

Preparation and property of waterborne UV-curable chain-extended polyurethane surface sizing agent: Strengthening and waterproofing mechanism for cellulose fiber paper

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ABSTRACT: Waterborne UV-curable polyurethane (UWPU) dispersions with different hydrophilicity and functionalities were prepared by varying the content of dimethylol butanoic acid (DMBA) and pentaerythritol triacrylate (PETA). And linear and cyclic chain extenders with different functionalities were also incorporated into the UWPU backbone, including isophorone diamine (IPDA), diethylene triamine (DETA), and ethylene diamine (EDA). Effects of DMBA content, PETA content, photoinitiator content, UV curing time, chain extender on the properties of UWPU dispersions and films, as well as the properties of the unsized and sized paper were investigated. The water resistance and mechanical properties of sized paper were greatly relied on the particle size, the molecular weight, the crosslinking density, and penetrability of UWPU. UWPU dispersion chain extended with IPDA (IPDA-UWPU) displayed smaller particle size than that of UWPU. The paper sized with IPDA-UWPU was endowed with best water resistance, tensile strength, folding strength and surface strength. XPS depth analysis revealed that IPDA-UWPU exhibited better penetrability into the paper substrate than UWPU. SEM and AFM demonstrated that the smoothness of sized paper was improved, and the bond strength between fibers was enhanced. The obtained UWPU could be directly used as an effective and fast drying surface sizing agent for cellulose fiber paper. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42354.

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INTRODUCTION

Paper, which is made from hydrophilic cellulose fibers, is very sensitive to both liquid water and moist air. Therefore, desirable water resistance is required for paper products. It can be achieved through sizing treatments during the papermaking process.^{1–3} The purpose of sizing is to modify the surface of the fibers to control the penetration of aqueous liquids into the paper, and provide paper with water resistance.^{2,4} Paper sizing treatments typically include internal sizing, surface sizing or both. Internal sizing is a very common papermaking operation, accomplished by adding hydrophobic but reactive sizing agents into the pulp slurry.^{5–7} Surface sizing is accomplished by applying sizing agents to the paper surface at the dry end of papermaking process. In addition to improve the water resistance, surface sizing treatment is also supposed to increase the surface strength and the tensile strength of paper.⁸ Waterborne polymers, such as styrene butadiene rubber latex,⁹ polyvinyl alcohol (PVA),¹⁰ chitosan,¹¹ silicon-acrylic copolymer,¹² and styrene-maleic anhydride copolymers,^{13–15} have been extensively utilized

as surface sizing agents. The surface sizing agent waterborne polyurethane (WPU) has recently received increasingly attention in the papermaking industry. However, only a few studies on WPU surface sizing agent have been reported.^{1,2} Guo *et al.*² found that the water resistance and mechanical properties of paper sheets sized with WPU are much better than the unsized paper sheets. In our previous work, anionic polyurethane-acrylate and polyurethane dispersion are also utilized as surface sizing agent,^{16–18} and effects of the structure and composition of polyurethane on the properties of sized paper are investigated.

Waterborne polyurethane has been increasingly used in various fields including as coatings, adhesives and inks because of its excellent mechanical properties, fire resistance, low toxicity, and low VOC.^{19,20} However, the drying speed, solvent resistance and abrasion resistance of WPU are still inferior to those of solvent-borne polyurethane.²¹ The disadvantages of waterborne systems can be overcome by crosslinking structure formed through UV-curing.^{22,23} UV-curing coating has been considered as an alternative to traditional solvent-borne coating, owing to its high

curing speed, reduced energy consumption, low solvent emission, high hardness, scratch, and chemical resistance.^{19,24} Waterborne UV-curable polyurethane (UWPU) dispersions combine the advantages of WPU and UV-curing and overcome the drawbacks of each other. Recently, UWPU has shown great potential as a green and environmentally friendly coating with unusual mechanical properties and solvent resistance. At present, the UWPU dispersions have been extensively applied in the coatings for wood, leather, plastic, cloth, and metal and so on. However, until now, the use of waterborne UV-curable polyurethane as a surface sizing agent in papermaking process has seldom been reported. The mechanism and factors that affect the properties of paper sized with UWPU still need systematic investigation.

The main objective of this article is to combine the merits of WPU and UV-curing technology to develop an efficient and fast-curing nano-sized waterborne UV-curable surface sizing agent. In addition to improving the water resistance of the sized paper, the UV-curable waterborne polyurethane dispersion is also expected to increase the wet strength, folding strength and surface strength of paper. In this case, the surface sizing can replace partial internal additives, such as internal sizing agent and wet strength additives. It can greatly decrease sizing cost, shorten curing time, prolong cleaning cycle, and reduce white-water pollution. However, the requirements for paper surface sizing agent are different from the requirements for wood coating, metal coating and so on. With respect to the coatings for wood and metal, high hardness is very necessary. While for paper, surface sizing agent with higher hardness will significantly weaken the folding strength of paper. Therefore, it is essential to make a balance between the tensile strength and flexibility, which can be controlled by the molecular weight and crosslinking density.

In this study, UV-curable waterborne polyurethane dispersions were synthesized by varying DMBA content, functionality, curing condition, and chain extender. Pentaerythritol triarylate (PETA) with hydroxyl group and three vinyl functionalities was incorporated by a reaction with NCO-terminated polyurethane prepolymer. Besides, linear and cyclic chain extender with different functionalities was incorporated into the polyurethane backbone through chain extension. In this method, the molecular weight can be increased by the introduction of chain extender, and the crosslinking density can be adjusted by changing functionalities.

Effects of DMBA content, functionality, curing condition and chain extender on the particle size of UWPU dispersions were analyzed, as well as their effects on the gel content and water absorption of UWPU films. The penetration and distribution of UWPU and chain-extended UWPU in the sized paper were studied by X-ray photoelectron spectroscopy (XPS). Moreover, the Cobb value, dry tensile strength, wet tensile strength, folding strength, and surface strength of sized paper were systematically investigated. The surface and cross-sectional morphology of original paper and sized paper were characterized by atomic force microscope (AFM) and scanning electron microscope (SEM).

MATERIALS AND METHODS

Materials

Polycaprolactone polyol (PCL₁₀₀₀, $M_n = 1000$), isophorone diisocyanate (IPDI) and dimethylol butanoic acid (DMBA) were purchased from Tyson Tianjin Chemical Group. (China). Dibutyl tin dilaurate (DBTDL) and acetone were purchased from Tianjin Chemical Reagent Factory (China). Pentaerythritol triacrylate (PETA) and triethyl amine (TEA) were purchased from Guangzhou Deco Composite Technology. (China). Isophorone diamine (IPDA) was purchased from Shanghai Huijin Chem. (China). Diethylene triamine (DETA) and ethylene diamine (EDA) were purchased from Xi'an Dingtian Chem. (China). Photoinitiator (Chemcure-73W) was purchased from Dongguan Hengqiao Commerce and Trade. (China). PCL₁₀₀₀ was dried and degassed at 80°C under vacuum for 2 h before use. IPDI and DMBA were vacuum-dried at 80°C for 24 h. Alkyl Ketene dimers (AKD) dispersion was purchased from Henan Hongrui Chemical (China). Acetone was dehydrated by immersion in 4 Å molecular sieves for one week. All other materials were directly used without further purification.

