

Synthesis of blocked and branched waterborne polyurethanes for pigment printing applications

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ABSTRACT: A series of blocked and branched waterborne polyurethanes (BBPUs) have been successfully synthesized and applied in pigment printing of cellulosic substrate. The branched structure was based on an “ $A_2 + CB_2$ ” approach with diisocyanate prepolymer and diethanol amine. The terminal isocyanate groups were blocked by sodium bisulfite to lower curing temperature and improve the color fastness. The prepolymerization and chain extending could be considered as the end at 70°C after 90 min and at 80°C after another 90 min, respectively. It was suitable for sodium bisulfite to block isocyanate groups at 0°C–5°C for 40 min. The microphase separation of BBPU based on the longest polyethylene glycol (PEG) soft segment appeared. Both curing rate and pencil hardness of BBPU films distinctly reduced as the molecular mass of PEG soft segment ascended. The moisture rate increased from 18.1% to 49.2% with increasing the molecular weight of PEG, indicating that water resistance of the film became poor. Excellent acid and alkali resistances of the BBPU films were obtained. Color fastness to washing, rubbing, and light of the printed cotton fabrics was remarkably enhanced as the BBPU amount ascended to 10% which were cured at 85°C for 6 min. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42780.

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INTRODUCTION

Waterborne polyurethanes (WPU) have been extensively employed as adhesives and coatings for various applications including textiles, papers, wood, and rubber, due to their flexibility, versatility, and environmental friendliness.¹ Unfortunately, WPUs still have some shortcomings, such as poor waterproof, weak mechanical properties, slow drying rate, and poor fastness to substrate and dyes, which inhibit their extensive application. Many efforts have been made to compensate for these drawbacks and further endow polyurethanes with unique properties through molecular structure design,² copolymerization with other polymers,³ and composition with inorganic nanomaterials.^{4,5} Among these methods, branching is an exciting example to obtain polyurethanes with tailored outstanding performances.

Branched polyurethanes (BPUs) are a kind of highly branched macromolecules with three-dimensional axiolitic architecture and large amount of terminal functional groups.^{6,7} This unique structure leads to some particular properties in comparison with conventional linear polyurethanes, such as good solubility and compatibility, low melting viscosity, and many empty internal cavities.⁸ Additionally, the numerous terminal functional groups offer multiple covalent sites for cross-linking reaction, which will further enhance the chemical resistance, durability, and mechanical properties of the film.⁹ Thus, BPUs are competitive candidates for a

variety of fields, including coatings, films, drug delivery, and other functional materials. Recently, numerous studies on synthesis routes, polymerization kinetics, and structure–property relationships of BPUs have been reported. A series of BPUs were synthesized by direct polycondensation of diisocyanates (A_2 monomers) with polyols (B_n monomers) or amido-polyols (CB_n monomers) and the influence of reaction conditions was detailedly discussed.⁸ The structure–property behavior of highly branched poly(urethane-urea) and its linear analog were comparatively studied and it was concluded that the tensile strength and viscosity of the highly branched polymer were lower than those of the linear analog.¹⁰ Hyperbranched shape-memory polyurethane can be prepared via $A_2 + B_3$ approach and it offered twofold higher shape-recovery rate compared with its linear counterpart.¹¹ Isocyanate-terminated prepolymer and hyperbranched poly(amide-ester) polyol were used to synthesize BPU by graft copolymerization, which also showed outstanding thermal and mechanical properties.¹²

In textile applications, isocyanate (NCO) groups are usually designed as end groups of polyurethanes in order to improve the adhesive strength between polyurethanes and fiber substrates. However, producing BPUs with terminal NCO groups is seriously limited by self-reactivity and high moisture sensitivity of the NCO groups, making a loss of available NCO groups

during emulsification, storage, and other processes.^{9,13} Therefore, it is essential to temporarily protect NCO groups before application. The temporarily blocked NCO groups can de-block at a certain temperature, and the regenerated NCO groups undergo cross-linking and curing reaction with fiber substrates that contain active hydrogen functional groups.¹⁴ The frequently used blocking agents are ketoxime, phenol, amines, lactams, sodium bisulfite, and others.^{14–16} Among them, sodium bisulfite is cheap, easily available, pollution-free, and especially it offers low deblocking temperature, which is beneficial to fabric finishing process.¹⁷

