Synthesis and characterization of waterborne polyurethane emulsions based on poly(butylene itaconate) ester

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ABSTRACT
Waterborne polyurethane (WPU) prepolymer was synthesised by the reaction of poly(butylene itaconate) ester (PBI, Mn = 1109 g/mol), 1,6-hexanediol, dimethylol propionic acid (DMPA), 2,4-toluene diisocynate (TDI), hydroxyethyl acrylate (HEA), and absolute ethanol as blocking agent, triethylamine as neutralizer. Cross-linked WPU was synthesized by trimethylolpropane (TMP) as crosslinker. The influences of PBI, DMPA, and TMP content on WPU emulsions and films were investigated. The structure of WPU was determined by Fourier transform infrared (FTIR) spectra, thermal properties and glass transition temperature of WPU films were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively, and morphology of the emulsion particles was observed by transmission electron microscopy (TEM). Through TGA, the heat resistance of the cross-linked WPU film was better than WPU film. By DSC analysis, glass transition temperature of cross-linked WPU film (21 °C) was higher than WPU film (10 °C).

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1. Introduction
Recently, waterborne polyurethane (WPU) emulsions have increasingly attracted attention because of their environment-friendly properties and wide applications in paper-making, paint, ink, leather, and adhesive industries.[1–3] All the applications utilize the ideal properties of the formed film, such as wide adhesion substrates, high abrasion resistance, high solvent resistance, great flexibility, and excellent elasticity.[4,5]

WPU macromolecules usually possess alternating hard and soft segments. The hard segments originated from the isocyanates and low-molecular weight diols, while the soft segments are mainly from high-molecular weight polyols.[6] Generally, WPU is synthesized by the prepolymerization of soft segments and hard segments, followed by chain extension reaction and neutralization. In the preparation process, the polyols, such as polyether and polyester, are generally used as the soft segments of polyurethane molecules. The commonly used polyols are synthesized from monomers from fossil resources. However, environmental consequences caused by petrochemical industry and the exhaustion of petroleum resources, with global warming and sustainability awareness, greater attention has been drawn to develop and utilize environment-friendly, renewable raw materials for polyurethane syntheses. For example, Lu et al. reported the successful synthesis of WPU from soybean oil [7] and modified rapeseed oil.[8] Larock et al. prepared a new WPU and urethane–acrylic hybrid latex based on modified soybean oil.[7] Recently, Saetung et al. prepared a series of WPU using modified nature rubber.[9] Besides direct utilization of natural or modified biomass materials, self-made polyols using monomers derived from renewable resources is also considered to reduce the fossil resource dependency. Existing studies have shown that the WPU prepared from polyester materials can provide perfect mechanical strength and adhesive force from polar ester groups. Furthermore, the polyester-based polyurethane coating films have greater heat and oxidation resistance than polyether-based polyurethane films. So, synthesis of bio-based polyesters with new structure and better performances from the large-scaled biomass monomers are in pressing need.

Itaconic acid (IA) has been widely used in the field of polymers and copolymers.[10–12] IA is a dicarboxylic acid produced by fermentation as one of the key platform chemicals derived from biomass. The IA-based polyester has been synthesized through condensation polymerization of the carboxyl groups of IA and the hydroxyl groups of butanediol.[13]

To date, very few reports have described IA-based polyester WPU synthesis. In comparison with polyethylene glycol (PEG) and polypropylene glycol (PPG), IA-based...
polyester contains unsaturated carbon–carbon double bonds for further polymerization, affecting the structure and properties of its final product.

In this study, the IA-based polyester type WPU emulsion was synthesized from poly(butylene itaconate) ester (PBI), 2,4-toluene diisocynate (TDI), 1,6-hexanediol (HDO), dimethylol propionic acid (DMPA), trimethylolpropane (TMP), hydroxyethyl acrylate (HEA), absolute ethanol (ET), and triethylamine (TEA) by melting copolycondensation method, and the structure and properties of polyurethane were characterized.