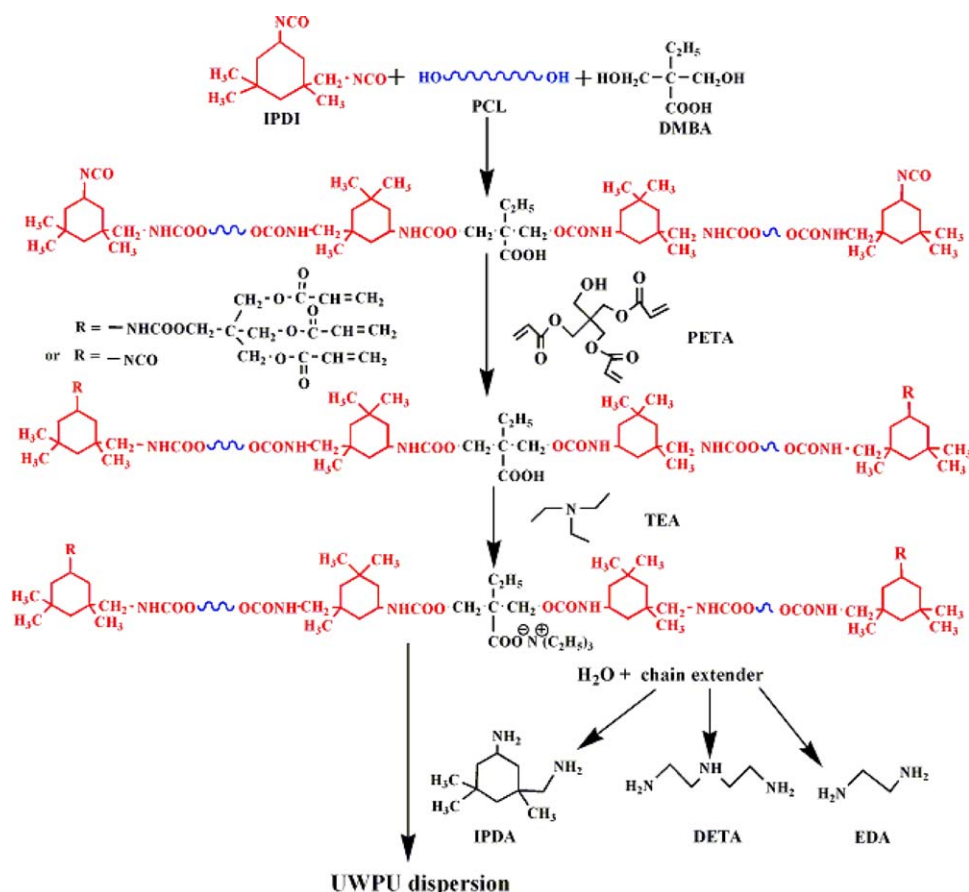
Synthesis of Waterborne UV-Curable Polyurethane Dispersions and Films

IPDI and PCL₁₀₀₀, and DMBA containing 0.03% (based on the weight of reaction monomers) DBTDL were added into a four-necked flask equipped with a digital thermometer, a mechanical stirrer, a reflux condenser and a nitrogen gas inlet. The reaction mixture was mixed uniformly and kept at 80°C for 2 h to obtain NCO-terminated polyurethane prepolymer. Then, a stoichiometric amount of PETA in acetone was added to cap part of the terminal NCO groups. The capping reaction was continued for another 4 h. Subsequently, the reaction temperature was cooled down to 50°C, and TEA was added dropwise into the flask to neutralize the polyurethane prepolymer. The neutralization reaction was kept for 30 min. Afterwards, deionized water and chain extender were added into the reaction system to form chain-extended UWPU dispersion, the chain extension was carried out at 50°C for 1 h. Finally, the UWPU dispersion with 35% solid content was obtained after the acetone was removed. The UWPU dispersions were prepared and outlined in Scheme 1.

The UV-cured UWPU films were prepared by casting UWPU dispersion containing various amounts of photoinitiator onto leveled tetrafluoroethylene (TFE) plates. Then, the films were cured by a 200 W UV (365 nm) irradiating lamp after a water flash-off step.

Surface Sizing of Cellulose Fiber Paper

A sheet of pristine 30 × 30 cm² cellulose fiber paper was placed on the working plate of a ST-1-260 coater (Shaanxi University of Science and Technology, China). Before surface sizing, the paper sheet was firmly pressed onto the working plate to prevent any folding or curling and was then fixed. Next, the mixture containing the UWPU sizing agent dispersion and the photoinitiator was poured on one side of the paper sheet, and a coating roller was used at a constant rate of 3.0–4.0 mm/s for the purpose of sizing the paper uniformly. The sized paper sheet was dried for 5 min at 100°C. Then the sized paper was cured



Scheme 1. The preparation scheme of waterborne UV-curable polyurethane dispersions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with UV light at different curing times. For each type of UWPU dispersion, five paper sheets were obtained. The amount of sizing agent used on each paper sheet was 10 ± 0.36 g/m². The sized paper sheets were conditioned at $23 \pm 1^\circ\text{C}$ and $50 \pm 2\%$ RH for 24 h before characterization.

In addition, a typical AKD surface sizing agent was formulated to make a comparison between UWPU sizing agent and typical AKD sizing agent. Firstly, a mixture of 7 g starch, 93 g deionized water and 2 g ammonium persulfate (APS) was heated to 95°C and stirred for 30 min to obtain a starch solution. Then, 0.2 g AKD dispersion was added into the starch solution and stirred until the mixture became uniform. In this way, AKD surface sizing agent was thereby obtained. The amount of surface sizing agent applied to each paper sheet was 10 ± 0.41 g/m².

Characterization of UWPU Dispersions and Films

The particle size of the UWPU dispersions was determined by a dynamic light scattering analyzer (Zetasizer Nano-ZS, Malvern Instruments, Worcestershire, UK). The samples were diluted to 0.1% with distilled water, and all samples were redispersed by a sonicator before analysis.

