, USA. Aluminum acetylacetonate (purity: >99 %, density: 1.27 g/mL) was purchased from LiDa, Yangzhou, China. Rosin glycerol ester resin GA-AT (Mn: 810, PDI: 1.3, softening point: 85°C), rosin pentaerythritol ester resin GA-100 (Mn: 1100, PDI: 1.3, softening point: 100°C) and terpene phenolics resin (Mn: 520, PDI: 1.3, softening point: 95°C) were purchased from Wuzhou Arakawa Chemical Industries, Guangxi, China. All products were used without further purification.

Synthesis of PSAs

In a four-necked round bottom flask with 1 L, 1/6 amount of total initiators, 48.6 g BA, 5.4 g VAc, 2.86 g AA monomers and 120 g ethyl acetate were mixed. The temperature was raised to 85°C within 0.3 h. The reaction was maintained for 0.5 h and 145.51 g BA, 17.6 g VAc, 8.67 g AA, 50 g solvent, and 2/5 amount of total initiators were fed dropwise over 3 h. The reaction was continued for another 1.5 h before the remaining 2/5 amount of initiators and 40 g solvent were fed dropwise over 0.5 h. The reaction was then maintained for 2.5 h. Then the solution was diluted by ethyl acetate/methanol to a 40 wt %

solid content to reduce the viscosity in the reaction system and also to decrease the temperature of the system. In the above reaction design, BA was chosen as a soft monomer, VAc as a hard monomer, AA as a functional monomer, and TMSPMA as a modified monomer. The monomer feeding ratio was fixed as BA : VAc : AA = 85 : 10 : 5 by weight to obtain a constant T_g of the copolymer as -42°C . The cross-linker AlACA was dissolved in toluene to prepare a 10% (m/m) solution, which was added with the dilution agent. Tackifier resin was dissolved in ethyl acetate to prepare a 50% (m/m) solution, which was added with the dilution agent based on PSA-11. Methanol was chosen as the stabilizer for its favorable cost and boiling point. Different amounts of initiator, AlACA, and TMSPMA were used for the experiments summarized in Table I.

The amount of BA (194.11 g), VAc (23.00 g), and AA (11.53 g) were identical for all experiments. Initiator amount = initiator/total monomers. AlACA amount = AlACA/total adhesive. TMSPMA amount = TMSPMA/total monomers.

Preparation of PSAs Films

The adhesives obtained above were coated on polyethylene terephthalate (PET) films with 50 μm thickness using a baker (Elcometer 3520). Such made PSAs films were dried at 120°C for 4 min, during which the crosslinking reaction occurred. The thickness of the PSAs layer obtained was $30 \pm 2 \mu\text{m}$. All PSAs were placed in an aging chamber which was set to 30°C for 24 h before the instrumental analysis.

Characterization of Synthesized Adhesives

Molecular Weight. The molecular weights of the synthesized adhesives were measured by GPC (GPCmax VE 2001 Malvern). 20 mg of dry adhesive was dissolved in 5 mL of tetrahydrofuran (THF) and shaken for 24 h in a shaker (KS 4000 IKA). The solution was then filtered through 0.2 μm polytetrafluoroethylene (PTFE) filters and placed in an auto sampler vial. The GPC instrument has a refractive index detector (VE 3580) and a viscosity detector (270 DUAL). The mobile phase was THF with a 1 mL/min flow rate and the injection volume was 100 μL .

Glass Transition Temperature (T_g). T_g was measured by DSC (Pyris-1 PE). 5 mg of dry adhesive was weighed into aluminum DSC sample pans that were then hermetically sealed. The temperature scanning program range was from -50°C to 50°C and heating rate was $20^\circ\text{C}/\text{min}$.

Shear Modulus. Dynamic mechanical properties were measured by DMA (Q-800 TA). The shear sandwich clamp was chosen to hold the PSA samples during the test. A frequency sweep from 0.1–100 Hz (including 0.1, 1, 10, 30, 50, 60, 70, 80, 100 Hz) at a constant temperature of 30°C and a temperature sweep from -70°C to 50°C at constant frequency of 1 Hz were conducted. The samples sizes were fixed at 0.2 mm \times 10 mm \times 10 mm.

Contact Angle. Contact angle was measured by OCA (DSA-100 Kruss) at room temperature. The dispersion and polar components of surface tension were calculated using the Owens-Kaelble-Chan method.²⁶

180° Peel Strength. 180° peel strength was measured according to the Pressure Sensitive Tape Council standard PSTC-1.

Table I. Recipes for Adhesive Synthesis

Experiment	Initiator amount (wt %)	AIACA amount (wt %)	TMSPMA amount (wt %)	Solvent	Dilution agent
PSA-01	AIBN (0.7)	0	0	Ethyl acetate	Ethyl acetate
PSA-02	AIBN (0.4)	0	0	Ethyl acetate	Ethyl acetate
PSA-03	AIBN (0.1)	0	0	Ethyl acetate	Ethyl acetate
PSA-04	AIBN (0.05)	0	0	Ethyl acetate	Ethyl acetate
PSA-05	AIBN (0.02)	0	0	Ethyl acetate	Ethyl acetate
PSA-06	BPO (0.7)	0	0	Ethyl acetate	Ethyl acetate
PSA-07	BPO (0.7)	0.05	0	Ethyl acetate	Ethyl acetate Methanol
PSA-08	BPO (0.7)	0.075	0	Ethyl acetate	Ethyl acetate Methanol
PSA-09	BPO (0.7)	0.1	0	Ethyl acetate	Ethyl acetate Methanol
PSA-10	BPO (0.7)	0	0	Ethyl acetate Methanol	Ethyl acetate Methanol
PSA-11	BPO (0.7)	0	0.25	Ethyl acetate Methanol	Ethyl acetate Methanol
PSA-12	BPO (0.7)	0	0.5	Ethyl acetate Methanol	Ethyl acetate Methanol
PSA-13	BPO (0.7)	0	1	Ethyl acetate Methanol	Ethyl acetate Methanol
PSA-14	BPO (0.7)	0	2	Ethyl acetate Methanol	Ethyl acetate Methanol

The amount of BA (194.11 g), VAc (23.00 g), and AA (11.53 g) were identical for all experiments. Initiator amount = initiator/total monomers. AIACA amount = AIACA/total adhesive. TMSPMA amount = TMSPMA/total monomers.

