Preparation and Characterization of Polyacrylate/Polymerized Rosin Composite Emulsions by Seeded Semicontinuous Emulsion Polymerization

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ABSTRACT: Polyacrylate/polymerized rosin composite emulsions were prepared by seeded semicontinuous emulsion polymerization of acrylate monomers in which polymerized rosin was dissolved. The effects of polymerized rosin content on the polymerization stability, monomer conversion, polymer structure, and adhesive properties were studied. Polyacrylate/polymerized rosin composites were characterized by gel permeation chromatograph (GPC), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogracvimetry (TG). The results showed that with an increase of polymerized rosin content from 0 to 6 wt %, gel fraction and sol molecular weight decreased obviously but monomer conversion was basically unchanged. In contrast, with a further increase of polymerized rosin content, the decreasing rates of gel fraction, and sol molecular weight were slowed down. Meanwhile, monomer conversion decreased remarkably. Moreover, interface failure changed into cohesive failure after the addition of polymerized rosin, and the peel adhesion and shear resistance of composite latex films declined with the increase of polymerized rosin content. Thermal analysis showed that polymerized rosin and polyacrylate were compatible and the composite latex films had good thermal stability. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4694–4701, 2012

Key words: emulsion polymerization; composites; polymer synthesis and characterization; adhesives

INTRODUCTION

As a kind of renewable material obtained from the exudation of pines, rosin, which is primarily composed of abietic acid and its isomers, is widely used in many fields such as rubbers, coatings, adhesives, painting inks, and papermaking, etc.[1–3] However, its further applications are greatly limited due to its low softening point and easy oxidization of C=C double bonds in the structure of abietic acid and its isomers. Therefore, various chemical modifications were utilized to overcome these shortcomings, such as hydrogenization, disproportionation, polymerization, and esterification.[4–6]

Rosin and its derivatives used as tackifying resin were usually introduced into polymer matrixes such as natural rubber (NR),[7] styrene-butadiene-styrene block copolymer (SBS),[8] unsaturated polyester resin (UP),[2] epoxy resin (EP),[9] and polyacrylate (PA),[10–12] to improve their adhesion properties. Especially, adding rosin and its derivatives to acrylate emulsion into prepare the composite emulsions has attracted more and more attentions, which is due to two aspects in comparison with solvent-borne polyacrylate as follows: first, polyacrylate composite emulsions have the advantages of low-cost, nonflammable, and environment-friendly; second, polyacrylate composite emulsions can achieve much higher solid contents at low viscosity which brings further benefits in formulation, transportation, and coating.[13–16] Moreover, the tackified polyacrylate emulsion can solve the common technical problem on bonding to the nonpolar or low energy surfaces, such as polyfluortetraethylene (PFTE), polyethylene (PE), and polypropylene (PP).[11,17–19]

Typically, by using appropriate surfactants, tackifying resin can be dispersed in water and blended with polyacrylate emulsions to prepare the composite emulsion.[20–25] Kim et al.[20,25] prepared water-borne acrylate emulsion as pressure sensitive adhesive by adding different aqueous dispersions of rosin ester, and they found that the blends with low molecular weight tackifying resin exhibited only one glass transition temperature (T_g), whereas the blends showed two T_g with high molecular weight tackifying resin. The probe tack and 180° peel strength of the blends were affected by the structure, content,

and miscibility of the tackifying resin. Tobing and Klein[21] added the aqueous dispersion of glycerol ester rosin to the copolymerization emulsion of acrylates, and the results showed that the formation of gel during emulsion polymerization of acrylic monomers brought inherent weakness to the tackified film properties owning to lack of network entanglements. Furthermore, Mallegol et al.[22] also studied acrylate emulsion/tackifying resin dispersion blends and found that suitable tackifying resin could improve the compatibility of blends through particle coalescence. However, the problems in the blends of acrylate emulsion and aqueous dispersion of tackifying resin, such as colloidal stability, compatibility, and the migration of surfactants, have not been well solved.

