

Effect of 2-Ethylhexyl Acrylate and N-Acryloylmorpholine on the Properties of Polyurethane/Acrylic Hybrid Materials

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ABSTRACT: A hybrid synthesis technology was used to prepare waterborne polyurethane/acrylic hybrid emulsions by polymerization of methyl methacrylate, butyl acrylate, 2-ethylhexyl acrylate(EHA), and N-acryloylmorpholine (AMCO) in presence of acrylic-terminated PU dispersion. Various characterization methods were used to investigate the effect of EHA and AMCO content on the properties of the hybrid emulsions and their resultant films. The research results show that the introduction of EHA can enhance the elasticity of their films, meanwhile, AMCO endows the film with high gloss, adhesion on substrate, toughness, and hardness. Mixing the two monomers leads to yield the hybrid materials with moderate properties. While increasing the weight ratio of AMCO/EHA, the average particle size of the hybrid emulsions increases and their viscosity decreases. For the resultant films, their surface water contact angle, adhesion on substrates, tensile strength, and hardness increase, but the water resistance and elasticity decrease. It has been found that EHA and AMCO have a synergistic effect on gloss of the hybrid films and the hydrogen bond interaction increases with an increase in the AMCO content. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41463.

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INTRODUCTION

As environment-friendly materials, polyurethane (PU) dispersions are well known for their application in surface coatings on the wood, metal, fabrics, leather, paper, and plastics because the formed films have desirable properties, such as good adhesion, chemical resistance, abrasion resistance, toughness, and excellent elasticity. However, PU dispersions are relative expensive, which restricts their application in some cases. Acrylic polymers (AP) are considered to be low cost and have good water resistance, weather resistance, and mechanical properties. Hybridization of the two polymers is expected to take the advantages of their potential cost reduction and tunable properties. Therefore, development of waterborne polyurethane/acrylic (WPUA) hybrid materials has attracted a lot of attention over the years.

Various reports describe the synthesis technology of these hybrid materials. In the research works, the emulsion polymerization process is one of the approaches used for preparing WPUA hybrid emulsions.^{1–3} By this process, acrylic-terminated

PU polymers with an amphiphilic molecular structure are synthesized by reaction of hydroalkyl acrylate with isocyanate-terminated PU prepolymer (a polyaddition of diisocyanate, dimethylolpropionic acid, hydroxyl-terminated polyether, or polyether) and then neutralizing with triethylamine. As an emulsifier and an acrylic monomer, the PU polymer copolymerizes with acrylic monomers in presence of initiators to prepare WPUA hybrid emulsions via emulsion process. Compared to the blend of PU and AP dispersions, the hybrid films exhibit superior quality, such as gloss, adhesion and the other mechanical properties.⁴

As a major component, acrylic monomers play a crucial role in the performance of WPUA hybrid materials. As mentioned above, hydroxylalkyl acrylate is always used to synthesize acrylic-terminated PU, which builds up chemical bonds between PU and AP to enhance their compatibility.^{3–5} Hydrophilic acrylic monomers, such as acrylic acid, acrylamide, or hydroalkyl acrylate, can be used as the hydrotrope monomers to obtain stable hybrid emulsions because most of acrylic

Table I. The Recipe of Different WPUA Hybrid Emulsions

System	H0:0	H0:100	H25:75	H50:50	H75:25	H100:0
PU dispersion						
PPG				36.0		
PPA				24.0		
IPDI				33.3		
DMPA				8.1		
HEA				16.2		
TEA				6.0		
water				343		
Acrylic monomer						
MMA	33.5	27.0	27.0	27.0	27.0	27.0
BA	51.7	41.1	41.1	41.1	41.1	41.1
EHA	-	17.1	12.9	8.4	4.2	-
ACMO	-	-	4.2	8.4	12.9	17.1
K ₂ S ₂ O ₈				0.678		
water				120		

monomers are hydrophobic.⁵⁻⁷ Methyl methacrylate (MMA) and butyl acrylate (BA) are the most popular monomers for the preparation of WPUA hybrid emulsions because balance of the hard and soft monomers provides the resultant films with tunable physical properties.⁸⁻¹¹ The introduction of fluorinated acrylates can endow the hybrid films with good chemical resistance, low water absorptivity, excellent flexibility, good wearing ability, and high weatherability.^{12,13} The acrylate with trimethoxysilane group are used to prepare self-crosslink WPUA hybrid emulsions which form the films with high thermal stability, low water absorptivity, good scratching, and abrasion resistance.^{14,15}

The application of polymers is mainly dominated by their properties, which in turn depends on their chemical architecture. With a long aliphatic chain, 2-ethylhexyl acrylate (EHA) is used to prepare polymers with high viscoelasticity.^{16,17} Alternatively, N-acryloylmorpholine (ACMO) is useful for the preparation of semipermeable membranes, polymeric supports for gel chromatography and superabsorbent composite, etc.^{18,19} However, to our knowledge, the preparation of WPUA modified with EHA and ACMO has not been reported until now. In this study, we prepared WPUA materials by polymerization of MMA, BA, EHA, and ACMO in the presence of acrylic-terminated PU dispersion via emulsion process. To investigate the EHA and ACMO on the properties of WPUA materials, the weight ratio of ACMO/EHA was varied and the content of MMA, BA, and PU was fixed. The average particle size and viscosity of the hybrid emulsions were determined, meanwhile, the properties of resultant hybrid films were also evaluated.

