

Hydrogenated rosin ester latexes/waterborne polyacrylate blends for pressure-sensitive adhesives

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ABSTRACT: Diethylene glycol ester of hydrogenated rosin (DGE-HR) emulsion was prepared via phase inversion method and then blended with waterborne (wb) polyacrylate for pressure-sensitive adhesives (PSAs). The preparation conditions of DGE-HR emulsion were studied. DGE-HR emulsion with an average particle size of about 220 nm was obtained. Furthermore, the thermal, adhesive, and viscoelastic properties and the morphology of DGE-HR/polyacrylate composite were investigated. Thermal analysis indicated that glass transition temperatures (T_g) of the DGE-HR/polyacrylate blends became higher as the DGE-HR content increased and DGE-HR did not have a significant influence on thermal stability of the blend films. Atomic Force Microscopy (AFM) observation revealed that the DGE-HR particles added had a good miscibility with acrylic particles. Additionally, for these tackified acrylic PSAs, positive correlations between mechanical performance and viscoelastic response at bonding and debonding frequencies were also found.

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INTRODUCTION

Pressure-sensitive adhesives (PSAs) are viscoelastic materials that can adhere strongly to solid surfaces upon application of light contact pressure and short contact time.¹ Among the different base polymers used in making PSAs, acrylic waterborne (wb) PSAs have enjoyed the fastest growth in commercial applications due to their excellent optical clarity, aging performance, low toxicity, and relative low cost.^{2,3} Strict environmental regulations in the production of PSAs have led to a shift away from solvent-cast formulations to aqueous dispersions of polymer colloids, i.e., latex. However, the bonding strength of acrylic wb-PSAs to polyolefins or other low surface energy materials is not high enough.

In order to improve adhesion strength between polyolefins and acrylic PSAs, it is common practice to modify the PSAs by introducing bulky and low-molecular-weight hydrophobic monomers, such as petroleum resin, terpene resin, and abietic resin, which could enhance the bonding strength of the wb-PSAs to low energy surfaces.^{4–6} As a kind of renewable material, rosin resin or its derivatives are widely used in the field of modification of adhesion strength between polyolefins and acrylic

PSAs, because the polarity of the molecular structure between acrylic resin and rosin resin or its derivatives is similar with each other. The incorporation of the rosin resin or its derivatives into acrylic PSAs not only can reduce the cost for PSAs, but improve the wettability of acrylic wb-PSAs on the low surface energy materials.^{7–10}

Modification of polyacrylate using rosin resin or its derivatives mainly includes blending and copolymerization. Chen *et al.*¹¹ prepared polyacrylate/polymerized rosin composite emulsions by seeded semicontinuous emulsion polymerization, in which polymerized rosin was dissolved. Canetta *et al.*¹² developed a miniemulsion way to incorporate the tackifier into acrylic particles leading to a better incorporation between tackifier and polyacrylate at nanometer scale. However, for copolymerization modification, C–C conjugated double bonds in rosin molecular would function as effective polymerization inhibitor and chain transfer agent, which could cause the decrease of both monomer conversion and molecular weight of PSAs. Nevertheless, even using hydrogenated rosin in the reaction, the low content of unhydrogenated rosin would also retard the polymerization. Although polymerizable side chain can be introduced in rosin ring, its cost is higher.^{13,14} Considering these factors, blending

method was used in this study. Low-molecular-weight hydrophobic rosin ester resins dissolved in a solvent for the solvent-cast PSAs has been studied by a few researchers.^{7,15,16} There are also some reports about the influence of waterborne rosin latex on acrylic PSAs. Kim *et al.*⁴ elucidated that rosin ester with the molecular weight about 800 was miscible well with wb-acrylic emulsion and the blend systems only had one T_g . Jeusette *et al.*¹⁷ developed a novel symmetric four-arm star “all-acrylate” block copolymers synthesized by atom transfer radical polymerization (ATRP) and mixed the copolymer with glycerol ester rosin. As we all know, high-softening-point resin can keep PSAs good cohesion, while low-softening-point resin not only have low temperature resistance but also have a good compatibility with the polymer.¹⁸ In those papers, the rosin resins used were high-softening-point resin and purchased, furthermore, there was no mention of the preparation method of waterborne rosin resin latex used in wb-PSAs. In comparison to high-softening-point resin, studies on low-softening-point resin for tackifying wb-PSAs are much less reported.

In this article, low-softening-point diethylene glycol ester of hydrogenated rosin (DGE-HR) emulsion (softening point is 35°C, average particle diameter is about 220 nm, and polydispersity index, PDI=0.049) was prepared firstly by phase inversion method, in which the commercial OP-10 (OctaphenylPolyoxyethylene-10) and SDS (sodium dodecyl sulfate) were used as the emulsifier for wb-PSAs applications. Subsequently, the DGE-HR emulsion was mixed with acrylic emulsion. Finally, the influences of DGE-HR on mechanical and viscoelastic properties of acrylic wb-PSAs were studied.

EXPERIMENTAL MATERIALS AND METHODS

Materials

Hydrogenated rosin was provided by Guangxi Wuzhou Chemical, China. Diethylene glycol, sodium bicarbonate (NaHCO_3), sodium dodecyl sulfate (SDS), butyl acrylate (BA), methyl methacrylate (MMA), acrylic acid (AA), and 2-hydroxyethyl acrylate (2-HEA) were purchased from Shanghai Lingfeng chemical, China. OctaphenylPolyoxyethylene-10 (OP-10) was supplied by Jiangsu Hai'an petrochemical, China. Sorbitan stearate (Span-60) and Sorbitan oleate (Span-80) were obtained from Nanjing Chemical Reagent, China. Ammonium persulfate (APS) was offered by Aladdin Reagent Co., Ltd. (Shanghai, China). All chemicals were analytical grade and used as received. In addition, Milli-Q water was used in all experiments.