Most reported literatures were focused on synthesis and characterization of novel BPU with highly branched polyols.^{6,18–20} However, the highly reactive NCO group was not designed as terminal group to further improve the adhesive strength between polyurethanes and substrates. Thus, the present work is concentrated on synthesis of blocked and branched waterborne polyurethane (BBPU) with polyurethane prepolymer (A_2 monomer), diethanol amine as branching unit (CB_2 monomer), and sodium bisulfite as blocking agent. The reaction conditions for prepolymerization and blocking reaction were optimized. The chemical and physical structures of the polyurethane were analyzed. The film properties including hardness, resistances to water and chemicals, as well as curing rate were investigated. The synthesized BBPU was also employed in pigment printing on cellulosic substrate and the color fastness was discussed in detail.

EXPERIMENTAL

Materials

The BBPUs were synthesized via the reaction of diisocyanate, polyether polyol, chain extender, and blocking agent. Isophorone diisocyanate (IPDI, 99 wt %) and dimethylolpropionic acid (DMPA, 98 wt %) employed as hard segment and hydrophilic chain-extender, respectively, were both purchased from Aladdin (Shanghai) Co., Ltd. Polyethylene glycol (PEG) with molecular weights of 200, 400, 600, 1000, and 2000 (supplied by Sinopharm Chemical Reagent Co., Ltd.) was used as polyether polyols. Dibutyltin dilaurate (DBTDL) that was bought from Sinopharm Chemical Reagent Co., Ltd., served as a catalyst. Diethanol amine (DEOA, chemically pure), sodium bisulfite ($NaHSO_3$, analytically pure), and triethylamine (TEA, analytically pure) which were all available from Sinopharm Chemical Reagent Co., Ltd., served as branching agent, blocking agent, and neutralization agent, respectively. Acetone (analytically pure, bought from Sinopharm Chemical Reagent Co., Ltd.) was used as a solvent to adjust viscosity. Dibutyl amine, hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and sodium hydroxide (NaOH) were all analytically pure and were purchased from Sinopharm Chemical Reagent Co., Ltd. The thickening agent DM-5263 was supplied by Wuxi Huishan Dymatic Chemical Co., Ltd. Pigment Red 21 was gifted by Hangzhou Hengsheng Chemical Co., Ltd. PEG was vacuum dehydrated at 80°C for 2 h and was kept at 60°C for 24 h prior to use. Acetone was stored with 5 Å type molecular sieves at least for a week. Other chemicals were utilized without further purification. The 100%

cotton woven fabric with density 153 g/m² was provided by Jiangsu Hongdou Industrial Co., Ltd. (China).

Preparation of BBPUs

BPU blocked with blocking agents were synthesized through the following procedures. First, PEG (0.01 mol) was added into a dry four-neck flask equipped with a motor stirrer, a condenser-tube, and a thermometer, which was heated up to 70°C. IPDI (0.04 mol) was added dropwise to react with PEG at 70°C under continuous stirring until residual isocyanate groups reached the theoretical value. The system was further increased to 80°C, followed by adding a calculated amount of DMPA (0.005 mol) and three to four drops of DBTDL. The linear polyurethane prepolymer was obtained from above prepolymer process. Acetone (20 mL) was added to reduce viscosity during the above process. Subsequently, DEOA (0.01 mol) was added after the temperature was decreased to 60°C and the branching reaction was continued for another 4 h. Afterward, the system was cooled to 0°C–5°C and required amount of $NaHSO_3$ (0.02 mol) and Na_2SO_3 (0.02 mol) were added to react for 40 min. TEA (0.005 mol) was then added to neutralize the carboxylic acid moieties in DMPA at 40°C for 40 min. Finally, the BBPUs were emulsified with deionized water under high speed for 60 min. The emulsion was distilled and filtered to remove residual acetone and unreacted reagents. The BBPU film which was used for following characterizations was obtained by casting the emulsion on a glass slide and then dried at room temperature. BBPU-1, BBPU-2, BBPU-3, BBPU-4, and BBPU-5 were synthesized with PEG 200, PEG 400, PEG 600, PEG 1000, and PEG 2000, respectively. The whole synthesis process for BBPUs is shown in Scheme 1.

