Properties and paper sizing application of waterborne polyurethanemicroemulsions: Effects of extender, cross-linker, and polyol

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ABSTRACT: A series of waterborne polyurethane (WPU) microemulsions were synthesized through self-emulsification methodology, using toluene-2,6-diisocyanate, polytetramethylene glycol (PTMG), poly-caprolactonediol (PCL), and dimethylol propionic acid (DMPA) as monomers; isophorone diamine (IPDA) as chain extender; and aziridine as cross-linking agent. The resultant WPU microemulsions were utilized as surface-sizing agents for cellulose fiber paper. The influences of IPDA content, PTMG/PCL molar ratio, and aziridine content on the physicochemical properties of the resultant emulsions and sized paper have been investigated in detail. The WPU microemulsion displayed better surface sizing properties when it was prepared under the following conditions: the IPDA content of 2.96%, PTMG/PCL molar ratio of 0:4, and aziridine content of 2.0 wt %. The relationships between the WPU structure and properties of WPU films and sized paper were clearly illustrated. The mechanical properties and water resistance of sized paper were not only depended on the interactions, chain entanglements, and cross-linking density among the WPU chains, but also relied on the interactions among polymers and fibers, as well as the polarity and stiffness of surface sizing agent. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2016, 133, 43211.

INTRODUCTION

With the rapid development of modern industry, enhanced mechanical property and water resistance are required for paper products. Paper sizing,[1–3] including internal sizing and surface sizing, was typically adopted to improve paper strength and reduce the rate of liquid penetration into the cellulose fiber paper. Internal sizing was carried out by adding hydrophobic but reactive sizing agents into the pulp slurry. Internal sizing agents included rosin,[4,5] alkyl ketene dimer (AKD),[6–11] and alkenyl succinic anhydride (ASA),[12] and so on. In contrast with internal sizing, surface sizing was performed by applying sizing agents on the surface of paper. The retention of sizing agent can reach approximately 100%. And the white water pollution can thereby be weakened if the internal sizing can be replaced or partially replaced by surface sizing. The surface sizing agent was able to form a continuous film on the paper surface and simultaneously penetrate into the paper to build chemical and physical bonds among fibers.[13] Various categories of surface sizing agents have been utilized, such as starch,[14–16] chitosan,[17] alginate,[18] poly (vinyl alcohol) (PVA),[19] styrene butadiene rubber

latex,[20] poly(styrene-maleicanhydride) copolymer (SMA),[21,22] and polyacrylate.[23]

Waterborne polyurethane (WPU) emulsions, used as paper surface-sizing agents, have recently received increasing concerns in the papermaking industry.[3,24,25] Heretofore, a lot of work has been done on WPU emulsions. WPU is commonly prepared by the incorporation of ionic groups into the PU backbone to enhance the hydrophilicity and promote the water dispersability.[26] Because of their environment-friendliness, excellent mechanical property, wear, and aging resistance, WPU materials have been abundantly used in the field of paint, adhesive, and ink industries.[27–31]

Various factors that are affecting the performance of WPU have been investigated, such as structure of soft and hard segment,[32–34] NCO/OH molar ratio,[35–38] chain extender,[39–41] cross-linker,[42–44] and so on. However, few reports on WPU surface sizing agent can be found in the literature.[3,25,45] Guo *et al.*[3,25] studied the water resistance and mechanical properties of paper sized with WPU based on different NCO/OH molar ratio, DMPA content, hard segment structure (TDI/IPDI molar ratio),

Table I. Detailed Formulae, Film Cross-Link Density, and Water Absorption of the Different WPU

Sample	IPDA (mol)	IPDA (wt %)	PTMG/PCL molar ratio	Aziridine content (wt %)	Cross-linking density (10^4 mol/cm^3)	Water absorption (%)
Group one						
A1	0	0.00	0:4	-	0.225 ± 0.007	27.43 ± 0.52
A2	0.0029	1.50	0:4	-	0.384 ± 0.031	24.68 ± 0.42
A3	0.0058	2.96	0:4	-	1.059 ± 0.072	18.92 ± 0.52
A4	0.0087	4.37	0:4	-	1.241 ± 0.092	13.95 ± 0.52
A5	0.0116	5.74	0:4	-	1.546 ± 0.082	12.06 ± 0.58
Group two						
A3	0.0058	2.96	0:4	-	1.059 ± 0.072	18.92 ± 0.52
B1	0.0058	2.96	1:3	-	0.778 ± 0.067	19.37 ± 0.51
B2	0.0058	2.96	2:2	-	0.448 ± 0.047	21.19 ± 0.70
B3	0.0058	2.96	3:1	-	0.229 ± 0.062	25.44 ± 0.52
B4	0.0058	2.96	4:0	-	0.177 ± 0.107	32.82 ± 0.71
Group three						
A3	0.0058	2.96	0:4	0	1.059 ± 0.072	18.92 ± 0.52
C1	0.0058	2.96	0:4	0.5	6.995 ± 0.111	13.12 ± 0.68
C2	0.0058	2.96	0:4	1	12.529 ± 0.565	8.24 ± 0.72
C3	0.0058	2.96	0:4	2	12.529 ± 0.724	6.88 ± 0.75
C4	0.0058	2.96	0:4	3	14.998 ± 0.781	5.19 ± 0.51

chemicals-adding sequence, and acetone content. Li et al.[45] reported that the water resistance and mechanical properties of paper sheets sized with waterborne UV-curable polyurethane (UWPU) are much better than the unsized paper sheets.

In this study, we attempted to synthesize WPU microemulsions with the different soft segment, chain extender, and cross-linker. The microemulsions were utilized as surface sizing agents for cellulose fiber paper. Different ratios of soft segment poly-caprolaclonediol (PCL) to polytetramethylene glycol (PTMG) were adopted. The influence of soft segment structure, chain extender, and cross-linker content on the particle size and distribution of WPU microemulsion were investigated, as well as the cross-linking density, water resistance, and mechanical properties of WPU films. In addition, the physicochemical properties of pristine paper and sized paper were discussed.