The infrared spectra of UWPU films before and after UV-curing were obtained on a FTIR spectrometer (Vector-22, Bruker Optics, Ettlingen, Germany) with a resolution of 4 cm^{-1} in the $4000\text{--}400\text{ cm}^{-1}$ range.

The UWPU films were cut into $2 \times 2\text{ cm}^2$ squares, and the weight was determined as W_0 . Then, the films were put into a sorbite extractor with acetone for 24 h at 50°C and subsequently dried for 72 h at 30°C to a constant weight (W). The gel content was calculated according to eq. (1):²⁵

$$\text{Gel content (\%)} = W / (W_0) \times 100 \quad (1)$$

The water resistance of the UWPU films was characterized by the water absorption ratio (ω), and the results reported are the mean values of five replicates. First, the films were cut into $30 \times 30\text{ mm}^2$ squares and dried in a vacuum oven for 24 h to determine the dry weight (W_1). Then, the UWPU films were immersed in water at 25°C . After 24 h, the UWPU films were taken out, and the water on the surface of the films was wiped off with a piece of filter paper. The weight was determined as W_2 . The water absorption was then calculated using the eq. (2):²⁶

$$\omega(\%) = (W_2 - W_1) / W_1 \times 100\% \quad (2)$$

Characterization of Unsized and Sized Cellulose Fiber Paper

The water resistance was measured by a Cobb tester (Sichuan Changjiang Paper Instrument, China), which is composed of a metallic cylinder with a height of 50 mm and a cross-sectional area of 100 cm^2 . Distilled water (100 mL , $23 \pm 1^\circ\text{C}$) was poured into the cylinder. Then, a circle with a surface area of 125 cm^2 was cut from the paper sheet, weighed, and placed on the

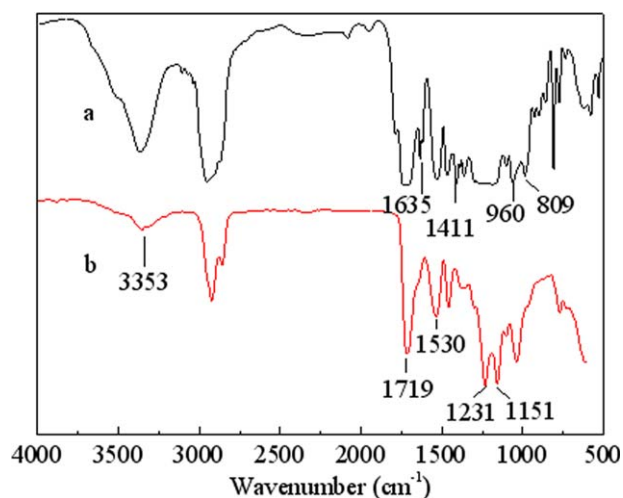


Figure 1. FTIR spectra of the UV-curable polyurethane: (a) before UV curing; (b), after UV curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cylinder with the testing surface facing the water. Afterwards, a sample lid was used to cover the sheet, and the cylinder was turned upside down. After 60 s, the sample was taken out, placed on a sheet of filter paper, covered with two other filter paper sheets, and rolled twice in a time of 4 s using a 10-kg roller. Finally, the sample was weighed and the Cobb value (g m^{-2}) was defined as the amount of water absorbed per unit area of the paper sheet.¹

Both the dry and wet tensile strength of unsized and sized papers were measured on a TS2000-S universal testing machine according to GB453–2002 (Scientific and Technological Limited Company of High Iron, Taiwan). The width and length of the sample were 25 mm and 250 mm, respectively. And the distance between clamps was 180 mm. The measurements were repeated a minimum of five times. The wet paper was prepared by immersing the paper in water for 10 min at ambient temperature, then the water on the surface of the paper was wiped off with a piece of filter paper.

For each folding endurance test, 10 specimens ($15 \times 100 \text{ mm}^2$) were prepared, and all tests were performed on an YQ-Z-31

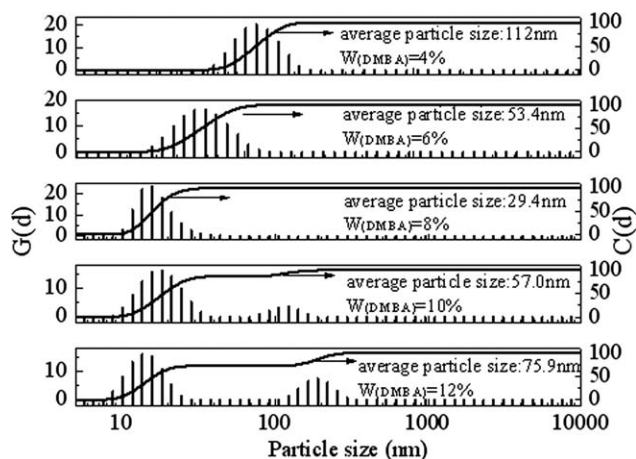


Figure 2. Effects of DMBA content on the average particle size of UWPU dispersions. ($n(\text{NCO})/(\text{OH}) = 1.6$, $w(\text{PETA}) = 6\%$, $w(\text{Chemcure-73W}) = 3\%$, and the curing time is 12 s).

vertical folding tester (Sichuan Changjiang Paper Instrument, China).

For each surface strength test, six specimens ($200 \times 15 \text{ mm}^2$) were prepared, and all tests were measured by an IGT picking speed detector (Sichuan Changjiang Paper instrument, China).

The XPS experiments were performed on a PHI Quantum 2000 scanning spectrometer through monochromatized Al K α excitation, and charge neutralization was implemented by using electron filament and an electron gun. Measurements were carried out at three different spots. The binding energy (BE) scale was calibrated with reference to the C1s line at 284.6 eV. The elemental composition and distribution in sized paper were studied with XPS depth profiling technique through ion sputtering, and the depth was up to 600 nm. The curve fitting program (Multipak v6.1A, Physical Electronics) supplied with the spectrometer was utilized, and Gaussian curves were fitted for deconvoluted high resolution spectra of C1s.

The topography of the paper surface was studied with an atomic force microscope (AFM) (SAC400-SPI3800N, Seiko, Japan). All measurements were made in the contact mode.