Printing with BBPUs

About 0%–20% BBPU dispersion (solid content 30%), 12.5% thickening agent, 10% pigment, and deionized water were mixed and stirred to obtain homogeneous color paste. And then the color paste was printed on cotton fabrics, followed by curing at 70°C–100°C for 3–6 min.

Characterization

The content of free isocyanate group (NCO%, mass fraction) was determined by dibutyl amine titration method and calculated according to the following equation:²¹

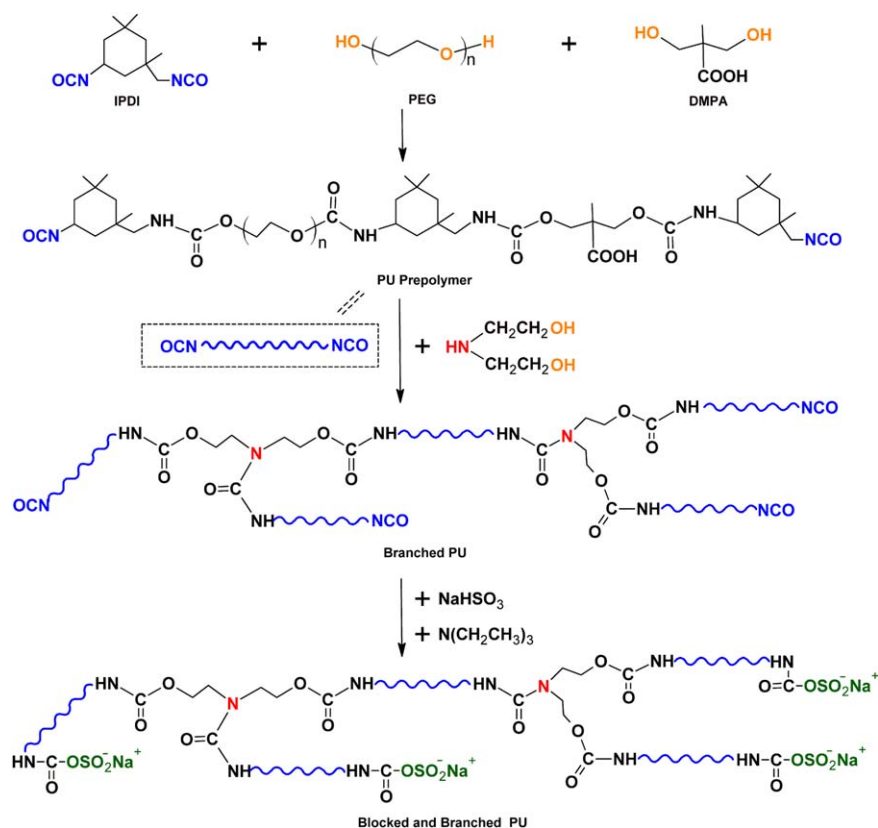
$$NCO\% = \frac{42c(V_0 - V_s)}{1000m} \times 100\% \quad (1)$$

where c represented hydrochloric acid concentration (mol/L), m is the mass of samples (g), V_0 and V_s represented the volume of hydrochloric acid (mL) consumed in the control and sample titrations, respectively.

