

Siloxane-modified polyacrylate low-residual pressure-sensitive adhesive with high peeling strength

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ABSTRACT: A low-residual siloxane-modified polyacrylate pressure-sensitive adhesive (PSA) with a high peeling strength was prepared by seeded semicontinuous emulsion polymerization. 3-Glycidyoxypropyltrimethoxysilane was introduced into the acrylic (AC) PSA through a thermal posttreatment method to crosslink with AC. To improve the adhesion properties, a polymeric emulsifier, 2-acrylamido-2-methyl-1-propanesulfonic acid, was introduced into the system with the conventional emulsifier. Several key polymerization conditions, such as the initiator concentration, mass ratio of soft monomer to hard monomer, the content of polymeric emulsifier, and siloxane dosages were examined in detail. Then, the optimal conditions and a proper preparation process were established. The results show that we achieved not only a low repeeling residue with high tack and peeling strength but also excellent properties of high-temperature aging resistance and water resistance. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42975.

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INTRODUCTION

Pressure-sensitive adhesives (PSAs) are viscoelastic materials that can adhere feasibly to a variety of surfaces with the application of slight pressure.^{1–3} PSAs are used in various fields and range from protective films, medical tape, and masking tape to removable labels or office notes.^{4–6} With the rapid development of electronic products, protective PSA films with better adhesive properties are needed, in particular PSAs with lower peeling residues.

The problem, which pertains to the packing of the electronic products, is the residue left on the surface when the PSA is peeled off. The electronic product's surface, such as a touch screen or shell, gets stained. There are some methods for reducing this glue residue. The most effective routes are the addition of extra crosslinker to the system and the modification of the PSA with silane to increase the inner cohesion.^{7–11} Although the addition of extra crosslinker can improve the cohesion and high-temperature resistance, this occurs at the expense of the peeling strength.¹² Silane-modified polyacrylate PSAs are better alternatives. The use of silane-modified polyacrylate PSAs has drawn considerable attention from a wide range of scientific and applied viewpoints

because these PSAs usually exhibit excellent performance of both silane and polyacrylate (AC). The combination of these two polymers gives the product better properties, including a higher reliability, a remarkable water resistance, and excellent thermal stability, and other novel properties.^{13–19}

Previous studies have shown that it has proven difficult to improve the tack, peeling strength, and shear strength simultaneously.²⁰ Moreover, the conversion of silane-modified AC latex was low.^{20,21} So far, most studies have focused on improving the conversion and adhesive properties of silane-modified polyacrylate PSAs. The effects of the pH value of the polymerization system, species, dosage, and feeding time of siloxane on the emulsion polymerization and film formation have been studied systematically.^{18,22,23} The effects of the chain-transfer agent, gel fraction, molecular weight, and crosslinking reactions on the AC emulsion and adhesive properties have been examined as well.^{24,25} Marcu *et al.*²⁰ studied the mechanism of alkoxy silane-based crosslinking and the copolymerization between siloxane and AC. They found that reducing the hydrolysis of the siloxane was a better way to solve the problem. To prevent hydrolysis and coagulation, alkoxy silane is usually added in the latter stage

of the semicontinuous process. Recently, the influence of the polymer microstructure on the performance of posttreated PSA was investigated.^{26,27} Posttreatment methods were found to be effective. They could improve the tack and peeling strength with little sacrifice of shear strength of pure AC PSA.²¹

However, few studies have been reported so far on the incorporation of siloxane into polyacrylate systems through a new manner of thermal postheating processes. To increase the cohesion and reduce the residue of PSA without sacrifices in the tack and peeling strength, 3-glycidyoxypropyltrimethoxysilane (KH560) was used in this study. The hydrolysis and coagulation issues were resolved by the thermal postheating process. A polymeric emulsifier was incorporated into the system to improve the tack and peel strength. Before this study, the effects of siloxane on the properties of PSA had not been studied. To achieve these goals, in this study, AC-Si emulsions were obtained through a seeded semicontinuous emulsion polymerization method²⁸ with different amounts of siloxane. The acrylic (AC) groups of the functional monomer acrylic acid (AA), the amino groups of the polymeric emulsifier surfactant 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), and the epoxy groups of the KH560 reacted with each other during the thermal posttreatment process of film formation. Thus, siloxane was grafted onto the polyacrylate chains. The effects of KH560 on the microstructure and adhesive properties of PSA were also studied.

EXPERIMENTAL

Materials

AA (99%), butyl acrylate (BA; 99%), and anhydrous calcium chloride (CaCl_2 ; 98%) were purchased from Tianjin Kernel Chemical Reagent Co. (China).