Preparation of DGE-HR

About 300 g hydrogenated rosin was added into four-necked round-bottomed flask equipped with an electric mixer, a water diversion device with condenser pipe, a dropping funnel, and a thermometer, and nitrogen was used as shielding gas. The rosin was heated and stirred as it was melted. Then 0.3 g zinc oxide and 122 g diethylene glycol were slowly added into the molten rosin when the temperature rose to about 200°C. After reacting for 2 h, the temperature was elevated to 230°C, the reaction was continued until the acid value of the product was less than 20 mg KOH/g. The DGE-HR obtained has a softening point of 35°C as measured by the ring-and-ball method.

Preparation of DGE-HR Emulsion

A certain amount of emulsifier was dissolved into a flask equipped with an electric mixer, a dropping funnel, and a thermometer. Then the DGE-HR obtained in the preceding step was placed into the flask, heated to 55~65°C and stirred at 200~300 RPM for 1 min. Subsequently, 65~70°C deionized water was added to the molten rosin resin keeping 30~40 drops min^{-1} , and then the stirring speed was increased to 800~1000 RPM. Within 3 min, the dispersion seemed to appear the phase inversion, which indicated the dispersion from water-in-oil state to oil-in-water state. Finally, the dispersion was cooled to 30°C, passed through a 100-mesh screen and placed into a glass bottle. No coagulant was found on the screen. The DGE-HR content of the obtained waterborne emulsion was 50 wt %.

Preparation of Waterborne Polyacrylate

Amounts of 90 g of deionized water and 1.5 g of surfactants (1 g SDS+0.5 g OP-10) were added to a 500 mL, four-necked, and round-bottomed flask and stirred rapidly to make the emulsifier dissolve sufficiently. Then the mixture of the monomers (90 wt % BA, 5 wt % MMA, 2 wt % 2-HEA, and 3 wt % AA) was slowly added to the water-surfactant mixture through a constant pressure funnel over 20 min. After that, the pre-emulsion was stirred for further 30 min. Then, 10% pre-emulsion and 10 wt % aqueous APS solution (0.6 g APS was dissolved in 10 g deionized water) were added into a flask. The seed-emulsion polymerization was carried out at 75°C. After stirring for 0.5 h, the system was heated to 80°C and 0.2 g NaHCO_3 was added as buffer. The pre-emulsion and remaining initiators were added dropwise into the reactor within 2 h, respectively. Upon finishing the addition, the reactant was held for 1 h at 85°C. After the hold period, the acrylic emulsion was cooled to 40°C, filtered, and adjusted the pH to 6~8 by ammonia solution. The synthesized waterborne acrylic PSA was found to have the following characteristics: polymer content was 50.1 wt %; viscosity was 35.4 mPa s; and Z-average diameter was 253 nm.

Preparation of Tackified wb-PSAs

Firstly, the polymer content of waterborne acrylic emulsion (the original polymer content was 50.1 wt %) was adjusted to be 50 wt % by adding a certain amount of water. Then acrylic emulsion was added into a flask and stirred at room temperature, and the stirring speed was 300 rpm. Subsequently, waterborne DGE-HR emulsion (DGE-HR content was 50 wt %) was slowly added drop wise into the flask and blended with acrylic emulsion, and the adding speed was 20 drops min^{-1} . The mixtures were made at different weight ratios of DGE-HR emulsion and acrylic emulsion and the total solid content of all mixtures was estimated to be 50 wt %. Blends of the dispersions were cast on 28 μm biaxially-oriented polypropylene (BOPP) sheets using a hand-held spiral bar coater. The films were dried at 110°C for 5 min under static air. The thickness of the dried films was determined to be about 10 μm by a coating thickness gauge.

Characterization of the DGE-HR Emulsion

A 10 μL of the 0.01 wt % DGE-HR emulsion was placed on a glow-discharged carbon-coated transmission electron

microscopy (TEM) copper grid. The excess liquid was absorbed by a piece of filter paper. After the specimen has been completely dried, it was introduced into the electron microscope. The sample was viewed using JET-2100 transmission electron microscopy (Hitachi, Japan) at an acceleration voltage of 200 kV. Particle size (diameter) and PDI (Polydispersity Index) of the DGE-HR were measured by dynamic light scattering (DLS, Zetasizer Nano Z, Malvern Instruments).

Characterization of PSAs

The glass transition of the polymers were measured by differential scanning calorimetry (DSC) using a Perkin Elmer Diamond Differential Scanning Calorimeter. 3~4 mg sample was enclosed in an aluminum pan. A nitrogen flow was used as a protective gas. The temperature was increased at a rate of 10 K min⁻¹. The second scan of the sample was used for measurement of glass transition temperature (T_g). Thermogravimetric (TG) analysis was performed by using NETZSCH STA 409 PC ranging from 30 to 700°C at a rate of 10°C min⁻¹ under nitrogen gas at a flow rate of 100 mL min⁻¹.

Films for AFM experiments were cast onto polypropylene sheets using a 10 μ m hand-held spiral bar coater. The films were dried at 110°C for 3 min under static air. The thickness of the dried films was estimated to be 5 μ m. A 1 cm \times 1 cm pieces were cut from the cast PSA films and mounted on the AFM sample holder. Samples were analyzed within 24 h after casting. Prior to AFM analysis, the film surfaces were rinsed with deionized water to remove the excess surfactants.¹⁹ The nanostructure of the PSA films was characterized by using a commercial AFM instrument (SPM-9600 AFM, Shimadzu, Japan) using AC240 (OLYMPUS) probes with a nominal resonant frequency at 70 kHz and a nominal spring constant at 2 N m⁻¹. All of the AFM experiments were performed in air at room temperature, and the phase and 3D images (scan sizes ranging from 5 μ m \times 5 μ m) were acquired using a scan rate of 1.56 Hz.