Shear Strength. Shear strength was measured according to the Pressure Sensitive Tape Council standard PSTC-7.

Shear Strength at High Temperature. The method to measure the shear strength at high temperature was similar to the regular shear strength test described above. The only difference was that test temperature was changed from room temperature to 150°C. The test device was placed in a 150°C oven.

Thermo-Resistance. A stainless-steel test panel was used as substrate from which polyester (PET) tapes coated with the adhesive samples were peeled. The tape samples were pressed three times with a 2 kg roller to be firmly bonded to the test panels. Then the test panels were placed in an oven of 150°C for 4 h. The PSA tapes were then removed from the stainless-steel panels and the surface conditions of the test panels were observed and the results were recorded with respect to the residue. The sample peeling tests were operated at various temperatures; i.e., for high temperature test, the peeling was operated in the oven at a designed temperature while for the room temperature test, the peeling was operated when the temperature of the test panels was cooled down to room temperature.

Measurement of Viscosity. The viscosities of the adhesive solutions were measured by a rotational viscometer (NDJ-1 ChangJi) at 25°C.

Composition Analysis. The product composition was analyzed by FTIR (Nicolet iS10 Thermo Fisher) with a smart iTR attachment assembled for solid sample and ¹H-NMR (Unity Inova 400 Varian) using CDCl₃ as a solvent.

RESULTS AND DISCUSSION

Confirmation of the Product Composition

Figure 1 is a typical FTIR spectrum of one adhesive sample, obtained at the condition of monomer ratio: BA : VAc : AA = 85

: 10 : 5 wt %, reaction temperature: 82°C, AIBN concentration: 0.4 wt % and reaction time: 8 h. The characteristic absorption bands of -COC, -C=O and -CH₃ were shown at 1162 cm⁻¹, 1740 cm⁻¹, and 2959 cm⁻¹, respectively. The absence of a band at 1640 cm⁻¹ was an indication of the absence of monomer residues, which would usually accompany if some of monomers BA, VAc, AA still existed after the reaction.

The ¹H-NMR for the PSA sample was shown in Figure 2-(d. ppm referenced by TMS, CDCl₃ as solvent), which included the expected peaks: 0.93 (-CH₃ on the butyl acrylate), 1.22 (-CH₂ on the butyl acrylate), 1.35-1.81 (-CH, -CH₂ on the polymer main chains), 2.04 (-CH₃ attached to the -COO side group of vinyl acetate), 3.69 (-CH₂ attached to the -COO side group of butyl

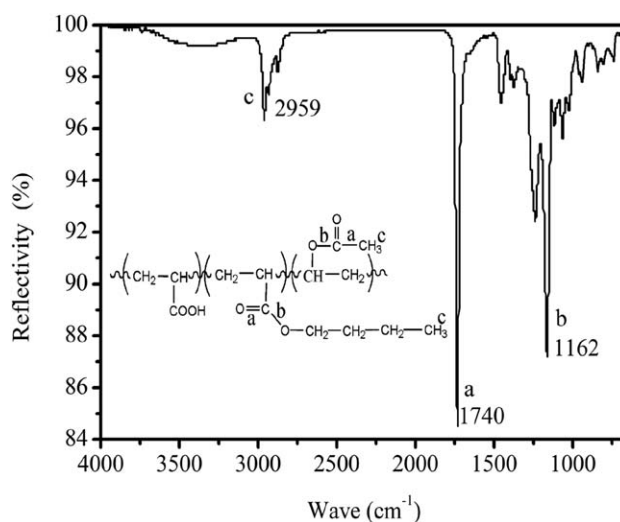


Figure 1. FTIR spectrum of the acrylic copolymer P(BA-VAc-AA). (Monomer ratio: BA : VAc : AA = 85 : 10 : 5 wt %; Reaction temperature: 82°C; AIBN concentration: 0.4 wt %; Reaction time: 8 h).

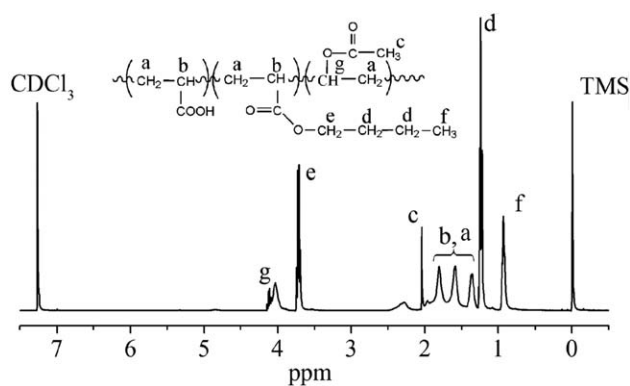


Figure 2. $^1\text{H-NMR}$ spectrum of the acrylic copolymer P(BA-AA-VAc). (Monomer ratio: BA : VAc : AA = 85 : 10 : 5 wt %; Reaction temperature: 82°C; AIBN concentration: 0.4 wt %; Reaction time: 8 h).

acrylate) and 4.11 (-CH on the polymer main chains attached to the OCO group of vinyl acetate). The absence of peaks in the 5.0–6.0 ppm regions (it they would show up if unsaturated bonds are detected) indicated the absence of monomers residues.

Both FTIR and $^1\text{H-NMR}$ spectra confirmed that the reactions were complete and the expected products were synthesized.

