

Morphology, Dynamic Rheology, and Cohesive Properties of Epoxy-Modified Polyurethane–Acrylate Microemulsions Prepared by *In Situ* Surfactant-Free Polymerization

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ABSTRACT: A series of organic, solvent-free, epoxy-modified polyurethane–acrylate (EPUA) adhesives were prepared through *in situ* surfactant-free polymerization. Stable EPUA microemulsions with average particle diameters of less than 100 nm and a unimodal distribution were obtained through control of the epoxy content. Transitions from irregular shapes with a heterogeneous size distribution to a regular spherical particle morphology with an apparent core–shell morphology were obtained for EPUA with an increasing epoxy content to 8 wt %. With epoxy addition, EPUA displayed pseudoplastic behavior instead of Newtonian behavior, and increases in the viscosity and pseudoplastic behavior were detected. In addition, the EPUA emulsion transferred from a viscous liquid to a solidlike liquid. The addition of epoxy was beneficial for phase mixing, interaction, and entanglements between polyurethane and polyacrylate, and the interactions between the EPUA colloidal particles were also enhanced. The thermal stability, mechanical properties, and water and solvent resistance were thereby improved, as was the cohesive properties. However, the corresponding properties were weakened with excessive epoxy, and this was ascribed to the greatly increased particle size, viscosity, and phase separation. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39886.

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INTRODUCTION

Polyurethane (PU) adhesives have extensive applications in upper sole joints in footwear; this can be attributed to their versatile properties, flexibility, good strength, and low-temperature performance. However, the growing awareness of the importance of reducing the emission of volatile organic components has forced the footwear industry to devote a major part of its research efforts to this matter.¹ Waterborne adhesives, because of their nonflammable nature and nontoxicity, will be a feasible and inevitable alternative in the footwear industry.² Waterborne polyurethane (WPU) adhesives are mainly prepared with the acetone process³ or prepolymer method.² However, volatile organic solvents, such as acetone, dimethylformamide, or *N*-methyl-2-pyrrolidone, are used during these processes.

At present, WPU is commonly prepared by the incorporation of ionic groups into the PU backbone to enhance the hydrophilicity and promote the water dispersability. Therefore, the properties of WPUs are generally inferior to that of solvent-based PUs. In addition, WPU adhesives often display lower cohesive

strengths; this can be attributed to their stiffness, low crystallinity, and phase separation.¹ Therefore, hybrid materials that combine PU and other polymers have gotten increasing attention because the resulting materials, such as the combination of PU and polyacrylate (PA), often exhibit superior properties over the individual components.^{4–6} Epoxy resins are also used as multifunctional polyols in the synthesis of WPU dispersions because of their superior physicochemical properties and multiple possibilities of crosslinking.^{7–10} Better solvent resistance and cohesive strength can be obtained by the introduction of epoxy resin to PU,⁷ but the brittleness also increases sharply.¹¹ In addition, the stability of PU–epoxy dispersions is often limited.¹⁰

To overcome the previously mentioned limitations, in this study, bisphenol A epoxy resin (E-44) was used as chain extender to increase the chain length of the PU prepolymer and introduce more crosslinking points; this, thereby, improved the mechanical and cohesive properties of the final product. Also, *in situ*, surfactant-free emulsion polymerization was adopted to prepare epoxy-modified polyurethane–acrylate (EPUA)

microemulsions. The organic solvent was completely prevented at the source, and vinyl monomers were used to replace the organic solvent in the preparation process of the PU prepolymer. The PU prepolymer/vinyl monomers blends were obtained first; after neutralization, an initiator was added to initiate the radical polymerization of vinyl monomers to obtain real eco-friendly EPUA microemulsions without volatile organic components. Heretofore, there have been few studies dealing with synthesis and characterization of EPUA microemulsions prepared by *in situ*, surfactant-free emulsion polymerization, especially those designed for shoe adhesive applications.

The main objective of this study was to develop efficient, nano-sized EPUA adhesives to be used in the footwear industry because smaller particles are preferred when deep penetration into a substrate is an essential step for adhesives.¹² Therefore, fundamental investigations into the relationships among the physicochemical properties of the EPUA microemulsions, EPUA films, and EPUA adhesives were systematically done, and this provided us with some information for the structural design of such adhesives. In this study, the effects of the E-44 content on the mechanical and cohesive properties of the EPUA system were comprehensively investigated on the basis of the dynamic rheology, morphology, interaction, and phase behavior.