The rheological measurements of dried bulk PSAs were performed with Haake Mars II. Free-standing PSA films (1 mm thick) were prepared by delaminating films that had been cast on release paper, dried for 10–15 days at ambient temperature, and then heated for 16 h at 50°C. Before analysis, the films were submitted to an additional heating at 110°C for 2 h. The sample was oscillated over a range of frequencies (0.01–100 Hz), with a monitored shear strain (10%) at a constant temperature (25°C). A 10 mm diameter stainless steel parallel plate and a gap size of 1 mm were applied.

According to GB/T 4582-2002 (China), the tack property was tested. A 100 mm \times 100 mm PSA tape was cut down and placed to an incline with an angle of 30°, and steel balls of different size tumbled from the top of the incline. The tack was represented by the measurement of the balls rolled onto the tape and the serial number of the biggest ball stopped on it was recorded.

According to GB/T 4581-1998 (China), the shear resistance was studied. A 25 mm \times 70 mm strip was cut down. A tape distance of 20 mm was pressed onto one of the steel sheet and the rest for another. After a dwelling time of 2 h, the sample was

clamped with a 1 kg load, which was applied to induce a shear stress. The shear resistance was measured by the time that elapsed between the application of load and the completed debond of tape from steel sheet. The same process was also performed three times and the average exfoliation time was defined as persistent adhesion property.

According to GB/T 2792-1998 (China), the 180° peel strength was evaluated. A tape of 25 mm in width was cut down. 25 mm \times 100 mm specimen was pressed onto the stainless steel substrate using three passes of a 1 kg rubber roller to make a good contact. After a dwelling time of 30 min at room temperature, the sample was tested by a tensile machine with a detachment rate of 300 mm min⁻¹. The peel force at a tape distance of 75 mm was defined as the 180° peel strength.

RESULTS AND DISCUSSION

The Choice of the Emulsifiers for the Preparation of DGE-HR Emulsion

Because of the special ring ester structure in rosin, it is difficult to manufacture a stable rosin emulsion by using only one single emulsifier. If the structure of the hydrophobic group in emulsifier is more similar with the rosin ester, the affinity between rosin ester and the emulsifier would be stronger. Anionic/non-ionic emulsifier complex is usually applied to satisfy these requirements. In general, the HLB (Hydrophile-Lipophile Balance) value required in the emulsification of rosin ranges from 13 to 18. Different anionic and nonionic surfactants were elected and compounded with each other, the emulsification effects of different surfactants compound are shown in Table I. Although the DGE-HR emulsion could be obtained when the Span-80/SDS mass ratio approximately ranged from 1.5 : 1 to 1.8 : 1, the particle size of the emulsion was more than 700 nm and the particle size distribution was large. However, when the OP-10/SDS complex was used and the mass ratio of OP-10/SDS was (5~6) : 1, the particle size of emulsion obtained was 214 nm and PDI was less than 0.05. This might be because that the benzene ring structure in OP-10 molecular structure serves as hydrophobic part and has more similarity with the phenanthrene ring in rosin ester, while there is only aliphatic long-chain structure in molecular structure of Span-80 serves as hydrophobic part. Furthermore, the particle size of the DGE-HR emulsion was also determined by TEM (Figure 1). It was found that particle size of emulsion obtained was about 180 nm, which was smaller than the particle diameter measured by DLS. This may be due to that the particle diameter measured by DLS includes the thickness of the water cladding on the surface of particles.

Preparation Conditions of DGE-HR Emulsion: Emulsifier Content and Emulsifying Temperature

In this experiment, the effects of emulsifier content and emulsifying temperature on the particle size and PDI of DGE-HR emulsion were investigated. It can be found from Figure 2 that both particle size and PDI roughly declined with the increase of emulsifier content or emulsifying temperature. In Figure 2(a), DGE-HR emulsions were obtained by OP-10/SDS complex as surfactants at 60°C and the OP-10/SDS mass ratio was 6 : 1. When the emulsifier content was up to 11% of the weight of

Table I. The Emulsification Effect of Different Surfactants on Preparation of DGE-HR Emulsion

Surfactant ^a	Mass Ratio	HLB _{mix} ^b	Emulsification result	Z-Average diameter/nm
OP-10:SDBS	1 : 1	12.6	*	-
	2 : 1	13.2	*	-
	3 : 1	13.5	*	-
Span-60:SDS	1.5 : 1	18.8	*	-
	2 : 1	16.5	*	-
	3 : 1	13.5	*	-
Span-80:SDS	1 : 1	22.2	*	-
	1.5 : 1	18.6	+	More than 700 ^c
	1.8 : 1	17.1	+	More than 700 ^c
OP-10:SDS	2 : 1	23.0	*	-
	4 : 1	19.6	*	-
	5 : 1	18.8	+	243 ^c
OP-10:SDS	6 : 1	18.1	+	214 ^c
	8 : 1	17.3	*	-

means creaming; + means ivory state; + means state of ivory with a bit blue light.

^aEmulsifier dosage is 8% of the weight of DGE-HR.

^bHLB_{mix}=HLB_AW_A%+HLB_BW_B%, which W_A % and W_B % are the weight percent of emulsifier A and B, respectively. HLB_A and HLB_B refer to the HLB of the two emulsifiers.