Potassium persulfate (KPS; 99.9%), 2-ethylhexyl acrylate (2-EHA; 99%), 2-hydroxypropyl acrylate (HPA; 98%), sodium dodecyl sulfate (SDS; 99%), hydroquinone (99.5%), KH560 (97%), and AMPS (98%) were purchased from Aladdin Reagent (Shanghai). Methyl methacrylate (MMA; 98%), styrene (St; 99%), tetrahydrofuran (THF; 99.5%), and polyoxyethylene alkyl phenyl ether (OP-10; 99%) were obtained from Jiangsu Yonghua Fine Chemicals (China). Ammonia solution and sodium bicarbonate (NaHCO_3 ; 99%) were purchased from Guangzhou Chemical Reagent Factory of China. All of these materials were used as received. Deionized water was used for all of the polymerization and treatment processes.

Preparation of Siloxane-Modified AC PSA Latexes and Films

A seeded semicontinuous emulsion polymerization was used to prepare the PSA emulsion latexes.^{28,29} All of the mixed acrylate monomers (BA, 2-EHA, MMA, St, AA, and HPA; the total mass of the monomers was 80 g) were charged into the aqueous solution of the surfactants (1.2 g of mixed AMPS, SDS, and OP-10 dissolved in 48 g of H_2O) and stirred at a high speed of 12,000 rpm to obtain the pre-emulsion. Polymerization was carried out in a 500-mL, four-necked, round-bottomed flask equipped with a condenser, thermometer, and mechanical stirrer rotating at 230 rpm. Persistent instillation was carried with two feed inlet tubes to pump the initiator and pre-emulsion into the flask. Seeded emulsions were prepared at 80°C for about 30

min with the addition of 46 g of H_2O , 0.2 g of NaHCO_3 , 10 wt % pre-emulsion, and 40 wt % of the total amount of KPS. When the seeded emulsions showed blue light, the remaining 90 wt % pre-emulsion and the initiator solution (one-half of the total amount of KPS dissolved in 24 g of H_2O) were pumped into the flask through two separate tubes at a constant rate for 180 min. Then, a certain amount of KH560 was added with stirring for 0.5 h. To increase monomer conversion, the remaining initiator solution (10 wt % of the total amount of KPS dissolved in 2 g of H_2O) was added to the flask, and the system was allowed to react for another 2 h at 80°C. After polymerization, hydroquinone was added to the latex to stop the reaction. Finally, the emulsion latex was obtained through the adjustment of the pH to 7 through the addition of ammonia with mechanical stirring after the mixture cooled down to 40°C.

A thermal posttreatment process was used to prompt the grafting of KH560 onto the polyacrylate molecular chains. The emulsion latexes were coated onto 20 μm thick poly(ethylene terephthalate) films with a bar coater. The coated films were dried in a convection oven at 90°C for 20 min to remove the residual water of the latex. Then, they were heated at 120°C for another 20 min to prompt the reaction of the functional groups from KH560, AMPS, AA, and HPA. The PSA films were conditioned at room temperature for 24 h before testing.

Characterization

Monomer Conversion. After the polymerization, samples withdrawn from the flask were short-stopped by hydroquinone and analyzed gravimetrically to determine the conversion (on the basis of the mass amount of monomer fed). The monomer conversion was calculated by the following equation:

$$\text{Conversion (\%)} = \frac{M_0 \times X - M_2}{M_1} \times 100\% \quad (1)$$

where M_0 is the total feeding amount, M_1 is the total feeding amount of the monomers, X is the solid content, and M_2 is the amount of nonvolatile components (emulsifier, initiator, and buffer).

Particle Size. The particle size was measured by dynamic light scattering. Analysis was performed with the a Malvern Nanowire 90 instrument at 25°C with a goniometer set to a scattering angle of 90°. The obtained results were used to calculate the average particle size of the latexes.

Viscoelastic Property Measurement. Rheological measurements were performed on an AR-G2 rotational rheometer (TA Instruments) equipped with a 40-mm steel plate to analyze the viscoelastic properties of the PSA.

Thermal Analysis. Differential scanning calorimetry was performed to determine the glass-transition temperature (T_g) of the PSAs before and after modification with KH560. A Mettler-Toledo DSC821 instrument with nitrogen cell purification was used to perform the analysis at a heating rate of 20°C/min from -80 to 120°C. The thermal curves of thermogravimetric analysis were recorded with a PerkinElmer analyzer. The temperature ranged from 40 to 600°C at a heating rate of 10°C/min under a nitrogen atmosphere.