EXPERIMENTAL

Materials

Isophorone diisocyanate, hexamethylene diisocyanate, polycaprolactone (PCL) polyol with an average molecular weight of 1000 g/mol (PCL1000), and dimethylol butanoic acid were purchased from Taisen Chemical (Japan). Dibutyl tin dilaurate, triethylamine (TEA), hydroxyethyl acrylate (HEA), and acetone were purchased from Tianjin Chemical Agent, Inc. Methyl methacrylate (MMA) and butyl acrylate (BA) were purchased from Hongyan Chemical Industry. A water-soluble azo initiator azobis (isobutylamide hydrochloride) (AIBA) was purchased from Deco Composite Technology Co., Ltd. E-44 was provided by Bluestar New Chemical Materials Co., Ltd. PCL1000 was dried and degassed at 80°C *in vacuo* for 2 h before use. All other materials were used as received without further purification.

Preparation of the *In Situ* EPUA Microemulsions

In situ, surfactant-free polymerization was performed in a 250-mL, four-necked glass reactor equipped with a reflux condenser, a mechanical stirrer, and a digital thermometer. Certain amount of isophorone diisocyanate, hexamethylene diisocyanate, PCL, DBMA, MMA, and BA were added to the reactor, and it was kept at 70°C for 1.5 h to obtain an NCO-terminated PU prepolymer. Then, the prepolymer was chain extended with different contents of E-44 (on the basis of the total weight of PU). After 1.5 h, HEA was introduced into the reactor, and the reaction was allowed to continue for another 30 min. Then, the temperature was decreased to 30°C, and the PU prepolymer was neutralized by TEA. Deionized water was slowly dropped into the solution under vigorous stirring, and the AIBA initiator solution was subsequently added to the reactor to initiate the radical copolymerization of the vinyl monomers. The reaction was allowed to proceed for an additional 2 h. Finally, EPUA

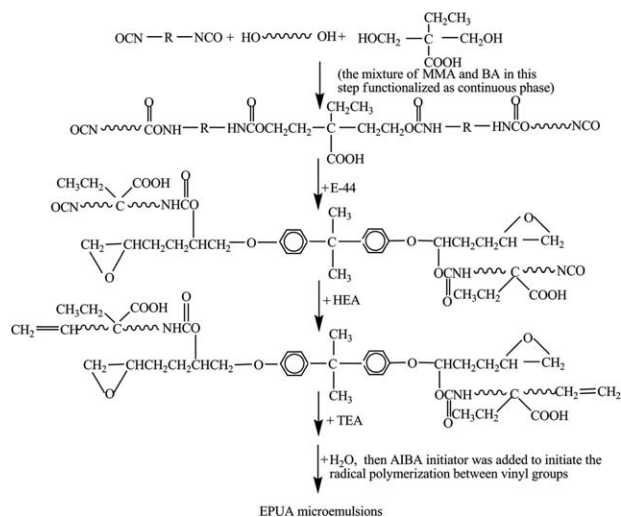


Figure 1. Preparation of the EPUA hybrid microemulsions.

hybrid microemulsions with a 35% solid content were obtained. The reaction process for the *in situ* polymerization of EPUA is shown in Figure 1.

Preparation of the EPUA Adhesive Films

EPUA microemulsions were cast on leveled tetrafluoroethylene plates to allow them to dry at room temperature for 5 days, and then at 60°C *in vacuo* for 12 h. After demolding, the films were kept in a desiccator to avoid moisture.

Characterization

We determined the centrifugal stability by submitting 10 g of microemulsions to a TDL-10B centrifuge (Shanghai Anting Scientific Instrument Factory, China) for 30 min at a speed of 3000 rpm. The coagulation ratio (σ) was calculated by eq. (1):¹³

$$\sigma(\%) = (w_c / w_m) \times 100 \quad (1)$$

where w_c is the weight of the dried coagulates and w_m is the total weight of all of the monomers.

The particle size of the microemulsions was analyzed by Version 2.14 dynamic light scattering (Zeta-plus, Brookhaven Instruments Co.). Its morphology was observed by a Hitachi S570 transmission electron microscope (Japan) with phosphotungstic acid as the staining agent.

The rheological properties of the microemulsions were analyzed in an AR2000ex rheometer (TA Instruments Co.). All of the tests were carried out at 25°C with a DIN concentric cylinder geometry. Strain (γ) amplitude experiments (0.01–100%) were performed at a frequency of 0.1 Hz to determine the linear viscoelastic region. Then, frequency sweeps (0.01–1000 Hz) were performed at a strain of 1% at 25°C.