^cThe Z-Average diameter of the latex was measured by DLS.

DGE-HR, homogeneous latex was prepared with a particle size of about 160 nm and PDI less than 0.05. However, considering large number of emulsifier would impair the adhesive properties of PSAs, emulsifier content chosen for preparing the latex was 7–9% of the weight of DGE-HR. To study the effect of emulsifying temperature on the emulsification, DGE-HR emulsions were prepared at emulsifying temperature at 55, 60, 65, and 70°C when OP-10/SDS complex as surfactants, the OP-10/SDS mass ratio was 6 : 1 and emulsifier content was 8% of the weight of DGE-HR. As can be seen from Figure 2(b), the phase inversion rate was slower and particle size distribution was

larger as the temperature was below 60°C. In addition, the latex with narrowest diameter distribution and the average particle size of 174 nm could be obtained as the emulsifying temperature was higher than 70°C, it indicated that the higher the temperature of the process was, the smaller average particle of emulsion would be. However, given that the cloud point of OP-10 is about 70°C, emulsifying temperature in range between 60°C and 70°C was selected for the preparation of DGE-HR emulsions.

Effect of DGE-HR Content on T_g of Latex Films

The glass transition temperature (T_g) of a polymer is determined by the amorphous region of a partially crystalline polymer when a viscous or rubbery state is transformed into a hard, brittle, glasslike state. The T_g evaluated by DSC has been generally used in the determination of blend miscibility. The phase structure of a blend is assessed by the number of T_g values observed in the thermogram. Two transitions are a clear indication of phase separation, while a T_g located at a temperature intermediate between those of the pure components indicates miscibility.¹⁸

Figure 3 presents the DSC curves of polyacrylate composites with different DGE-HR contents: (a) 0 wt %; (b) 10 wt %; (c) 20 wt %; (d) 30 wt %; (e) 40 wt % (f) 50 wt %; and (g) 100 wt %. As shown in Figure 3, the T_gs of the composites were elevated as the DGE-HR at greater concentrations. One reasonable explanation may be that the T_g of DGE-HR itself is higher than the T_g of polyacrylate. Moreover, the endothermic peak at 1.93°C (T_g of DGE-HR) was not found in DSC curves of composites, which indicated that the DGE-HR had a good miscibility with polyacrylate in the composites.

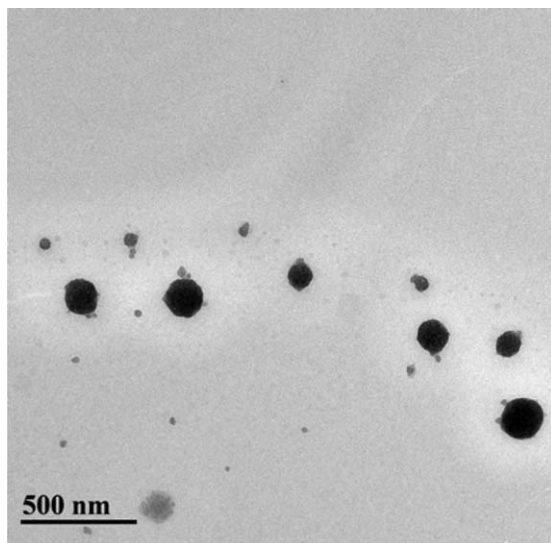


Figure 1. TEM image of DGE-HR emulsion particles.

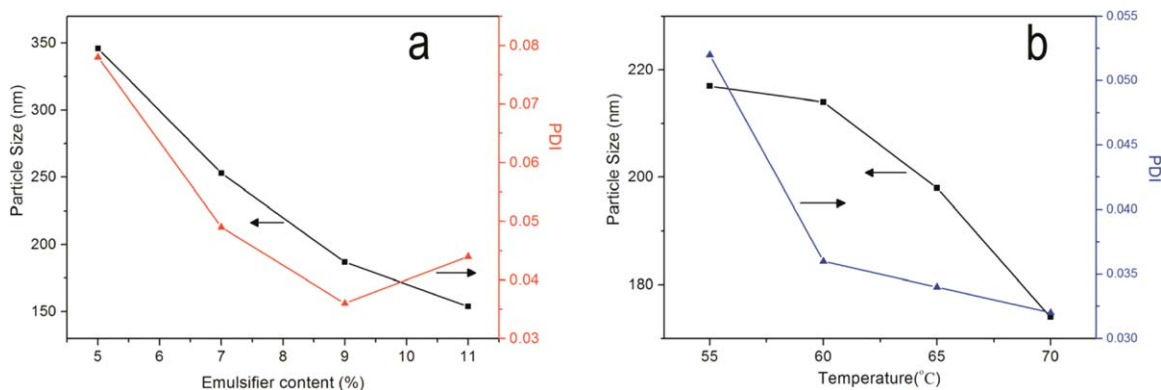


Figure 2. The effects of (a) emulsifier content and (b) emulsifying temperature on the particle size and PDI of DGE-HR emulsion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of DGE-HR Content on Thermal Stability of Latex Films

Figure 4 shows TG and DTG curves of pure polyacrylate, DGE-HR, and their composites. The corresponding onset temperature of thermal decomposition at weight loss of five (T_{onset}) and the corresponding temperature at the maximum rate of weight loss (T_{max}) were analyzed and displayed in Table II. As shown in Figure 4 and Table II, the mass loss of DGE-HR lasted for a wide temperature range with T_{onset} at 319.8°C, and there were two degradation steps in TG curve with the corresponding T_{max} peaks in DTG curve at 377.7 and 433.9°C. Owing to the excess of diethylene glycol it was believed that two kinds of rosin ester would form, which were diethylene glycol monoabietate and diethylene glycol biabietate, respectively. These two kinds of DGE-HR might be the result of the two thermal decomposition points in DTG curve of DGE-HR. Compared with pure polyacrylate, the T_{onset} and the T_{max} of composites with DGE-HR were a little bit higher. This might be because the structure of the composites seemed to act like “wattle-and-daub” structure in which the two components synergistically complemented each other. The synergy did not play the dominant role with the

increase of DGE-HR, and the T_{onset} and T_{max} decreased slightly when the DGE-HR content was 30 wt % compared with the pure polyacrylate. The slight decrease of decomposition temperature of the composite with 30 wt % DGE-HR indicated the addition of DGE-HR did not have a significant influence on thermal stability of the blend films.