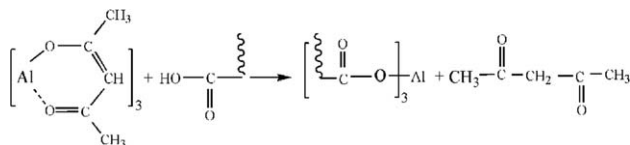
Design and Mechanism of Synthesizing Single-Component Acrylic PSAs

In order to realize stable single-component PSAs, preventing the PSAs from developing crosslinking is important. AlACA is a coordination compound with aluminum cation and acetylacetonate ligand. The crosslinking reaction occurs between metal ions and carboxyl groups. The mechanism of crosslinking reaction of AlACA and the resulting acrylic copolymer was shown as Scheme 1.

The long acrylic main chains containing carboxyl groups form a continuous network by coordination; simultaneously a product pentanedione is generated. In practical applications, pentanedione or alcohol solvents (methanol or isopropanol), used as stabilizing agent, are added to restrain the activity of crosslinking reaction. The viscosity of the resulting adhesive does not increase significantly if a stabilizing agent is added and the storage time can be prolonged without affecting the performance.

It can be seen from Figure 3 that the viscosity of PSAs without stabilizer increased significantly with the storage time even within 12 h. The viscosity of PSAs with stabilizer (20 wt % methanols) increased only slightly during the first hour after adding AlACA, then, it tended to be stable.

An organosiloxane monomer used in this work refers to 3-methacryloxypropyl trimethoxy silane (TMSPMA). TMSPMA contains a vinyl group which can participate in copolymerization with acrylic monomers, as well as an alkoxy group which may



Scheme 1. Mechanism of crosslinking reaction of AlACA and acrylic copolymer.

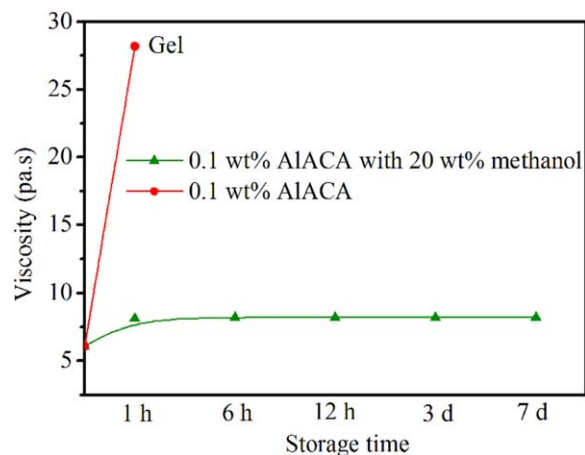


Figure 3. Effect of stabilizer solvent methanol on the viscosity of cross-linked PSA during storage. (Monomer ratio: BA : VAc : AA = 85 : 10 : 5 wt %; Reaction temperature: 82°C; BPO concentration: 0.7 wt %; Reaction time: 8 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

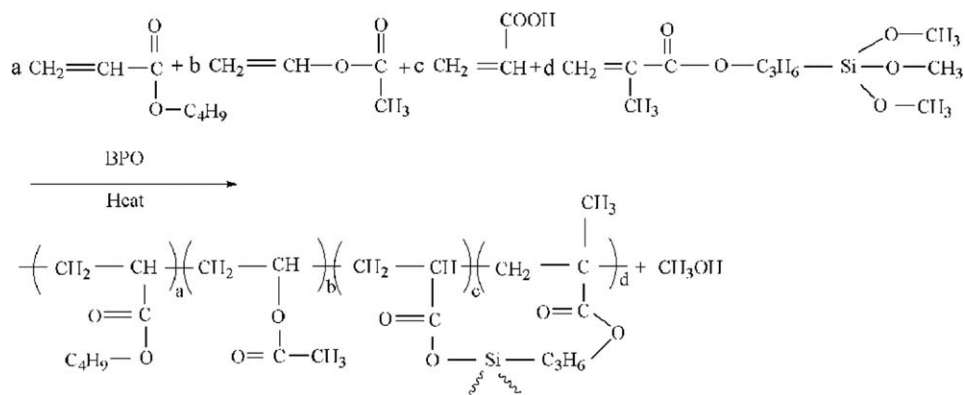
react with carboxyl groups to form crosslinking structure. In the solution polymerization process, the viscosity increases extremely quickly as TMSPMA is fed with the existence of acrylic acid. This gelling phenomenon can be avoided effectively by adding methanol to the solution. This can be explained that methanol is the byproduct of the crosslinking reaction so the sufficient methanol existence in the system will retard the crosslinking reaction. The crosslinking reaction occurs only in the process of solvent evaporation. This principle improves the storage property of organosiloxane-modified acrylic PSAs. The mechanism of crosslinking reaction of TMSPMA and acrylic copolymer was shown as Scheme 2, which was similar to the ether exchange reaction that occurred when a carboxylic or hydroxyl acrylic resin was cross-linked by the etherified melamine formaldehyde resin.

Effect of Molecular Weight on Adhesive Properties

To study the influence of the molecular weight, five samples of PSAs were prepared with which had the same glass transition temperature ($T_g = -42^\circ\text{C}$). Polymer molecular weights were regulated using different initiator concentrations. Figure 4 indicated that an increase in the initiator (AIBN) concentration resulted in the decrease in M_w as expected, which also led to the decrease in the viscosity. The molecular weight distribution narrowed as M_w decreased. It was found that shear strength was improved as molecular weight increased as shown in Figure 5. The research indicated that the shear strength varied from 20 min to 32 h when the molecular weight varied from 1.226×10^5 g/mol to 12.16×10^5 g/mol. Dahlquist²⁷ proposed a formula for the relationship between the shear resistance time and the zero-shear viscosity, as shown by eq. (1).

$$t = \frac{l^2 \cdot b \cdot \eta_a}{2W \cdot g \cdot a} \quad (1)$$

t : time to failure in seconds, g : acceleration of gravity, b : width of PSAs tape in cm, l : shear creep length in cm, W : mass of loaded weight in grams, a : thickness of PSAs tape, η_a : viscosity of the PSAs in poises.