Thermogravimetric analysis (TG) and differential thermogravimetry (DTG) were performed in a Q500 thermal analyzer (TA Instruments Co.) from 20 to 650°C under an N₂ atmosphere at a heating rate of 10°C/min.

Dynamic mechanical analysis was carried out on a Q800 dynamic mechanical analyzer (TA Instruments Co.) at a

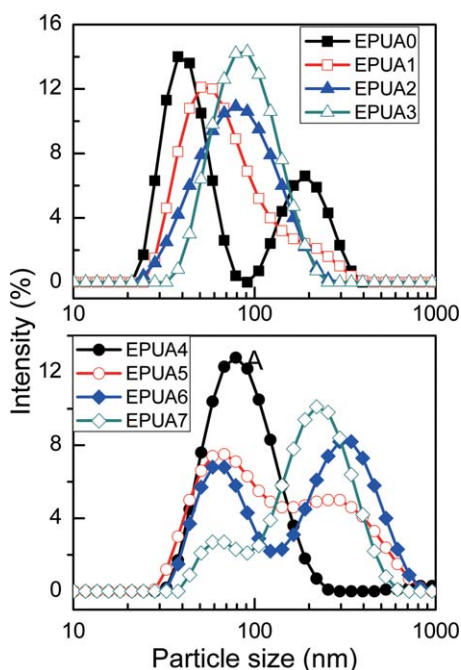


Figure 2. Effects of the E-44 content on the particle diameter and distribution of the EPUA microemulsions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

frequency of 2 Hz and a rate of 3°C/min over a temperature range from −100 to 150°C.

The tensile strength and elongation at break of the films were measured on a TS2000-S universal test machine (Scientific and Technological Limited Co. of High Iron, Taiwan). The results reported are the mean values of three replicates.

The water and toluene absorption of the films was determined by the immersion of the films in a beaker of medium for 24 h. After the surface water was wiped off with filter paper, the film weight (W_1) was determined. The swelling ratio (A) of the films was calculated by eq. (2):

$$A = (W_1 - W) / W \times 100\% \quad (2)$$

where W is the dry weight of films before immersion.

The cohesive properties of the EPUA microemulsions were studied by T-peel strength tests of leather/EPUA/rubber joints according to GB/2791-1995. The T-peel strength tests were performed in a TS2000-S universal test machine with a crosshead speed of 500 mm/min. The values obtained were the average of three replicates.

RESULTS AND DISCUSSION

Particle Size and Distribution Analysis

The average particle diameter and polydispersity index (PDI) values of the EPUA microemulsions with different E-44 contents were determined by a light-scattering technique, as shown in Figure 2. The particle size increased from 63.92 to 83.94 nm with increasing E-44 content, but the PDI decreased from 0.461 to 0.141 when the E-44 content was lower than 6 wt %. Simultaneously the particle size distribution transferred from a bimodal distribution to a unimodal distribution. In this study,

E-44 was functionalized as a hydrophobic chain extender and crosslinker in the preparation of the PU prepolymer. The reason EPUA0 displayed a bimodal distribution was mainly the lack of interactions between PU and PA. In the phase inversion, polymer chains rich in hydrophobic PA formed bigger colloidal particles, whereas polymer chains rich in hydrophilic PU formed smaller colloidal particles; this resulted in a bimodal distribution. With E-44 addition, the hydrophobicity and molecular weight of the polyurethane-acrylate (PUA) chains increased, and this resulted in an increase in the particle size. However, an interpenetrating network was simultaneously formed with the introduction of E-44, and the interactions between the PU and PA chains were thereby enhanced, as was the miscibility among PU and PA.¹⁴ In addition, PA had a promising compatibility with epoxy resin. All of the previously mentioned phenomena may have been responsible for the decrease in PDI. The decreased PDI also indicated the relatively uniform distribution of hydrophobic and hydrophilic segments in each polymer chain. It also suggested enhanced interaction between the PU and PA chains.