EXPERIMENTAL

Materials

Polypropylene glycol (PPG, $M_n = 2000$) and polypropylene glycol adipate (PGA, $M_n = 2000$) were supplied by Shandong Dongda Chemical, China. Isophorone diisocyanate (IPDI) was purchased

from Rongrong Chemical, China. Dimethylol propionic acid (DMPA), potassium persulfate (KPS), triethylamine (TEA), and dibutyltin dilaurate (DBTDL) were bought from Tianjin Chemical, China. MMA, hydroxyethyl acrylate (HEA), EHA, and ACMO were obtained from Zhangjiagang Huarui Chemical, China. Deionized water was used throughout the work. All the above chemicals were used as reserved without further purification.

Synthesis of WPUA Hybrid Dispersions

The recipes for the synthesis of WPUA hybrid emulsions with and without EHA and ACMO are given in Table I.

To a 1000 mL of four-necked round bottomed flask equipped with a mechanical stirrer, a thermometer, a nitrogen inlet and a condenser, PPG and PGA were charged and stirred at the temperature of 110°C for 2 h to remove the moisture. After the temperature was cooled to 65°C, IPDI, DMPA, and 0.1 g of DBTDL were added into the mixture at nitrogen atmosphere and the reaction was carried out at 80°C until the theoretical NCO value of the prepolymer was reached as determined by the di-n-butylamine back titration.¹ Then, HEA was added into the system and reacted for 4 h at the same temperature to end the NCO groups completely. After the viscous product was diluted with the mixture of MMA and BA, the solution was cooled to 50°C and TEA was added to neutralize the COOH content for 1 h. Deionized water was added slowly into the flask under vigorous stirring (ca. 1000 rpm) for 25 min. Acrylic-terminated PU dispersion was obtained.

The mixture of EHA and ACMO were introduced into the dispersion under stirring. The temperature was raised to 75°C and 1 wt % KPS aqueous solution was added for 3 h and the reaction was continued for another 2 h at 80°C. WPUA hybrid emulsions with about 31 wt % solid content were obtained.

Characterization of the Hybrid Emulsions

The morphologies of the hybrid particles were observed by a JEM-1011 transmission electron microscopy (TEM, Japan). To

perform the measurement, the emulsion was diluted with water at a high dilution level. Then, a drop of the sample was deposited onto a copper grid and stained with 2 wt % phosphotungstic acid hydrate before drying.

The particle size of the emulsion was determined by a Bertter-size2000 laser particle size analyzer (LPSA, Dandong Baxter, China). The emulsion was diluted with water to adjust the solid content to about 1 wt % under ultrasonic dispersing and the measurements were carried out at 25°C.

The viscosity of the emulsion was analyzed with a NDJ-79 rotary viscometer (Shanghai Scientific Instruments, China) at 25°C.

Preparation and Performance Evaluation of WPUA Hybrid Films

WPUA hybrid films were prepared by casting certain amount of the emulsions onto polytetrafluoroethylene plates at room temperature for 48 h, followed by drying at 80°C for 4 h. Then the films were stored in a desiccator at room temperature for characterization.

The temperature and humidity may have a slight influence on the test results of the hybrid films.⁴ Therefore, all the determinations of the films were carried out at ambient temperature and humidity (22–25°C/50–70 RH) and the test error was not taken into consideration.

FTIR spectra of the prepared thin films were obtained on a KBr pellet using a Thermo Nicolet-360 Fourier transform infrared spectrometer (USA). Each sample was scanned 32 times with a resolution of 2 cm⁻¹ in the range of 1500–3500 cm⁻¹. The individual -NH band in FTIR spectrum was resolved by employing Fourier self-deconvolution (FSD) and Gaussian curve-fitting techniques using Origin software. A program was established to analyze FTIR spectrum according to the literature.²⁰

The water contact angle of the films was determined on a DSA20X contact angle goniometer (Germany) using the sessile drop method. Drops of water were deposited onto the surfaces of hybrid film and the direct microscopic measurement of the water contact angle was done with software for drop shape analysis.