Effect of DGE-HR on Morphology of Latex Films

In order to further investigate the effect of DGE-HR on the structure of the PSA film. The morphology of pure acrylic PSA film and blending acrylic PSA film with 15 wt % DGE-HR added were studied by AFM, respectively. Prior to AFM analysis, the film surfaces were rinsed with deionized water to remove the excess surfactants. For the neat PSAs latex [Figure 5(a)], particles evenly assembled and were deformed from their spherical shape to hexagon forming a continuous film. There was very little contrast in the phase image. However, for blending emulsion film, the addition of 15 wt % DGE-HR to the acrylic latex led to the appearance of an evident second phase in the morphology of the adhesive film [Figure 5(c)] even though only one T_g was observed in the DSC analysis of all composites. This result was in good agreement with the works reported by Mallégo²⁰ and Canetta¹². Small sizes of dispersed phase particles might be ascribed to this phenomenon in this blending system, and the relationship between size of dispersed phase and T_g is not clear and needs more efforts to study this problem in the future. Because the T_g of DGE-HR is higher than that of pure acrylic copolymer (DGE-HR, $T_g = 1.93^\circ\text{C}$; Pure acrylic copolymer, $T_g = -33.6^\circ\text{C}$) and acrylic copolymer are the main ingredients, we speculated that bright regions represent DGE-HR particles (hard segments), and the dark regions represent acrylic latex particles (soft segments). Furthermore, 1 (the neat acrylic film). It was found that each acrylate particle seemed to be surrounded by DGE-HR and only some rare aggregates of acrylate particles were observed. In addition, in Figure 5(d), two kinds of particles appeared to have coalesced and a completely homogeneous surface, which was not found from 3D image of the neat acrylic film, [Figure 5(b)] was also obtained. In other words, it revealed that DGE-HR particles could improve the smoothness of acrylic films and have a good miscibility with acrylic particles.⁹

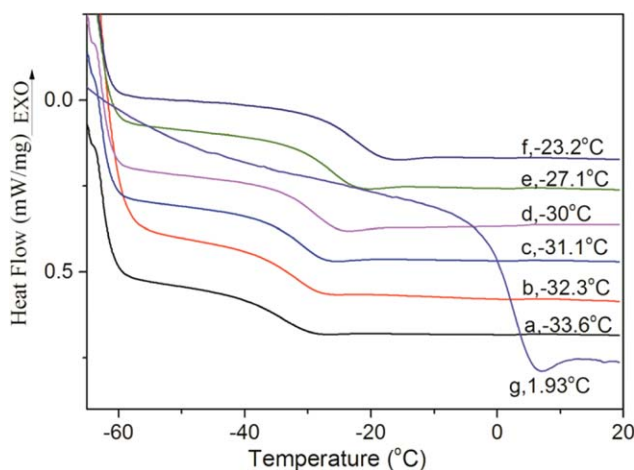


Figure 3. DSC curves of polyacrylate composites with different DGE-HR contents: (a) 0 wt %; (b) 10 wt %; (c) 20 wt %; (d) 30 wt %; (e) 40 wt %; (f) 50 wt %; and (g) 100 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

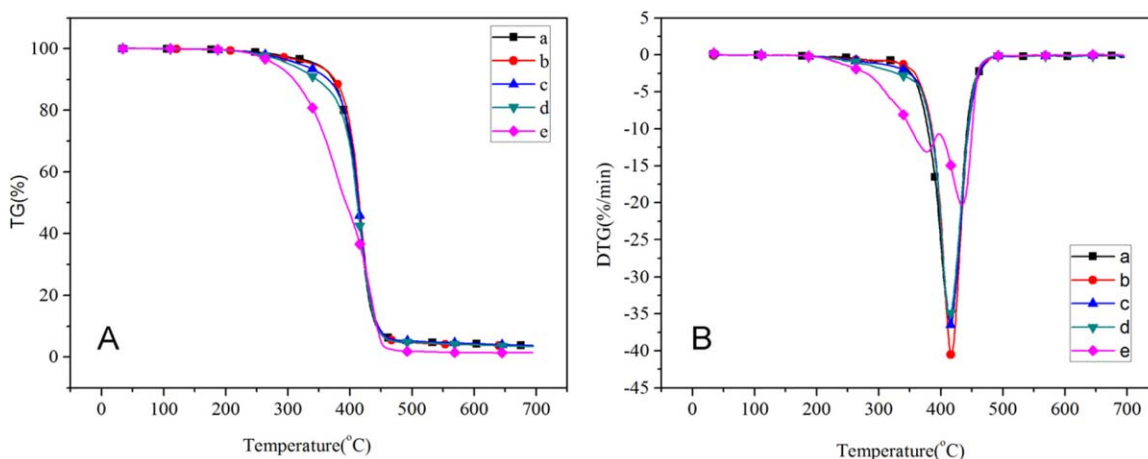


Figure 4. (A) TG and (B) DTG curves of polyacrylate composites with different DGE-HR contents: (a) 0 wt %; (b) 10 wt %; (c) 20 wt %; (d) 30 wt %; and (e) 100 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of DGE-HR Content on the Adhesive Properties of the Tackified Latex Films