With the further increases in the E-44 content, the PDI increased from 0.276 to 0.561; there was also a great increase in the particle size, especially for EPUA7. On the one hand, the entanglement and crosslinking among polymer chains were further increased, and the viscosity of the PU prepolymer became high. Therefore, the self-emulsifying ability of the PU prepolymer decreased and resulted in an increased particle size. On the other hand, when the E-44 content was excessive, the greater amount of E-44 might have preferentially located at the surface of the droplets because of the presence of its OH group. As a result, hydrophobic chain extension might have taken place at the droplet/water interface and promoted bridging flocculation and resulted in an increased particle size and PDI.⁴

Colloidal Stability

The coagulation ratios for the EPUA microemulsions are presented in Table I. These reveal that the EPUA microemulsions with E-44 contents of less than 10 wt % were stable, and no precipitation was observed for longer than 6 months during the storage at ambient temperature. However, increased coagulation ratios were detected when the E-44 content was higher than 10 wt %. In the case of EPUA7, phase separation was observed after 2 months, and complete separation was observed after 4 months. This may have been due to the higher particle size for EPUA7 compared with other emulsions, which led to sedimentation during storage.¹⁵ The result was consistent with the average size and distribution of the emulsion droplets. Therefore, we concluded that the crosslinking and phase behavior between PU and PA during the synthesis of the PUA microemulsions straightway played an important role in the average particle size and stability of the emulsions.

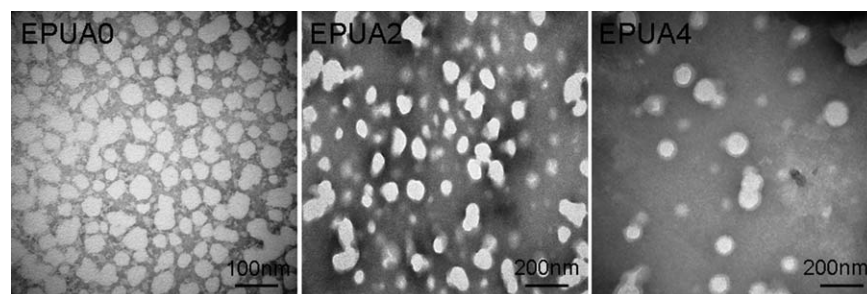
Morphological Analysis of the EPUA Microemulsions

Figure 3 shows the transmission electron microscopy morphology for the EPUA microemulsions without and with E-44. As to EPUA0 without E-44, an irregular shape with a heterogeneous size distribution was detected. This suggested a bigger deformability of the EPUA0 colloidal particles, which may have

Table I. Effects of the E-44 Content on the Properties of the EPUA Microemulsions

Designation	$n(\text{NCO})/n(\text{OH})$	$m(\text{MMA})/m(\text{BA})$	$m(\text{PU})/m(\text{PA})$	E-44 content (%)	Diameter (nm)	PDI	Coagulation ratio (%)
EPUA0	1.8	1:1	6:4	0	63.92	0.406	0.00
EPUA1	1.8	1:1	6:4	2	71.86	0.334	0.00
EPUA2	1.8	1:1	6:4	4	77.96	0.263	0.00
EPUA3	1.8	1:1	6:4	6	83.94	0.141	0.00
EPUA4	1.8	1:1	6:4	8	86.49	0.276	0.32
EPUA5	1.8	1:1	6:4	10	99.02	0.364	2.43
EPUA6	1.8	1:1	6:4	12	125.2	0.433	5.67
EPUA7	1.8	1:1	6:4	14	202.6	0.561	7.98

$n(\text{NCO})/n(\text{OH})$ is the molar ratio of NCO groups to OH groups; $m(\text{MMA})/m(\text{BA})$ is the weight ratio of MMA to BA, the others are the same.

**Figure 3.** Particle morphology of the EPUA microemulsions without and with E-44.

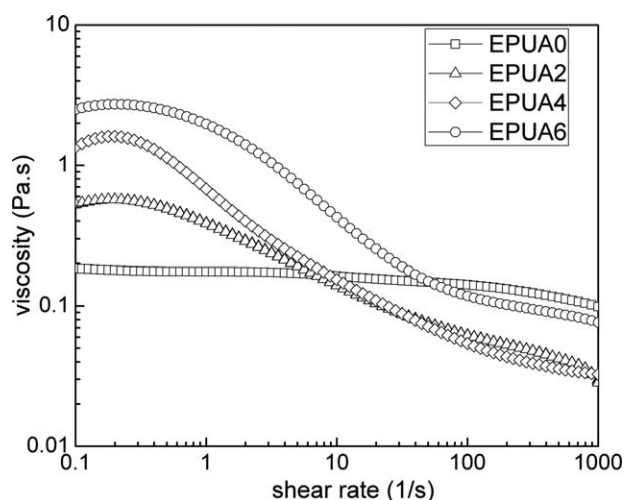
been due to the lack of rigidity or interactions among the polymer chains. With the introduction of 4 wt % E-44, more than one kind of particle was observed, where some were core-shell particles, but others did not show any contrast at all. The particles that showed core-shell morphologies were composed of both PU and PA, whereas those that showed no contrast were composed of pure or nearly pure PU or PA components. When the E-44 content was increased to 8 wt %, spherical particles with an apparent core-shell morphology were observed for EPUA4. The darker region of the shell represented the PU domains, and the lighter region of the core was the PA domains because the electronic cloud density around the PU chains was higher than that of PA.¹⁶ The regular spherical structure for EPUA4 indicated that the rigidity of the colloidal particles was enhanced with E-44 addition, and the interactions between the PU and PA chains simultaneously increased.