Table I. Effect of the Initiator Content on the PSA Performance

$m(\text{initiator})/$ $m(\text{monomer})$	Appearance	Conversion (%)	Tack (ball no.)	180° peeling strength (N/25 mm)	Shear resistance (h)	Aging resistance
0.3:100	Milk white	94.0	9	5.8	510.3	–
0.5:100	Milk white	95.5	13	7.4	358.1	–
0.7:100	Blue light (weak)	96.0	16	8.3	315.2	–
0.9:100	Blue light (strong)	96.9	20	11.2	273.3	–
1.1:100	Blue light (strong)	98.0	12	10.4	146.8	++

All reactions were performed at 353 K. – and ++ represent no glue and a little ghost but no glue left on the panels, respectively.

Contact Angle. A DSA 10 video contact-angle measuring device was used to measure the wettability and water absorption properties of the AC films and KH560-modified AC films. Deionized water was used as the probe liquid. The film was dried at room temperature for 7 days through casting on latex onto glass slide. About three independent measurements were made on different parts of the film to calculate the average contact angle. Each sample was tested six times to obtain the final average contact angle.

Adhesive Properties. The tack was tested according to the national standard GB/T 4825-2002 (China). A series of steel balls with different diameters were tumbled from an incline of 30°. The test result was obtained by the number of the biggest ball being stopped at least three times. The peel adhesiveness at 180° was determined according to GB/T 2792-1998 (China). The shear resistance was tested according to GB/T 4851-1998 (China) at 25°C, and the holding power was expressed as the time required for the standard area of PSA strips to shear from the stainless steel panels. The high-temperature shear resistance was tested according to GB/T 4851-1998 (China) except that the temperature was set to 100°C.

Aging Resistance. The PSA film specimens were attached to stainless steel panels and placed for at least 24 h at 25°C, and then, they were put into the oven to be heated at 70°C for 48 h. When they were cooled to room temperature and repelled from the panels, the amounts of glue and ghost left on the surface of the panels were observed to determine the aging resistance properties of the PSA. A PSA with an excellent high-

temperature aging resistance has no glue and ghost residue left on the panels when peeling off. The abbreviations –, +, ++, and +++ in the tables (shown later) represent no glue and ghost, a little ghost but no glue, a small amount of glue, and a large amount of glue residue left on the panels, respectively.

Fourier Transform Infrared (FTIR) Spectroscopy. The IR spectra of the polyacrylate PSAs modified with KH560 were obtained on an RFX-65 A FTIR spectrophotometer in KBr. The spectra of the dried film were collected within the range of 4000–400 cm^{-1} .

Gel Content Measurement. The gel content of the PSAs was measured by continuous extraction with THF under reflux for 24 h at about 75°C.³⁰ About 1 g of dried latex film was wrapped by two pieces of filter paper to be extracted. After extraction, the gel left in the filter paper was dried and weighed. The gel content was calculated by the following equation:

$$\text{Gel content (\%)} = \frac{M_5 - M_3}{M_4 - M_3} \times 100\% \quad (2)$$

where M_3 , M_4 , and M_5 are the masses of the filter paper, the initial dried latex film with filter paper, and dried latex film with filter paper after extraction, respectively.

Sol Molecular Weight. The sol average molecular weight was determined by an Agilent 1200 Infinity Series gel permeation chromatograph. The dried film was extracted in THF for 24 h to obtain the colloidal dispersion of the sol and gel polymer. The dispersion was filtered before it was injected into the gel

Table II. Effect of the $m(\text{Soft Monomer})/m(\text{Hard Monomer})$ Ratio on PSA Adhesion Properties

$m(\text{soft monomer})/$ $m(\text{hard monomer})$	Theoretical T_g (°C)	Tack (ball number)	180° peeling strength (N/25 mm)	Shear resistance (h)	Aging resistance
21.2:1	–54.6	27	14.1	111.7	+++
18.2:1	–53.4	23	13.6	360.1	+
15.2:1	–52.5	21	8.9	540.8	+
12.2:1	–51.1	16	7.3	716.9	–
9.2:1	–49.0	10	6.9	148.3	+
6.2:1	–45.1	6	4.8	46.5	–

The soft monomers were 2-EHA and BA. MMA and St were the hard monomers. All reactions were performed with $m(\text{BA}/2\text{-EHA}) = 1:1$, $m(\text{MMA}/\text{St}) = 1.3:1$, $m(\text{AA})/m(\text{monomer}) = 2:100$, $m(\text{HPA})/m(\text{monomer}) = 4.5:100$, and $\text{mass } m(\text{KPS})/m(\text{monomer}) = 0.9:100$ at 353 K. –, +, and +++ represent no glue and ghost, a small amount of glue, and a large amount of glue residue left on the panels, respectively.