Mentioned emulsion polymerization, there are mainly two methods commonly used: batch and semicontinuous.[26] In a batch polymerization, all ingredients are added at the beginning of the reaction. The higher quantity of monomers droplets can give a decrease in colloid stability, with excessive amounts of coagulum formed during the reaction, whereas the semicontinuous process can be used as a seeding technique, i.e., a small particle size seed latex is charged to the reactor as a preformed latex or is prepared in the first stage of a two-stage polymerization.[27] This technique process can precisely control over various aspects including the rate of polymerization, the particles number, copolymer composition, and particle morphology to avoid the colloid instability and coagulum formation and to obtain the desirable properties of the polymers.[27,28]

In this article, polymerized rosin was first dissolved in mixed acrylate monomers, and then the mixture was added into the aqueous solution of surfactants to prepare the monomers preemulsion. At last, polyacrylate/polymerized rosin composite emulsions were prepared by seeded semicontinuous emulsion polymerization. The effects of polymerized rosin content on monomer conversion, polymerization stability, gel fraction, and adhesive properties were investigated, and the polyacrylate/polymerized rosin composites were characterized by GPC, FTIR, DSC, and TG.

EXPERIMENTAL

Materials

Butyl acrylate (BA), 2-ethylhexyl acrylate (2-EHA), methyl methacrylate (MMA), acrylic acid (AA), hydroxy 2-ethyl acrylate (2-HEA), and potassium persulfate (KPS) were purchased from Tianjin Chemical Reagent Factory (China). Allyloxy nonylphenol polyoxyethylene (10) ether (ANPEO$_{10}$) and its ammonium sulfate (DNS-86) were supplied by
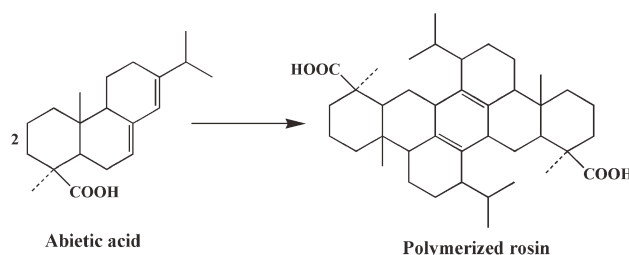
Figure 1 Polymerization reaction of abietic acid.

Guangzhou Shuangjian Trading (China). Commercial polymerized rosin (softening point: 130–140°C; acid value: 150 mg KOH g^{-1}), which is formed by the polymerization of abietic acid and the reaction equation is shown in Figure 1, was obtained from Wuzhou Sunshine Forestry and Chemicals (China). Ammonia (NH$_3$·H$_2$O, 25–28 wt %) was purchased from Guangzhou Donghong Chemical Factory (China). BA, 2-EHA, and MMA were distilled under vacuum before use and the other chemicals were used as received. Deionized water was used throughout all the polymerizations.

Preparation of polyacrylate/polymerized rosin composite emulsions

Polymerized rosin was first dissolved in the mixed monomers (60 g BA, 30 g 2-EHA, 5.5 g MMA, 2.5 g AA, and 2 g 2-HEA), then the mixture was added into the aqueous solution of surfactants (0.3 g DNS-86, 0.3 g ANPEO$_{10}$, and 40 g H$_2$O) and stirred with a high-speed dispersion homogenizer (Shanghai Suoying equipments, China) to obtain the preemulsion. Polymerizations were carried out batchwise in a 500 mL four-necked flask equipped with a thermometer, a mechanical stirrer rotating at 200 rpm, an ascendant condenser and two feed inlet tubes. All reactions were seeded and the seed emulsions were made at 80°C for 30 min by the addition of 10 wt % preemulsion in 40 g H$_2$O in the presence of 0.15 g KPS. Then the rest components (90 wt % preemulsion and the initiator solution including 0.35 g KPS and 20 g H$_2$O) were added into the flask through the two inlet tubes at a constant flow rate for 180 min. After the addition, the system was allowed to react for additional 1.5 h at 85°C. At last, polyacrylate/polymerized rosin composite emulsions were obtained after cooling to room temperature and adjusting pH to 7 by ammonia.

Measurements and characterization

Monomer conversion and coagulum ratio

Monomer conversion, which is defined as the weight ratio of the obtained polymer to monomers, was determined gravimetrically. The coagulum was

collected after the experiment and the coagulum ratio was calculated as the weight ratio of the dried coagulum to the sum of monomers and polymerized rosin.