Rheological Properties of the EPUA Microemulsions

Figure 4 shows the viscosity versus shear rate curves of EPUA microemulsions with different E-44 contents. We considered that there were many factors, including the molecular architecture, molecular weight, solid content, interaction, and dispersion medium, which affected the rheology of the emulsions.¹⁷ EPUA0 displayed Newtonian behavior. It has been reported that the lack of entanglement in polymers may lead to Newtonian behavior.¹⁸ EPUA microemulsions with E-44 addition exhibited a pronounced deviation from Newtonian behavior. The EPUA2, EPUA4, and EPUA6 microemulsions showed pseudoplastic behavior; that is, there was a decrease in the viscosity as the shear rate increased. Chain entanglements could be rapidly formed because of the increase in the molecular weight with

E-44 addition;¹⁸ this may have been responsible for the pseudo-plastic behavior. It could have also been due to the polar interactions among the molecules, which resulted from the numerous peripheral polar groups.¹⁷ We also found that the viscosity and pseudoplastic behavior increased with increasing E-44 content. This was ascribed to the formation of enhanced interactions between the EPUA colloidal particles.

Oscillatory measurements offer a nearly nondestructive measuring method that allows structural studies on complex systems. Figure 5 shows the frequency dependence of the storage modulus of EPUA microemulsions (G') and loss modulus (G'') for

**Figure 4.** Viscosity versus the shear rate of EPUA microemulsions with different E-44 contents.

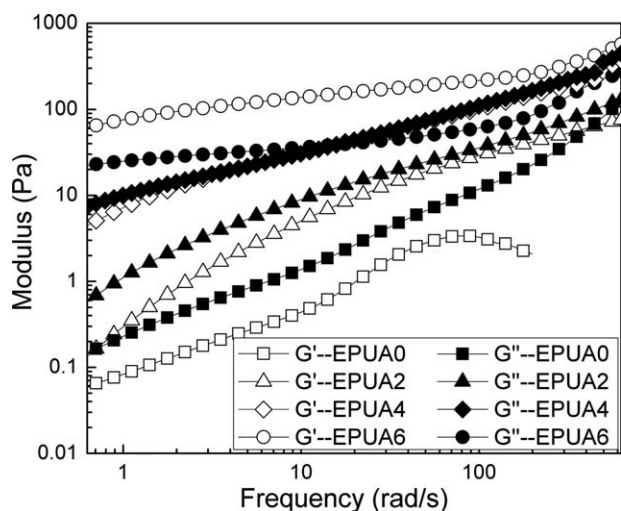


Figure 5. Modulus versus the frequency curve of EPUA microemulsions with different E-44 contents.

EPUA microemulsions with different E-44 contents (carried out in the linear viscoelastic region at $\gamma = 1\%$). G' quantified the mechanical properties of the respective emulsions. Hence, it was also a measure of the molecular and colloidal interactions in the sample.¹⁹ For EPUA0, the microemulsion behaved like a viscous liquid, showing $G' < G''$ in the frequency region. The EPUA2 microemulsion behaved as a viscoelastic liquid because G' was lower than G'' in the lower frequency regime and G' became equal to G'' in the higher frequency regime. The EPUA4 microemulsion was gel-like and characterized by $G' = G''$ and loss factor ($\tan \delta$) = 1,²⁰ this suggested a self-similar relaxation time spectrum at the gel point. EPUA6, with a higher E-44 content, behaved in solidlike manner ($G' > G''$).²¹ The apparent liquid-to-solid transition could be ascribed to enhanced particle–particle interactions with increasing E-44 content.

Thermal Stability

Figure 6 shows the TG and DTG curves of EPUA modified with different contents of E-44. The thermal stability was evaluated by the degradation temperatures at 10% weight loss ($D_{0.1}$) and 50% weight loss ($D_{0.5}$). It is worth noting that $D_{0.1}$ increased from 262 to 269°C, and $D_{0.5}$ increased from 326 to 360°C with increasing E-44 content to 8 wt %. This behavior was attributed to the presence of stronger interactions between the PU and PA

chains with the introduction of E-44.¹² However, the thermal stability was weakened with further addition of E-44.