Table I. Effects of DMBA Content on the Properties of the Sized Paper

DMBA content (%)	Gel content (%) ^a	Water absorption (%) ^a	Cobb value (g m^{-2}) ^b	Dry tensile index (N m g^{-1}) ^b	Wet tensile index (N m g^{-1}) ^b	Folding strength (time) ^b	Surface strength (m s^{-1}) ^b
Unsize paper	–	–	172 ± 1.2	32.1 ± 2.2	5.72 ± 0.3	42 ± 6	1.3 ± 0.1
4	81.5 ± 3.1	32.1 ± 1.7	37.7 ± 1.2	39.3 ± 2.1	10.1 ± 0.2	60 ± 4	2.3 ± 0.1
6	84.4 ± 3.6	29.2 ± 2.2	32.9 ± 1.1	43.2 ± 1.9	14.8 ± 0.4	92 ± 8	3.0 ± 0.2
8	88.8 ± 3.4	28.5 ± 1.7	29.8 ± 1.4	48.7 ± 1.7	17.7 ± 0.2	88 ± 6	2.8 ± 0.2
10	83.5 ± 4.2	39.6 ± 1.9	42.2 ± 1.7	46.4 ± 2.2	12.3 ± 0.6	59 ± 7	2.0 ± 0.1
12	77.5 ± 5.2	57.2 ± 2.0	58.6 ± 2.2	45.2 ± 2.7	11.5 ± 0.4	44 ± 4	1.8 ± 0.1

^aProperties of UWPU films.

^bProperties of the unsized and sized paper.

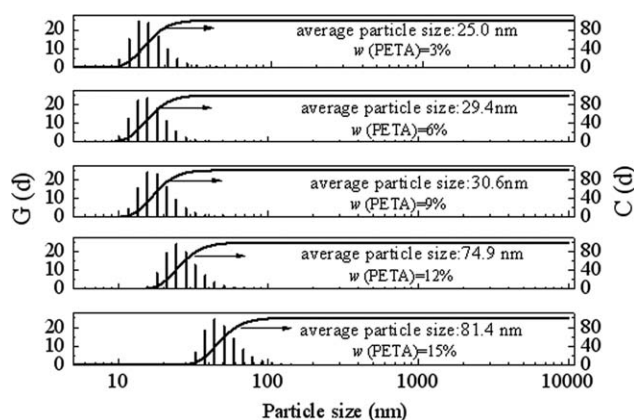


Figure 3. Effects of PETA content on the particle size of UWPU dispersions. ($n(\text{NCO})/(\text{OH}) = 1.6$, $w(\text{DMBA}) = 8\%$, $w(\text{Chemcure-73W}) = 3\%$, and the curing time is 12 s).

The surface and cross-sectional morphology of the paper sheets were observed on an environmental scanning electron microscope (SEM, s-4800 Hitachi, Tokyo, Japan). All of the samples were coated with gold under a vacuum before SEM observation. The samples were torn by hand to obtain the interfacial cross-section.

RESULTS AND DISCUSSION

FTIR Analysis

Figure 1 shows the FTIR spectra of the UWPU films before and after UV curing. The absorption peak at 3353 cm^{-1} and 1719 cm^{-1} can be ascribed to the stretching vibration of hydrogen-bonded -NH .^{27,28} Before UV curing, the absorption peaks of the $\text{C}=\text{C}$ double band at 1635 cm^{-1} ($\text{C}=\text{C}$), 1411 cm^{-1} ($=\text{CH}_2$), and 809 cm^{-1} ($=\text{CH}$)^{19,29,30} are observed, suggesting that UWPU is functionalized with vinyl groups. It is worthy to note that the characteristic peaks of the vinyl groups disappear after UV-curing, indicating the crosslinking reaction among vinyl groups.

Effects of DMBA Content

Fixed the NCO/OH molar ratio (1.6), the PETA content (6%, based on the weight of all monomers, the following is the same), the content of Chemcure-73W (3%), and the curing time (12 s), a series of UWPU dispersions and films were prepared through changing the DMBA content.

Table II. Effects of PETA Content on the Properties of Paper Sized with UWPU Dispersion

PETA content (%)	Gel content (%) ^a	Water absorption (%) ^a	Cobb value (g m^{-2}) ^b	Dry tensile index (N m g^{-1}) ^b	Wet tensile index (N m g^{-1}) ^b	Folding strength (time) ^b	Surface strength (m s^{-1}) ^b
3	78.5 ± 3.8	55.4 ± 2.1	57.1 ± 2.6	38.6 ± 1.4	13.8 ± 1.3	64 ± 3	1.9 ± 0.1
6	88.8 ± 3.4	28.5 ± 1.7	29.8 ± 1.4	48.7 ± 1.7	17.7 ± 0.2	88 ± 6	2.8 ± 0.2
9	89.9 ± 3.5	21.2 ± 1.2	22.4 ± 0.9	51.2 ± 1.4	20.9 ± 0.6	96 ± 4	2.9 ± 0.2
12	90.5 ± 4.1	9.8 ± 0.8	11.1 ± 0.9	50.4 ± 1.2	20.1 ± 0.5	42 ± 6	3.2 ± 0.2
15	92.9 ± 3.2	9.9 ± 1.1	11.3 ± 0.8	48.6 ± 1.9	19.4 ± 1.3	35 ± 4	3.3 ± 0.3

^aProperties of UWPU films.

^bProperties of the sized paper.

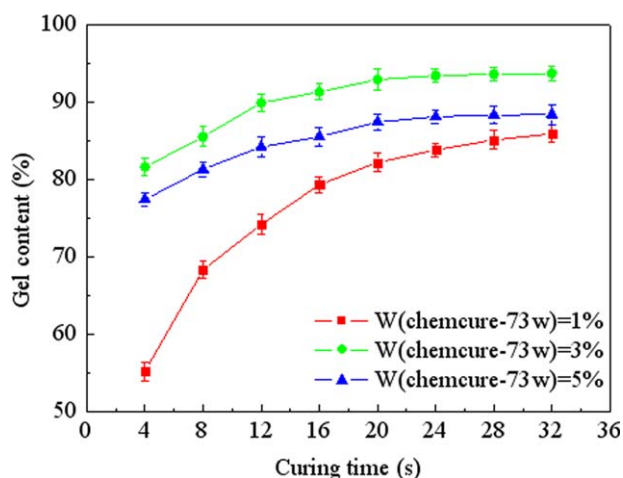


Figure 4. Effects of curing time and photoinitiator content on the gel content of UWPU films. ($n(\text{NCO})/(\text{OH}) = 1.6$, $w(\text{DMBA}) = 8\%$, $w(\text{PETA}) = 9\%$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In this study, DMBA is incorporated into the PU backbone to endow the PU chains with hydrophilicity and allow the homogeneous dispersion of the PU prepolymer in water, as well as to build up the molecular weight.³¹ The carboxylic ions not only stabilize waterborne PU dispersions, but also form the curing sites. Figure 2 shows the effects of DMBA content on the particle size and distribution of UWPU dispersions. It is clear that the particle size of UWPU dispersions decreases from 112 nm to 29.4 nm with increasing DMBA content of 4% to 8%, owing to the increasing hydrophilicity.³² However, the particle size increases from 29.4 nm to 75.9 nm when the DMBA content increases from 8% to 12%, and the particle size distribution changes from unimodal distribution to bimodal distribution. It can be ascribed to the great increase in the system viscosity with increasing DMBA content,³³ which may lead to particle aggregation. In addition, PU having high content of hydrophilic groups will change from micellar state to the verge of solution state; stable colloidal particles do not exist in the system. This phenomenon may be also responsible for the bimodal distribution of UWPU dispersion prepared at higher DMBA content.^{32,33}