Gel fraction

Gel fraction was measured by continuous extraction with tetrahydrofuran (THF) under reflux for 8 h at about 75°C.[29,30] About 1g latex was dried on PTFE board and then the film was wrapped by two pieces of filter-paper. After extraction, the gel left in the filter-paper was dried and weighted. Gel fraction was calculated as the following eq. (1):

$$\text{Gel fraction (wt\%)} = \frac{W_2 - W_0}{W_1 - W_0} \times 100\% \qquad (1)$$

where W_0, W_1, and W_2 are the weight of filter-paper, the initial polymer with filter-paper, and polymer after extracted including filter-paper, respectively.

Gel permeation chromatograph (GPC)

The sol average molecular weight was determined by GPC instrument (Waters, USA). Dried polymer was immersed in THF for 24 h, resulting in a colloidal dispersion of sol and gel polymer in THF. The dispersion was filtered before injected into the GPC instrument. Polystyrene standards were used for the calibration.

Fourier transform infrared spectroscopy (FTIR)

Samples were analyzed by Bruker Vector 33 Fourier transform infrared spectrometer (Germany). Polymerized rosin sample was ground and mixed with KBr to make pellets, polyacrylate emulsion and composite emulsions were coated on the KBr pellets and put under the infrared lamp until dried. FTIR spectra were recorded in the range of 450–4000 cm^{-1} in absorbance mode.

Differential scanning calorimetry (DSC)

The glass transition temperature (T_g) of polyacrylate/polymerized rosin composite latex films was measured by Netzsch DSC 204F differential scanning calorimeter (Germany). Samples of 6–10 mg were placed in a standard aluminum crucible and heated from −80 to 150°C at a heating rate of 20°C min^{-1} under nitrogen atmosphere. In the first heating run, the samples were heated from −80 to 150°C to erase the thermal history, and immediately quench-cooled and reheated at the same heating rate and in the same temperature range. The second heating run was used to determine the glass transition temperature.[31,32]
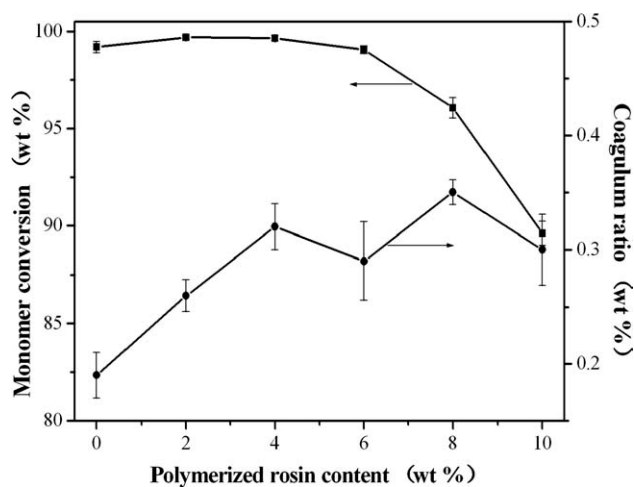
Figure 2 Effect of polymerized rosin content on monomer conversion and coagulum ratio.

Thermogravimetry (TG)

Dried polymerized rosin, polyacrylate and their composite latex films were determined by Netzsch TG 209F thermogravimeter (Germany). Samples of 6–10 mg were placed in a platinum sample pan and heated from 30 to 600°C at a heating rate of 20°C min^{-1}. Nitrogen was used as purge gas at flow rate of 200 mL min^{-1}, and the weight loss and temperature difference were recorded as a function of temperature.[33,34]

Adhesive properties

The obtained composite emulsions were coated on the corona treated PET film with an average thickness of 36 μm by a Mayer bar on the pilot coating machine. The thickness of dried adhesive was 25 ± 2 μm. The coated emulsions were dried for 5 min in an electric drying oven with forced convection at 120°C. Then, the test strips with the width of 25 mm and the minimum length of 175 mm were cut and used to test the adhesive properties at 23°C ± 2°C and 60% ± 5% RH employing the FINAT test methods. The peel adhesion at 180° (FTM 1) is defined as the force required to remove pressure sensitive coated material, which has been applied to a standard test plate under the angle of 180° and the speed of 30 mm min^{-1}. The shear resistance (FTM 8) is defined as the time required for a standard area of pressure sensitive coated material to slide from a standard flat surface in a direction parallel to the surface.[35,36]