The gloss of each film was measured at 60° and 85° by a BYK4446 micro-TRI gloss meter with standard holder (Germany) according to the ASTM standard D-523. Measurement was taken in quintuplicate for each film.

Water absorption of the films was tested as follows: A piece of the film with known weight (W_0) was immersed in water at room temperature. After 48 h, the sample was taken out and the film was weighed again (W). The water absorption was calculated as follow:

$$\text{Water absorption (\%)} = (W - W_0) \times 100 / W_0$$

The adhesion of the hybrid materials was evaluated according to the ISO2409:2007 standard. After the hybrid emulsion was coated and dried on the melamine board and tinplate, respectively, the coating was scratched by multiblade cutting device and then a scotch adhesive tape was used to tape the scratched coating. The coating retentions were measured to evaluate the

adhesion of the WPUA on melamine board and tinplate. The values obtained were the average of three replicates.

The tensile strength and elongation at break of the films were determined by an electronic universal testing machine (Shenzhen SANs Testing Machine, China) with a crosshead speed of 20 mm/min. Dumbbell specimens were cut from the films by a sheet-punching machine. An average value of five replicates of each sample was taken to report.

The hardness of the films was measured at room temperature by HT-6510A Shore A Hardness Tester (Landtek Instruments, China) according to ASTM D 2240. Results are the average value of five measurements.

RESULTS AND DISCUSSION

The primary objective of this study is to investigate the effect of the EHA and ACMO content on the properties of WPUA hybrid materials. Compared to 2-EHA bearing a long hydrophobic chain, ACMO presents several special features: solubility in aqueous solutions and organic solvent, ability to increase the hydrogen bond interaction in polymers. Therefore, the hybrid emulsions modified with EHA and ACMO were synthesized by copolymerizing different weight ratio of ACMO/EHA with a fixed content of MMA and BA in presence of acrylic-terminated PU dispersion by emulsion polymerization process. Meanwhile, WPUA without the two monomers was also prepared by keeping the same content of PU and AP. Figure 1 shows the preparation scheme of WPUA. It is expected that modification of WPUA with of EHA and ACMO can improve the performance of their hybrid emulsions and resultant films.

Effect of EHA and ACMO on the Properties of WPUA Hybrid Emulsions

Figure 2 shows WPUA hybrid particle morphologies observed by TEM. It can be observed that the particles are irregular spheres with sizes ranging from about 50 to 250 nm and the spherical particles exhibit a semi-interpenetrating network structure, meanwhile, the particle sizes seem to be slightly reduced with an increase in the weight ratio of ACMO/EHA. The phenomenon may be explained by the schematic representation of the formation of the hybrid particle showed in Figure 3. During preparation of PU dispersion, MMA and BA are used as dilution solvent to reduce its viscosity. As the result, MMA and BA swell or diffuse into the PU particles [Figure 3(a)]. When the reaction is initiated, the introduced EHA and ACMO copolymerize with MMA, BA, and acrylic-terminated PU, which results in grafting AP into both sides of urethane linkages to form MMA/BA/EHA/ACMO/PU copolymer through the colloidal particles [Figure 3(b)]. Simultaneously, the PU chains propagate and start re-arranging PUA chains to minimize the enthalpy penalty by placing their hydrophilic groups (carboxylic anion and morpholine group) on the particle surface as much as possible. This rearrangement leads to the formation of relatively stable PUA particles with semi-interpenetrating network structure.²¹ The formation of particles is dependent on the content of hydrophilic groups. This higher content of hydrophilic groups naturally results in the formation of smaller particles, and vice versa.²²