The blocking rate was calculated according to the content of NCO before and after blocking reaction as follows:²²

$$\text{Blocking rate}\% = \frac{W_0 - W_1}{W_0} \times 100\% \quad (2)$$

where W_0 and W_1 are the mass fraction of NCO groups before and after blocking, respectively.



Scheme 1. Synthesis process of BBPUs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Fourier transform infrared (FTIR) spectra for the BBPU was performed on a spectrometer (NICOLET.is10, Thermo Scientific) in the range of 350–4000 cm^{-1} via liquid-film method.

¹³C nuclear magnetic resonance (¹³C NMR) of the synthesized BBPU was recorded with DMSO-*d*₆ as solvent and tetramethylsilane (TMS) as an internal standard on a Bruker Avance III 400 MHz spectrometer.

The molecular weight of the BBPU was estimated by gel permeation chromatography (GPC, BREFZE, Waters) with a flow rate of 1 mL/min at 30°C. Tetrahydrofuran (THF) and polystyrene (PS) standards were used as the eluent and the molecular weight calibration, respectively.

Differential scanning calorimetry (DSC) measurements were recorded on a TA instrument (Q200, United States) thermal analyzer. Liquid aluminum crucibles containing 3–5 mg of samples were heated from –90°C to 150°C at a heating rate of 10°C/min in nitrogen atmosphere.

The glass slides coated with BBPU samples were cured at 85°C. After curing, the BBPU films were immersed in ethanol for 30 min. The sample was taken out, wiped off the residual solvent, and dried. If the weight of the film before and after immersion was unchanged (namely the gel yield was almost 100%), and the film was considered as complete curing.²³

BBPU samples were uniformly coated on a glass slide and then cured to be films, followed by soaking in deionized water for

24 h. The glass slide was taken out and wiped to remove any residual water. The moisture ratio (*W*, %) can be obtained by the following formula:

$$W = \frac{m_2 - m_1}{m_1 - m_0} \times 100\% \quad (3)$$

where, *m*₀ was the weight of a glass slide (g), *m*₁ and *m*₂ were the weight of a glass slide coated with BBPU film before and after soaking (g), respectively.

The BBPU films were immersed into 10% H₂SO₄ and 10% NaOH, respectively. If the film is damaged within 12 h, the acid or alkali resistance is judged 1 grade; if the film is damaged within 12–24 h, the acid or alkali resistance is rated 2 grade; if the film is intact within 24–48 h, the acid or alkali resistance is considered 3 grade.

Pencil hardness of the BBPU films was evaluated on the basis of ASTM D 3363-05 standard. The scale from soft to hard of the pencil hardness for the films is as follows: 6B – 5B – 4B – 3B – 2B – B – HB – F – H – 2H – 3H – 4H – 5H – 6H.

The colorfastness to rubbing, washing and light of the printed fabrics after application of BBPUs was estimated according to AATCC 8-2007, AATCC 61-2006, and AATCC 16-2004, respectively.

The surface morphology of cotton fabrics before and after printing was observed with a scanning electron microscope (SEM, TM3030, Hitachi) at a magnification of 3000×.

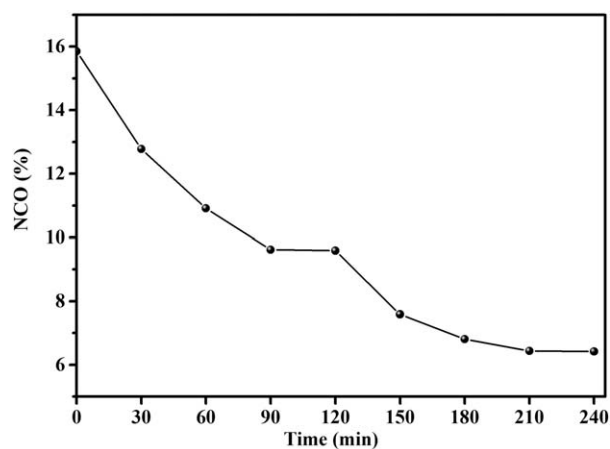


Figure 1. Relationship of $-\text{NCO}$ content and reaction time.