Table I shows the effects of DMBA content on the gel content and water absorption of UWPU films. With increasing DMBA

Table III. Effect of Curing Time on the Properties of Paper Sized with UWPU Dispersion

Curing time (s)	Cobb value (g m ⁻²)	Dry tensile index (N m g ⁻¹)	Wet tensile index (N m g ⁻¹)	Folding strength (time)	Surface strength (m s ⁻¹)
4	40.3 ± 1.2	35.6 ± 1.7	13.8 ± 0.7	59 ± 3	2.2 ± 0.2
8	32.6 ± 1.1	43.3 ± 2.1	18.4 ± 0.4	66 ± 4	2.6 ± 0.1
12	22.4 ± 0.9	51.2 ± 1.4	20.9 ± 0.6	96 ± 4	2.9 ± 0.2
16	15.6 ± 1.2	54.1 ± 1.0	23.8 ± 0.3	39 ± 3	3.3 ± 0.1
20	15.4 ± 1.4	54.4 ± 1.3	24.2 ± 0.6	23 ± 5	3.4 ± 0.2
AKD	40.4 ± 1.7	39.5 ± 1.6	8.61 ± 0.8	36 ± 3	1.7 ± 0.3

content from 4% to 8%, the gel content increases from 81.5% to 88.8%, the water absorption gradually decreases from 32.1% to 28.5%. As the DMBA content is increasing, the molecular weight of UWPU prepolymer increases and a crosslink reaction between COOH and NCO groups may take place.¹ The aforementioned structure is beneficial to the formation of the chain entanglement, hydrogen bond, and Coulomb force in the rigid segments.^{19,34,35} Therefore, the intermolecular interactions are enhanced, resulting in the increase in gel content and water resistance. Furthermore, denser films can be formed with the decrease in particle size.

However, the gel content and water resistance decrease when DMBA content is greater than 8%. On one hand, owing to the enhanced intermolecular interactions with increasing DMBA content, the molecular motion is restricted, and the molecular movement inside the film is hindered after the film surface is cured so that the curing degree is reduced,³⁶ resulting in decreased gel content and water resistance. On the other hand, the great increase in the DMBA content promotes the formation of more hydrophilic microdomains, leading to an abrupt decrease in gel content and water resistance.

Table I also shows the effect of DMBA content on the properties of sized paper. As shown in Table I, the Cobb value of unsized papers is 172 g m⁻², which is much higher than that of the sized paper. The Cobb value decreases from 37.7 g m⁻² to 29.8 g m⁻² as DMBA content increases from 4% to 8%; it then

increases to 58.6 g m⁻² when the DMBA content is increased to 12%. Similar phenomena are also detected for the dry and wet tensile strength, folding strength and surface strength of sized paper. It indicates that the water resistance and mechanical properties greatly depend on the balance between particle size of UWPU dispersion, hydrophobicity, intermolecular interaction, and interactions between fibers. The smaller particle size allows for easy penetration into the porous cellulose fiber paper substrate and thereby builds up new interactions among fibers. In addition to physical entanglement, chemical crosslinking networks are uniformly formed inside and on the surface of paper substrates after UV-curing, which is favorable to improve the water resistance and the mechanical strength of the sized paper.

It is also worthy to note that the folding strength and surface strength start to decrease when the DMBA content is greater than 6% instead of 8%. The decrease in the folding strength can be attributed to the enhanced rigidity induced by the increasing content of DMBA hard segment. In addition, the viscosity increases with a further increase in the DMBA content. Therefore, it becomes difficult for the UWPU dispersion to form a uniform coating and penetrate into the paper sheet, resulting in a decrease in surface strength.

Effect of PETA Content

Fixed the content of Chemcure-73W (3%), the curing time (12 s), the NCO/OH molar ratio (1.6) and the content of DMBA (8%), a series of UWPU dispersions and films were prepared through changing the PETA content.

The particle size and particle size distribution of UWPU dispersions prepared with different PETA contents are shown in Figure 3. It can be seen that the particle size displays a unimodal distribution. The average particle size increases from 25.0 nm to 81.4 nm as the PETA content increases from 3% to 15%. This increase can be attributed to the increased hydrophobicity as the PETA content is increased.

Table II shows the effect of PETA content on the gel content and water absorption of UWPU films. The gel content increases from 78.5% to 92.9% when the PETA content increases from 3% to 15%, indicating the increase of crosslink density. With increasing the PETA content, the functionality of the UWPU increases, which is able to strongly increase the curing rate and the final conversion,²² leading to an increase in the crosslinking density. It is also observed that the UWPU film prepared with a higher PETA content is endowed with better water resistance. It

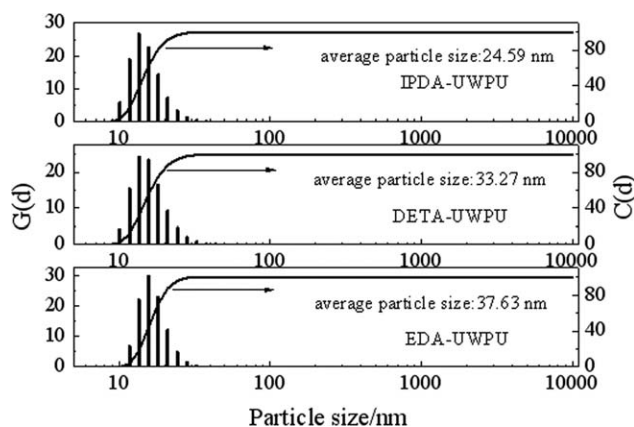


Figure 5. Effects of chain extenders on the particle size of the UWPU dispersion. (*n(NCO)/(OH) = 1.6, w(DMBA) = 8%, w(PETA) = 9%, w(Chemcure-73W) = 3%, the curing time is 12 s, and the chain extension degree is 60%).