In EPUA0, there three stages were identified: (1) the first stage (150–261°C), displayed as a shoulder, was ascribed to urethane degradation, (2) the second stage (261–337°C) was mainly due to PCL degradation,^{22,23} and (3) the third stage (337–600°C) was mainly attributed to PA degradation. With 8 wt % E-44 addition, the three degradation stages merged together to form a broad degradation peak with a maximum peak temperature of 348°C (EPUA4). This indicated that the phase compatibility between PU and PA was enhanced with a certain amount of E-44 addition. However, two separate degradation peaks were detected when the E-44 content was greater than 10 wt % (EPUA6 and EPUA7); this suggested the occurrence of phase separation.

Dynamic Mechanical and Phase Behavior

To further study the effects of E-44 content on the phase behavior of PUA, dynamic mechanical analysis for EPUA0 and EPUA4 was also performed. Figure 7 shows the temperature dependence of the storage modulus of EPUA films (E') and $\tan \delta$ of EPUA0 and EPUA4 films. The behavior of E' showed a plateau in the region between -100 and -85°C . This area was determined as a glass area and could be characterized by the low mobility of the polymeric chains.²⁴ With increasing temperature, a steeper fall in E' was observed, characterizing the glass-transition region, that is, the change of the glass state into the rubbery state. After all of the chains acquired mobility (rubbery behavior), a transition peak was generated. The maximum $\tan \delta$ value was used to define the glass-transition temperature (T_g) in this study.

The temperature range in the glass plateau region increased with E-44 addition. We also observed that E' of EPUA4 was higher than that of EPUA0; this indicated that EPUA4 had a higher crosslinking degree²⁵ and cohesive strength.²⁶ Two T_g values at -52.12 and 21.29°C with $\tan \delta$ values of 0.2276 and 0.3085 were detected for EPUA0. This suggested microphase separation in EPUA0.²⁷ With 8 wt % E-44 addition, T_g shifted to a higher temperature, and the two separate T_g 's merged together to form a peak at 32.36°C with a higher $\tan \delta$ value of 0.4862. This result indicated that the introduction of E-44 improved the interaction and compatibility between the PU and PA chains and resulted in phase mixing. The higher $\tan \delta$ value also revealed that the introduction of E-44 was beneficial to the

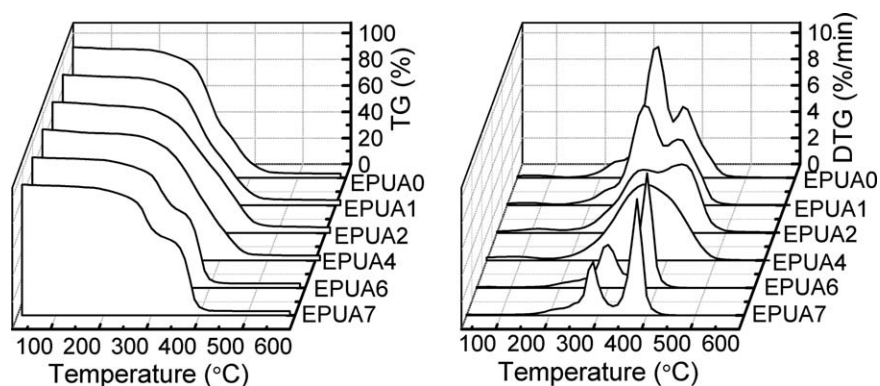


Figure 6. TG and DTG curves of EPUA films with different E-44 contents.