All of the blending emulsions were prepared by mixing the DGE-HR emulsion and the polyacrylate emulsion with the ratios of 0/100, 5/95, 10/90, 15/85, 20/80, 30/70, 40/60, and 50/50 by weight. The average particle size of DGE-HR emulsion and polyacrylate emulsion were 214 nm and 253 nm, respectively, measured by DLS. And the DGE-HR emulsion used here was prepared when emulsifier dosage was 8% of the weight of DGE-HR, the emulsifier mass ratio of OP-10 and SDS was 6 : 1, and the reaction temperature was 60°C. The blending emulsions were cast onto BOPP films using 60 μm hand-held spiral bar coater and dried at 110°C for 5 min under static air. The thickness of the obtained adhesive films were about 10 μm measured by a TT210 coating thickness gauge. The adhesive properties of these tackified PSAs were tested and shown in Table III.

It was observed that with the increase of DGE-HR content, tack, and 180° peel adhesion increased up to a maximum with 40 wt % and 15 wt % DGE-HR, respectively, while the shear resistance roughly decreased. It could be explained by the fact that the introduction of DGE-HR enhanced the wettability and chain mobility of the blending latex on adherent surface, which, in turn, resulted in higher bonding strength and 180° peel adhesion between the substrate and adhesive layer. However, as can be seen from Table III, if more DGE-HR was added, the effects of higher T_g of the PSAs and higher viscosity of the mixed

emulsion would definitely dominate, leading to the decrease of tack and 180° peel adhesion. On the other hand, when the polyacrylate was blended with rosin ester, the shear resistance of the PSAs became poorer, which was attributed to the decrease of the crosslink density and the average molecular weight of the adhesive. These results were in good agreement with the works of Tobing and Kelin.²¹ Furthermore, although 20 wt % DGE-HR was added, the PSAs displayed good tack (8 #), shear resistance (>60 h) and 180° peel adhesion (330.7 N m^{-1}) properties.

Effect of DGE-HR Content on the Viscoelastic Properties of the Tackified Latex Films

In order to further investigate the mechanistic properties of blending PSAs, the viscoelastic studies of the acrylic PSAs blends were carried out by dynamic thermomechanical analysis (DMA) over a range of frequencies (0.01–100 Hz), with a monitored shear strain (10%) at constant temperature (25°C). The storage modulus (G'), loss modulus (G''), complex viscosity (η^*), and damping factor ($\tan\delta = G''/G'$) were discussed, respectively.

Figure 6 shows the plots of complex viscosity (η^*) against sweep frequency. All the samples exhibited monotonically decreasing curves and falling tendency as the shear frequency increases, in other words, all the samples put out the shear thinning behaviors, behaved as pseudoplastic non-Newtonian materials.²² It was interesting to note that the addition of DGE-HR did not reduce the viscosity of blend system, instead, it improved the viscosity compared to the pure polyacrylate when the content of DGE-HR was less than 30 wt %. The miscibility between DGE-HR and acrylic PSAs, which had already discussed previously by AFM images and DSC analysis, might make for this phenomenon. The interaction force between the two phases resulted in the increase of flow resistance in the blends when the content of DGE-HR was less than 30 wt %, and if more DGE-HR was added, the phase inversion would occur and then the viscosity decreased.

Figure 7 shows the plots of $\tan\delta$ versus sweep frequency. It was observed that $\tan\delta$ of the blending system became higher as the DGE-HR content increased. Compared with the neat polyacrylate, $\tan\delta$ curves of the blends had same trend against frequency

Table II. TG Results of Pure Polyacrylate, DGE-HR, and Their Composites

Samples	DGE-HR content (wt %)	T_{onset} (°C)	T_{max} (°C)
a	0	388.1	415.6
b	10	393.3	416.8
c	20	390.5	416.4
d	30	387.6	413.9
e	100	319.8	377.7/433.9