EXPERIMENTAL

Materials
Poly-caprolaclonediol (PCL, 99.99%, number-average molecular weight of 1000) and polytetramethylene glycol (PTMG, 99.99%, number-average molecular weight of 1000) were supplied by Daicel Corporation, Japan. Toluene-2,6-diisocyanate (TDI, 80/20, 99.99%) was purchased from Tianjin Fuchen Chemical Reagents Factory, China. Dimethylol-propionic acid (DMPA, 98%) and isophorone diamine (IPDA, 99.5%) were obtained from Sigma-Aldrich Co. LLC. USA. N-methyl-2-pyrrolidinone (NMP, AR), triethylamine (TEA, AR), and acetone (AR) were purchased from Tianjin Guangfu Fine Chemical Co. Ltd., China. Aziridine (99%) was supplied by Shanghai Ewan Chemical Co., LTD. China. Double-distilled and deionized water was self-made and used through all the experiments.

Before conducting the WPU synthesis, PCL and PTMG were all dehydrated at 110 °C under the condition of vacuum pressure of −0.09 MPa for 1 h. As well, NMP and acetone were both dehydrated by immersing 4A zeolite in the solvent for more than 1 week prior to any use.

Preparation and Synthesis Progress of the WPU Emulsions
The emulsions used were synthesized with TDI, PCL, PTMG, and DMPA as monomers and IPDA as the chain extender by means of a two-step synthesis method consisting of prepolymerization and chain-extending reaction. In Step 1, the monomers of TDI, PCL, PTMG, and DMPA were reacted to obtain a low-molecular-weight NCO-terminated prepolymer. In Step 2, the prepolymer thus obtained was further reacted with a chain-extending agent of IPDA to result in final WPU polymers with high molecular weight.

Group 1 and Group 2 in Table I presented the detailed formulae used in this study for having synthesized different WPU emulsions. The reaction was conducted in a 500-mL four-neck flask equipped with a reflux condenser, a mechanical stirrer, a thermometer, and a nitrogen gas inlet. Figure 1 showed the detailed preparation protocol for synthesizing WPU emulsions with PCL and PTMG. PCL (0.02 mol) and PTMG mixed soft segment (the specific proportion seen in Table I) were initially added into the flask and heated up to 80 °C. When the PCL and PTMG melted, TDI (0.0592 mol) was added under stirring with N$_2$ protection. After 2 h reaction and when the –NCO content reached the theoretical value, 0.017 mol of DMPA solution in NMP (mass ratio of DMPA/NMP = 1:3) were added in the flask and reduced the temperature to 65 °C. The reaction continued for 3 h, resulting in the WPU prepolymer. Later, the system cooled down to 30 °C, and the viscosity-reducing agent acetone
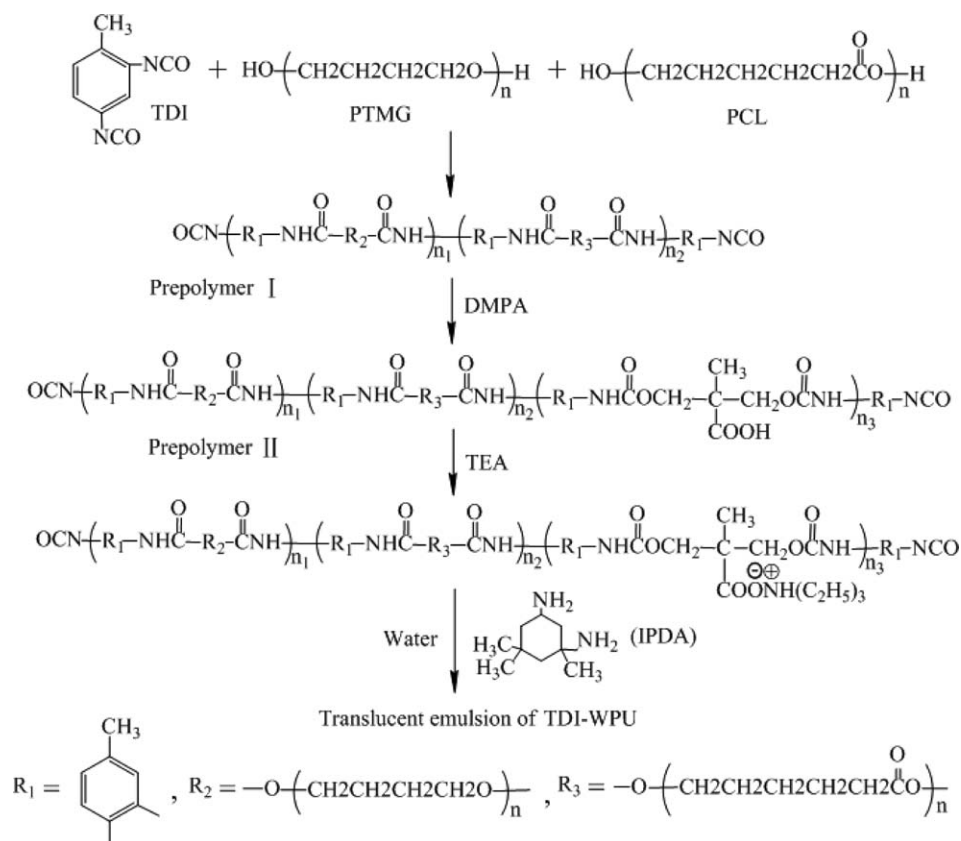
Figure 1. Preparation process of the WPU films synthesized with PCL and PTMG as the monomers.

and the neutralizer TEA (0.0187 mol) was subsequently added under stirring. Kept for 20 min, the system was further cooled down to below 2 °C using an ice-water bath, followed by sequential addition of deionized water and the chain extension agent IPDA (IPDA dosage was shown in Table I) under the shear rate of nearly 3000 revolutions per minute. The resultant mixture was then heated to 40 °C for further chain extension reaction for 2 h, and then the acetone was removed by vacuum distillation, yielded the final WPU emulsions with a theoretical solid content of 30 wt %.

Preparation of the WPU Films

WPU emulsions were cast on leveled teflon plates to allow them to dry at room temperature for 5 days, and then at 60 °C *in vacuo* for 24 h. After demolding, the films were kept in a desiccator to avoid moisture.

Characterization of the WPU Films and Emulsions

Fourier transform infrared (FT-IR) spectra of all samples were recorded on an American Perkin-Elmerspectrum 100 FT-IR spectrometer in the range of 4000–500 cm^{-1}.