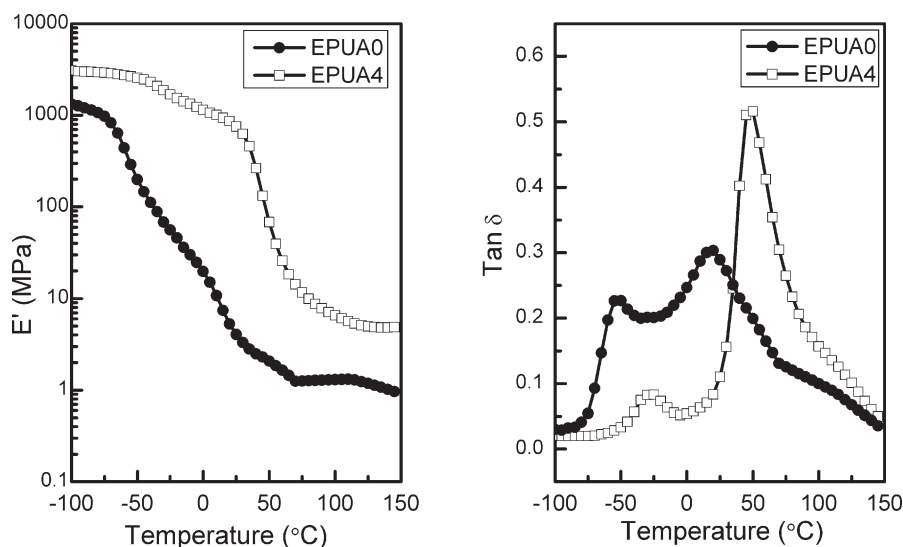


Figure 7. Temperature dependence of the storage modulus and $\tan \delta$ for the EPUA0 and EPUA4 adhesive films.

improvement of the EPUA flexibility.²⁵ The increased E' , together with the increased $\tan \delta$, suggested that the chain extension reaction of PU with E-44 increased the molecular weight of PU, and E-44 simultaneously served as a crosslinker-like moiety.²⁸ On the one hand, with the chain extension of E-44, the PUA chain contained more dangling PU chains, which were able to connect into bridges when additional E-44 was available.⁴ On the other hand, the soft segment molecules of PU and the PA molecules were intertwined in a manner similar to that of an interpenetrating network. More crosslinking points were introduced between the PU and PA chains. Therefore, the compatibility between PU and PA could be significantly improved because of higher degrees of interpenetration, cross-linking, and entanglement.²⁹

Mechanical Properties

To determine whether the increased E-44 content in the formulation affected the polymer network architecture inside each colloidal particle, the mechanical and cohesive properties were also investigated. The tensile strength and elongation at break of the EPUA films with different E-44 contents are illustrated in Figure

8. The tensile strength increased from 8.12 to 22.3 MPa when the E-44 content was lower than 8 wt %; this was followed by a decrease with a further increase in the E-44 content. A similar phenomenon was also detected for elongation at break. The elongation at break also increased slightly and then decreased greatly. The molecular weight was increased with increasing E-44 content, and more bridges between PU and PA were formed; this resulted in increases in the tensile strength and elongation at break. The decreased tensile strength and elongation at break at higher E-44 contents could be ascribed to the larger particle size and phase separation, which led to poor film-forming properties. In addition, more rigid benzene ring structures were simultaneously introduced into the polymer structure; this may have been responsible for the steep decrease in the elongation at break at higher E-44 contents. Furthermore, the increased bridging between PU and PA resulted in a reduction of the mobility of the PU and PA chains and thereby reduced the elongation at break.³⁰

Water and Solvent Resistance

Figure 9 shows the effects of E-44 content on the water swelling and toluene swelling ratio of the EPUA adhesive films. We

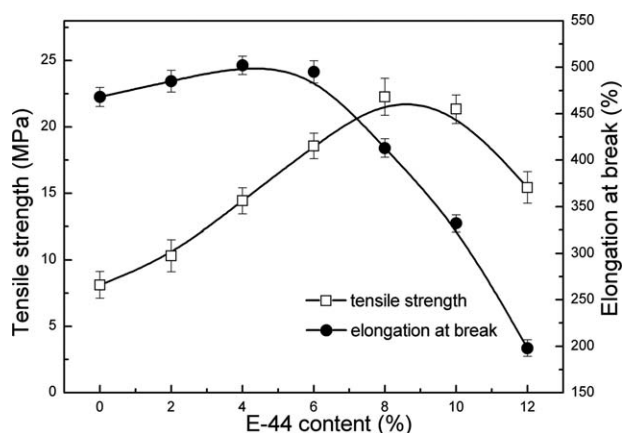


Figure 8. Effect of the E-44 content on the tensile strength and elongation at break.

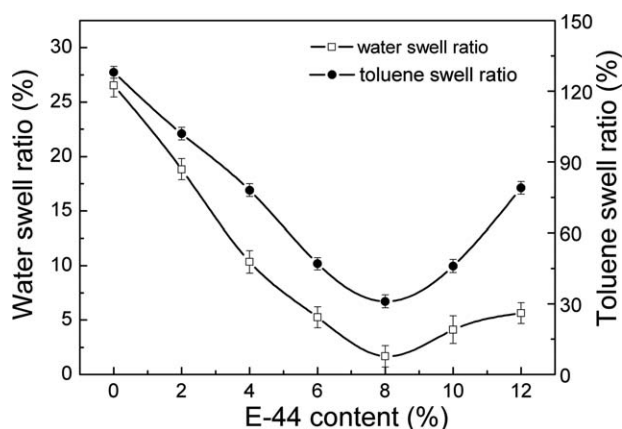


Figure 9. Effect of the E-44 content on the water swelling and toluene swelling ratio.