Scheme 2. Mechanism of crosslinking reaction of TMSPMA and acrylic copolymer.

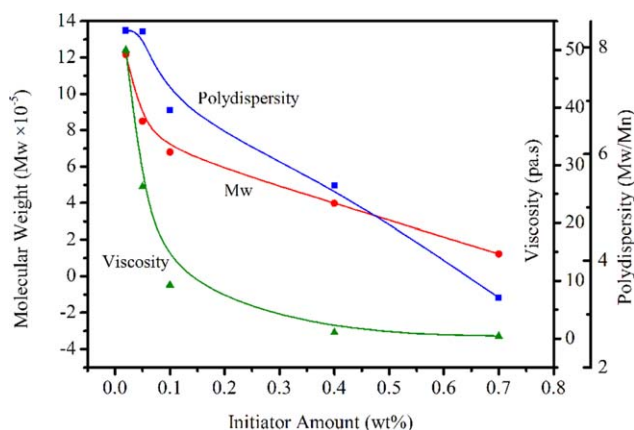


Figure 4. Effect of initiator amount on molecular weight and viscosity. (Monomer ratio: BA : VAc : AA = 85 : 10 : 5 wt %; Reaction temperature: 82°C; Reaction time: 8 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The justifiability of this equation is restricted by that the shear slip is negligible, initial rate of shear is very low, the time to failure should be long enough, and the failure mode is cohesive failure. The steady shear viscosity is proportional to the 3.4

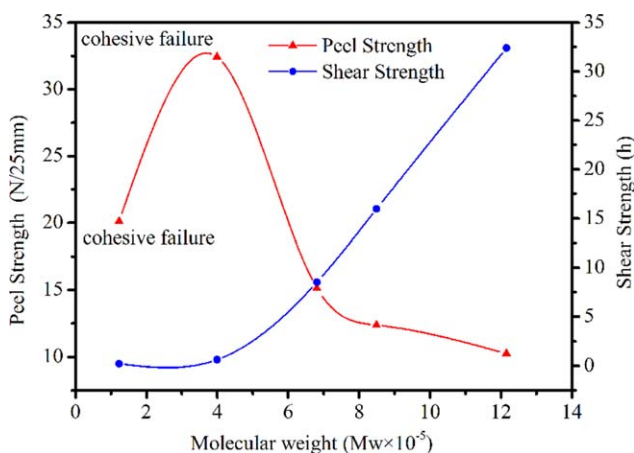


Figure 5. Effect of molecular weight on adhesive properties. (Monomer ratio: BA : VAc : AA = 85 : 10 : 5 wt %; Reaction temperature: 82°C; Reaction time: 8 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

power of Mw for a monodisperse polymer. This equation suggests that the higher the molecular weight, the higher the shear strength; however, when the molecular weight is too high, the internal flow may not obey shear flow and possible slip may occur. Furthermore, the shear strength is also influenced by entanglement molecular weight (M_e) calculated according to this eq. (2) below⁵:

$$M_e = \frac{\rho RT}{G_n'} \quad (2)$$

ρ : density of polymer, R : 8.31 J/(mol·K), T : absolute temperature for the onset of rubbery plateau, G_n' : G' at the onset of rubbery plateau region. Tobing²⁸ and Klein's research proved that a higher M_w/M_e ratio resulted in a higher shear strength. When the side chain length of acrylic monomers increased, the entanglement molecular weight became higher, which represented it was more capable of forming fibrils during peeling.²⁹ These factors were maybe the reasons that eq. (1) could qualitatively but not quantitatively describe our data.

Figure 5 also indicated that when the molecular weight was below 4×10^5 g/mol, cohesive failure could occur during the peeling test. A PSA with a low M_w tended to be viscous flow, which helped increase the peel strength; however, it did not have sufficient viscoelastic energy dissipation (VED) during the peeling process which resulted in cohesive failure. When the molecular weight was above 6×10^5 g/mol, a complete interface adhesion failure occurred during the peeling process as shown in Figure 5, which proved that the internal cohesive energy tended to be higher than the interface adhesion energy for the PSAs when the M_w increased. Thus the M_w in a suitable range should be selected in order to achieve both the internal cohesive strength and interface adhesion strength, and for our case the optimal M_w was 6.8×10^5 g/mol.

Effect of Crosslinking on Adhesive Physical Properties

The cross-linker AICA and the organosiloxane monomer TMSPMA were added to improve the shear strength of the PSAs for applications at high temperature (150°C). It can be seen from the Figure 6 that AICA had a significant influence on the shear strength of PSAs. The cohesive strength of adhesive was improved as a result of the formation of crosslinking network. For the PSA crosslinked by AICA, shear strength of 24 h

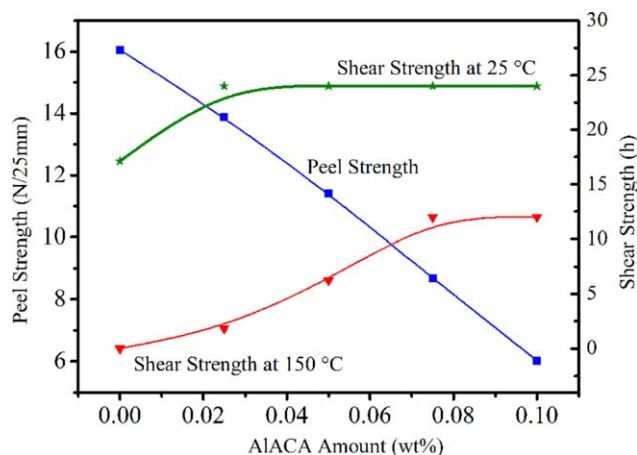


Figure 6. Effect of cross-linker (AlACA) amount on adhesive properties. (Monomer ratio: BA : VAc : AA = 85 : 10 : 5 wt %; Reaction temperature: 82°C; BPO concentration: 0.7 wt %; Reaction time: 8 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