The average particle size and particle-size distribution of the emulsions was analyzed by light scattering using Malvern Zetasize Model 3000HS. Approximately 0.2 mL of the emulsions were diluted with deionized water to an approximate concentration of 0.01% and was measured at 25 °C.

The rheological properties of the microemulsions were analyzed in an AR2000ex rheometer (TA Instruments Co.). All the tests were carried out at 25 °C with a DIN concentric cylinder geometry.

Samples of approximately 3×3 mm were immersed in glass flasks containing dimethyl formamide (DMF) and allowed them to stand at ambient temperature. After 7 days of equilibrium, samples were removed from DMF and patted with lint-free tissue paper to remove excess solvent, and the percentages of the quality increase were measured again. The cross-link density [mol/cm^3] was estimated using eq. (1) which was proposed by Flory and Rehner[20,35]:

$$V = -\left[\frac{\ln(1-V_r) + V_r + X \cdot V_r}{V_s(V_r^{1/3} - V_r/2)} \right] \quad (1)$$

Where V_s was the molar volume of solvent, X was the polymer–solvent interaction parameter; in this study, the polymer–solvent interaction parameter (X) was determined to be 1.093×10^{-2}. V_r is the volume fraction of polymer in swollen gel, which was obtained according to eq. (2):

$$V_r = 1/(1 + Q\rho_r/\rho_s) \quad (2)$$

Where Q was the percentages of the quality increase after swelling, ρ_s was the solvent bulk density, and ρ_r was the sample density.

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 were the mean values of three replicates. The tensile

strength and elongation at break of the WPU films were studied by T-peel strength tests according to GB/1040-92. The T-peel strength tests were performed in a TS2000-S universal test machine with a cross-head speed of 500 mm/min. The values obtained were the average of three replicates.

The water 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 films was calculated by eq. (3) as

$$A = \frac{W_1 - W}{W} \times 100\% \qquad (3)$$

Where W is the dry weight of films before immersion.

The water absorption of the WPU films was measured according to GB/1034-2008. The values obtained were the average of the three replicates.

Paper Surface Sizing

The paper was made of pure cotton fiber (75 ± 0.2 g/m^2, Chengdu Jinding Papers, Inc., China), were one-by-one placed on the K303 MULTI COATER (RK. Print Coat Instruments Ltd, U.K.). After the paper sheet was secured firmly onto the working plate, the WPU emulsion was diluted to 10%, and added aziridine (according to Table I), then poured on the sheet and coated with a coating roller at a constant rate of 3.0–4.0 cm/s. The paper sheets were subsequently transferred onto a photo drying machine (SX-70, Hefei Kesai Machinery Manufacturing Co., Ltd. Anhui Province, China) for drying about 5 min at 105 °C. For each of the emulsions considered, about 20 paper sheets were used for examining the surface sizing effect.

The sized papers were conditioned at 25 ± 1 °C and $50 \pm 2\%$ RH for 24 h before property testing. The cross-sectional morphology of paper sheets was observed on scanning electron microscope (SEM, JSM-6460 Japanese electronics co., LTD). Before the SEM examinations, the samples were chilled in liquid nitrogen for at least 30 s and then folded with forceps to make a sharply broken interfacial cross-section, followed by gold coated under vacuum by a sputter coater.

The water resistance was measured using a Cobb tester (Changjiang Paper Co. Ltd., Sichuan, China), which mainly consisted of a metallic cylinder of 50 mm in height and 100 cm^2 at the cross-sectional area. Distilled water (100 mL, 23 ± 1 °C) was added into the cylinder. Then, the paper sheet was circularly cut with a surface area of 100 cm^2, weighed, and placed on the cylinder with the testing surface facing the water. The sample lid was used to cover the sheet. Then, the cylinder was turned upside down, and a stopwatch was started. After 30 s, the sample was taken out, placed on a sheet of filter paper, covered with two other filter paper sheets, and rolled twice in 4s using a 10 kg roller. Finally, the sample was weighed to obtain the Cobb value (g/m^2), indicating the amount of water absorbed per unit area of the sheet.

The printing surface strength was measured using an AIC2-5Printability Tester (IGT Co. Ltd., Netherlands). For each sample, 10 strips of 35 ± 0.1 mm in width and 350 mm in length
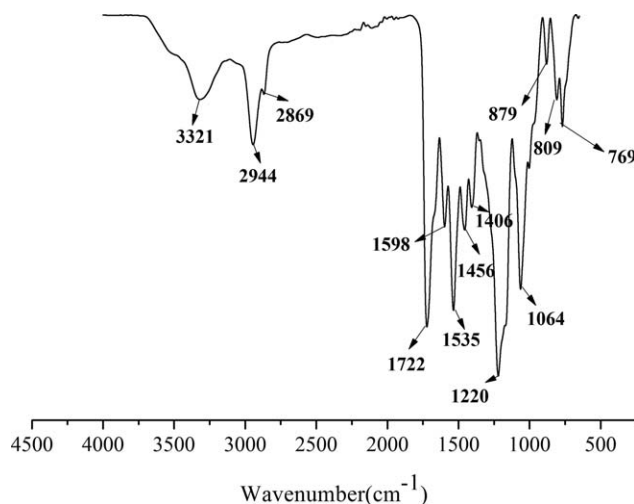

Figure 2. FTIR spectra of the WPU film.

were prepared with 5 for transverse direction (TD) tests and the remaining for machine (MD) tests according to ISO 186:186, MOD.

The stiffness was surveyed by a 160 bending tester (LORENT-ZEN & WETTRE Ltd., Switzerland). For each sample, 20 strips of 15 ± 0.1 mm in width and 140 mm in length were prepared with 10 for transverse direction (TD) tests and the remaining for machine (MD) tests.

The folding resistance was measured using a DIN/ISO 5626 folding tester (PTI Co. Ltd., USA). For each sample, 20 strips of 15 ± 0.1 mm in width and 140 mm in length were prepared with 10 for transverse direction (TD) tests and the remaining for machine (MD) tests. The strip was double-folded over a span of 135° with 9.81 N force until it broke. The folding times recorded were averaged over the strips measured for each sample.

The tensile strength of sized papers was measured using an SE062 tensile strength tester (Lorentzen & Wettre Co. Ltd., USA). For each sample, 40 strips of 15 ± 0.1 mm in width and 140 mm in length were prepared with 20 for transverse direction (TD) tests and the other 20 for machine direction (MD) tests. The measurements were carried out by adjusting the testing rate to make the samples break within 15–25 s and then the tensile strength was recorded. The values were obtained for each sample by averaging over the strips measured. The tensile index was obtained as the ratio of tensile strength to the basic weight (75 g/m^2) of pristine paper sheets.

