Preparation and Properties of Epoxy-modified Waterborne Polyurethane/polyacrylate Composite Emulsion with the Action of Polymerizable Emulsifier

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Abstract

With the introduction of glycidyl methacrylate (GMA) and allyloxy hydroxyl propanesulfonic salt (AHPS) to the waterborne polyurethane/polyacrylate (WPUA) emulsion, a stable epoxy-modified waterborne polyurethane/polyacrylate (EPUAS) composite emulsion with high solid content had been obtained. The structure and morphology were characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron microscope (TEM) and X-ray diffraction (XRD). The GMA content and the AHPS content on properties of the emulsion and films were discussed. The FTIR results showed that GMA and AHPS both reacted with WPUA. A core-shell structure is observed by TEM. The properties of EPUAS emulsion and films were improved by modification.

Key Words: Polymerizable Emulsifier, Epoxy-modified, Polyurethane/polyacrylate, Properties

1. Introduction

As we all know, environmental protection and energy conservation have become the development trend from now on. Waterborne polyurethane has also been widely used due to its non-toxic, non-polluting properties [1,2]. Polyurethane not only has a number of advantages such as oil, acid, wear resistance but also several disadvantages such as poor water resistance, hardness etc [3,4]. However, there are many methods to modify polyurethane, one of the main methods is modification with acrylate. The polyacrylate (PA) has the good properties of mechanical and water-resistance, but their wear resistance and solvent resistance are poor. Therefore, the aqueous resin with the combination of polyurethane and polyacrylate having the two advantages were prepared successfully in this paper [5–7]. As the enhancement of people’s awareness of environmental protection, water-based polyurethane coatings are increasingly paid attention. Polymerizable emulsifier may be able to reduce the interfacial energy, and it can be used in the radical polymerization with its functional groups. The polymerizable allyloxy hydroxypropyl sulfonate (AHPS) linked with the surface of latex particles through chemical bond, then it can also improve the emulsion stability and performance of films [8,9]. This paper introduces AHPS and glycidyl methacrylate (GMA) to the polymer molecular chain, which have the double bond and epoxy group that can be reacted with carboxyl group of the waterborne polyurethane to form a crosslinking structure, thus to improve water resistance and hardness of the polymer properties [10,11]. AHPS is the polymerizable emulsifier, the emulsifier is combined to the surface of polymer particle by chemical bond, which can not only increase the charge density of the polymer particle surface, but also the emulsion stability, thereby improving the solid content [12]. The EPUAS whose solid content was 43% was prepared with the combination of AHPS and GMA, the combined EPUAS have the stable performance, stable emulsion storage stability, under the best ratio of raw materials, and the film’s water resistance, hardness and adhesion have also been significantly improved.
2. Experimental

2.1 Reagents
Poly(caprolactone) glycol (PCL1000), Shenzhen Guanghua WeiYe Industrial Co. Ltd., Industrial; isophorone disocyanate (IPDI), Guangzhou City long Fung Trading Co. Ltd., Industrial; 2,2-bis(hydroxymethyl) butyric acid (DMBA), Guangzhou Jinsheng Ji Chemical Co. Ltd., Industrial; methyl methacrylate (MMA), butyl acrylate (BA), hydroxyethyl acrylate (HEA), triethylamine (TEA), potassium persulfate (KPS), AR, Tianjin Hongyan Reagent Factory; Dibutyl tin dilaurate (DBTDL), chemically pure, Tianjin Guangcheng Chemical Reagent Co. Ltd; glycidyl methacrylate (GMA), industrial pure, Beijing Chemical Plant; allyloxy hydroxypropyl sulfonate (AHPS), industrial products, Xiangtan Hi-tech Zone Linsheng chemical Co. Ltd.