can be achieved without any shift at room temperature when the amount of AlACA larger than 0.02 wt %, best larger than 0.05 wt % was applied. When the amount of AlACA added was less than 0.05 wt %, the quantity of crosslinking points formed by metal ions was limited, resulting in a lower shear strength and cohesive failure during high temperature tests. When the amount of AlACA was higher than 0.08 wt %, the shear strength remained above 12 h at 150°C, which reached the same level of a high thermo-resistance PSA, which was synthesized by an acrylate base polymer and a metal-chelate cross-linker.¹⁵ As the crosslinking density increased, the gel amount increased, which was responsible for good shear strength. The shear strength can also be reflected by the average molecular weight between crosslinking points (M_c), which can be calculated by the equation below³⁰:

$$M_c = \frac{V_1 \rho [\varphi^{1/3} - \varphi/2]}{-[\ln(1-\varphi) + \varphi + x\varphi^2]} \quad (3)$$

V_1 : molar volume of toluene (106 cm³/mol), χ : polymer-solvent interaction parameter, φ : volume fraction of polymer in toluene, ρ : density of polymer.

Tobing and Klein's research revealed that acrylic linear polymers were able to form a continuous network when the $M_c \geq M_e$.⁹ It was reported that the increase of cross-linker amount led to a decrease in M_c , resulting in an increase in crosslinking density and cohesive strength of PSAs. As shown in Figure 7, shear strength also increased with an increase in TMSPMA amount for PSA 10 - PSA 14.

The peel strength exhibited a decrease tendency as the concentration of cross-linker increased. It can be attributed to the enhancement of crosslinking density reduced the wetting degree between the bonding surfaces and the adhesives. The M_c decreased with the enhancement of crosslinking density, which therefore, resulted in a lower VED during debonding.

The effects of the cross-linker AlACA and organosiloxane monomer TMSPMA on the thermo-resistance property were

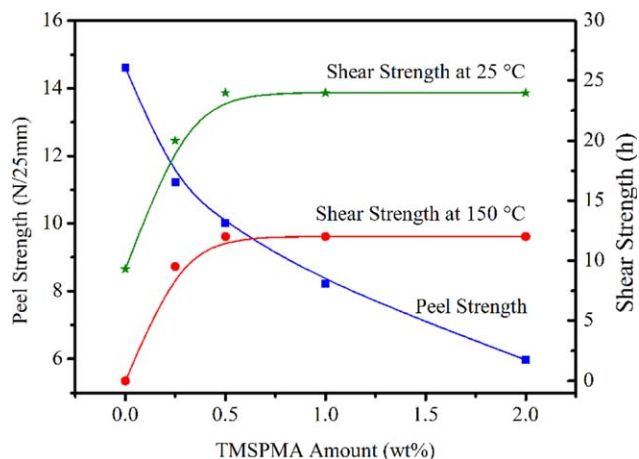


Figure 7. Effect of TMSPMA amount on adhesive properties. (Monomer ratio: BA : VAc : AA = 85 : 10 : 5 wt %; Reaction temperature: 82°C; BPO concentration: 0.7 wt %; Reaction time: 8 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

also investigated. Figure 8(b) indicated that the uncrosslinked PSA had a poor peeling resistance and no matter whether it was at room temperature or 150°C, there was always a residue left on the test panel. The PSAs crosslinked by AlACA had an improved peeling property that the PSA did not have residue left at room temperature although it had an obvious residue when it was peeled at 150°C, which implied that crosslinking by AlACA was insufficient and the cohesive strength of the PSAs was not high enough to be used as a thermo-resistance PSA, as shown in Figure 8(a). Figure 8(c) demonstrated that when TMSPMA was used as the cross-linker, the peeling performance was significantly improved and no matter whether it was applied at room temperature or 150°C, no residue was left on the test panel for a peeling operation. The thermo-resistance test showed evidence that single-component acrylic PSAs cross-linked by TMSPMA remained effective at 150°C. The single-

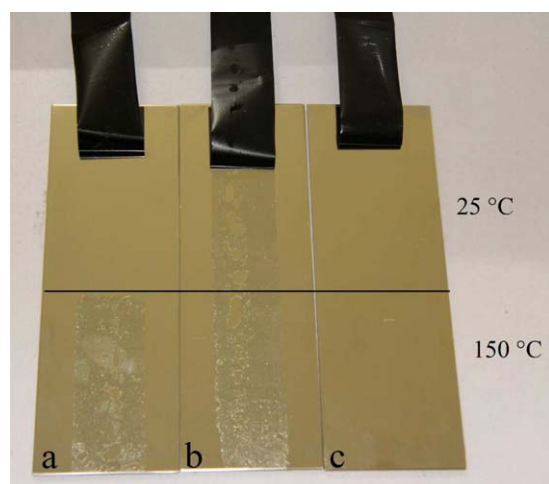


Figure 8. Thermo-resistance test of the PSA at 150°C and 25°C peeling temperature. (a) PSA crosslinked by 0.1 wt % AlACA; (b) PSA uncrosslinked; (c) PSA crosslinked by 2 wt % TMSPMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

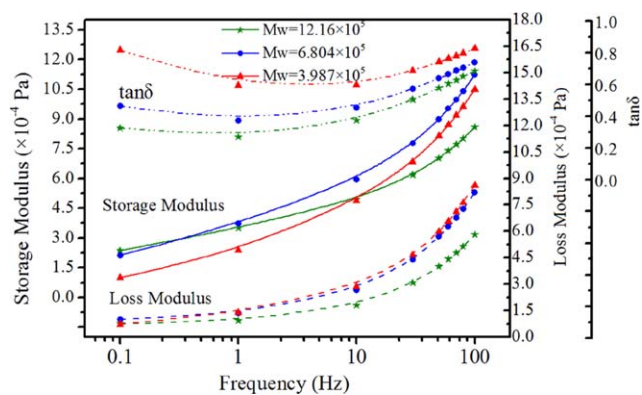


Figure 9. Effect of molecular weight on storage modulus, loss modulus, and $\tan\delta$ of the synthesized adhesives in frequency sweep measurement. (Monomer ratio: BA : VAc : AA = 85 : 10 : 5 wt %; Reaction temperature: 82°C; Reaction time: 8 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

component PSAs provided possibility of replacing majority of multi-component crosslinked PSAs for its convenience in real coating process and its stable property in storage process.