RESULTS AND DISCUSSION

Synthesis and Characterization of BBPU3

Optimization of Synthesis Conditions. Generally, the reaction between isocyanate ($-\text{NCO}$) groups and polyols will be accelerated via increasing the reaction temperature and time. Nevertheless, $-\text{NCO}$ groups can react with urethane at an excess temperature and generate unstable structures which will continue to decompose. If the temperature is too low, the reaction period will be too long, leading to low efficiency. Therefore, the reaction temperature and time should be controlled in a certain range. According to available references,^{24–27} the temperature for prepolymer process is generally controlled in 70°C – 80°C , whereas the reaction time is diverse in different system. So it is focused on discussing the reaction time for the prepolymer process by monitoring the content of $-\text{NCO}$ groups.

The theoretical values after PEG600 and DMPA reacted with IPDI were designed to be 9.49% and 6.34%, respectively. Figure 1 represented that the content of NCO groups notably decreased in the beginning of prepolymerization (within 60 min). Then the reaction rate slowed down, and the content of NCO groups reached 9.62% at 90 min and 9.59% at 120 min which approached to the first theoretical value. DMPA was then added to continue reaction with NCO groups, and the content of NCO groups was 6.42% at 210 min and 6.40% at 240 min, both of which approximated to the second theoretical value. Taking the reaction efficiency into consideration, it is suitable for PEG and DMPA to react with IPDI at 70°C for 90 min and at 80°C for another 90 min, respectively.

The reaction temperature of NaHSO_3 and NCO is generally set to be 0°C – 5°C because it is an exothermic reaction.²⁸ Nevertheless, the reaction rate varies with the system. Here, the influence of time on the blocking reaction with NaHSO_3 at 0°C – 5°C was investigated. As shown in Figure 2, the blocking rate increased as a function of reaction time, and achieved 86.8% at 40 min and 87.0% at 50 min, respectively. It almost kept constant beyond 40 min, indicating the end of blocking reaction. Consequently, it was proper to terminate the blocking reaction at 40 min.

Structure Characterization. The successful synthesis and curing of BBPU-3 were confirmed by FTIR. As shown in Figure 3(a), the absorption bands near 3320 cm^{-1} and 1530 cm^{-1} are ascribed to the presence of $-\text{NH}-$ stretching and bending vibration, respectively. The absorption peaks corresponding to the carbonyl groups ($-\text{C}=\text{O}$) in urethane group ($\text{NH}-\text{CO}-\text{O}$) and urea group ($\text{NH}-\text{CO}-\text{NH}$) separately appear at 1700 cm^{-1} and 1630 cm^{-1} . A narrow peak around 1100 cm^{-1} belongs to stretching vibration of ether linkage ($\text{C}-\text{O}-\text{C}$) in PEG. These characteristic peaks indicate the formation of polyurethane. Additionally, the absorption band at about 2270 cm^{-1} due to free isocyanate groups (NCO) is absent, meanwhile, new characteristic peaks at 1460 – 1240 cm^{-1} are assigned to sulfites ($-\text{SO}_3-$), which demonstrate the completion of the blocking reaction and formation of blocked polyurethane. However, the absorption of NCO group at 2270 cm^{-1} appears in Figure 3(b) after curing at 75°C , indicating the deblocking of the blocked polyurethane.

The ^{13}C NMR of the synthetic BBPU-3 was measured as shown in Figure 4. The signals are assigned as follows: 174.43 ($-\text{COOH}$ in DMPA), 156.71–156.45 ($-\text{NHCON}-$, urea), 155.30–155.06 ($-\text{NHCOO}-$, urethane), 124.26–121.50 ($-\text{N}=\text{C}=\text{O}$), 69.86–68.96 ($-\text{CH}_2\text{CH}_2-$ in PEG), 65.47–60.27 ($-\text{NCH}_2\text{CH}_2-$ in DEOA), 56.57–45.62 ($-\text{NCH}_2\text{CH}_2-$ in DEOA), 36.15–23.03 ($-\text{CH}_2$ or $-\text{CH}_3$ in IPDI). These signals confirmed the formation of BPU.