2.2 Synthesis of EPUAS Emulsion
PCL1000 and DMBA after vacuum dehydration were charged into a 500 ml three-necked flask equipped with a stirrer, then MMA, BA were added into the flask, stirring at 60°C until DMBA completely melted, then heating to 75°C. Then a certain amount of IPDI and catalyst DBTDL were added, after reacting for several hours, HEA was added as capping agent and reacting for an hour. Then after neutralizing by TEA, AHPS and deionized water were added to the mixture to emulsify under high speed stirring, after the completion of emulsification, temperature was increased to 80°C, in which the initiator (KPS) accounted for 2% of the amount of PA, and 1/3 of the initiator should be dropped within 1 hour. Then the rest of the MMA, BA and an certain amount of GMA are added by dropping, then continue dropping the remaining 2/3 of the initiator within 2 hours at the same temperature and reacted for 2 hours, and a EPUAS emulsion with the stable performance was obtained. The reaction scheme of EPUAS emulsion is shown in Figure 1.

3. Preparation and Characterization

3.1 Preparation of Films
The prepared emulsion was casted on the polytetrafluoroethylene plate, naturally dried for three days, then placed in a drying oven at 60°C for 24 h, and it is stored in a desiccator.

3.2 FTIR Analysis
The FTIR spectroscopy of the film was analysed by the potassium bromide coating method using VECTOR-22-type Fourier transform infrared spectrometer (BRUKER Co. Ltd, German), the scanning area ranges from 500 cm^{-1} to 4000 cm^{-1}.

3.3 Latex Particle Characterization
The particles morphology stained was observed with H-600 transmission electron microscope (HITACHI Co. Ltd, Japan).

3.4 X-ray Diffraction (XRD) Testing
The X-ray diffraction (XRD) measurements were performed with D/Max-automatic X-ray diffractometer with a CuKα radiation source at room temperature. Patterns were recorded by monitoring diffractions from 5° to 60°. The scan speed was 0.02°/min.

3.5 Emulsion Particle Size and Stability Testing
The particle size, size distribution and zeta potential of the emulsions were measured with BI-200SM’s dynamic light scattering (Brookhaven Co. Ltd, USA). The tests were carried out at 25°C, taking the measuring angle at 90°, and the stable emulsion was measured according to the standard of GB/T6753.3-1986.

3.6 Water and Ethanol Absorption Testing of Films
The test films were cut in the shape of 10 mm × 10 mm × 1 mm. The completely dry specimens were weighed to obtain the initial weight, \( W_0 \). The specimens were immersed in deionized water or ethanol for 24 h. The specimens were then removed from the water, one at a time, and surface water on the specimens was removed with filter paper. The specimens were weighed immediately to obtain the weight, \( W_1 \). The percentage increase in the weight of the samples was calculated by using the formula \( (W_1 - W_0)/W_0 \times 100\% \).

3.7 Mechanical Performance Testing
The film hardness testing refers to the standard of
GB/T 6739-2006. The tensile strength and elongation at break of films were measured with XWW-20B tensile testing machine, according to the standard of GB/T1040.3-2006. Determination of film adhesion was tested according to the ISO2409-1992 standard.

3.8 Determination of Solid Content and Conversion Rate
The emulsion solid content was measured according to GB1725-2007, the conversion rate was determined according to [13].

3.9 Storage Stability and Gel Content Testing
The storage stability of the emulsion was measured according to the standard of GB6753.3-86. The method of testing gel content is as follows: the dried composite polymer membranes weighed \( M_0 \) was placed in a Soxhlet extractor, then extracted with acetone as the solvent at 65 °C. The process consisted in a 24 h continuous extraction under reflux in a 250 mL round bottom flask.
After the extraction, crosslinked polymer was assumed to remain in the thimble while linear polymer went down to the acetone balloon by acetone circulation, and the rest weight \( (M) \) of the membranes were obtained after drying for 72 h at 30 \( ^\circ\)C. Then the gel content was calculated according to the following formula: \( G (%) = \frac{M}{M_0} \times 100\% \).