2. Experimental

2.1. Materials

Poly(butylene itaconate) ester (PBI, Mn = 1109 g/mol) was synthesized according to the reference.[13] 2,4-toluene diisocynate (TDI), 1,6-hexanediol (HDO, AR) and hydroxyethyl acrylate (HEA, AR) were purchased from Sinopharm., China. Trimethylolpropane (TMP, AR), absolute ethanol (ET, AR) and triethylamine (TEA, AR) were purchased from Bodi Chemicals Company, China. Dimethylol propionic acid (DMPA, AR) and N-methylpyrrolidone (NMP, CP) were purchased from Aladdin and BASF, respectively. Dibutyltin dilaurate (DBTDL, AR) and hydroquinone (HQ, AR) were purchased from Guangcheng Chemicals Company, China.

2.2. Preparation of WPU

Polymerization was performed in a 250 mL round-bottom, four-necked flask with a mechanical stirrer, thermometer, and condenser with drying tube. Firstly, a mixture (PBI, DMPA, HDO and TMP) was added to the flask, followed by water removal by distillation at 100 °C. The reaction mixture was then cooled to room temperature, and NMP was added to dissolve DMPA (Scheme 1). Afterwards, TDI and organic solvent (Mass ratio was 1:1), DBTDL (0.3% relative to TDI quantity), and triethylamine (TEA) by melting copolycondensation method, and the structure and properties of polyurethane were characterized.

2.3. Characterization

2.3.1. Fourier transform infrared spectroscopy

The structure of WPU was obtained by Fourier transform infrared (FTIR, Bruker Vertex 70, Germany) spectra. KBr disk was dried in a vacuum oven at 40 °C for 5 days with −0.08 Mpa. The sample was scanned from 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹.

2.3.2. Particle size and polymer disperse index measurement

The particle size and polymer disperse index (PDI) of the WPU emulsion was measured by a laser particle sizer (Malvern Nano-ZS 90, England) at 25 °C. The sample was prepared by diluting with deionized water to adjust the content to about 1 wt% and followed by ultrasonic wave treatment.
2.3.3. Viscosity measurement
The viscosity of the WPU emulsion was measured with a rotational viscometer (Brookfield DV-II, USA) at room temperature.

2.3.4. Morphology of emulsion particles measurement
The morphology of the emulsion particles was observed by a transmission electron microscopy (TEM, JEM-1200 EX, Japan). The emulsion was diluted to 0.5 wt% with deionized water. Then, a drop of sample was deposited onto a copper grid.

2.3.5. Sample preparation
For the measurements of WPU films properties, the WPU emulsion was cast on a polytetrafluoroethylene plate and dried for one week at room temperature. Then, the resulting film was dried in a vacuum oven at 70 °C for 24 h.

2.3.6. Water absorption measurement
The water absorption of the film was measured by immersing the WPU film in deionized water for 24 h at room temperature. The percentage of swelling for a film was determined by measuring its weight increase.

\[
\text{Water absorption} = \frac{X_2 - X_1}{X_1} \times 100\%
\]

where \(X_1\) was the weight of film sample and \(X_2\) was the swelling film sample in water.

2.3.7. Thermal properties measurement
The thermal properties of WPU film by thermogravimetric analysis (TGA, Netzsch 209 F1, Gernany). The measurement was performed under a \(N_2\) flow of 60 mL/min. Sample was heated from 25 to 700 °C at a heating rate of 10 °C /min.

2.3.8. Glass transition temperature measurement
The glass transition temperature of WPU film was tested by differential scanning calorimetry (DSC, Netzsch 204 F1, Germay) at a heating rate of 10 °C /min under a \(N_2\) flow of 20 mL/min.

2.3.9. Pencil hardness and adhesive force measurement
The pencil hardness of WPU film was measured according to Chinese national standard GB/T 6739-2006, and the adhesive force according to GB/T 1720-89.