Table III. Effect of the $m(\text{Polymeric})/m(\text{Conventional})$ Emulsifier Ratio on PSA Adhesion Properties

$m(\text{PE})/m(\text{CE})$	Conversion (%)	Tack (ball no.)	180° peeling strength (N/25 mm)	Shear resistance (h)	Aging resistance	Ca ²⁺ stability	Contact angle (°)
0:3	96.9	16	8.4	240.1	–	–	90.2
1:2	95.8	20	10.1	391.7	–	–	97.5
1:1	96.0	22	12.5	>720	–	–	113.3
2:1	95.1	23	13.7	>720	++	–	110.8
3:0	85	15	6.4	25.8	+	+	106.9

All reactions were performed with $m(\text{emulsifier})/m(\text{monomer}) = 3:100$ and $m(\text{SDS})/m(\text{OP-10}) = 2:1$. –, +, and ++ represent no glue and ghost, a little ghost but no glue, and a small amount of glue residue left on the panels, respectively. Mass (m); polymeric emulsifier (PE); conventional emulsifier (CE).

permeation chromatograph. Polystyrene standards were used for calibration.

RESULTS AND DISCUSSION

Effect of Polymerization on the Adhesive Properties of the Latex Films

To obtain PSA films with excellent performance, the factors that affected the stage of emulsion polymerization were studied first; these included the amount of initiator, the mass ratio of soft monomer to hard monomer, and the ratio of polymeric emulsifier and conventional emulsifier.

As shown in Table I, the monomer conversion and stability of the emulsion basically rose with increasing amount of initiator (KPS). More initiator also caused a decrease in the molecular weight of the copolymer and led to a smaller particle size. A slight decrease in the molecular weight improved the soaking of the PSA to the substrate. The tackiness and 180° peeling strengths were increased. The shear resistance and aging resistance decreased because of the softness of the polymer chains. An excess amount of initiator caused a sharp decrease in the shear resistance; this resulted in glue residue in the aging resistance test. With all of these properties, when the initiator was 0.9 wt % of the total monomers, the stability of the emulsion and adhesive properties of the PSA were better.

Then, the effect of the mass ratio of soft monomer to hard monomer on the performance of the PSA films was studied; the initiator amount was 0.9 wt % of the total monomers. The adhesive properties of the PSA are shown in Table II. When the soft monomer content decreased, the theoretical T_g (calculated according to the Fox equation¹²) increased. Because the stiffness of the polymer chains became stronger, the soaking of PSA to substrate became poorer. Then, the tackiness decreased from 27 to 6 (ball number), the 180° peeling strength decreased from 14.1 to 4.8 (N/25 mm). When the mass ratio of soft monomer to hard monomer decreased from 21.2 to 12.2, the cohesion increased; this was helpful for preventing cohesion destruction during peeling off from the adherent. Therefore, there was less glue residue or ghost left on the surface when the PSA was peeled off. When the ratio was lower than 9.2, the polymer chain became too hard to wet the substrate. It was hard for the PSA to adhere to the surface, so the shear resistance tested was

lower too. So, 18.2:1 was regarded as the proper mass ratio of soft monomer to hard monomer.

As reported by previous studies,^{30–35} emulsifiers play important roles in emulsion polymerization and in the adhesive properties of PSA. To reduce the migration of small molecules to the surface of the PSA and to improve the wettability, a polymeric emulsifier (AMPS) was introduced into the system with a conventional anion and nonionic emulsifier, which produced very good compatibility effects. The effect of the emulsifier ratio on the PSA adhesive properties was investigated as well. As shown in Table III, $m(\text{polymeric})/m(\text{conventional})$, where (m) refers to mass, mass ratio of emulsifier increased from 0:3 to 2:1, the adhesive properties improved notably because of better wettability. The rise in the contact angle from 90.2 to 113.3° was attributed to the reduction of the conventional emulsifier (SDS/OP-10), which had hydrophilic groups in the molecular structure that would have imposed a negative effect on the water resistance of the films.³⁶ However, the addition of an excess amount of AMPS led to a decrease in the monomer conversion to 85% because of the delimitation of the pre-emulsion. This effect might have been related to the coalescence in the latex particles