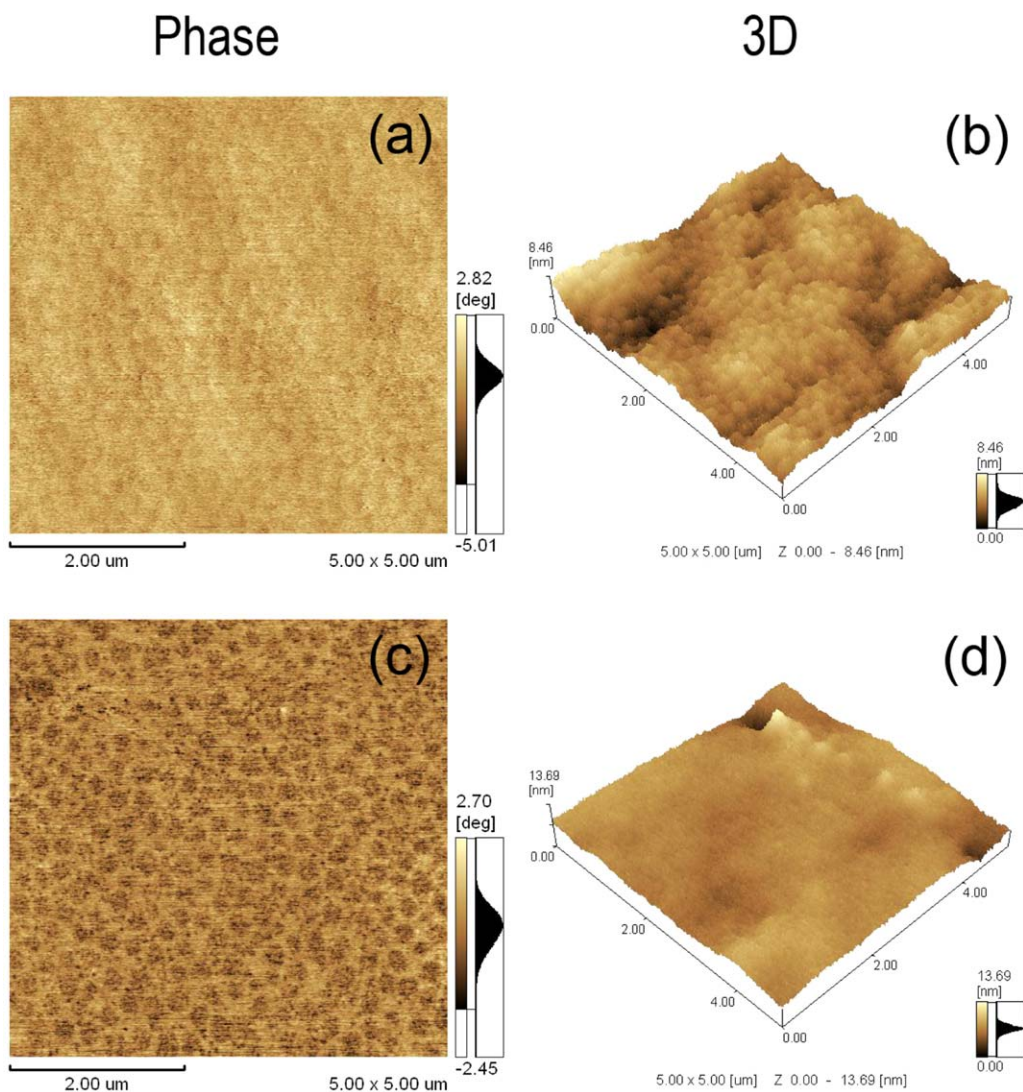


Figure 5. (a) Phase and (b) 3D AFM images of the top surface of film cast from neat acrylic latex; (c) Phase and (d) 3D images of the top surface of films acrylic with 15 wt % DGE-HR added. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as the DGE-HR content was less than 30 wt %. However, the $\tan\delta$ curves of the blends had a different variation tendency against frequency as the DGE-HR content was more than 30 wt %, this may have been due to the phase inversion in the composites as addition of DGE-HR increased continuously.

Figures 8 and 9 illustrate the plots of G' and G'' against sweep frequency, respectively. As the DGE-HR content was less than 30 wt %, both the values of G'' and G' of the blends and pure polyacrylate seemed to have the same sensitive to the frequency, indicating again that miscibility between DGE-HR and acrylic polymer was good. The viscoelastic information at low frequency (0.01 rad s^{-1}) represents the bond formation, whereas that at high frequency (100 rad s^{-1}) describes the behavior of debonding. Shear performance can be correlated with G' at 0.01 rad s^{-1} . Generally, the higher the G' at 0.01 rad s^{-1} and the better the shear resistance.²³ It could be found from Figure 8 that the G' at 0.01 rad s^{-1} of composites were in good agreement with their respective shear resistance. Peel performance

Table III. Effects of DGE-HR Content on Adhesive Properties of Polyacrylate/DGE-HR Composite Latex Films

DGE-HR content (wt %)	Tack (#)	180° peel adhesion (N m^{-1})	Shear resistance (h)
0	5	263.5	>72
5	5	282.5	>72
10	6	327.2	>72
15	7	337.3	>72
20	8	330.7	66
30	9	328.9	23.5
40	9	326.2	12
50	7	320.2	4.5

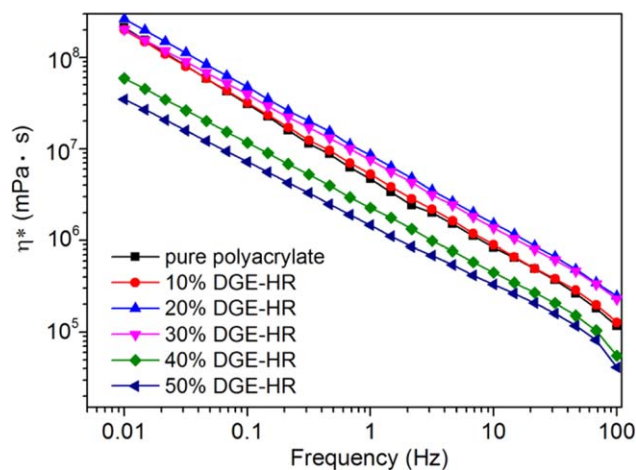


Figure 6. The plots of complex viscosity (η^*) of polyacrylate/DGE-HR blend PSAs versus sweep frequency with different DGE-HR contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

relies on both the bonding efficiency (G' at 0.01 rad s^{-1}) and debonding resistance (G' and G'' at 100 rad s^{-1}). The lower the G' (0.01 rad s^{-1}), the more favorable the bonding, and the higher the peel strength. Furthermore, G' at 100 rad s^{-1} indicates the cohesive strength of adhesive and G'' at 100 rad s^{-1} shows the energy of dissipation.^{23,24} Therefore, the higher the G' (100 rad s^{-1}) and G'' (100 rad s^{-1}), the higher the peel strength. Compared with the neat polyacrylate film, the samples with 10 wt %, 20 wt %, and 30 wt % DGE-HR added had similar G' (0.01 rad s^{-1}) but much larger G'' (100 rad s^{-1}) and G' (100 rad s^{-1}), which favored bonding efficiency and corresponded to their higher peel strength. The samples with 40 wt % and 50 wt % DGE-HR had smaller G'' (100 rad s^{-1}) and G' (100 rad s^{-1}) but the G' (0.01 rad s^{-1}) was also smaller, which resulted in relatively large value in peel strength. Similar to peel correlation, tack performance also depends on the bonding efficiency and debonding resistance (G' and G'' at 100 rad s^{-1}),