RESULTS AND DISCUSSION

FTIR Analysis

As seen in Figure 2, the completion of the polyester polyol and TDI reaction was confirmed by the absence of -NCO characteristic peak at 2260 cm^{-1} and the presence of –NH characteristic peak at 3321 cm^{-1}. As for the –CH groups, unsymmetrical and symmetrical stretching vibration appeared at 2944 and 2866 cm^{-1}, respectively. The peaks at 1722, 1535, 1220, and 1064 cm^{-1} were attributed to stretching absorption of –NH, –C=O, C–O– and –C–N in urethane –NHCOO groups, were

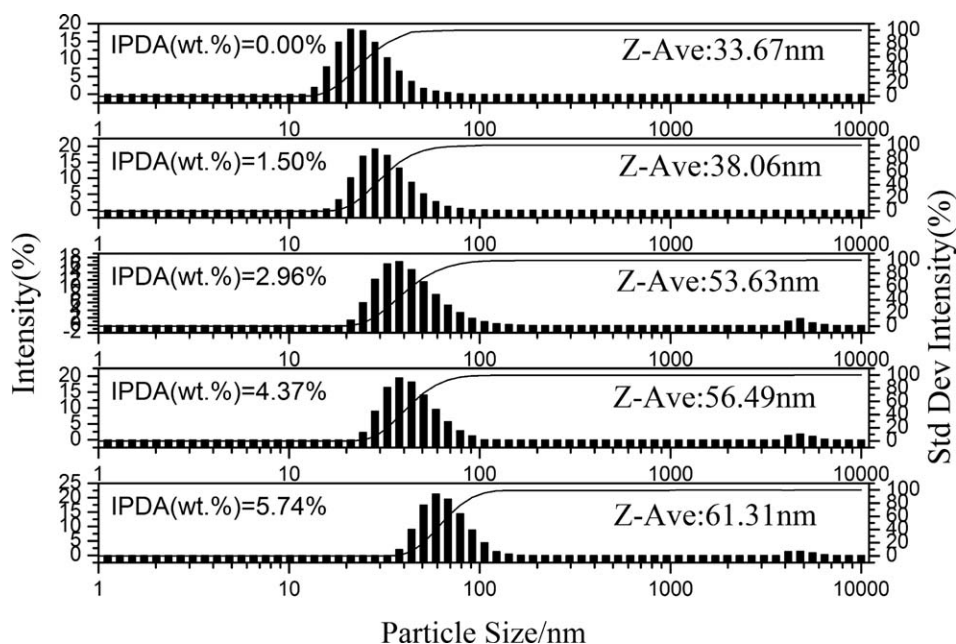**Figure 3.** Effect of IPDA content on the emulsion particle size.

generated by the reaction of –NCO and –OH. The peak at 1456 cm^{-1} was due to the deformation vibration of CH$_2$ and CH$_3$, the C–C stretching vibration band appeared at 879 cm^{-1}. The peaks at 1598 and 769 cm^{-1} were corresponding to the characteristic peaks of benzene.

Effect of IPDA Content

Effect on the Particle Size. The effect of IPDA content on the emulsion particle size was shown in Figure 3. As can be seen in the figure, with the increase in the IPDA content, the average particle size of the emulsions obviously increased from 33.67 to 61.31 nm. On one hand, the molecular weight of polyurethane increased with the increase of the IPDA content. On the other hand, IPDA quickly reacted with the rest of the isocyanate generated polyurea,[46] which had stronger molecular polarity compared with polyurethane groups. So with the increase of IPDA content, high polarity polyurea structure content increased, resulting in stronger hydrogen bonding among polymer chains and increased cross-linking density. The above scenario was responsible for the increase in the WPU particle size.

Effect on the Rheological Properties of the WPU Microemulsions. Figure 4 shows the viscosity versus shear rate curves of WPU microemulsions with different IPDA contents. All the WPU microemulsions showed pseudoplastic behavior of non-Newtonian fluid; there was a decrease in the viscosity as the shear rate increased. We also found that the viscosity and pseudoplastic behavior increased with increasing IPDA content. It could have also been due to the polar interactions among the molecules, which resulted from the numerous peripheral polar groups of polyurea structure.

Effect on the Film Cross-Link Density and Water Absorption. Table I showed the dependence of film cross-linking density and water absorption on the IPDA content. As the IPDA content increases from 0.0 to 5.74%, the cross-linking density

increased from 0.22594 to 1.54671 $\times$ 10^{-4}mol/cm^{-3}, the water absorption decreased from 27.43 to 12.06%. With the increase of IPDA content, more polyurea structure and hydrophobiccyclic structure were introduced into the polymer chains, which were favorable to improve the rigidity and intermolecular hydrogen bonding force, resulting in dramatic increase in the cross-linking density and water resistance.

Effect on the Film Tensile Strength and Elongation. The variations in the tensile strength and elongation at break with the IPDA content were investigated as shown in Figure 5. The tensile strength of WPU increased from 21.64 to 39.97 MPa with increasing the IPDA content, whereas the elongation at break increased first and then decreased when the IPDA content was >1.50%. As discussed above, the cross-linking density increased
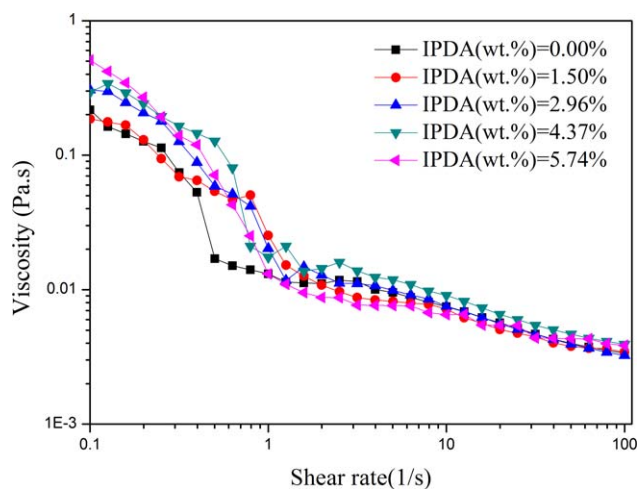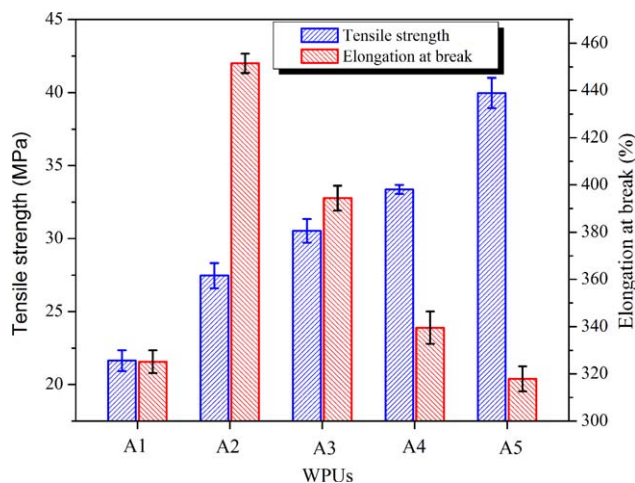