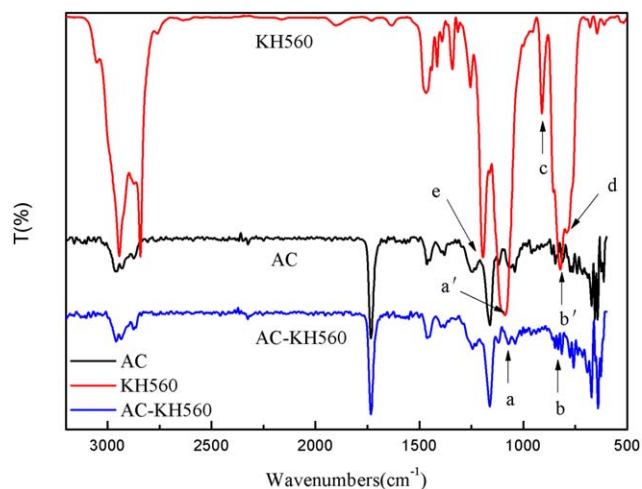


Figure 1. FTIR spectra of KH560, AC, and AC-KH560 with 2.5 wt % KH560. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

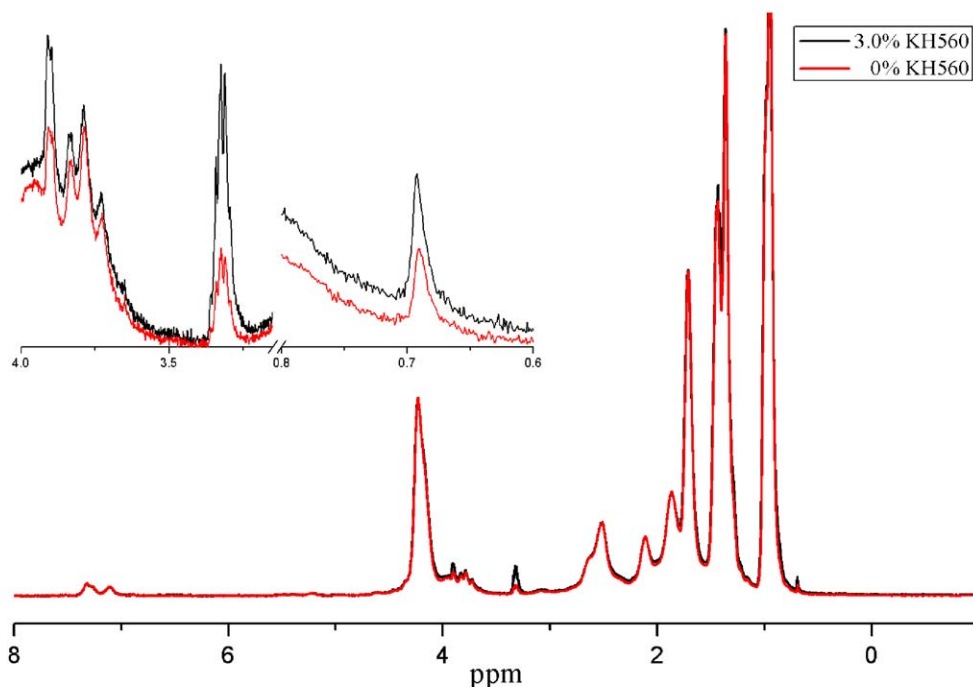


Figure 2. $^1\text{H-NMR}$ spectra of AC-KH560 with 3.0 and 0 wt % KH560. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and the increased gel content induced by self-homopolymerization and the homopolymer of AMPS.³⁷ The incomplete dispersion of unreacted emulsifier in the system caused by the reactive emulsifier AMPS also contributed to the increase in coagulum and the instability of polymerization.³⁸ When the conversions decreased, the adhesive properties declined sharply. Meanwhile, the calcium ion stability decreased. In addition, the extra hydrophilic group provided by the excess amount of AMPS also led to a slight decrease in the contact angle to 106.9° ; this resulted in a decline in the water resistance.³⁹ Therefore, the quantity of the polymeric emulsifier AMPS needed to be better controlled to 50 wt % of the total amount of emulsifier.