Table IV. Effects of Chain Extender on the Properties of the Sized Paper

chain extender	UWPU	IPDA-UWPU	DETA-UWPU	EDA-UWPU
Weight average Molecular weight Before UV curing (M_w , g mol^{-1})	14500	25400	23700	21800
Gel content (%) ^a	89.9 ± 3.5	96.8 ± 2.1	93.9 ± 3.1	92.3 ± 2.3
Water absorption (%) ^a	21.2 ± 1.2	8.64 ± 0.9	10.4 ± 1.3	15.5 ± 1.1
Cobb value (g m^{-2}) ^b	22.4 ± 0.9	10.1 ± 0.3	12.3 ± 0.5	17.9 ± 0.8
Dry tensile Index (N m g^{-1}) ^b	51.2 ± 1.4	67.5 ± 1.1	60.1 ± 1.7	58.7 ± 1.8
Wet tensile index (N m g^{-1}) ^b	20.9 ± 0.6	39.7 ± 0.7	35.9 ± 1.0	34.2 ± 1.2
Folding Strength (time) ^b	96 ± 4	149 ± 2	132 ± 1	128 ± 3
Surface strength (m s^{-1}) ^b	2.9 ± 0.2	3.5 ± 0.1	3.3 ± 0.2	3.1 ± 0.2

^aProperties of UWPU films.^bProperties of the sized paper.

can be due to the higher functionality and increased crosslinking density.³⁷

Table II also shows the effects of PETA content on the properties of sized paper. The water resistance and mechanical properties of sized paper are improved with appropriate amounts of PETA. In this research, nanosized UWPU dispersion is able to penetrate into the fiber wall and in this way, strengthens the fiber wall, which is important for the improvement of wet strength.³⁸ In addition, more and more three-dimensional networks are formed with increasing PETA content. A network with a high crosslinking density has better resistance to an external extension force,²² and the strength of the joint between the fibers can be improved, resulting in improved water resistance, tensile strength, and surface strength.

However, a slight decrease in the tensile strength is detected when PETA content is larger than 9%, since it becomes more difficult for the UWPU dispersion with larger particle size to penetrate into the paper substrate, resulting in the decrease of tensile strength. And the folding strength decreases greatly from 96 times to 42 times when the PETA content is greater than 9%, owing to the greatly increased crosslinking density and rigidity.

Effect of Curing Condition

Fixed the NCO/OH molar ratio (1.6), the DMBA content (8%) and the content of PETA (9%), a series of UWPU dispersions

Table V. Carbon, Nitrogen, and Oxygen Contents for Sized Paper at Different Depth

Designation	Depth (nm)	C (%)	N (%)	O (%)
UWPU	0 nm	72.45	3.83	23.72
	50 nm	82.90	2.13	14.97
	100 nm	87.25	1.83	10.92
	150 nm	87.49	1.23	11.28
IPDA -UWPU	0 nm	77.69	4.06	18.25
	50 nm	88.61	3.68	7.71
	100 nm	89.59	3.42	7.66
	150 nm	89.74	2.74	7.52

and films were prepared through changing curing time and the content of photoinitiator.

Figure 4 shows the variation of gel content with Chemcure-73W photoinitiator content and curing time. In the process of photo-polymerization, the photoinitiator content determines the curing degree of the polymer.³⁶ As shown in Figure 4, the gel content greatly increases when the Chemcure-73W content increases from 1% to 3%. It can be ascribed to the UV-curable velocity, which is depended on the forming velocity of free radicals on the film surface.^{19,36} According to the Lambert-Beer law, the light intensity is degressive in the form of an exponential function when the content of photoinitiator increases.

However, the gel content decreases when the Chemcure-73W content is excessive. The excessive photoinitiator closed to the film surface will absorb most of the UV light, and the light flux reached to the film interior would decrease sharply.^{19,36} The number of free radicals generated by the photoinitiator thereby decreases, as well as the UV-curable velocity. Therefore, the gel content decreases when the content of Chemcure-73W is 5%.

With increasing the curing time from 4 s to 32 s, the gel content increases abruptly from 55.2% to 85.9% when the content of Chemcure-73W is 1%. However, when the content of Chemcure-73W is 3% and 5%, the increase rate in the gel content decreases and becomes almost invariable when the curing time reaches 16 s.

Table III shows the effects of the curing time on the properties of the sized paper. It is found that the water resistance, tensile strength, and surface strength are improved with curing time. Since the conversion of double bond and crosslinking density keeps increasing with increasing curing time, and more chemical crosslinking networks among fibers are formed.

However, the folding strength decreases sharply when the curing time is greater than 12 s. The water resistance, tensile strength, and surface strength keep almost invariable when the curing time is greater than 16 s. It suggests that moderate crosslinking is favourable to increase the folding strength, but excessive crosslinking density will significantly reduce the folding strength.

A comparison between a typical AKD surface sizing agent and UWPU was also made, as shown in Table III. It is found that

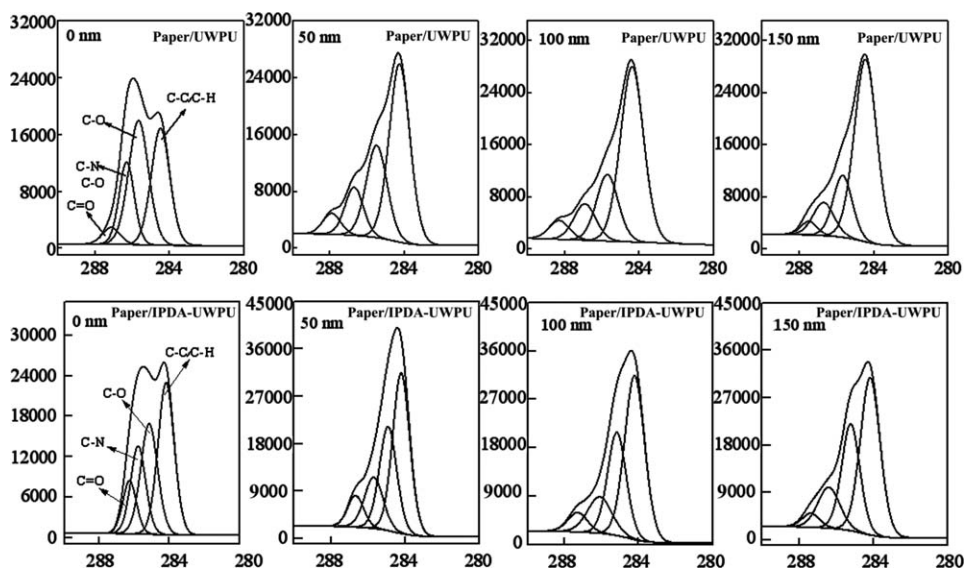


Figure 6. High resolution C1s XPS spectra at different depth for paper sized with UWPU and IPDA-UWPU. (*n(NCO))/(OH) = 1.6, w(DMBA) = 8%, w(PETA) = 9%, w(Chemcure-73W) = 3%, the curing time is 12 s, and the chain extension degree is 60%, the followings are the same).

the paper sized with UWPU exhibits better performance than the paper sized with the AKD dispersion.