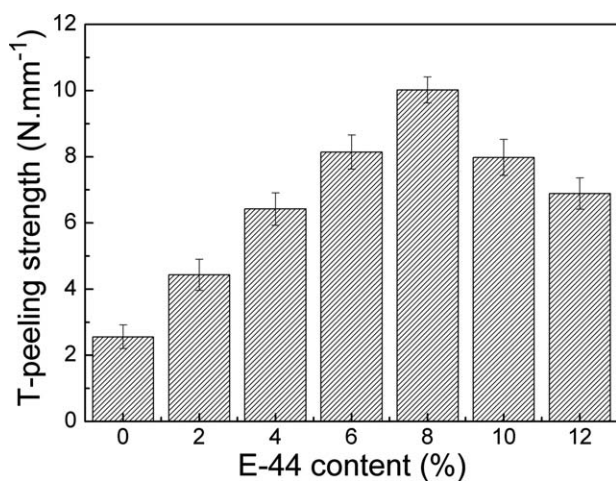


Figure 10. Variation of the T-peel strength as a function of the E-44 content.

found that the introduction of E-44 increased the crosslinking and entanglement between the PU and PA chains and led to an increase in the water resistance and solvent resistance. However, when excessive hydrophobic E-44 was used, the increased hydrophobicity greatly decreased the self-emulsifying ability of the PUA chains; the particle size of the resulting emulsions was larger. Therefore, it was difficult to obtain continuous and closely packed films, and this resulted in decreases in the water and solvent resistance.

Cohesive Properties

Finally, the cohesive properties of EPUA with different E-44 contents were determined, as shown in Figure 10. The T-peel strength increased with E-44 content; this was followed by a decrease when the E-44 content was greater than 8 wt %. In general, the small particle size allowed for easy penetration into the porous leather and rubber substrate, and chemical bonds were formed. This resulted in better cohesive properties.⁹ However, the particle diameter increased with increasing E-44 content from 0 to 8 wt %. This indicated that the slight increase in the particle size had little impact on the cohesive properties. The increased intermolecular entanglement, interaction, and compatibility between the PU and PA chains and the interaction between the EPUA colloidal particles were able to account for the enhanced T-peel strength. However, when the E-44 content was higher than 8 wt %, the steep increases in the particle size and viscosity were detrimental to the infiltration of the EPUA adhesive to the substrate and leather, and this resulted in a decrease in the cohesive properties.⁹ On the other hand, the decreased mechanical strength caused by excessive E-44 content was also responsible for the decrease in the T-peel strength.

CONCLUSIONS

With E-44 as a chain extender and with a crosslinking composition, an efficient and ecofriendly EPUA microemulsion that could find applications in bonding leather in the footwear industry was successfully prepared through an *in situ*, surfactant-free polymerization. The crosslinking, entanglement, and phase behavior between the PU and PA during the synthesis

of the EPUA microemulsions affected straightaway the average particle size and stability of the emulsions. With 8 wt % E-44 addition, the particle diameter increased gradually from 63.92 to 86.49 nm, and the particle size distribution transferred from a bimodal distribution to a unimodal distribution. The morphology of the EPUA colloidal particles transferred from an irregular shape to a spherical core-shell structure. In addition, the mechanical, thermal stability, solvent resistance, and cohesive properties were certified to have resulted from a good balance between the morphology, interaction, rheological behavior, and phase behavior of the EPUA system. The pseudoplastic EPUA microemulsion with a moderate viscosity and a particle diameter less than 100 nm, displaying viscoelastic or gel-like behavior, was found to be endowed with good cohesive properties. The improved thermal stability, mechanical properties, solvent resistance, and cohesive properties were ascribed to the enhanced phase mixing, interaction, and entanglements between PU and PA and the increased interactions between EPUA colloidal particles. However, the particle size, PDI, and viscosity increased abruptly when the E-44 content was greater than 8 wt %. Enhanced phase separation was also certified. These factors were responsible for the decreases in the related properties. Therefore, the introduction of a suitable amount of E-44 into the PUA chain improved the cohesive properties of the copolymer and, more importantly, coordinated the structure and properties of the copolymer to be in favor of promoting the interactions among the substrate, leather, and PUA.

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