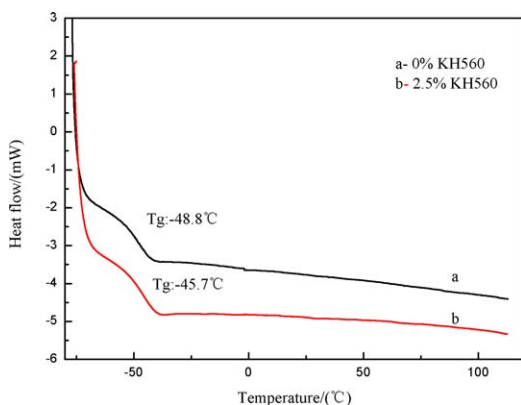


Figure 3. Differential scanning calorimetry thermograms of PSA with and without KH560. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Confirmation of the Grafting of Siloxane onto Polyacrylate

Next, the incorporation of siloxane onto polyacrylate, the microstructure, and its effect on the adhesive properties were studied. The reactions were performed under the optimal conditions of the emulsion polymerization. The initiator dosage was controlled to be 0.9 wt % of the total amount of the monomers. The mass ratio of the soft monomer to hard monomer was 18.2:1. Moreover, the amount of polymeric emulsifier was one-half the amount of the total emulsifier.

To determine the amount of grafting between polyacrylate and siloxane (KH560), the FTIR spectra (shown in Figure 1) of the dried films of the pure AC PSA and the PSA modified with AC-KH560 were studied. Pure AC was prepared according to the procedure of KH560-modified AC except without the addition of the KH560. To demonstrate a clear contrast, the typical IR spectrum of the pure KH560 is also shown in Figure 1.

The FTIR spectra of AC and AC PSA showed that the characteristic absorption peak of the stretching vibrations of the C—H bond from C=C at $3000\text{--}3100\text{ cm}^{-1}$ and the C=C double bond at $1630\text{--}1660\text{ cm}^{-1}$ disappeared; this offered evidence in favor of the completion of the polymerization reaction.³⁵

As shown by a comparison of the IR spectra in Figure 1, the AC-KH560 Spectrum presented a weak peak at 1085 cm^{-1} , which was related to the asymmetric stretching vibrations of Si—O—Si (peaks a and a' in Figure 1). The AC-KH560 spectrum also exhibited a weak peak at 819 cm^{-1} , which was related to the bending vibration absorption of Si—CH₂ (peaks b and b' in Figure 1). These peaks were attributed to the KH560 composite.⁴⁰ The disappearance of the peaks at 1197 cm^{-1} (peak e

Table IV. Effect of the Siloxane Content on the Microstructure of PSA

$m(\text{siloxane})/m(\text{monomer})$	Gel content (wt %)	M_w (g/mol)	M_n (g/mol)	MWD
0:100	77.4	118,000	34,360	3.43
0.5:100	77.3	165,800	47,810	3.47
1.0:100	72.7	158,700	43,790	3.63
1.5:100	73.9	161,600	40,570	3.98
2.0:100	73.8	201,470	49,960	4.04
2.5:100	76.6	219,400	54,700	4.01
3.0:100	76.2	165,300	37,700	4.38

M_w weight average molecular weight; M_n number average molecular weight; MWD molecular weight distribution width.

in Figure 1) and 910 cm^{-1} (peak c in Figure 1) and the peak at 790 cm^{-1} (peak d in Figure 1), attributed to the epoxy group, were assigned to the completion of the reaction between the epoxy group from KH560 and the carboxyl group from the AA unit and the reaction of the epoxy group from KH560 with the amino group from the surfactant AMPS. All of these peaks detected in the FTIR spectra confirmed that KH560 was grafted onto the AC chains during the thermal posttreatment process and the silicone groups were successfully introduced into the copolymer.

In a comparison of the $^1\text{H-NMR}$ spectra in Figure 2, the enhancement of the signal at 0.69 ppm, which was attributed to the hydrogen atom of Si-CH_2 of KH560, was due to the introduction of KH560 into the system. The enhancement of the signals at 3.32 and 3.90 ppm, which were attributed to the hydrogen atom adjacent to the oxygen after the ring opening of the epoxy of KH560, also indicated the graft of KH560 onto the polyacrylate chains.

The differential scanning calorimetry thermograms of the pure AC PSA and KH560-modified PSA (Figure 3) demonstrated that both had only one T_g . This indicated the homogeneous phase between the polyacrylate copolymer and siloxane; this could be regarded as evidence of the successful prevention of the homopolymerization of both acrylate and siloxane at a siloxane content of 2.5 wt %. On the other hand, the cross-

linked network of the KH560-modified PSA provided a higher T_g value than that of the pure AC PSAs.