Figure 4. Viscosity versus the shear rate of WPU microemulsions with different IPDA contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. Effect of IPDA content on the film tensile strength and elongation at break. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with increasing the IPDA content, which was beneficial to increase the tensile strength. Because IPDA forms the cyclic rigid segment in WPU macromolecules, its presence tends to make the molecular chains more rigid, thus improving the film tensile strength. On the other hand, IPDA forms the hard component of the polyurethane, and its existence seems to debase plasticity and elasticity to the films. Therefore, as the IPDA content increases, the resultant films acquire high tensile strength and low elongation.

Effect of PTMG/PCL Molar Ratio
Effect on the Particle Size. Figure 6 showed the dependence of the emulsion particle size on the PTMG/PCL molar ratio. As seen in Figure 6, with the increase of PTMG/PCL molar ratio, the particle size of the emulsions reduced from 53.63 to

28.57 nm. Compared with WPU prepared by polyester PCL, the polarity of WPU prepared with polyether PTMG was weakened. The molecular interactions were thereby decreased with the increase of PTMG content, resulting in the increased molecular motion ability. Therefore, the hydrophilic groups were more easily migrated to the surface of colloidal particles, leading to the decrease of particle size.

**Effect on the Rheological Properties of the WPU Microemulsions.** The viscosity versus shear rate curves of WPU microemulsions with different PTMG/PCL molar ratio were shown in Figure 7. All the WPU microemulsions showed pseudoplastic behavior of non-Newtonian fluid; there was a decrease in the viscosity as the shear rate increased. We also found that the viscosity increased first and decreased later with increasing PTMG/PCL molar ratio. We considered that there were many factors, including the molecular architecture, molecular weight, solid content, interaction, and particle size, which affected the rheology of the emulsions.[47] Figure 6 shows that with the increase of content of PTMG, latex particle size was reduced, the total surface area of colloidal particles increased, and so viscosity at the same shear stress of C1 was greater than the A3; however, with PTMG content increased continuously, intermolecular hydrogen bonding force reduce, so that the viscosities of C2, C3, and C4 were lower than A3.

Effect on the Film Cross-Link Density and Water Absorption. The cross-linking density and the water absorption of WPU films modified with different PTMG/PCL molar ratio were shown in Table I. As seen in Table I, with the increase of PTMG/PCL molar ratio, the cross-linking density of the WPU films decreased from 1.05901 to 0.17702×10^{-4} mol cm^{-3}, the water absorption of the films increased from 18.92 to 32.82%. Since the polarity of the ester bond was stronger than the ether bond, the molecular interactions were decreased with increasing the PTMG content.
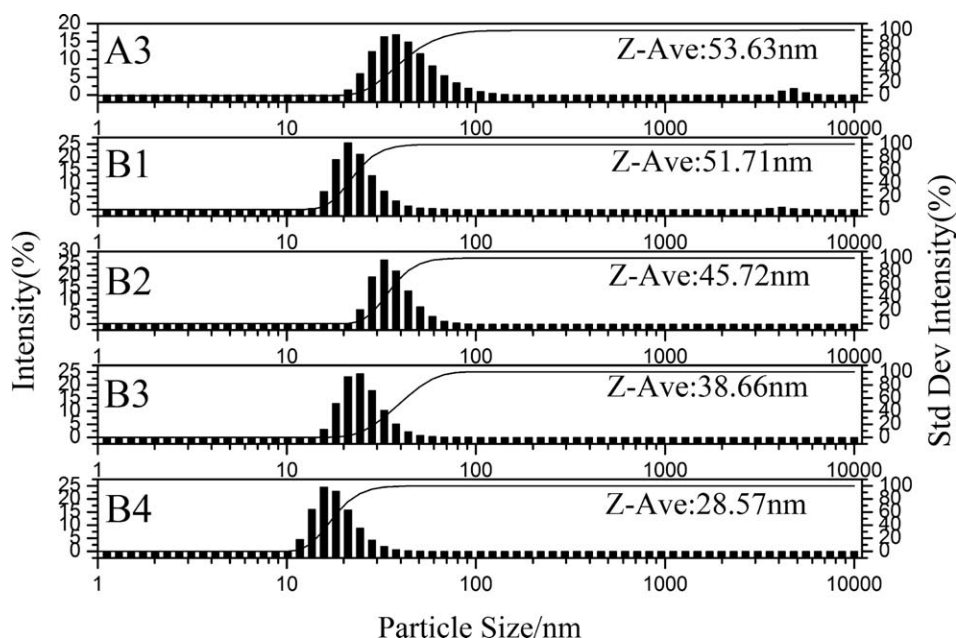
Figure 6. Effect of PTMG/PCL molar ratio on the emulsion particle size: (A3) 0:4, (B1) 1:3, (B2) 2:2, (B3) 3:1, and (B4) 4:0.
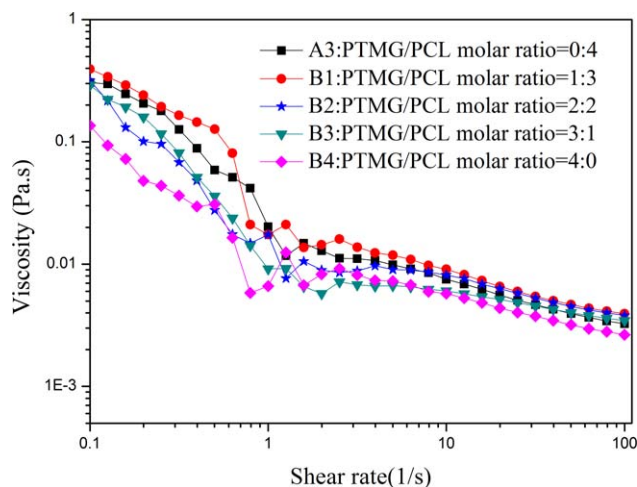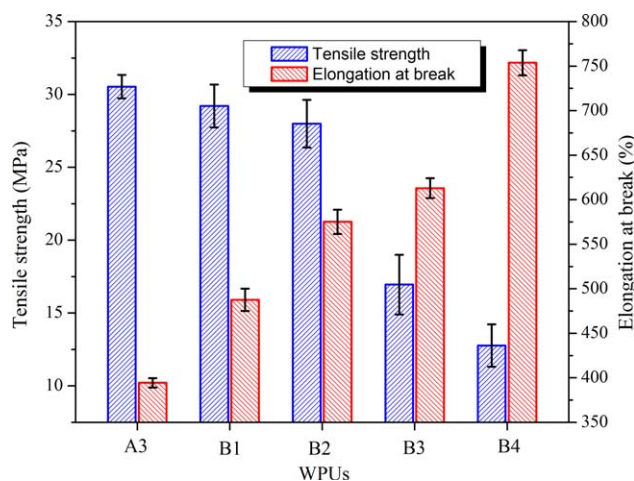
Figure 7. Viscosity versus the shear rate of WPU microemulsions with different PTMG/PCL molar ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect on the Film Tensile Strength and Elongation. The variations in the tensile strength and elongation with the PTMG/PCL molar ratio were investigated, as illustrated in Figure 8. As can be seen, the tensile strength kept almost invariable with increasing the PTMG content from 0% to 50%, and then decreased from 27.99 to 12.77 MPa with further increase of PTMG content. However, the elongation at break continuously increased with increasing the PTMG content. It can be attributed to the higher flexibility and lower molecular interactions for polyether PTMG-based WPU.