Effect of Chain Extender

Fixed the content of Chemcure-73W (3%), the curing time (12 s), the NCO/OH molar ratio (1.6), the content of DMBA (8%), the content of PETA (9%), and the chain extension degree (60%), a series of UWPU dispersions and films were prepared through changing the type of chain extender.

Figure 5 depicts the particle size of UWPU dispersions prepared with different chain extenders. It is found that the UWPU dispersion chain extended with IPDA (IPDA-UWPU) exhibits the smallest particle size, and the UWPU dispersion chain extended with EDA (EDA-UWPU) displays the highest particle size. It indicates that IPDA has better compatibility with the hard segment of polyurethane owing to its similar structure with the IPDI hard segment. The chain extension may take place inside the colloidal particles, leading to the smallest particle size. It is also reported that the hydrogen bonds in polyurethane are

altered by the incorporation of chain extender.³⁹ The polyurethane synthesized with IPDA shows better miscibility between soft and hard segments, compared to those chain-extended with EDA.³⁹ This phenomenon may also be responsible for the smallest particle size of UWPU dispersion chain extended with IPDA.

In addition, the particle size of the chain-extended UWPU by DETA and EDA was higher than UWPU. Since the flexibility of UWPU polymer chains can be enhanced with the introduction of linear chain extender DETA and EDA, the hard segments thereby tend to aggregate together, and the hydrogen-bonding interactions among polymer chains are greatly improved, as well as the intermolecular entanglements. As a result, the viscosity of prepolymer increased, and the phase inversion becomes more difficult, resulting in increased particle size. On the other hand, the hydrophilicity of DETA and EDA is higher than that of IPDA, chain extension tends to take place on the particle surface, leading to the increase of particle size. Besides, the UWPU dispersion chain extended with trifunctional DETA (DETA-UWPU) has smaller particle size than the UWPU dispersion by bifunctional EDA. It may be due to the better compatibility between DETA and polyurethane backbone, since DETA with more than two amino groups has higher reactivity with NCO groups than EDA.

As shown in the Table IV, the paper sized with chain-extended UWPU dispersion displays better performance than that of paper sized with UWPU. The molecular weight of UWPU is lower than that of chain-extended UWPU, the intermolecular void may be larger in the process of film-forming, which is beneficial to the formation of water channels. However, the molecular weight of UWPU is increased, and hydrophobic structure is incorporated into UWPU chains after chain extension, resulting in enhanced water resistance. In addition, urea bonds are formed by chain extension. The hydrogen bonding interactions are thereby enhanced, which leads to increased tensile strength.

Table VI. Qualitative and Quantitative XPS Analysis for Sized Paper at Different Depth

Designation	Assignment	0 nm/%	50 nm/%	100 nm/%	150 nm/%
UWPU	C—C,C—H	44.90	53.63	60.68	66.13
	C—O	31.21	27.74	21.88	19.07
	C—N	17.76	12.92	11.98	11.26
	C=O	6.14	5.71	5.46	3.55
IPDA-UWPU	C—C,C—H	38.63	45.75	49.68	50.02
	C—O	29.31	29.99	29.72	31.42
	C—N	20.74	15.90	14.68	14.21
	C=O	11.32	8.37	5.92	4.35

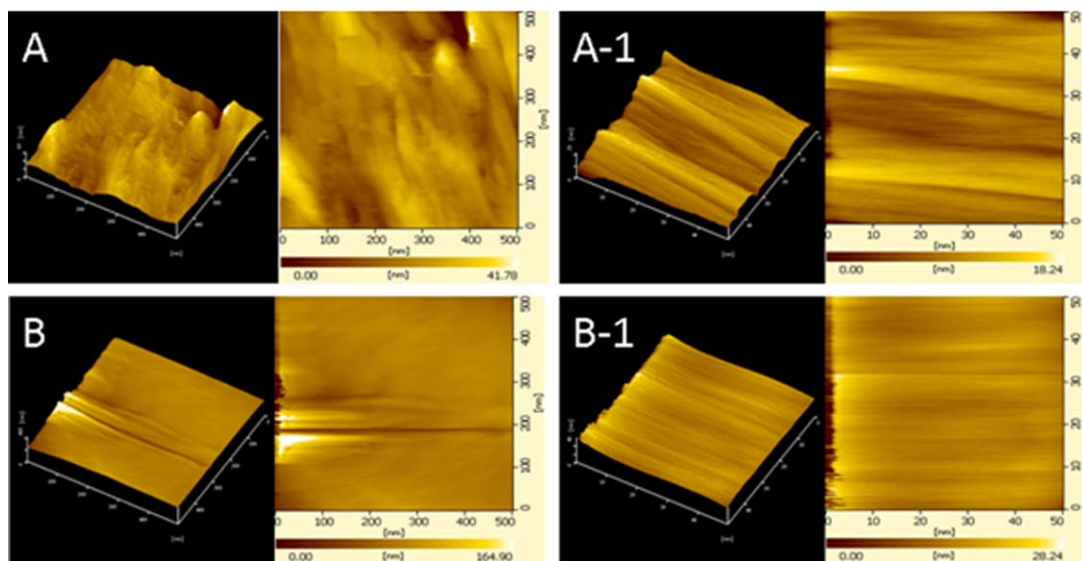


Figure 7. AFM morphology for the surface of unsized paper (A) and sized paper (B) at different magnification (left: 3D surface morphology; right: phase image). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The paper sized with IPDA-UWPU dispersion displays the best performance. Since the polyurethane synthesized with IPDA shows better miscibility between soft and hard segments, compared to those chain-extended with EDA.³⁹ The enhancement function of IPDA-IPDI hard segment on soft segment is better than that of DETA-IPDI and EDA-IPDI. In addition, the rigidity of UWPU chain prepared with the cyclic structure IPDA is higher than those prepared with linear DTEA and EDA. Furthermore, IPDA has the biggest hydrophobic groups in comparison with DETA and EDA, leading to improved water resistance and decreased Cobb value.

The properties of paper sized with DTEA-UWPU are superior to that of paper sized with EDA-UWPU. It suggests that the incorporation of trifunctional linear chain extender is more effective in improving the performance of UWPU and sized paper compared with bifunctional linear chain extender.