Effect of Siloxane on the Microstructure and Adhesive Properties of the Composite Latex and Films

To further understand how the siloxane KH560 affected the properties of PSA, the microstructure of the latex films was investigated. Table IV shows the gel content and sol molecular weight and distribution of the PSAs with different amounts of KH560. According to the following equation,⁴¹ the shear resistance was directly proportional to the zero-shear viscosity (η):

$$T = \frac{WL^2\eta}{2tMg} \quad (3)$$

where T is the time to failure, W is the width of the tape, L is the length of the overlap, t is the adhesive thickness, M is the mass weight of the load, and g is the gravitational constant. According to the empirical formulas $\eta = K_1M_w$ ($M_w < M_C$) and $\eta = K_2M_w^{3.4}$ ($M_w > M_C$),⁴² η increases with increasing M_w . So, the increase in average molecular weight (M_w), entanglement molecular weight (M_C). K_1 and K_2 are both proportionality coefficient (shown in Table IV) led to apparent increases in the shear resistance and high-temperature shear resistance (shown in Table V).

Usually, an increase in the cohesion tends to decrease the tack and peel strength and vice versa.⁴³ This phenomenon was

Table V. Effect of the Siloxane Content on the PSA Adhesion Properties

$m(\text{siloxane})/m(\text{monomer})$	Conversion (%)	Tack (ball number)	180° peeling strength (N/25 mm)	Shear resistance (h)	Aging resistance	High-temperature shear resistance (h)	Contact angle (°)
0:100	96.1	17	11.6	163.8	+	2	92
0.5:100	95.7	23	12.7	400.6	-	10.3	103.3
1.0:100	95.9	23	13.5	631.7	-	13.2	108.5
1.5:100	95.6	25	14.2	>720	-	17.7	110.5
2.0:100	95.5	22	13.5	>720	-	26.7	113
2.5:100	95.3	22	13.3	>720	-	>72	113.5
3.0:100	95.1	22	13.0	>720	-	72	111.5

All reactions were performed with $m(\text{polymerizable})/m(\text{conventional})$ emulsifier = 1:1. - and + represent no glue and ghost left on the panels, respectively.

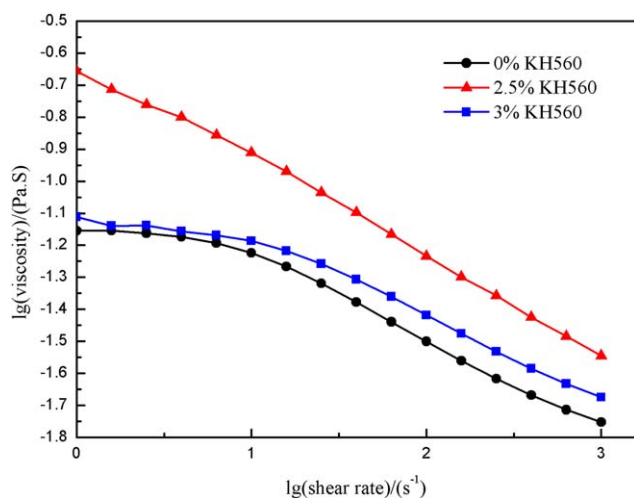


Figure 4. Static steady-shear viscosity curves of PSA with different amounts of KH560. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

particularly evident in the PSA that was modified by the addition of extra crosslinker. To improve the cohesion of the PSAs without sacrifices in the tack and peeling strength, KH560, a siloxane with unique and better dry and wet adhesion properties, was selected to modify the polyacrylate PSA. In contrast to the decreases in the tack and peeling strength of the PSA modified by the commonly used vinyl silicone,⁴⁴ PSA modified by KH560 showed a better adhesive performance. Table V shows that when the content of KH560 was in excess of 2.0 wt % of the total monomer, the tack and peeling strength decreased slightly. This was attributed to their higher values of both gel fraction and M_w (as shown in Table IV).^{11,43,45}

η of PSA was extrapolated from the static steady-shear viscosity curves shown in Figure 4. we deduced that the addition of KH560 to the system lead to the increase in η . Compared with

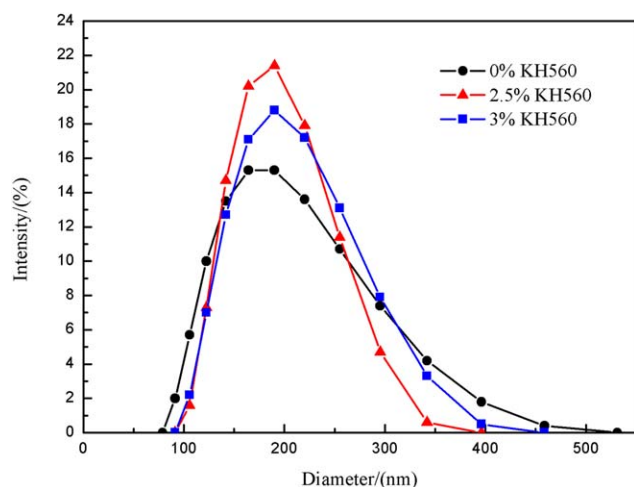


Figure 5. Particle size distributions of PSA with different amounts of KH560. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