4. Results and Discussion

4.1 FTIR Spectra Analysis

The FTIR spectra of the polymers were shown in Figure 2. As shown in Figure 2, spectra (a) shows the stretching vibrations of C-H were observed at 2984 \( \text{cm}^{-1} \) and 2945 \( \text{cm}^{-1} \). The band at 1744 \( \text{cm}^{-1} \) and 1635 \( \text{cm}^{-1} \) were characteristic stretching vibrations absorption of C=O and C=C, and the bands at 932 \( \text{cm}^{-1} \), 832 \( \text{cm}^{-1} \) and 800 \( \text{cm}^{-1} \) were attributed to the characteristic absorption peak of epoxy groups of GMA. The spectra (b) and spectra (c) are respectively represent the composite emulsion (PUAS) just without GMA, and composite emulsion (EPUA) only without AHPS; (d) and (e) are FTIR spectras of WPU and EPUAS respectively. From spectra (d) and (e), we can conclude that the stretching vibrations absorption peak and bending deformation absorption peak of N-H are detected at 3380 \( \text{cm}^{-1} \) and 1530 \( \text{cm}^{-1} \). The band at 1729 \( \text{cm}^{-1} \) is attributed to the characteristic absorption peak of C=O in urethane. The three peaks we talk above are the characteristic absorption peaks of polyurethane. The disappearance of the peak at 2270 \( \text{cm}^{-1} \) which corresponded to –NCO group in FTIR spectra proved the completed polymerization. The spectra (e) shows that the bands nearby 1090 \( \text{cm}^{-1} \) is stronger and wider than spectra (d), which is due to the C-O stretching vibration absorption peak in polyurethane/polyacrylate overlaps each other, this proved that polyurethane/polyacrylate was successfully prepared. In comparison with a, b, and e, spectra (e) shows the disappearance of the peak at 1680–1620 \( \text{cm}^{-1} \) which corresponded to C=C in FTIR spectra proved that the double bond within GMA involved in the copolymerization reaction, simultaneously the epoxy group peak disappeared indicates that epoxy group totally participate in the reaction. At the same time, compared to EPUA infrared spectra, (e) spectra shows the absorption band at 1250 \( \text{cm}^{-1} \) which was the characteristic absorption peak of –SO3 in AHPS, the stretching vibrations of C-O bond were observed at 1162 \( \text{cm}^{-1} \) range, and the peak at 1065 \( \text{cm}^{-1} \) represent stretching vibrations of C-O-C. The above results showed that AHPS was combined to the polymer particles by chemical bond.

4.2 TEM Analysis

The morphologies of EPUAS and WPU particles were observed by transmission electron microscope, the TEM photograph of WPU is shown in Figure 3(a) and the TEM photograph of EPUAS is shown in Figure 3(b). In comparing with the two figures we can clearly see the shell structure in (b) which proved the composite emulsion is core-shell structure, which is mainly due to the different electron density of core layer and shell. As is shown in the picture, the lighter part is the core layer.
polyacrylate, and the darker part shows the shell polyurethane.

4.3 XRD Analysis

The curves a, b and c in Figure 4 show the XRD of WPU, WPUA and EPUA respectively. From the X-ray diffraction analysis, we can conclude that diffraction peak of the three are at \( 2\theta = 20^\circ \), and the integral area of the three curves (a, b, c) gradually decrease indicating that the crystallinity of the three successively weakened. In the polyurethane material, the crystallization is generally thought to be the effect of hydrogen bond and the formation of ordered soft segments [15]. WPUA is an acrylate-modified polyurethane that proved acrylic and polyurethane was crosslinked to form a three-dimensional network structure which destroyed the ordered arrangement of the original segment, while the EPUA with GMA made crystallization property weaker, indicating the epoxy-carboxy group reaction to form a crosslinked network structure after adding the GMA.

4.4 Effects of the AHPS Content on Particle Size and Zeta Potential of EPUAS Emulsion

From Figure 5, it is observed that, with the increase of AHPS content, the absolute value of the Zeta potential is increased, then decreased with the further increase AHPS content, and the potential maintains from -39.3 mV to -48.4 mV. This is because with the increase of AHPS content, particle diameter of latex decreases, the system is stable, the absolute value of the Zeta potential increased. However, self polymerization of excessive AHPS easily lead to the instability of the polymerization system, therefore, the absolute value of the Zeta potential decreased.