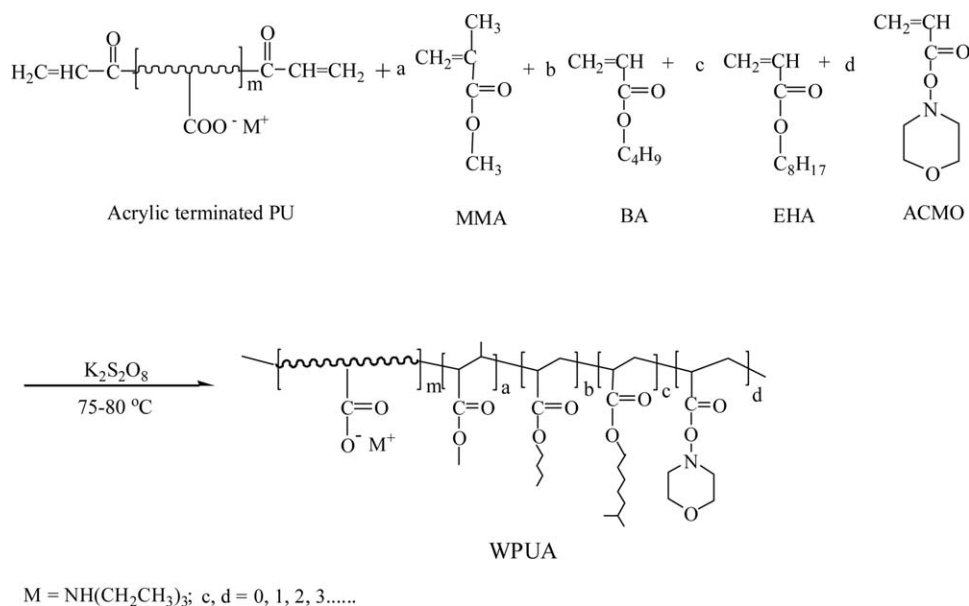


Figure 1. Scheme for the preparation of WPUA hybrid materials.

This result can be confirmed by the average particle size of the hybrid emulsions determined by LPSA, and the result is given in Figure 4. It can be found that the average particle size of the hybrid emulsions is bigger than that measured by TEM. When the weight ratio of ACMO/EHA is increased from 0 : 100 to 100 : 0, the average particle size of the emulsions decreases gradually from 236 to 215 nm though the content of EHA and ACMO accounts for only 8.1 wt % of the synthetic material.

This phenomenon is reasonable because the average particle sizes determined by LPSA are in emulsion state and their average size is bigger than the particle size observed by TEM in dried condition. Although the content of EHA and ACMO accounts for only 8.1 wt % of the synthetic material, they can slightly affect the average particle size of the hybrid emulsions because of the change of hydrophilic group content. In the experiment, it is interesting to find that the average particle size

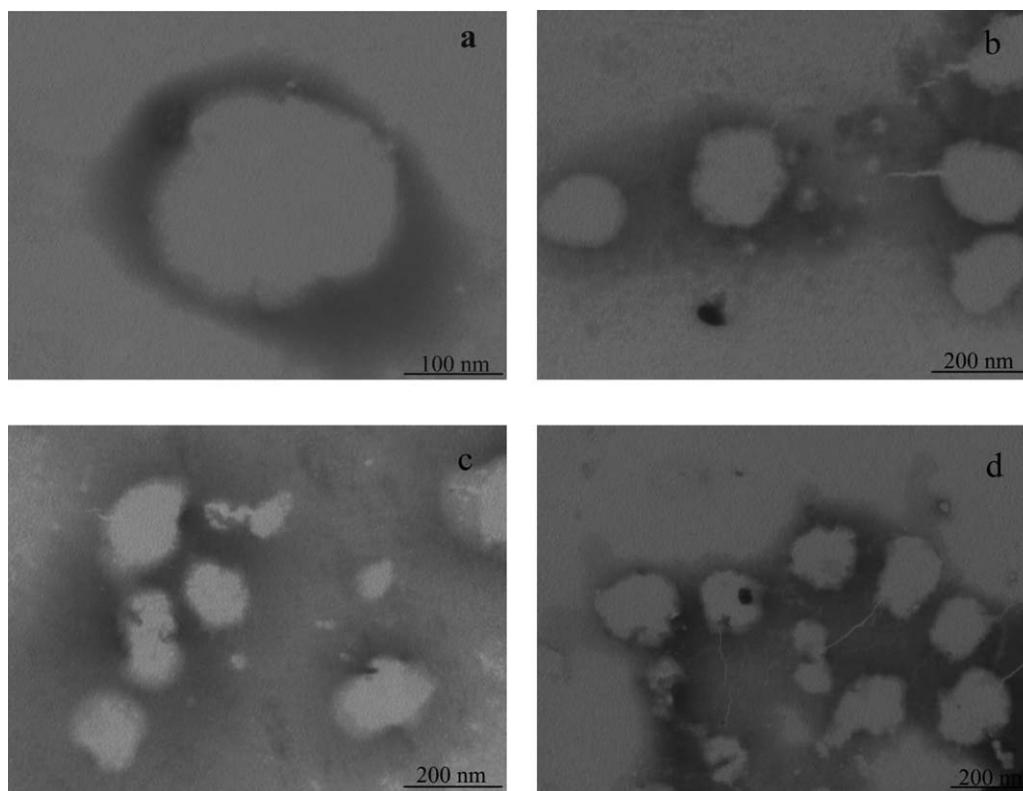


Figure 2. TEM morphology of WPUA hybrid particles (a) typical particle, (b) H0:100, (c) H50:50, and (d) H100:0.