RESULTS AND DISCUSSION

Effect of polymerized rosin content on monomer conversion and coagulum ratio

Figure 2 shows the monomer conversion and coagulum ratio of emulsion polymerization of acrylates
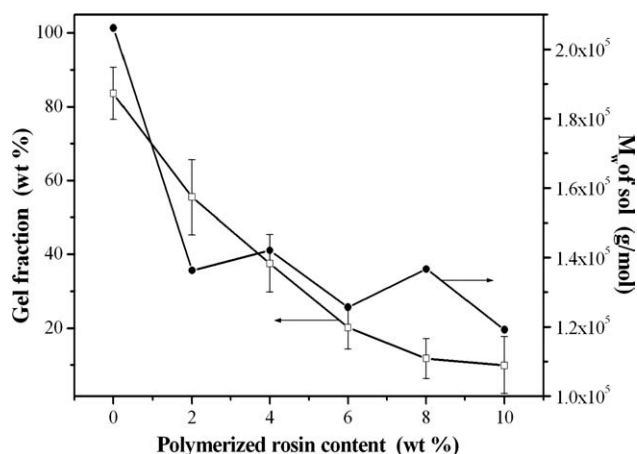
Figure 3 Effect of polymerized rosin content on gel fraction and M_w of sol.

with different polymerized rosin contents. It can be seen that the coagulum ratio increased slightly from 0.19 to 0.35 wt % with an increasing loading of polymerized rosin. This low coagulum was due to the accumulation of few impurities in polymerized rosin which had low compatibility with polyacrylates matrix. The results showed that the addition of polymerized rosin had little effect on the stability of polymerization.

Meanwhile, it also can be observed that the monomer conversion was almost independent of the loading of polymerized rosin below 6 wt %. The monomer conversion, however, decreased remarkably from 99.0 to 89.6 wt % when the polymerized rosin content increased from 6 to 10 wt %. This might be attributed to the fact that the small amount of abietic acid in polymerized rosin could function as effective chain transfer agent and inhibitor,[11,37] which consumed both the initiator radical and the propagation radical. As a result, when polymerized rosin content was low, the monomer conversion exceeded 99 wt % although the microstructure of polymer might be affected. As the content of polymerized rosin increased, abietic acid could decrease the monomer conversion by eliminating more active radicals.

Effect of polymerized rosin content on gel fraction and sol molecular weight

Figure 3 shows gel fraction and sol molecular weight of composites with different polymerized rosin contents. It can be seen that the addition of polymerized rosin led to an obvious decrease of gel fraction and sol molecular weight. According to the previous reports,[38–40] during the emulsion polymerization of acrylates, gel was formed by the intermolecular chain transfer to polymer followed by termination via combination, and the intermolecular chain trans-