3. Results and discussion

3.1. FTIR spectroscopy of WPU
The chemical structure of the WPU was investigated by FTIR. As shown in Figure 1, the characteristic peaks at 3261 and 1725 cm\(^{-1}\) were assigned to \(-\text{NH}\) and \(-\text{C}=\text{O}\) stretching vibration, respectively. The peak at 1228 cm\(^{-1}\) was assigned to \(-\text{COO}–\) stretching vibration. In addition, the peaks at 2956 and 1452 cm\(^{-1}\) corresponded to the \(-\text{CH}\) stretching vibration of \(-\text{CH}_2\) and \(-\text{CH}_3\) groups, respectively. The peak at 1670 cm\(^{-1}\) was assigned to the stretching vibration of \(=\text{C}=\text{C}\), which implied that the double bonds were success-fully introduced to WPU macromolecular chains. There was no peak at 2270 cm\(^{-1}\) indicating that the \(-\text{NCO}\) had been fully reacted. Through analysis, the product was the desired.

3.2. Effect of PBI content on WPU emulsions
Figure 2 shows the effect of PBI content on particle size and PDI of the WPU emulsions. It can be seen that particle size and PDI decreased first and then increased with the increase in PBI content. When the amount of PBI was 50%, particle size and PDI both reached the minimum values (58.93 nm and 0.30, respectively).

When PBI content was in the range of 35–50%, the amount of DMPA increased in order to keep molar ratio of NCO/OH groups constant. The introduction of more hydrophilic groups \(-\text{COOH}\) from DMPA resulted in forming smaller particles at the dispersion stage. Hence, particle size and PDI both decreased. When the amount of PBI further increased, the particle size and PDI of emulsions increased simultaneously. PBI was a hydrophobic ester, so the hydrophobicity of WPU molecular chain increased as more PBI was added into polymerization system, which caused less likely to crimp to nucleate at the dispersion stage. Consequently, the particle size and PDI increased. On the other hand, hard segment content reduction improved the possibility of soft segment–hard segment phase separation, which might result in increasing particle

![Figure 1. FTIR spectra of WPU based on PBI.](image-url)
size and PDI. This phenomenon was inconsistent with the results reported by Sariah et al. [14–17].

Figure 3 shows the dependence of viscosity of WPU emulsions on PBI content. It can be seen that the viscosity decreased with the increase in PBI content. In addition to external factors, such as the shearing force and temperature, the viscosity of WPU emulsions was mainly governed by the hydrophilicity of macromolecular chains. [18] Generally, the stronger the hydrophilicity of chain segments, the higher the viscosity of emulsion. Because PBI was a hydrophobic ester, the hydrophilicity of WPU chains decreased gradually as more and more PBI was used in synthetic process. On the other hand, the amount of urethane bonds decreased with the increase in amount of PBI, the inter/intramolecular action of WPU macromolecule chains was reduced. Consequently, the viscosity of emulsion decreased. This phenomenon was also different from the tendency of other WPU systems synthesized by other raw materials.[14,16]

3.3. Effect of PBI content on WPU films

As shown in Figure 4, water absorption decreased with the increase in PBI added in the WPU formula. This was because that PBI was a hydrophobic component, which formed the core of the particles as the prepolymer was dispersed in aqueous phase. The chain of PBI was longer than HDO, so the hydrophobicity of PBI was higher than HDO. On the other hand, the longer the carbon chains were, the easier the polar groups were buried by the hydrophobic groups. These made the hydrophilicity of WPU macromolecular chains decreased when more PBI added to emulsion. Consequently, the water absorption of WPU films decreased with increased PBI.

As shown in Table 3, pencil hardness and adhesive force decreased with increasing PBI content. Pencil hardness and adhesive force of WPU films were influenced by the chemical structure of WPU. The amount of urethane bonds with high polarity decreased with the increase in PBI content. The higher the polarity of WPU macromolecular chain was, the higher the pencil hardness was and the stronger the adhesion to substrate was, and thus pencil hardness and adhesive force decreased with PBI content increasing.

3.4. Effect of DMPA content on WPU emulsions

DMPA was commonly used for synthesizing various emulsions, which introduced –COOH to side chains of WPU. It could be seen that the particle size and PDI of WPU

| Table 3. Effect of PBI content on pencil hardness and adhesive force of WPU films. |
|-----------------|----------|----------|----------|----------|----------|
| PBI/%           | 35       | 43       | 50       | 55       | 60       |
| Pencil hardness | 3H       | 2H       | 3B       | 5B       | 6B       |
| Adhesive force  | 1        | 1        | 2        | 4        | 4        |
emulsions decreased gradually with the increase in DMPA content (Figure 5) and the viscosity increased with increasing DMPA (Figure 6).