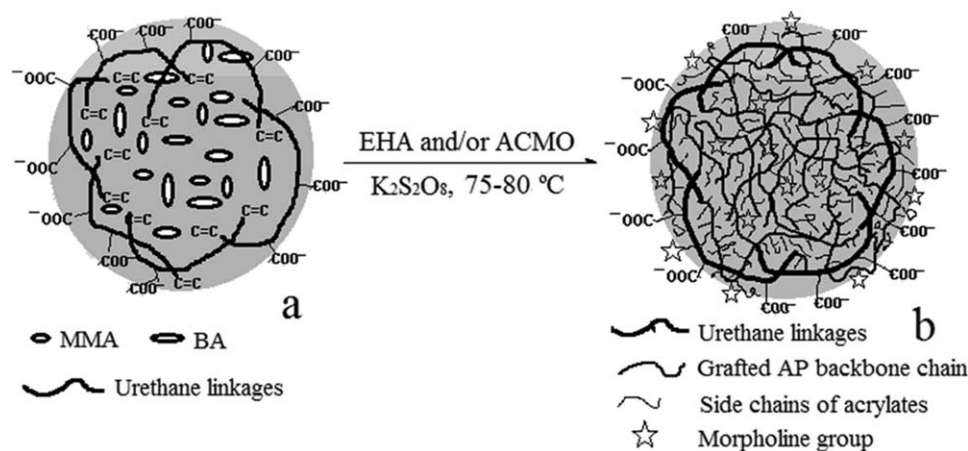


Figure 3. The schematic representation of the formation of (a) the acrylic-terminated PU and (b) WPUA particle.

of PU dispersion is 233 nm, which is similar to H0:100 but bigger than that of the others. This result also supports above conclusion that the particle sizes of the self-emulsifying dispersions are mostly decided by the content of hydrophilic groups rather than the polymer compositions.

As seen in Figure 4, the content of EHA and ACMO also impacts the viscosity of the hybrid emulsions. While increasing the weight ratio of ACMO/EHA from 0 : 100 to 100 : 0, the viscosity of the hybrid emulsions increases from 5.1 to 29.1 mPa s. It is because the viscosity of emulsion is mainly governed by the number of particles under the constant external factors such as the shear force and temperature. Increasing the content of ACMO leads to a decrease in average particle size and an increase in the number of particles because the polymer content has not changed. As the result, collisions between particles and the hydrodynamic volume increase, which results in a slight increase in the viscosity of their emulsions.²²

Effect of EHA and ACMO on the Properties of WPUA Films

Figure 5 shows the dependence of the hybrid film gloss on the content of EHA and ACMO. In the figure, the gloss of the films at 85° is higher than those at 60° because the light reflection is enhanced when the incidence angle is increased. Interestingly,

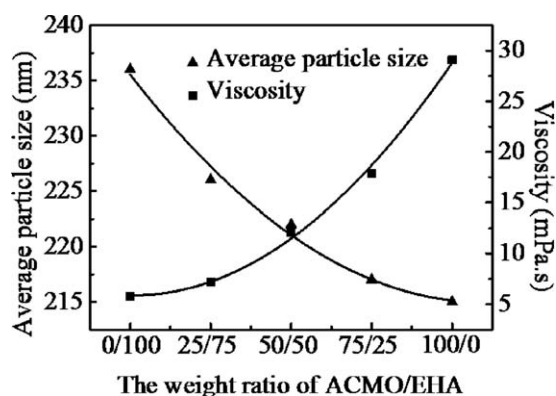


Figure 4. Effect of the ACMO and EHA content on the average particle size and viscosity of WPUA hybrid emulsions.

the gloss of H100:0 is higher than that of H0:100, but the glosses of the hybrid films synthesized from mixture of two monomers are higher than both of them. When the weight ratio of ACMO/EHA is 50 : 50, the film exhibits highest gloss. The possible reason is that the polymeric films with rigid ring group can increase their gloss because the rigid ring can scatter light.²² However, mixing the monomers with rigid rings and soft chains leads to formation of mutual chain entanglement and interpenetrating polymer network, which has synergistic effects on the gloss of the hybrid film.^{23,24}

Water contact angle is an indicator of the water wetting ability of the film's surface. In Figure 6, the water contact angle of H0:100 is highest and the H100:0 is lowest. An increase in the weight ratio of ACMO/EHA leads to a decrease in the contact angle of their hybrid films, correspondingly, the wetting ability is increased. The results indicate that EHA can increase the hydrophobicity of the hybrid film's surface because of its long aliphatic chain, whereas, ACMO possess a hydrophilic morpholine group which increase the wetting ability of the polymeric surface.