fer to polymer required labile H at tertiary carbon atoms in the backbone of the polyacrylate chain. In this study, the labile H is supplied by the structure units of BA, 2-EHA, and 2-HEA and the esterification section of 2-EHA. The mechanism is displayed in Scheme 1.
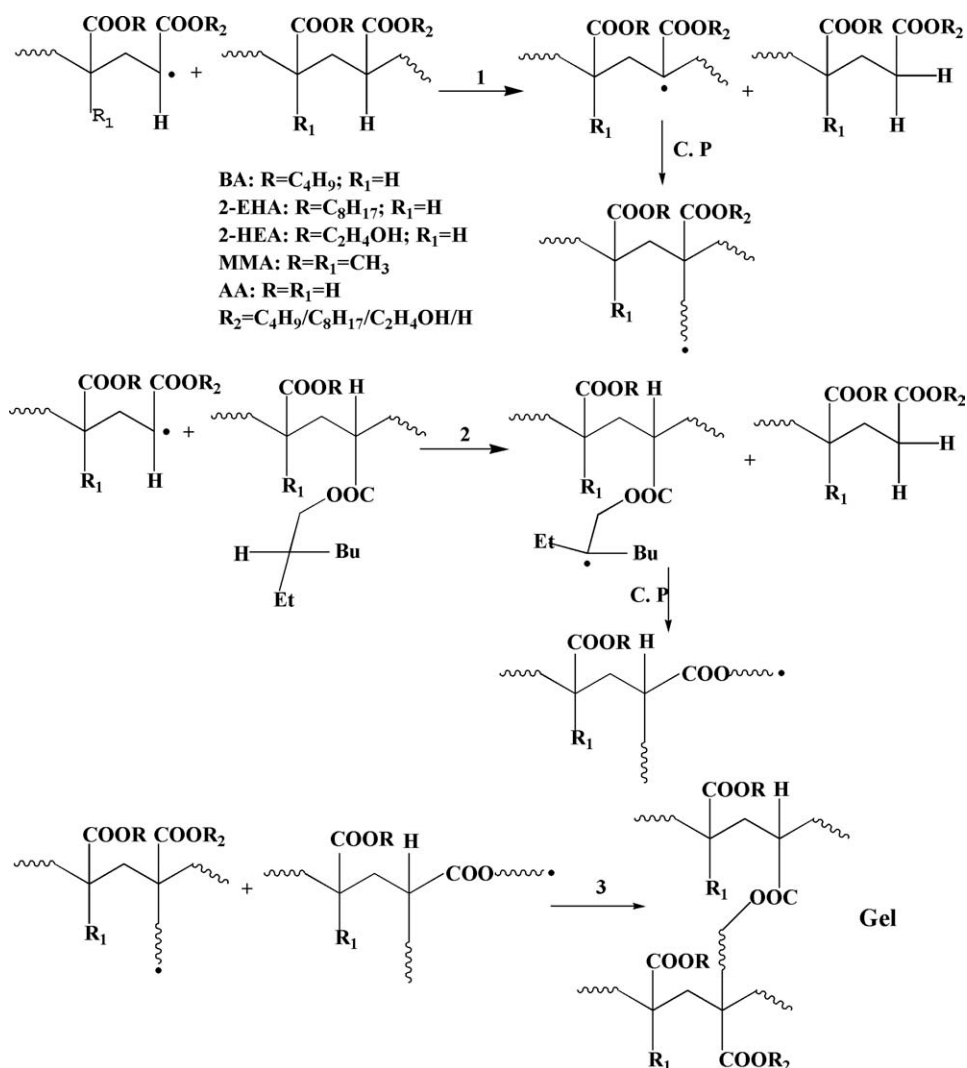
When polymerized rosin was added into the polymerization system of acrylates, two effects should be considered. On the one hand, polymerized rosin was free in the polyacrylate and had a negative effect in form of physical separation on the occurrence of hydrogen abstraction of radical from tertiary carbon atoms. On the other hand, the little residual abietic acid around polymer chain consumed a part of radical and made them inactive, and then led to the decrease of monomer conversion, which hindered gel formation and the chain transfer of sol molecules to gel. Therefore, with the increase of polymerized rosin content, both effects were more obvious, which could contribute to the decrease of gel. The decrease of sol molecular weight can be explained by the reducing of the kinetic chain length via chain transfer of propagating chain radicals to abietic acid.[11]

Effect of polymerized rosin content on adhesive properties

Table I shows the effect of polymerized rosin content on the adhesive properties of polyacrylate/polymerized rosin composite latex films. As shown in Table I, the addition of polymerized rosin to the polyacrylate led to cohesive failure of adhesive in the test of peel adhesion and shear resistance compared to the interface failure of pure polyacrylate. When 2 wt % polymerized rosin was added, the peel adhesion increased remarkably, and then it decreased with the further increase of polymerized rosin. But the shear resistance decreased continuously as polymerized rosin content increased.