Dynamic Viscoelastic Properties

The storage modulus (G') is determined by the elasticity property of PSAs, while the loss modulus (G'') is determined by the viscosity property. The damping factor ($\tan\delta$) is equal to G''/G' , reflecting the proportion of viscous component. According to test standards PSTC-1 and PSTC-7, the shear strength test is conducted with a static force applied at a very low frequency (0.01–1 Hz) while the 180° peel test is conducted with a dynamic force at high frequency (50–100 Hz). The relationship between peel energy and shear modulus is according to Yang's formula.³¹

$$P \propto I \times G''(\omega_1) / G'(\omega_2) \quad (4)$$

P : peel energy in J/m^2 , I : intrinsic surface energy in J/m^2 , G' : shear storage modulus in Pa, G'' : shear loss modulus in Pa, ω_1 : debonding frequency at 70 Hz, ω_2 : bonding frequency at 0.1 Hz. This formula indicates that peel strength is proportional to the ratio of loss modulus (G'') at debonding frequency to storage modulus (G') at bonding frequency. Figure 9 presented the effect of molecular weight on the modulus at both bonding and debonding frequency. The $G''(\omega_1)$ value for molecular weight at 3.987×10^5 g/mol, 6.804×10^5 g/mol and 12.16×10^5 g/mol were 70972 Pa, 67576 Pa and 47753 Pa, respectively, where $\omega_1 = 70$ Hz; and the $G'(\omega_2)$ values were 9206 Pa, 21190 Pa and 23659 Pa, respectively, where $\omega_2 = 0.1$ Hz. Therefore the $G''(\omega_1)/G'(\omega_2)$ ratio were 7.709, 3.189 and 2.018 respectively. The decrease in modulus ratio as presented in Figure 9 was correspondent to the decrease in peel strength as presented in Figure 5.

Figure 9 demonstrated that the storage modulus (G') and the loss modulus (G'') increased as the test frequency increased. At the bonding frequency (0.1 Hz), adhesive synthesized with higher M_w exhibited higher storage modulus, which was consistent with the finding that adhesives synthesized with higher M_w

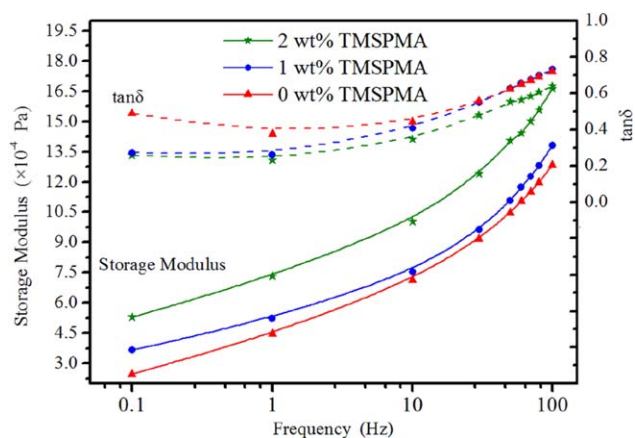


Figure 10. Effect of TMSPPMA amount on storage modulus, $\tan\delta$ of the synthesized adhesives in frequency sweep measurement. (Monomer ratio: BA : VAc : AA = 85 : 10 : 5 wt %; Reaction temperature: 69°C; BPO concentration: 0.7 wt %; Reaction time: 8 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

exhibited higher shear strength, as shown in Figure 5, indicating that increasing M_w improved the PSA elasticity.

The loss modulus (G'') decreased with the increase in the M_w , especially in the debonding frequency range (50–100 Hz). The $\tan\delta$ decreased with the increase in the M_w in the entire investigated frequency range. This was consistent with the conclusion that the adhesive synthesized with lower M_w exhibited higher 180° peel strength when the M_w was above 3.987×10^5 g/mol, indicating that the decrease of M_w improved the PSA viscosity in the investigated range.

Figure 10 revealed that crosslinking played an important role in the viscoelasticity of PSAs. The storage modulus increased with the increase in the TMSPPMA amount, especially at the bonding frequency while the $\tan\delta$ value of the adhesive decreased with the increase of TMSPPMA amount. The results proved that the samples with higher amount of TMSPPMA exhibited a higher G' and a lower $\tan\delta$, which implied a higher cohesive strength and improved shear strength. In other words, the crosslinking reaction improved elasticity proportion of PSAs. In order to achieve superior shear strength or heat resistance, the storage modulus at bonding frequency should be high enough, or at least be 3.0×10^4 Pa in the investigated range.