The water absorption of WPUA films was determined by immersing the film in water for 48 h and the results are also given in Figure 6. As expected, the water absorption of H0:100

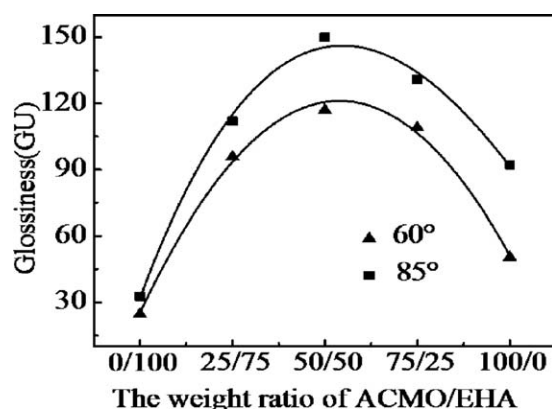


Figure 5. Effect of EHA and ACMO content on the gloss of WPUA hybrid films.

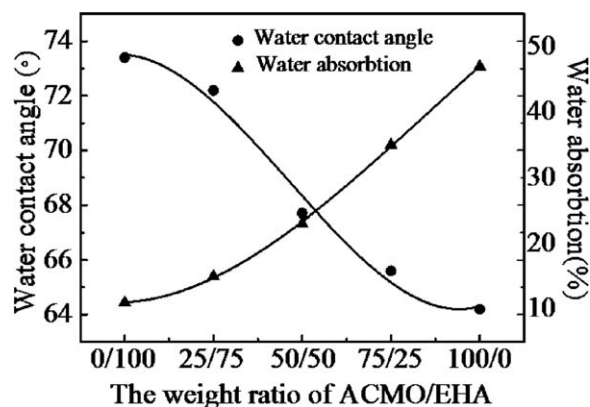


Figure 6. Effect of EHA and ACMO content on the water contact angle and water absorption of WPUA hybrid films.

is 9.2%, but it reaches to 45% while weight ratio of AMCO/EHA is 100 : 0. Mixing EHA and ACMO can obtain the hybrid film with moderate water resistance. This is because the water absorption of polymers mostly depends on the hydrophilicity of their segments.¹¹ High EHA content leads to formation of the hybrid film with low water absorption because of its hydrophobic chains. However, introduce of ACMO is unfavorable for the improvement of the polymeric water resistance because of its hydrophilic character.

The adhesion properties of WPUA on melamine board and tinplate were determined by scratch test and the results are showed in Figure 7. As seen in figure, the adhesion of WPUA on melamine board is higher than that on tinplate. When H0:100 are coated on the two substrates, there are only about 42% and 63% coating retentions on the tinplate and melamine board, respectively, after test. However, an increase in the weight ratio of ACMO/EHA leads to an enhancement in their adhesion on substrates. When the weight ratio of AMCO/EHA reaches to 100 : 0, there are no scratches on melamine board and about 90% coating retention on tinplate after scratch test. It can be concluded that ACMO can increase the adhesive of WPUA on substrate, but EHA do not. It is well known that the polymers with aliphatic chains weaken the their adhesion on substrates, but introducing the polar groups into polymers can improve their adhesive force with substrate because of the formation of

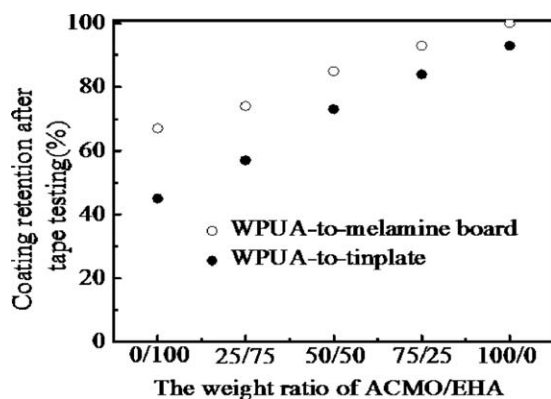


Figure 7. Effect of EHA and ACMO content on adhesion of WPUA on melamine board and tinplate.

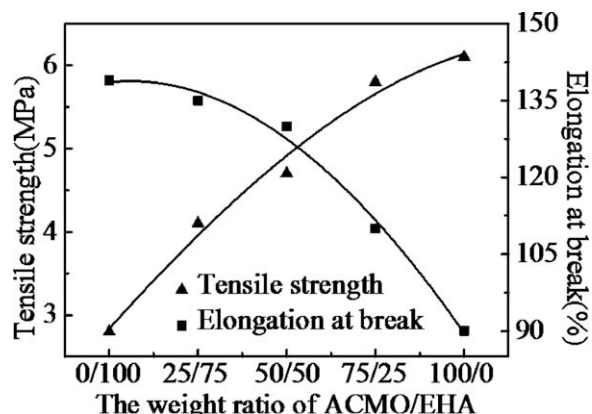


Figure 8. Effect of EHA and ACMO content on the mechanical properties of the hybrid films.