For the pure polyacrylate, the gel fraction and M_w of sol were high up to 83.6 wt % and 2.05×10^5 g mol^{-1}, respectively (as shown in Fig. 3). That is to say, it had the considerable high crosslinking density of polymer network and sol molecular entanglement, which provided the good cohesive strength of adhesive, but caused the weak wettability of adhesive. Consequently, the force of cohesive failure at debonding process was much greater than that of the interface failure, and the interface failure appeared in the peel adhesion and shear resistance was longer than 1500 min. When a small amount of polymerized rosin (2 wt %) presented in the composite, the gel fraction and M_w of sol decreased sharply (as shown in Fig. 3). On the one hand, this could improve the wetting of adhesive on substrate and hence enhanced the interfacial adhesion strength, and on the other hand, the cohesive

BA: R=C₄H₉; R₁=H
2-EHA: R=C₈H₁₇; R₁=H
2-HEA: R=C₂H₄OH; R₁=H
MMA: R=R₁=CH₃
AA: R=R₁=H
R₂=C₄H₉/C₈H₁₇/C₂H₄OH/H

Scheme 1   Mechanism of gel formation in the emulsion polymerization of acrylates.

strength of adhesive could be consequently lowered. The result indicated that the force of cohesive failure at debonding process was lower than that of interface failure. Therefore, cohesive failure occurred and peel adhesion increased. In addition, with the increase of polymerized rosin content from 2 to 10 wt %, the peel adhesion and shear resistance of composite latex films decreased obviously. It was possibly due to the general decrease gel fraction and M_w of sol.
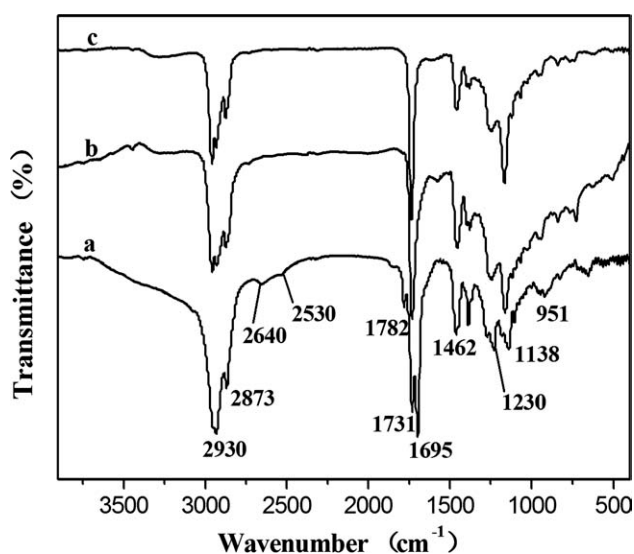
FTIR analysis

FTIR spectra of polymerized rosin, pure polyacrylate, and polyacrylate composite with 6 wt % polymerized rosin are shown in Figure 4. In the spectrum of polymerized rosin, the peaks at 1695 and 1273 cm^{-1} were assigned to the stretching vibration of C=O and the C—O, respectively; the peaks at 2640, 2530, and 952 cm^{-1} were contributed to the O—H···O (hydrogen bonding) stretching vibration and bending vibration, respectively. Moreover, the

TABLE I
Effect of Polymerized Rosin Content on Adhesive Properties of Polyacrylate/Polymerized Rosin Composite Latex Films

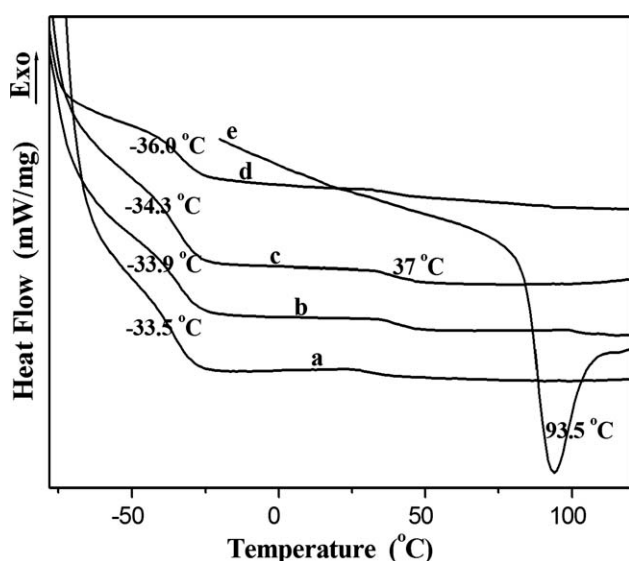| Adhesive properties	Polymerized rosin content (wt %)					
	0	2	4	6	8	10
180° peel adhesion (N/25 mm)	8.5 ± 0.3	20.8 ± 1.5[a]	10.5 ± 0.7[a]	10.0 ± 0.5[a]	9.0 ± 0.5[a]	8.3 ± 0.3[a]
Shear resistance (min)	>1500	373 ± 33[a]	44 ± 5[a]	39 ± 5[a]	16 ± 3[a]	7 ± 1[a]

[a] Represents cohesive failure.