Figure 11 indicated the effect of TMSPPMA on the storage modulus, loss modulus, and $\tan\delta$ of the synthesized adhesives in temperature sweep. As the temperature increased, the storage modulus decreased while the loss modulus increased. The $\tan\delta$ peak temperature was at around 0°C. For samples crosslinked with 2 wt % TMSPPMA, the onset storage modulus was higher than that of samples without any crosslinking. In the whole scanning process, the samples crosslinked with 2 wt % TMSPPMA remained solid-like state ($G'' < G'$, $\tan\delta < 1$), which indicated that the elastic component dominated the viscoelastic behaviors. However, the samples without crosslinking transformed from solid-like state ($G'' < G'$, $\tan\delta < 1$) to fluid-like state ($G'' > G'$, $\tan\delta > 1$). The viscous component started to dominate the viscoelastic behaviors when temperature

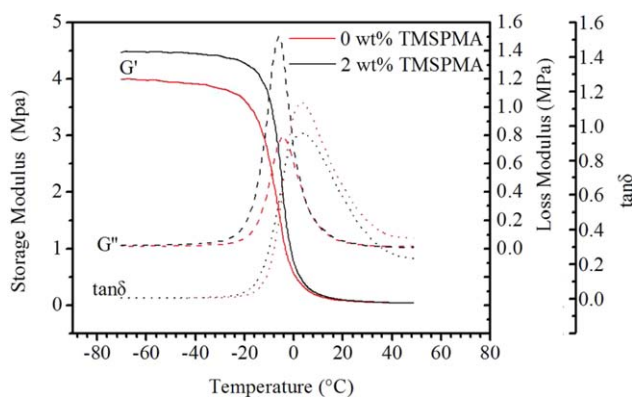


Figure 11. Effect of TMSPMA amount on storage modulus, loss modulus, and $\tan\delta$ of the synthesized adhesives in temperature sweep measurement. (Monomer ratio: BA : VAc : AA = 85 : 10 : 5 wt %; Reaction temperature: 69°C; BPO concentration: 0.7 wt %; Reaction time: 8 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

approached to -10°C . This result indicated that the existence of crosslinking network was responsible for making the PSA remain elastic-dominated state throughout the temperature ranged from -75°C to 55°C .

Figure 12 revealed the effect of tackifier resin on the viscoelastic behaviors of the PSAs. The blend of tackifier resin and adhesive led to higher loss modulus compared to neat acrylic PSAs, especially in the debonding frequency range. The $\tan\delta$ of the tackified adhesive was higher than that of neat adhesive in the debonding frequency range. The $G''(\omega_1)$ values for neat PSA, PSA with 10% rosin resin and PSA with 10% terpene resin were 100600 Pa, 123,300 Pa and 149,900 Pa, respectively, where $\omega_1 = 70$ Hz; and the $G'(\omega_2)$ values were 39,720 Pa, 33,050 Pa, and 33,090 Pa, where $\omega_2 = 0.1$ Hz respectively. Therefore the $G''(\omega_1)/G'(\omega_2)$ ratio were 2.532, 3.731, and 4.530, respectively. According to our discussion above, the result suggested adhe-

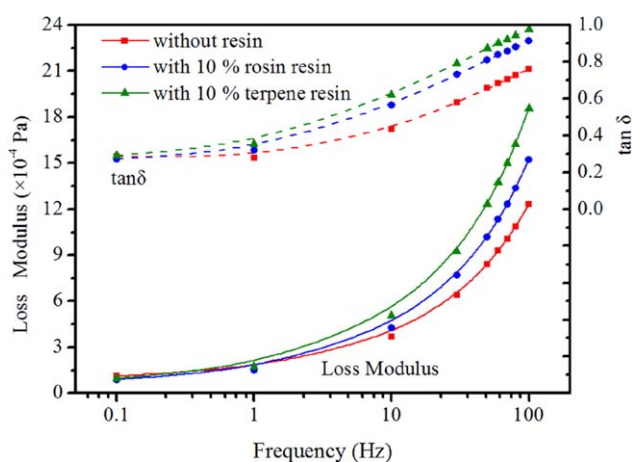


Figure 12. Effect of tackifier resin on loss modulus and $\tan\delta$ of the synthesized adhesives in frequency sweep measurement. (Monomer ratio: BA : VAc : AA = 85 : 10 : 5 wt %; Reaction temperature: 69°C; BPO concentration: 0.7 wt %; Reaction time: 8 h; TMSPMA amount: 0.5 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sives with tackifier resin had a higher peel strength because a higher $G''(\omega_1)/G'(\omega_2)$ ratio gave a higher VED. Besides, the adhesive tackified with 10% terpene resin showed the highest loss modulus in the debonding frequency range, indicating the adhesive might have the highest peel strength due to the excellent wetting degree between the adhesive and the surface.

Surface Energy and Work of Adhesion

The viscoelasticity of PSAs determined the properties that PSAs could generate viscous flow when a slight pressure applied, however, the tight contact would not bring out the high adhesion when the wetting degree between the PSAs and surfaces was not effective or sufficient. The wetting degree can be evaluated by the interfacial tension and adhesion work (Wa) between the PSAs and bonding surfaces.³² In our research, the contact angle and surface energy were calculated to reveal the relationship between adhesion work and peel strength based on tackified acrylic PSA. Adhesion work, defined as thermodynamic work expended for separating two bonding phases into independent phase, can be calculated by this equation²⁶:

$$Wa = r_A + r_s - r_{AS} \quad (5)$$

Combined with equation²⁶:

$$r_{AS} = r_A + r_s - 2(r_A^d r_s^d)^{1/2} - 2(r_A^p r_s^p)^{1/2} \quad (6)$$

Then 26

$$Wa = 2(r_A^d r_s^d)^{1/2} + 2(r_A^p r_s^p)^{1/2} \quad (7)$$

where γ_A^d and γ_A^p represent disperse and polar contribution of adhesive surface tension in N/m, γ_s^d and γ_s^p represent disperse and polar contribution of bonding surface tension in N/m. These parameters can be calculated from the standard test liquid's contact angle ($\cos\theta$) using this equation²⁶:

$$\cos\theta = 2/r_A \times [(r_A^d r_s^d)^{1/2} + (r_A^p r_s^p)^{1/2}] - 1 \quad (8)$$