Generally, the emulsion has better stability when Zeta potential is from ±40 to ±60 mV [16], so that the emulsion stability will be good after adding the functional monomer AHPS, and when AHPS content is 2%, the absolute value of Zeta potential reaches the largest, the system is most stable. It can also be seen from Figure 5, particle diameter of latex decreases with the increasing of the content of AHPS, because the molar ratio of the emulsifier and monomer are the main factors that affected the particle diameter at the beginning of the polymerization reaction. At the initial polymerization, the bigger the ratio is, the more micelles content are, and the latex particle diameter is smaller.

4.5 Effects of GMA Content and AHPS Content on the Properties of Emulsion and Films

Water absorption and ethanol absorption are important parameters for practical application of polymer. As can be seen from Table 1, with the adding of GMA, ethanol absorption and water absorption rate of the product decreased, the tensile strength was increased, and the tensile strength was decreased, when the content of GMA was increased to 5%, the water absorption and the ethanol absorption reached the lowest, while the tensile strength attained the largest, and elongation at break was the lowest. The reason is that the GMA was crosslinked

\[ \text{Intensity (\%)} \]

\[ \text{20 (\degree)} \]

\[ \text{Figure 4. X-ray diffraction of WPU and WPUA film.} \]

\[ \text{Figure 5. Effects of AHPS content on the particle size and zeta potential of emulsion.} \]

\[ \text{WPU: waterborne polyurethane; WPUA: waterborne polyurethane-polyacrylate emulsion} \]
with WPUA to form a crosslinked network structure. With the increasing of GMA content, the crosslinking reaction of epoxy carboxyl of the system increased and the crosslinking density of films were increased, in addition, the GMA belongs to the hard monomer, making the proportion of hard segment and hydrophobic groups of the macromolecules increased. However, while the GMA content is 6% of the polyacrylate mass, the film’s performance decreased, which may be because overmuch GMA content led to the emulsion unstable. At the same time, with the addition of GMA, pencil hardness shows a tendency to increase but the adhesion decreases, the precipitation began when the content of GMA increased to more than 5%, this is because, at the function of GMA, the crosslinking density, hardness and particle size increase gradually, which lead to the emulsion unstable.

As can be seen from Table 2, while fixing GMA content of 5%, with the increase of the content of AHPS, the water absorption and ethanol absorption rate gradually increased, which was because there were hydrophilic acid groups such as hydroxyl and sulfo group in the functional monomer AHPS. With the increasing amount of AHPS, the hydrophilic groups in this system increased, leading to a increase in the rate of water absorption and ethanol absorption. From Table 2, it can also be clearly seen that the solid content and conversion represent the trend with increase at first and then decrease, while the gel content was increased after the first decrease. It is concluded that a gel was formed via AHPS self-polymerization when AHPS is excessive, resulting in the solid content decreased and the conversion rate was not high. With the tensile strength increasing from 12.34 MPa to 15.04 MPa, the elongation at break reduced from 232.47% to 148.38%. In summary, the result can be conclude that the performance of emulsion and latex films were the best with the AHPS content at 2%.