The hydrophilic carboxyl group content of WPU increased as the amount of DMPA increased. DMPA introduced –COOH group into WPU side chain. After neutralization, the WPU could be dispersed in water. Water entered more easily into the hard segments to disperse the WPU molecules as the ionic character (DMPA) of the hard segments increased. The more hydrophilic the polyurethane chains were, the more likely to crimp to nucleate and form smaller particles.[18,19] Consequently, the particle size and PDI of WPU emulsions decreased.

As discussed above, the particle size decreased and number of particles increased with the increasing amount of DMPA. Simultaneously, a larger amount of WPU particles increased the friction resistance between particles and led to higher viscosity. On the other hand, the higher charge content, the thicker the electrical double layer. It also made the resistance of motion increased.[20,21]

3.5. Effect of DMPA content on WPU films

As shown in Figure 7, the water absorption increased with increasing DMPA content, which was due to the increase in hydrophilicity of WPU. On the other hand, more polar groups may be attracted to each other and even form hydrophilic microdomains. Water molecules could diffuse and penetrate readily into these hydrophilic microdomains after contacting with the film surface.

3.6. Effect of TMP content on WPU emulsions

TMP was used as an internal crosslinker to improve the properties of WPU. Cross-linked network structure could form after the introduction of TMP. As shown in Figures 8 and 9, particle size and PDI of WPU emulsions reached maximum as the percentage of TMP content was 0.8% (236.10 nm and 0.85, respectively) and then decreased, but the tendency of viscosity was just the opposite. The minimal viscosity value was 27.01 cP when TMP content was 0.8%.

When the dosage of TMP was less than 0.8%, the degree of crosslinkage increased with the addition of TMP, which made WPU harder to be emulsified and resulted in the increases in particle size and PDI. Before the tri-functional monomer TMP was added, the action between WPU macromolecule chains was physical force, molecule chains were easy to slide. After introducing TMP, the cross-linking structures were formed and prevented molecules from sliding to a certain extent, and thus the viscosity of emulsions decreased. On the other hand, the number of particles in dispersion system decreased because of
and the water molecules could penetrate easily into the amorphous areas, and therefore the dispersibility of WPU was improved and the particle size and PDI decreased.[23] With the density of WPU particles increasing, the friction resistance between particles increased, and the viscosity of emulsions increased.

3.7. Effect of TMP content on WPU films

Figure 10 shows the effect of TMP on water absorption of WPU films. It can be seen that water absorption reached minimum (20.46%) as TMP content was 0.8%, which was the result of introduction of TMP. Crosslinkages were formed and prevented the penetration of water after introducing TMP. However, if TMP content was larger than 0.8%, with the increase in cross-linking degree, the compatibility between WPU particles was poor, and it was easier for water molecules to penetrate into polymer chains. Consequently, the water absorption increased.[24,25]

3.8. Thermal properties of WPU films

The thermodynamic properties of WPU films were investigated by TGA (See Figure 11). It can be seen that there were three stages. The first stage was the splitting of water and small molecular compounds. The second was the decomposition of WPU hard segments. Urethane bonds were decomposed into isocyanate and polyol, and further broken down into amines, CO₂, and olefins. The third was the decomposition of WPU soft segment.[26,27]

The onset decomposition temperature (T_{on}) of the non-crosslinked WPU1 was 220 °C and the crosslinked WPU2 was 263 °C. The weight loss temperature (T_{max}) corresponding to maximum rate of weight loss was 280 and 300 °C, respectively. The temperature of 50% weight loss was 310 and 320 °C, respectively, which indicated the heat endurance was greatly improved after crosslinking.
The increase in thermal stability was attributed to the crosslinked network structure by introduction of TMP, which prevented the decomposition of the WPU macro-molecular chains and improved the thermal stability of the polymer.[28] The amount of urethane bonds increased with the introduction of TMP, and the inter/intramolecular action of WPU chains was enhanced. Consequently, the heat endurance was improved.