Effect of the Aziridine Content

Effect on the Film Cross-Link Density and Water Absorption. The cross-linking density and the water absorption of WPU films modified with different aziridine content are shown in Table I. As seen in Table I, with the increase of aziridine content, the cross-linking density of the WPU films increased from 1.05901 to 1.499849×10^{-3}

Figure 8. Effect of PTMG/PCL molar ratio on the film tensile strength and elongation at break: (A3) 0:4, (B1) 1:3, (B2) 2:2, (B3) 3:1, and (B4) 4:0. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
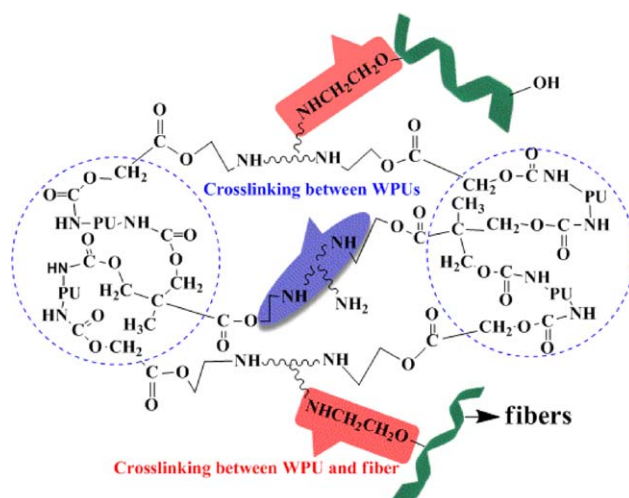
Figure 9. The cross-linking structure diagram of fiber and polyurethane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mol cm^{-3}. The water absorption of the films decrease from 18.92 to 5.19%. The main reason may be given as below. In the process of solidification, the cross-linking reaction might occur between aziridine and –COOH groups in WPU, as shown in Figure 9.

As seen from the above reaction scheme, network structures were formed in WPU through cross-linking, ester bond[48] was generated and the content of hydrophilic –COOH groups was reduced. In general, the water resistance decreased with increasing the –COOH content, since hydrogen bonding was more easily formed between water molecules and –COOH groups in the hydrophilic microdomains. Therefore, the water resistance could be improved through decreasing the content of –COOH groups. In addition, it became difficult for water molecules to penetrate into the film due to the formation of network structure.

Effect on the Film Tensile Strength and Elongation. Figure 10 showed the dependence of the films tensile strength and elongation on the aziridine content. With the increase of the aziridine content, the tensile strength of the WPU films increased from 30.53 to 52.119 MPa, the elongation decreased from 394.38 to 151.65%. Hence, more chemical interactions between aziridine and WPU resulted in more chemically cross-linked network structures in the polymers because of trifunctional ethyleneimine of aziridine. It was well known that the network structure of the polymer was favorable for reinforcing mechanical strength. With the increase of the aziridine content, the cross-linking density of WPU increased, and the tensile strength of polyurethane film enhanced the elongation at break decrease.

Effect of the Emulsions on Paper Surface Sizing

In this study, the WPU emulsions were adopted as surface sizing agent for cellulose fiber paper. Figure 11 showed the SEM micrographs of paper surfaces sized with and without the WPU emulsions. It can be seen that the sized papers possess a relative smooth and glossy surface compared with the crude surface of unsized papers. The cross-section SEM images of the unsized and sized paper showed that the paper surfaces were apparently coated by a continuous layer of the WPU emulsion after the
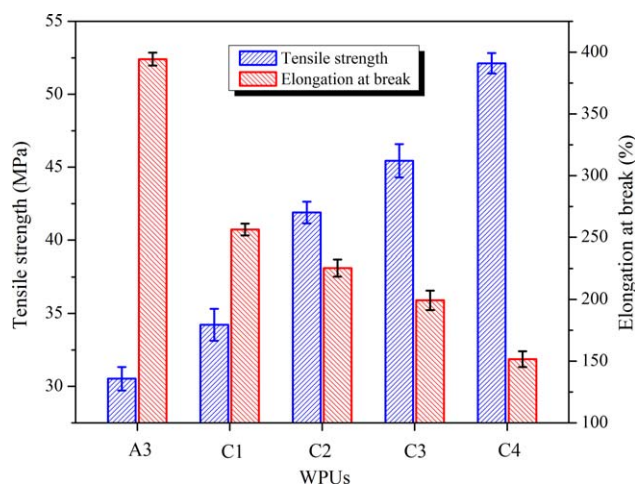
Figure 10. Effect of the aziridine content on the film tensile strength and elongation at break: (A3) 0.0%, (C1) 0.5%, (C2) 1.0%, (C3) 2%, and (C4) 3%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surface sizing treatment. And part of WPU emulsions were able to penetrate into the inner structure of paper, and build bonding among cellulose fibers.