### Table 1. Effects of GMA content on the properties of film at 0 AHPS content

<table>
<thead>
<tr>
<th>GMA content/%</th>
<th>Water absorption/%</th>
<th>Ethanol absorption/%</th>
<th>Tensile strength/MPa</th>
<th>Elongation at break/%</th>
<th>Pencil hardness/H</th>
<th>Adhesion/grade</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25.3</td>
<td>39.11</td>
<td>6.89</td>
<td>537.43</td>
<td>2B</td>
<td>1</td>
<td>Stable</td>
</tr>
<tr>
<td>1</td>
<td>18.36</td>
<td>28.47</td>
<td>6.92</td>
<td>508.83</td>
<td>HB</td>
<td>1</td>
<td>Stable</td>
</tr>
<tr>
<td>2</td>
<td>16.34</td>
<td>36.69</td>
<td>7.87</td>
<td>451.18</td>
<td>HB-H</td>
<td>1</td>
<td>Stable</td>
</tr>
<tr>
<td>3</td>
<td>13.03</td>
<td>20.10</td>
<td>8.82</td>
<td>358.32</td>
<td>2H</td>
<td>0</td>
<td>Stable</td>
</tr>
<tr>
<td>4</td>
<td>10.86</td>
<td>28.33</td>
<td>10.58</td>
<td>299.57</td>
<td>2H</td>
<td>0</td>
<td>Stable</td>
</tr>
<tr>
<td>5</td>
<td>7.23</td>
<td>16.28</td>
<td>12.34</td>
<td>232.47</td>
<td>2H</td>
<td>0</td>
<td>Stable</td>
</tr>
<tr>
<td>6</td>
<td>14.63</td>
<td>25.17</td>
<td>6.05</td>
<td>484.30</td>
<td>HB</td>
<td>1</td>
<td>Unstable, with sedimentation</td>
</tr>
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### Table 2. Effects of AHPS content on the properties of emulsion and films at 5% GMA content

<table>
<thead>
<tr>
<th>AHPS content/%</th>
<th>Water absorption/%</th>
<th>Ethanol absorption/%</th>
<th>Solid content/%</th>
<th>Gel content/%</th>
<th>Emulsion stability</th>
<th>Conversion/%</th>
<th>Tensile strength/MPa</th>
<th>Elongation at break/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.23</td>
<td>16.28</td>
<td>35.38</td>
<td>5.42</td>
<td>Unstable, with sedimentation</td>
<td>87.36</td>
<td>12.34</td>
<td>232.47</td>
</tr>
<tr>
<td>1</td>
<td>7.56</td>
<td>18.36</td>
<td>38.81</td>
<td>3.85</td>
<td>Without sedimentation</td>
<td>93.27</td>
<td>12.93</td>
<td>227.19</td>
</tr>
<tr>
<td>2</td>
<td>7.78</td>
<td>20.28</td>
<td>42.76</td>
<td>2.34</td>
<td>Without sedimentation</td>
<td>98.42</td>
<td>13.26</td>
<td>206.32</td>
</tr>
<tr>
<td>3</td>
<td>14.27</td>
<td>20.79</td>
<td>42.57</td>
<td>2.84</td>
<td>Without sedimentation</td>
<td>94.13</td>
<td>13.71</td>
<td>183.27</td>
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<tr>
<td>4</td>
<td>18.53</td>
<td>28.33</td>
<td>41.64</td>
<td>2.97</td>
<td>Without sedimentation</td>
<td>93.28</td>
<td>14.89</td>
<td>162.11</td>
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<tr>
<td>5</td>
<td>27.46</td>
<td>36.28</td>
<td>40.33</td>
<td>3.03</td>
<td>Without sedimentation</td>
<td>93.11</td>
<td>15.04</td>
<td>148.38</td>
</tr>
</tbody>
</table>
5. Conclusions

The epoxy-modified waterborne polyurethane/polyacrylate emulsion was prepared while adding the polymerizable emulsifier AHPS and epoxy groups simultaneously. The emulsions and structure of films before or after modification were characterized by FTIR, XRD, TEM, and we have studied the effects of GMA and AHPS content on WPUA emulsion and film properties. The study shows that, GMA and AHPS had been combined to the polymer molecules in the manner of chemical bond, making the WPUA molecules form a crosslinked network structure with the addition of GMA, and the water resistance, solvent resistance, and the mechanical properties had been improved as well as the hardness. In addition, the solid content of the emulsion has been significantly increased with the adding of AHPS obviously, which reaches 43%. When the content of GMA is 5%, AHPS is 2%, the polyurethane/polyacrylate emulsion and the films achieve the best performance and the emulsion have a good stability.

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