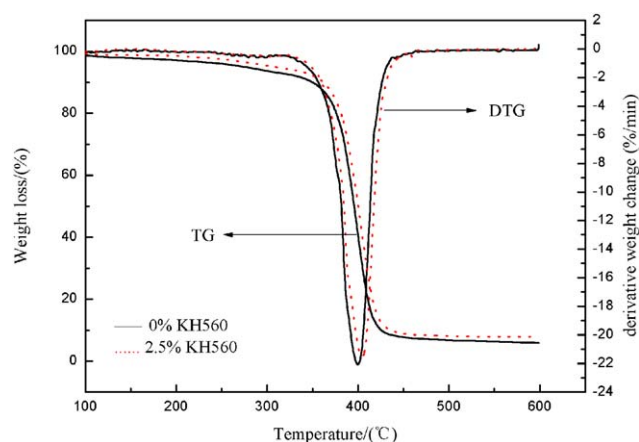


Figure 6. Thermogravimetry (TG) and differential thermogravimetry (DTG) curves of PSA with 0 and 2.5 wt % KH560. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the η of PSA with 2.5 wt % KH560, the slight decrease in η of the PSA with 3 wt % KH560 was due to the lower M_w (shown in Table IV) and the leading role of the plasticizing effect that siloxane played.⁴⁶ The lower η resulted in decreases in the shear resistance and high-temperature shear resistance; this was confirmed by the results shown in Table V. Therefore, the properties of PSA were predicted through the detection and analysis of the static steady-shear viscosity of the emulsion during the polymerization stage. The compliance of siloxane led to better adhesive properties, so when the content of KH560 was no greater than 1.5 wt %, and the tack and 180° peeling strength increased. The adhesive residue, when it was peeling off from the substrate, was reduced from 135 to 1 mg or less after modification with KH560. With the proper amount of KH560, there was only ghost left on the surface. Continuously adding more KH560 would cause decreases in the tack and 180° peeling strength. This could be explained by the fact that the entanglement density was too large.⁴⁷ The smaller polar Si—O bonds and the excellent hydrophobicity of siloxane contributed to a better water resistance in PSA.^{23,48}

As a result, the contact angle increased from 90 to 113.5°. The average particle size was evaluated, as shown in Figure 5. The average particle size of the KH560-modified AC latex was 190 nm. The pure AC latex particle size was 177 nm. The particle size distribution was most narrow when KH560 was 2.5 wt % of the total monomer amount because of the proper cross-linking density.

Siloxane migrated more easily to the surface of the latex films because of its lower surface energy. The more crosslinked network that formed in the surface increased the high-temperature shear resistance. Figure 6 shows that the initial decomposition temperature (5% weight loss temperature) increased from 366 to 381°C and the temperature at the maximum heat loss rate increased from 400 to 405°C. This was in accordance with the improvement of the high-temperature shear resistance shown in Table V. This was attributed to the reaction between the epoxy and the carboxyl groups from KH560 and AA units to form a larger polymer chain. The reaction between the epoxy and

amino groups from KH560 and AMPS units during the thermal posttreatment process of film formation also contributed to the formation of the crosslinked network. In addition, the reaction between carboxyl and hydroxyl groups from AA and HPA units also had positive effect on the improvement.^{26,27} Compared with the reported articles,^{26,27} the PSA synthesized here had better adhesive properties; the water resistance and high-temperature resistance properties were also improved.

CONCLUSIONS

An AC copolymer, which was synthesized by the seeded semi-continuous emulsion polymerization of BA, 2-EHA, MMA, St, AA, and HPA, was modified by KH560 through a thermal post-treatment process to prepare PSA films for electronic products. The shear resistance, tack, and peeling strength were improved simultaneously through this route of introducing the siloxane KH560 in the polymeric chain of PSA. The modified PSA showed a noticeable improvement in the high-temperature shear resistance, aging resistance, and water resistance. The AC PSA, which was modified by 2.5 wt % KH560, showed a satisfactory wetting ability and repealing ability as well. The peeling residue was significantly reduced for the optimal protection of electronic products.

From a practical point of view, the prediction of the adhesive properties of the PSA can be made through the detection and control of the static steady-shear viscosity of the emulsion to prevent the production of PSA films with poor adhesive properties. Low-residue PSAs with outstanding properties could find potential applications in self-cleaning coatings, optoelectronics, and so on.

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