hydrogen bond or covalent bonds between the polymer and substrate.^{17,25} As for the substrate, the active hydrogen and hydroxyl groups exist on the melamine boards, whereas, tinplate contains only metal element. When WPUA is coated on them, the formation of hydrogen bond and covalent bonds between WPUA and melamine board leads to yield higher adhesive force than only the covalent bonds formed between WPUA and tinplate.²⁵

Figure 8 shows the effect of EHA and ACMO on the mechanical properties of WPUA hybrid films. As seen in the figure, the film's tensile strength and elongation at break of H0:100 are 2.8 MPa and 144% respectively, but the corresponding data of H100:0 film are 5.8 MPa and 89%. Mixing two monomers leads to yield the films with tunable mechanical properties. In general, the mechanical properties of WPUA films are dependent on the factors such as the chemical structure of AP and PU, the weight ratio of PU and PA, the degree of hydrogen bond in the hybrid film.^{2,10,22} When the chemical structure of PU and the weight ratio of PU/ PA were fixed, this performance mainly results from the features of two monomers and hydrogen bond interaction formed in the polymers. With long aliphatic chain, EHA can endow the WPUA films with good elasticity, but ACMO enhances their toughness because of its rigid morpholine group.¹⁷ In addition, the hydrogen bond degree in the hybrid films is also an important factor which affects their mechanical properties.

The hydrogen bonds formed in WPUA films was confirmed by FTIR analysis. In the hybrid films, the hydrogen atom of the N–H group in the urethane linkages is the donor proton, while the acceptor group can be the carbonyl groups, the oxygen atom of the ester or ether linkage of the PU and AP segments. In this study, the nitrogen and oxygen atoms of morpholine group in ACMO segment must be taken into account. Figure 9 shows the FTIR spectra of EHA, ACMO, and the hybrid films with different weight ratio of ACMO/EHA. As seen in the figure, the morpholine group in ACMO exhibits the characteristic absorption peak at 1641.14 cm^{-1} and this peak is gradually intensified with an increase in the content of ACMO, which confirmed the grafting and interpenetration of ACMO in polymer.¹⁸ The characteristic peak of C=O group of WPUA is located in

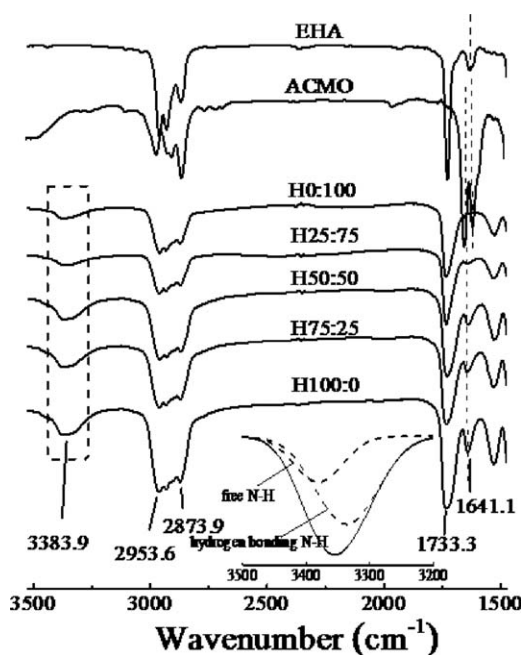


Figure 9. The FTIR spectra of EHA, ACMO and WPUA hybrid films.

1733 cm^{-1} and the adjacent peaks in the range of 2953–2873 cm^{-1} is attributed to asymmetric and symmetric stretching of $-\text{CH}$, $-\text{CH}_2$ and $-\text{CH}_3$ groups, respectively. The peak at about 3459 cm^{-1} corresponds to stretching of $-\text{NH}$ groups of urethane linkages, which is highly sensitive to hydrogen bond distribution. FSD is used to divide this peak into two peaks quantitatively, one for free and another for hydrogen-bonded $-\text{NH}$ bonds near 3380 and 3334 cm^{-1} respectively.^{20,24} Table II shows the divided peak's location and fraction. When the weight ratio of ACMO/EHA is increased from 0 : 100 to 100 : 0, the fraction of hydrogen-bonded $-\text{NH}$ peak increases from 64.3% to 76.3% and the free $-\text{NH}$ decreases simultaneously. In this study, the morpholine group of ACMO can form hydrogen bond with $-\text{NH}$ in the hybrid films. An increase in the ACMO content leads to yield high degree of hydrogen bond in polymers, which produces physical cross-links and reinforces the PUA matrix. Therefore, the polymeric toughness and stiffness are enhanced.²⁵

Figure 10 shows the hardness of WPUA hybrid films. As expected, the shore A hardness of H0:100 and the H100:0 films

Table II. The Location and Fraction of Free and Hydrogen-Bonded $-\text{NH}$ Bond in WPUA Films