XPS Depth Analysis

The elemental composition for sized paper at different depth was examined by XPS depth profiling technique. The C1s, O1s, and N1s signals, as unique elemental markers of polyurethane, are measured to confirm the distribution and penetration of UWPU in the sized paper. Table V shows the variation of atomic content of carbon (C), oxygen (O), and nitrogen (N) at different depth. Figure 6 presents the deconvoluted high resolution C1s spectra for UWPU sized paper and IPDA-UWPU sized paper at different depth. The deconvoluted peaks at 284.5–284.8, 285.6–285.9, 286.5–287.0, and 287.5–289.0 eV are attributed to the functional groups of C–C/C–H, C–O, C–N, and C=O, respectively. The composition and chemical state of different C components are listed in Table VI. As shown in Table V, the content of N element decreases with increasing depth. From Table VI, it is also found that the contributions of

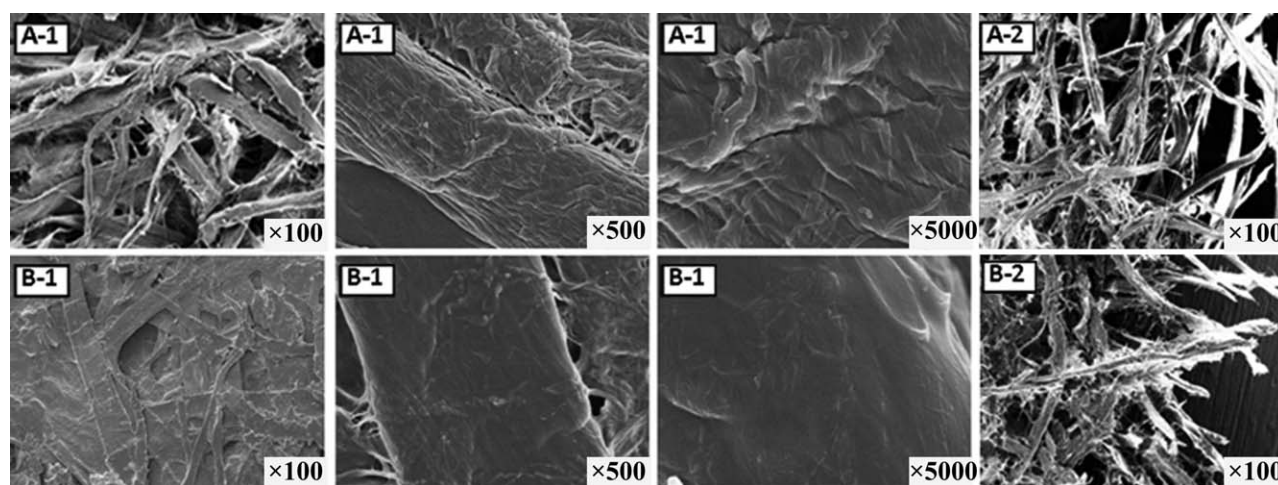


Figure 8. SEM surface and cross-section morphology of unsized paper (A) and sized paper (B) at different magnification (A-1, B-1: surface morphology; A-2, B-2: cross-section morphology).

C—N functions decrease with an increase in depth. Since nitrogen and C—N groups are present only in the hard segment, i.e., in urea and urethane functions. Therefore, these results suggest that the surface segregation nature of the hard segment towards the surface and away from the bulk. This phenomenon is different from the XPS results obtained for pure polyurethane-urea films.⁴⁰ In general, the hard segments preferentially reside towards the bulk of the polyurethane film instead of the top surface. The main reason can be attributed to the hydrogen bonding formed between urethane (or urea) groups in polyurethane and the —OH groups on the paper surface. This interaction provides a higher driving force for the hard segments to localize on the surface.

Furthermore, the data of chemical composition listed in Tables V and VI suggest that the content of nitrogen in paper sized with IPDA-UWPU is higher than that of paper sized with UWPU, as well as the content of C—N. It can be ascribed to the incorporation of nitrogen compound IPDA into UWPU. Slower decreasing rate of nitrogen content with depth for paper sized with IPDA-UWPU is detected. This result suggests that IPDA-UWPU with smaller particle size displays better penetrability into the paper substrate.

It is interesting to observe that changes in the relative intensities of the C—C and C—O peaks occur as the thickness of the probed layer increases. As to the paper sized with UWPU, the peak associated with C—O (286.5 eV) decreases with increasing depth. This suggests that the soft segment is in relatively higher concentration at the top layer. Soft segment in UWPU migrates to the surface due to their chain mobility.⁴⁰ While for the paper sized with IPDA-UWPU, the intensity of C—O peak slightly increases as a function of depth. It indicates that the mobility of soft segment is restricted owing to the enhanced hydrogen bonding interactions in IPDA-UWPU. These results confirm a more phase mixing characteristic for IPDA-UWPU and phase separation for UWPU.

Morphology Analysis

The nanoscale morphology is illustrated by an AFM image of unsized paper and sized paper. As shown in Figure 7, the surface of the sized paper is much smoother than the original paper. It indicates that the UWPU is able to form a continuous film on the paper surface and thereby increase the smoothness of the paper.

Figure 8 shows surface and cross-section SEM morphology of original paper and sized paper. It can be observed that fibers in the original paper have a rougher surface in comparison with fibers in the sized paper. The surface of fibers in paper sized with UWPU dispersion becomes smoother, suggesting that a homogeneous film of UWPU is able to form on the surface of the paper. In addition, the gap between fibers is filled with UWPU polymers.

It can be also observed from the SEM cross-section morphology that the fibers are broken when the sized paper is torn, and a burred feature is detected on the surface of fibers. These phenomena indicate that UWPU is able to penetrate into the paper and bridge the fiber together, and the bond strength between fibers is greater than the specific strength of the fiber.

CONCLUSIONS

Waterborne UV-curable nanosized polyurethane (UWPU) surface sizing agents displayed optimum performance when prepared under the following conditions: $n(\text{NCO})/(\text{OH}) = 1.6$, $w(\text{DMBA}) = 8\%$, $w(\text{PETA}) = 9\%$, $w(\text{Chemcure-73W}) = 3\%$, and the curing time is 12 s. Chain-extended UWPU was endowed with higher molecular weight, gel content, water resistance than UWPU. UWPU dispersion chain extended with IPDA (IPDA-UWPU) exhibited the smallest particle size and best sizing performance, and a more phase mixing characteristic for IPDA-UWPU was also confirmed. Besides, different from pure polyurethane-urea film, the hard segment in polyurethane resided towards the paper surface instead of the bulk.

The main factors leading to the enhanced properties of sized paper are summarized as following: (1) The decreased particle size of UWPU dispersions, as well as better penetrability into the paper substrate; (2) Moderate crosslinking density together with higher molecular weight. The folding strength is greatly affected by crosslinking density when the molecular weight of UWPU is lower. (3) Chain extender with bigger hydrophobic group and better compatibility with polyurethane backbone was also responsible for the improved performance. Besides, the smoothness of sized paper can be improved, and the bond strength between fibers was higher than the specific strength of the fiber. As compared with paper sized with a typical AKD surface sizing agent, paper sized with UWPU dispersion displayed much better performance, the obtained UWPU could be directly used as an effective and fast drying surface sizing agent for cellulose fiber paper.

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