### 3.9. The DSC analyze of WPU films

Glass transition temperature ($T_g$) of WPU and the crosslinked WPU were examined with DSC. $T_g$ of WPU1 was 10 °C and the crosslinked WPU2 was 21 °C. The flexibility of WPU decreased with the introduction of TMP, and the segmental mobility reduced significantly in crosslinked samples with TMP. Thus, the introduction of TMP decreased the free volume of WPU chains, resulted in the interaction between backbone chains increased.[29] There was hydrogen bond between urethane bonds, the amount of urethane bonds increased with the introduction of TMP, to a certain degree, which prevented molecules from sliding, and therefore, made the $T_g$ shift to a high temperature. As shown in Figure 12, $T_g$ of the crosslinked sample was increased by about 11 °C.[30]

### 3.10. Morphology and particle size of WPU by TEM

The morphology and particle size of the emulsion particles was determined by TEM. As shown in Figure 13, the WPU particles were spherical and distributed homogeneously. But the particle size measured by TEM (35.17 nm) was smaller than that measured by laser particle sizer (98.01 nm). This was due to different test conditions. The particle size measured by laser particle sizer was in emulsion state and the particle size observed by TEM was in dried condition. There was hydration layer around particles when measured by laser particle sizer.[9]

The average particle size of the WPU emulsion was 98.63 nm, and the index of size distribution was 0.33 (Figure 14). Generally, the smaller particle size, the longer stability of emulsion was, and then the water solubility of the resin was better. Diluting the resin with water, the result showed that the resin could be miscible with water in any ratios and no turbid phenomenon occurred.

### 4. Conclusion

In this paper, WPU was successfully synthesized by self-made PBI instead of traditional polyether and polyester diols. The structure of samples was characterized by FTIR. The influences of PBI, DMPA, and TMP content on WPU emulsions and films were investigated. Thermal properties
increasing PBI content. When PBI content was 50%, particle size and PDI both reached the minimum values, 58.93 nm and 0.30, respectively. But the viscosity of emulsions decreased and glass transition temperature of WPU films were determined by TGA and DSC, respectively.

Figure 14. Statistic distribution of the particle size in the WPU1 emulsion by intensity (formulation of WPU1 were listed in Table 2).

Scheme 1. Preparation of WPU based on PBI.

(1) Particle size and PDI of WPU emulsions decreased first and then increased with increasing PBI content. When PBI content was 50%, particle size and PDI both reached the minimum values, 58.93 nm and 0.30, respectively. But the viscosity of emulsions decreased
with PBI. For the cast films of WPU, water absorption decreased to 18.72%, as well as pencil hardness and adhesive force decreased with increasing PBI content.

(2) Increasing the DMPA content from 3.0 to 6.0%, particle size and PDI of WPU emulsions decreased to 98.01 nm and 0.31, respectively, but the viscosity of emulsions increased to 67.50 cP. For the cast films of WPU, water absorption increased to 27.77%.

(3) Particle size and PDI of WPU emulsions increased first and then decreased with increasing TMP content. When TMP content was 0.8%, particle size and PDI both reached the maximum values, 236.10 nm and 0.85, respectively. But the tendency of viscosity was just the opposite, which was 27.01 cP when TMP content was 0.8%. For cast films of WPU, water absorption reached minimum when TMP content was 0.8% (20.46%) and then increased.

(4) Thermal stability of WPU was substantial, and degradation started after 220 °C. Crosslinked WPU was more stable with higher $T_{on}$ (220 °C and 263 °C correspond to non-crosslinked WPU and crosslinked WPU, respectively) and $T_{max}$ (280 and 300 °C corresponding to non-crosslinked WPU and crosslinked WPU, respectively) due to the crosslinked network structure by introducing TMP.

(5) $T_g$ of the crosslinked WPU was increased by about 11 °C (10 and 21 °C corresponding to non-crosslinked WPU and crosslinked WPU, respectively) due to the flexibility of WPU decreased with the introduction of TMP.

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