Sample	Free N-H		Hydrogen bonding N-H	
	Location (cm^{-1})	Fraction (%)	Location (cm^{-1})	Fraction (%)
H0:100	3379.8	35.7	3332.4	64.3
H25:75	3380.6	33.6	3333.7	66.4
H50:50	3380.8	28.9	3334.4	71.1
H75:25	3380.2	25.4	3334.9	74.6
00:0	3380.6	23.7	3334.1	76.3

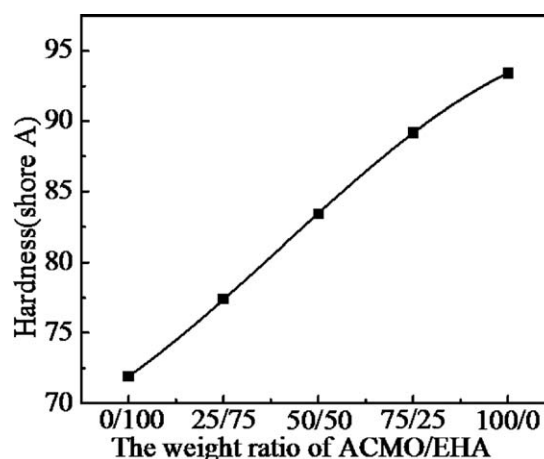


Figure 10. Effect of EHA and ACMO content on the hardness of the hybrid films.

are 72 and 94, respectively. The mixture of the two monomers can prepare the hybrid films with moderate hardness. This result also supports the above conclusion that ACMO can increase the hydrogen bonding interaction in the films, which hardens the WPUA films.

Comparison the Properties of the Hybrid Materials with and Without EHA and ACMO

To investigate their modified effect on the properties of WPUA, keeping the same weight ratio of PU and AP as WPUA modified with EHA and ACMO, PU/MMA-BA (H0:0) was prepared without EHA and ACMO and the characteristic results are given in Table III.

The average particle size and viscosity of H0:0 emulsion are 233 nm and 5.5 mPa.s, respectively, which are similar to that of H0:100 but different with that of WPUA modified by ACMO or the mixture of EHA and ACMO. As discussed above, because MMA, BA, and EHA are all hydrophobic, H0:0 and H0:100 exhibit the similar emulsion performance. However, when ACMO is introduced, the hybrid emulsion shows small average particle size and high viscosity because the hydrophilic content is increased.

Table III. The Characteristics of the Hybrid Material Without EHA and ACMO

Properties	Test results
Emulsion	
Average particle size (nm)	233
Viscosity (mPa.s)	5.5
Film	
Gloss (60°/80°)	34/45
Water contact angle (°)	73
Water absorption (%)	14.1
Adhesion on melamine board and tinplate (%)	60/38
Tensile strength (MPa)	3.5
Elongation at break (%)	117
Shore A hardness	76

The films of H0:0 and H0:100 has some similar properties, such as gloss, water contact angle, and water resistance, but H0:0 has lower adhesion on substrates, elongation at break, and higher tensile strength, hardness than that of H0:100. Compared with the hybrid materials modified with ACMO or mixture of EHA and ACMO, the film of H0:0 shows better water resistance and higher water contact angle, but H0:0 has the significant disadvantage in its gloss, adhesion on substrates, toughness, and hardness. It indicates that EHA can improve the elasticity of the hybrid films. Meanwhile, ACMO can increase the film's properties such as gloss, adhesion on substrates, toughness, and hardness.

CONCLUSIONS

In order to investigate the effect of EHA and ACMO on the properties of WPUA hybrid materials, WPUA hybrid emulsions were prepared by polymerization of EHA, AMCO, MMA, and BA in the presence of acrylic-terminated PU dispersion. The experimental results show that the particles exhibit semi-interpenetrating network structure when the hybrid emulsions were prepared by this process. The effect of EHA and ACMO on the properties of the hybrid emulsion and film can be concluded as follows:

1. The introduction of EA can increase the elasticity of the WPUA films, whereas, their hardness is reduced and the gloss, adhesion, and hardness of the film are not changed.
2. Modification with AMCO, the hybrid emulsions show decreased average particle size and increased viscosity. ACMO can endow the films with high gloss, adhesion on substrates, toughness and hardness, but worsen its water resistance and elasticity.
3. Mixing of EHA and ACMO can prepare the WPUA hybrid materials with moderate properties. With increase the weight ratio of ACMO/EHA, the average particle size of the hybrid emulsions decreases and their viscosity decreases. For the resultant films, the wetting ability of surface, water absorption, adhesion on substrate, toughness, and hardness increase. The EHA and ACMO have synergistic effect on the gloss of hybrid films.

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