Table II presented the physical properties obtained for the papers sized with different WPU emulsions. The performance parameters of paper were significantly improved after sized with the WPU emulsions. As shown in Table II, the tensile strength, stiffness, printing surface strength, and water resistance of paper increased as the IPDA content increased from 0.0 to 5.74% (A series). The cross-linking density and chain entanglements were enhanced with increasing the IPDA content, which was favorable for the improvement of mechanical properties and water resistance. However, the folding strength first increased and then decreased with the increase of IPDA content. On one hand, the mechanical properties could be increased with increasing the cross-linking degree and chain entanglements of WPU. On the other hand, the rigidity of WPU chain increased with the introduction of cyclic structure IPDA. The changing trend of folding strength could be ascribed to the synergetic effect from the above two opposite factors.

Table II presented the performance parameters for the paper sized with WPU emulsions of different PTMG/PCL molar ratio (B series). As the PTMG/PCL molar ratio increased from 0:4 to 4:0, the Cobb value (60 s) increased from 25.6 to 34.5 g/m^2, the tensile strength of machine direction decreased from 119.69 to 89.1 N·m/g, the folding resistance decreased from 857 to 577,
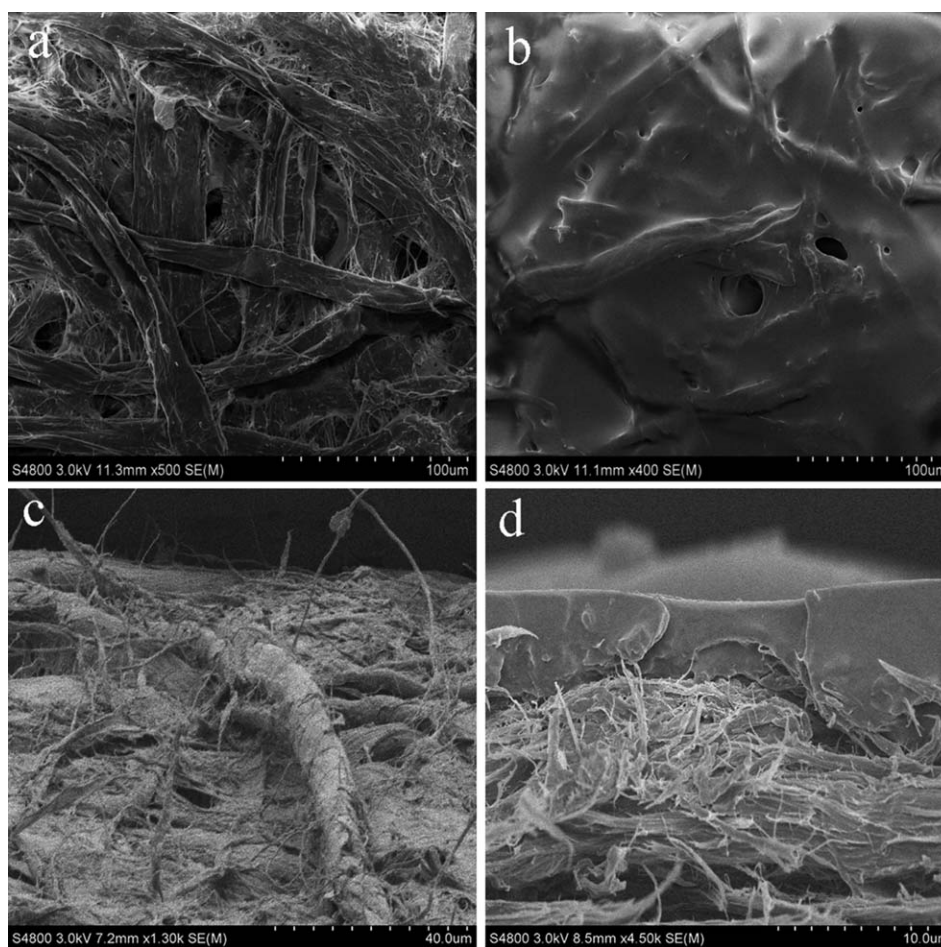
Figure 11. SEM images of the (a) unsized paper and (b) sized paper with the emulsion. (C3) Cross-sectional SEM images of the (c) unsized paper and (d) sized paper with the emulsion C3: the IPDA content = 2.96%, PTMG/PCL molar ratio = 0:1, Aziridine content = 2.0 wt %.

Table II. The Performance Parameters of Unsized Paper and Paper Sized with Different WPU Emulsions