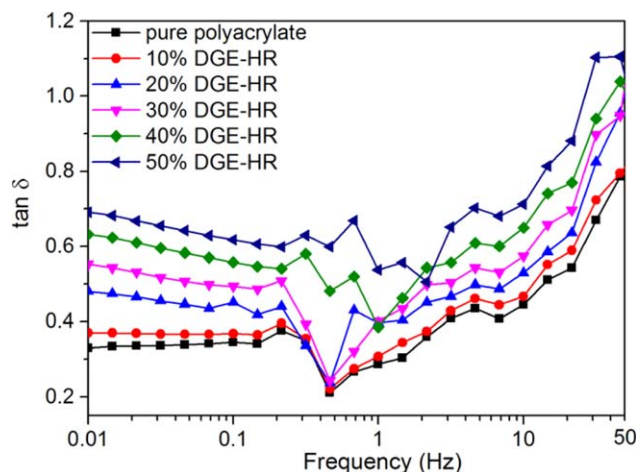


Figure 7. The plots of damping factor ($\tan \delta$) of polyacrylate/DGE-HR blend PSAs versus sweep frequency with different DGE-HR contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

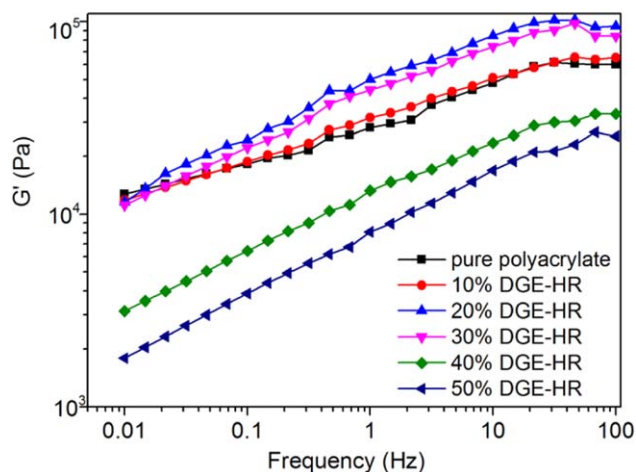


Figure 8. The plots of storage modulus (G') of polyacrylate/DGE-HR blend PSAs versus sweep frequency with different DGE-HR contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

except that the bonding frequency during tack measurement was about 1 rad s^{-1} rather than 0.01 rad s^{-1} .^{23,24} To some extent, the tack of composites also correlated well with their respective G' at 1 rad s^{-1} and G' and G'' at 100 rad s^{-1} .

CONCLUSIONS

DGE-HR emulsion with an average particle size of about 220 nm was obtained as the anionic/nonionic emulsifier complex of OP-10/SDS was used as emulsifier with a mass ratio of (5–6):1. DGE-HR emulsion was blended with waterborne polyacrylate for pressure-sensitive adhesives applications. The miscibility between waterborne acrylic emulsion and DGE-HR was investigated using DSC and AFM. DSC showed that there was only one single T_g of all blend systems and AFM revealed that a continuous film with 15 wt % DGE-HR added was formed, which both indicated that DGE-HR had a good compatibility

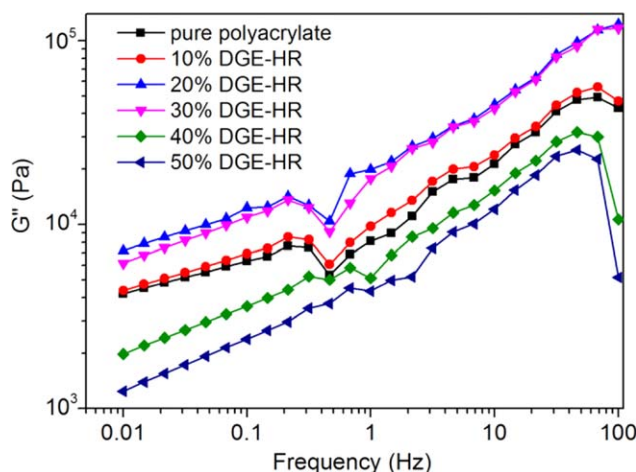


Figure 9. The plots of loss modulus (G'') of polyacrylate/DGE-HR blend PSAs versus sweep frequency with different DGE-HR contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with waterborne polyacrylate. TG analysis revealed that the addition of DGE-HR did not have a significant influence on thermal stability of the blend films.

PSAs films were laminated to corona-treated BOPP film of 10 mm average thickness. The tackified PSAs with 10–20 wt % DGE-HR had a good adhesive performance, which exhibited a maximal peel strength of 337 N m^{-1} , tack of 8 #, and shear resistance of over 60 h. Furthermore, the viscoelastic properties of these blends were determined as a function of frequency. The interaction force between the two phases resulted in the increase of viscosity in the blend, as the DGE-HR content was less than 30 wt %. In addition, $\tan\delta$ of the blend system became higher as the DGE-HR content increased. Additionally, positive correlations were also observed between the mechanical performance and the viscoelastic response at bonding and debonding frequencies for these tackified acrylic PSAs.

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