Figure 4 FTIR spectra of (a) polymerized rosin, (b) pure polyacrylate, and (c) polyacrylate composite with 6 wt % polymerized rosin.

absorption peaks at about 1782 and 1731 cm^{-1} might be due to the formation of anhydride caused by the dehydration of —COOH during the polymerization of abietic acid. In addition, the peaks at 1230 and 1138 cm^{-1} were contribution of the C—O stretching vibration in anhydride.[41,42]

Except for the peaks at ~ 2873, 2930, 1387, 1462, and 951 cm^{-1} associated with the CH$_2$ and CH$_3$ vibration, and the peaks at about 1730, 1245, 1160, and 1110 cm^{-1} related to C=O and C—O stretching vibration in the spectra,[43,44] it also could be found that the characteristic absorption peaks at 1695, 2640,

2530, and 952 cm^{-1} disappeared in the spectrum of composites as compared with the spectrum of polymerized rosin. This was because that the polymerized rosin was evenly dispersed in the latex particles, finally, the —COOH in the polymerized rosin was neutralized to carboxylate which took place of the original hydrogen bonds in crystal polymerized rosin. Meanwhile, the absence of the characteristic absorption peak at ~ 1782 cm^{-1} was ascribed to the hydrolysis of the anhydride in composite emulsion.

DSC analysis

Figure 5 presents the DSC curves of pure polyacrylate (a), polymerized rosin (e) and their composites with 2 wt % (b), 6 wt % (c), 10 wt % (d) polymerized rosin. As shown in Figure 5, the glass transition temperatures (T_g) of the composites decreased slightly with the increase of polymerized rosin content. One reasonable explanation was that the plasticization of polymerized rosin in composites could reduce the intermolecular force and increase free volume of polyacrylates.[45] Furthermore, with the increase of polymerized rosin content, gel fraction of polymer decreased. Namely, the crosslinking of polyacrylates was decreased and thus lowered T_g. In addition, the presence of T_g at about 37°C in all curves might be caused by the homogeneous nucleation of small amount of soft monomers with MMA dissolved in water and water-soluble AA. Meanwhile, the endothermic peak at about 93.5°C (T_g of polymerized rosin) was not found in DSC curves of composites, which indicated the good compatibility of polyacrylate and polymerized rosin in composites.
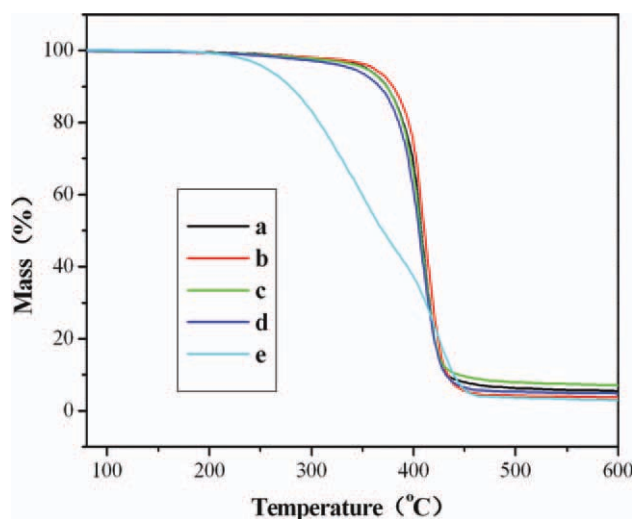