Sample	30 s Cobb g/m²	Folding resistance (times)		Tensile index (N·m/g)		Stiffness (mN/m)		Printing surface strength (m/s)	
		TD	MD	TD	MD	TD	MD	TD	MD
A1	33.2 ± 1.25	244 ± 9	516 ± 25	62.90 ± 6.27	114.50 ± 8.66	29 ± 3	64 ± 5	1.53 ± 0.11	2.06 ± 0.29
A2	27.9 ± 1.13	313 ± 10	722 ± 41	64.71 ± 7.13	117.80 ± 9.54	32 ± 3	65 ± 7	1.57 ± 0.15	2.19 ± 0.27
A3	25.6 ± 1.41	344 ± 14	857 ± 27	67.76 ± 6.59	119.69 ± 10.21	33 ± 5	68 ± 8	1.65 ± 0.13	2.32 ± 0.32
A4	24.1 ± 0.85	301 ± 12	646 ± 37	70.35 ± 5.92	122.19 ± 13.12	38 ± 6	75 ± 10	1.72 ± 0.19	2.35 ± 0.31
A5	23.0 ± 0.92	258 ± 17	578 ± 32	68 ± 6.31	122.59 ± 16.47	40 ± 6	81 ± 9	1.81 ± 0.14	2.46 ± 0.41
A3	25.6 ± 1.41	344 ± 14	857 ± 27	67.76 ± 6.59	119.69 ± 10.21	33 ± 5	68 ± 8	1.65 ± 0.13	2.32 ± 0.32
B1	27.7 ± 0.78	302 ± 18	757 ± 24	65.19 ± 7.49	115.76 ± 11.59	31 ± 7	64 ± 6	1.51 ± 0.15	2.17 ± 0.32
B2	28.2 ± 0.83	299 ± 13	719 ± 29	59.80 ± 5.17	106.51 ± 12.17	30 ± 5	60 ± 7	1.44 ± 0.09	2.05 ± 0.25
B3	31.4 ± 1.52	257 ± 14	593 ± 38	56.39 ± 5.28	98.19 ± 9.89	27 ± 2	59 ± 9	1.21 ± 0.11	2.01 ± 0.35
B4	34.5 ± 1.47	202 ± 11	577 ± 35	51.61 ± 4.96	89.1 ± 10.38	25 ± 3	59 ± 11	0.96 ± 0.15	1.86 ± 0.27
A3	25.6 ± 1.41	344 ± 14	857 ± 27	67.76 ± 6.59	119.69 ± 10.21	33 ± 5	68 ± 8	1.65 ± 0.13	2.32 ± 0.32
C1	22.7 ± 0.89	412 ± 17	922 ± 19	70.98 ± 7.15	132.08 ± 15.28	34 ± 4	71 ± 15	1.82 ± 0.17	2.52 ± 0.31
C2	21.4 ± 1.23	438 ± 21	981 ± 31	73.57 ± 7.34	137.49 ± 17.64	36 ± 5	74 ± 11	1.94 ± 0.19	2.76 ± 0.25
C3	20.8 ± 0.62	442 ± 15	1074 ± 25	77.25 ± 8.12	141.02 ± 18.92	39 ± 6	80 ± 16	2.13 ± 0.18	2.91 ± 0.28
C4	19.5 ± 0.91	357 ± 12	799 ± 21	80.08 ± 8.55	144.47 ± 17.45	45 ± 4	92 ± 13	2.35 ± 0.12	3.15 ± 0.42
Unsized paper	42.2 ± 2.6	159 ± 7	267 ± 13	40.31 ± 4.61	79.53 ± 6.42	24 ± 2	46 ± 5	0.52 ± 0.12	1.41 ± 0.37

stiffness decreased from 68 to 59 mN/m, and printing surface strength decreased from 2.32 to 1.86 m/s. Although easier penetration of WPU microemulsions into cellulose fiber paper was allowed for WPU of lower particle size, interactions between fibers could be enhanced. However, the cross-linking density and interactions between polymers and fibers were relatively lower for PTMG-based WPU in comparison with PCL-based WPU, owing to higher polarity of PCL. As a result, the mechanical properties of paper sized with WPU microemulsion of higher PTMG content were weakened. Therefore, in contrast with the particle size of microemulsions, it could be postulated that the polarity of polymer chain played a dominant role in improving the performance of sized paper. However, it was worthy to note that the folding strength of sized paper also decreased with increasing the PTMG content, and the tensile strength of sized paper also showed different trend compared with WPU films. In general, the folding strength is related to the flexibility of materials; it was found that the flexibility of WPU films increased with the increase of PTMG content, as shown in Figure 10. The reason why the folding strength and tensile strength of sized paper decreased is that the interactions among fibers and WPU polymers were weakened when paper is sized with WPU of lower polarity. Hydrogen bonding was easily formed between fiber with –OH groups and PCL-based WPU with more ester groups. The results indicated that the mechanical properties and water resistance of sized paper were greatly depended on the polarity of the surface sizing agents.

The effects of the aziridine content on the properties of unsized and sized paper had also been examined, and the experimental results were shown in Table II. The paper 30s Cobb value decreased from 25.6 (sample A3) to 19.5 g/m^2 (sample C4) when the aziridine content increases from 0 to 3.0 wt %. The folding resistance, tensile strength, stiffness, and printing surface strength have been significantly improved, except for the C4 sample which was sized with WPU emulsion of excessive cross-linking agent aziridine. A major contributor to this phenomenon was that the cross-linking density and interactions among polyurethane macromolecules and fiber increased, as illustrated in Figure 8. The cross-linking reaction between WPU and fibers improved the chemical bonds between the fibers and reduced the content of hydroxyl (–OH) groups on the fiber surface.[10,11] At the same time, the WPU emulsions were able to form a thin layer on the paper surface and fill the interspaces of the paper fibers, resulting in improved water resistance and physical strength properties, as shown in Table II. The folding resistance increased at first and then decreased, which could be attributed to the synergistic effect between the stiffness of polymer chain and interactions among polymers and fibers.

CONCLUSIONS

In this study, WPU surface sizing agents with different soft segments, various content of chain extender IPDA, and cross-linking agent have been synthesized through two-step synthesis methodology. Based on the results obtained, the following conclusions may be drawn:

1. With an increase in the IPDA content, the particle size of WPU microemulsion increased from 33.67 to 61.31 nm; for the WPU films, the water absorption decreased, the tensile strength increased, and the elongation at break elongation first increased and then decreased. For the sized papers, the water resistance, stiffness, and surface strength kept increasing. However, the folding resistance and tensile index increased first and then decreased.
2. With an increase in the PTMG/PCL molar ratio, the particle size of WPU microemulsions decrease from 53.63 to 28.57 nm. The water resistance of WPU films decreased and the elongation at break increased. The tensile strength slightly reduced at first and then greatly decreased. As to the sized papers, the water resistance, folding resistance, tensile index, stiffness, and printing surface strength decreased as the PTMG/PCL molar ratio increased.
3. With an increase in the aziridine content, for the WPU films, the water absorption decreased, the tensile strength increased from 30.53 to 52.119 MPa, the elongation at break decreased from 394.38 to 151.65%. With respect to the sized papers, the water resistance, tensile index, stiffness, and printing surface strength of the sized paper increased with appropriate amount of cross-linking agent aziridine; however, the folding resistance increased first and then decreased.

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