The contact angle results and calculated surface tension, adhesion work were summarized in Table II. Water and glycol were selected as standard liquid to obtain disperse and polar contribution of surface tension. The disperse component, polar component and surface tension of water were 21.8 mN/m, 51 mN/m, and 72.8 mN/m, respectively, while for glycol the values were 33.8 mN/m, 14.2 mN/m, and 48 mN/m, respectively. It was observed that contact angle decreased when the tackifier resins were added. The calculated adhesion work showed a dependent relationship with the measured peel strength in Table II. In other words, higher calculated adhesion work tended to result in higher peel strength. This conclusion can also be explained by the following equation established with the energy balance principle²¹:

$$P/b = \frac{Wa}{1 - \cos\theta} \quad (9)$$

P : peel strength, b : width of adhesive tape, θ : peel angle, Wa : adhesion work. This equation indicates that the peel strength is

Table II. Contact Angel and Calculated Surface Tension, Adhesion Work of Tackified PSAs

Samples	Average Contact Angel ^b (°)		Surface tension γ (mN/m)		Adhesion work (mN/m)	Average peel strength ^b (N/25mm)
	Water	Glycol	γ^d (mN/m)	γ^p (mN/m)		
0% resin	110.1(0.5)	86.9(0.7)	13.8	0.8	33.8	9.3(0.2)
20% GA-AT ^a	106.8(0.2)	85.9(0.4)	12.9	1.6	37.9	10.4(0.3)
10% GA-AT ^a	104.7(0.8)	83.7(0.3)	13.5	2.0	40.0	12.8(0.3)
10% GA-100 ^a	102.1(0.1)	81.4(0.5)	13.7	2.6	42.8	13.6(0.3)
10% TP-96 ^a	99.8(0.8)	78.3(0.8)	14.0	3.3	45.8	16.8(0.3)
Stainless Steel	52.2(0.5)	43.9(0.9)	9.5	38.6		

^aGA-AT: rosin glycerol ester (M_n : 810, PDI: 1.3, softening point: 85°C), GA-100: rosin pentaerythritol ester (M_n : 1100, PDI: 1.3, softening point: 100°C), TP-96: terpene phenolics resin (M_n : 520, PDI: 1.3, softening point: 95°C).

^bThe results quoted were the average of three determinations. The number in the brackets indicated the standard deviation of these determinations.

proportional to the adhesion work when the test condition is constant. According to the results presented in Table II, PSAs tackified with 10% terpene resin produced the highest adhesion work and highest peel strength on the stainless steel surface, which was consistent with the conclusion showed in Figure 12 that the highest $\tan\delta$ and VED were obtained due to the PSAs tackified with 10% terpene resin had the most effective wetting degree. The probably reason was the terpene resin had the lowest molecular weight, which made a great contribution to improving wetting degree.

DSC Analysis

The glass transition temperature of uncrosslinked and cross-linked PSA films was compared. The T_g of uncrosslinked copolymer obtained using the Fox equation was about -42°C for PSA 1–5, however, the measured value was -39°C , higher than the calculated value. The reason might be that hydrogen bonds in polymer chain were formed between the polar carboxyl groups, which made a contribution to physical crosslinking. Figure 13 revealed that T_g values increased with an increase of

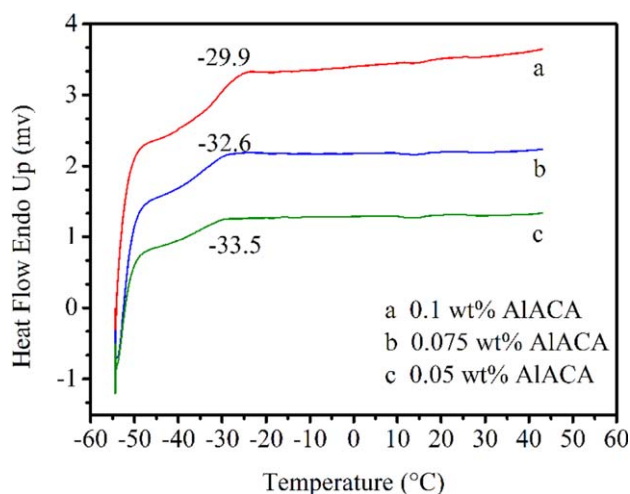


Figure 13. Effect of cross-linker (AlACA) amount on T_g . (Monomer ratio: BA : Vac : AA = 85 : 10 : 5 wt %, Reaction temperature: 82°C, BPO concentration: 0.7 wt %, Reaction time: 8 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cross-linker amount. The chemical network achieved by cross-linking reaction restricted the motion of molecular chains, which elevated the glass transition temperature of the PSAs.

CONCLUSIONS

Poly(butyl acrylate-vinyl acetate-acrylic acid) based acrylic pressure sensitive adhesives were synthesized by solution polymerization. A variation of initiator concentration resulted in different M_w and shear modulus. The dependence of the adhesive properties on initiator concentration could be explained by the modulation of viscoelastic property. The results demonstrated that higher storage modulus in bonding frequency represented higher shear strength properties and higher loss modulus in debonding frequency represented higher peel strength.

The thermo-resistant property of the PSAs was improved by the addition of the cross-linker AlACA and modified monomer TMSPMA. During storage, the addition of methanol was shown to prevent unwanted crosslinking and the associated increase in viscosity, which made the crosslinked PSAs a single-component system. The adhesive properties at elevated temperature were significantly improved due to the crosslinking network formation. The adhesive tapes remained effective at 150°C.

The T_g and shear storage modulus increased due to the formation of a crosslinking network. The shear storage modulus of crosslinked PSAs was higher than that of uncrosslinked PSAs, while the $\tan\delta$ was lower.

The peel strength increased as the tackifier resin was added, as a result of adhesion work improvement. The PSAs tackified by terpene resin exhibited the highest tackifying effect because it gave the highest VED.

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