Figure 5 DSC curves of polyacrylate composites with different polymerized rosin contents: (a) 0 wt %; (b) 2 wt %; (c) 6 wt %; (d) 10 wt % and (e) polymerized rosin.
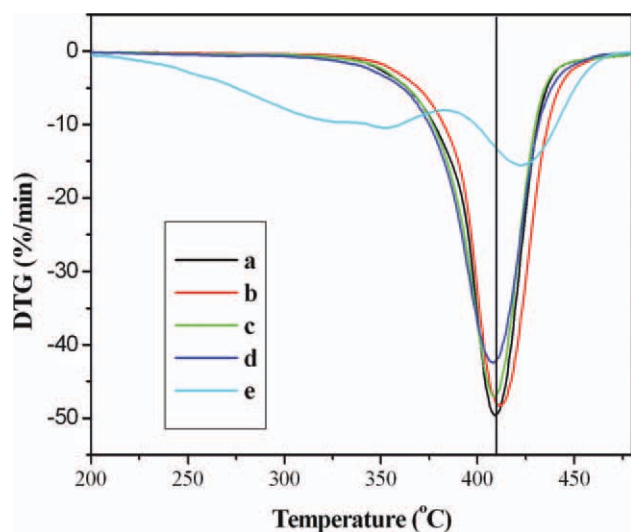

Figure 6 TG curves of polyacrylate composites with different polymerized rosin contents: (a) 0 wt %; (b) 2 wt %; (c) 6 wt %; (d) 10 wt % and (e) polymerized rosin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TG analysis

Figure 6 shows TG curves of pure polyacrylate (a), polymerized rosin (e) and their composites with 2 wt % (b), 6 wt % (c), 10 wt % (d) polymerized rosin, and Figure 7 shows the behavior of differential weight loss (DTG) curves of the samples. The corresponding onset temperature of thermal decomposition at weight loss of 5 wt % $(T_{onset})^{41}$ and the corresponding temperature at the maximum rate of weight loss (T_{max}) were analyzed and displayed in Table II.

As shown in Figure 6 and Table II, the mass loss of polymerized rosin lasted for a wide temperature range with T_{onset} at 263.3°C, and there were two degradation steps in TG curve with the corresponding T_{max} peaks in DTG curve at 352.2 and 426.2°C shown in Figure 7. These were due to the complicated structure change of polymerized rosin during the decomposition. Meanwhile, the complex compounds with better thermal stability were produced by decarboxylation and disproportionation[46] in the first stage of decomposition of polymerized rosin, which led to the second stage/peak in TG/DTG curve. Compared with pure polyacrylate, the T_{onset} and the T_{max} of composite with 2 wt % polymerized rosin were a bit higher, which might be due to the synergetic effect between the two components by grafting or cross-linking. The synergy did not play the dominant role with the increase of polymerized rosin, and the T_{onset} and T_{max} decreased slightly. However, the slight decrease of decomposition temperature of the composites with 6 and 10 wt %

TABLE II
TG Results of Pure Polyacrylate, Polymerized Rosin, and Their Composites

Samples	Polymerized rosin content (wt %)	T_{onset} (°C)	T_{max} (°C)
a	0	389.7	410.8
b	2	391.6	413.4
c	6	387.6	409.7
d	10	383.2	409.2
e	100	263.3	352.2/426.2

polymerized rosin indicated the good thermal stability of the composites.

CONCLUSIONS

Polyacrylate/polymerized rosin composite emulsions were successfully prepared by seeded semicontinuous emulsion polymerization via polymerized rosin dissolved in comonomers at the stage of preemulsion. With the increase of polymerized rosin content, the monomer conversion, gel fraction of polymer and sol molecular weight decreased because of the chain transfer and inhibition roles of abietic acid. The addition of a small amount of polymerized rosin (2 wt %) improved the wetting of adhesive on substrate and enhanced the interfacial adhesion strength, which led to the obvious increase of peel adhesion, but the failure modes of adhesive changed from interface into cohesion due to the decrease of cohesive strength of adhesive. Then the peel adhesion and shear resistance decreased with the increase of polymerized rosin content. In comparison with pure polyacrylate, the polyacrylate/polymerized rosin composites showed the lower glass transition temperature because of the plasticization of polymerized rosin and the decline of gel fraction. Furthermore, thermal analysis showed that the composite latex films obtained by this means exhibited good compatibility and thermal stability.

Figure 7 DTG curves of polyacrylate composites with different polymerized rosin contents: (a) 0 wt %; (b) 2 wt %; (c) 6 wt %; (d) 10 wt % and (e) polymerized rosin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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