Degree of branching (DB) is a vital parameter for branched polymers, indicating the branching efficiency. DB of the BBPU-3 was calculated according to Frey's eq. (4) because the branching agent was diethanolamine (CB_2).²⁹

$$DB = \frac{2D}{2D+L} \quad (4)$$

where D is the number of dendritic units, and L is the number of linear units which are determined by the integration of the peaks for the methylene groups linked with hydroxyl units in diethanolamine via ^{13}C NMR.

According to ^{13}C NMR, the resonances at 65.47, 63.08, and 62.88 ppm corresponded to methylene carbon linked with

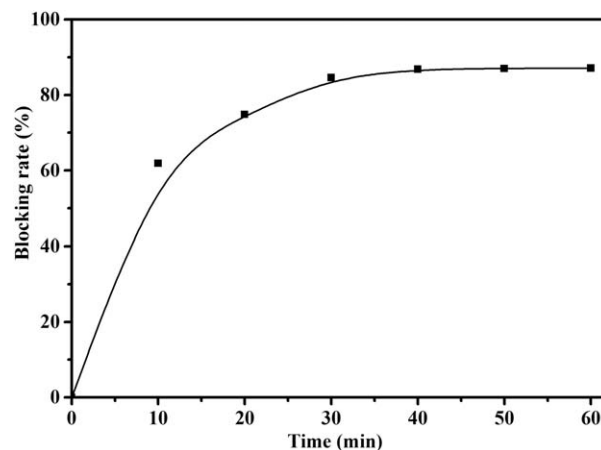


Figure 2. Relationship of blocking rate and reaction time.

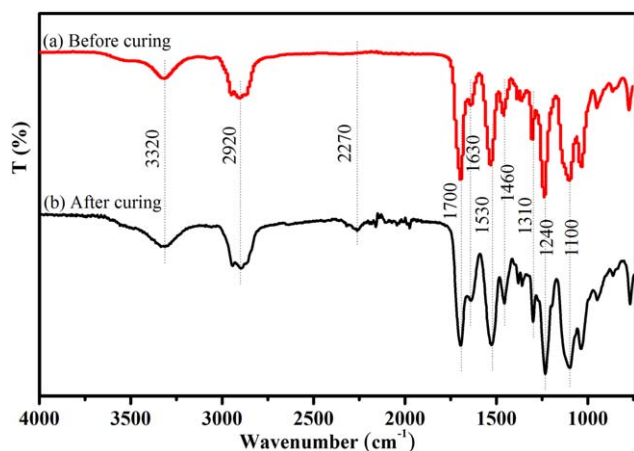


Figure 3. FTIR spectra of BBPU-3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydroxyl units for dendritic and linear structures, respectively.^{8,29} The integration for the methylene was 1.00 (*D*) and 2.15 (*L*), respectively. Consequently, DB of the synthetic BBPU-3 was 0.48.

The molecular weight of BBPU-3 was measured by GPC. As presented in Table I, the number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the BBPU-3 are 12,451 and 72,085 Da, respectively. And the polydispersity is 4.46, indicating a broad distribution of molecular weight.

Thermal Analysis. The thermal behavior of the BBPUs based on PEG with different molecular weights was obtained from DSC curves as displayed in Figure 5. BBPU-1–4 exhibited a single melting temperature (T_m) in the range of 106°C–122°C, which demonstrated complete mixing between the hard and soft segments.^{30–32}

Table I. Molecular Weight of BBPU-3

M_n (Da)	M_w (Da)	Polydispersity
12,451	72,085	4.46

Additionally, T_m of the BBPUs gradually decreased as molecular weight of PEG soft segment increased. This was because the relative amount of hard segment increased as the short PEG was used as soft segment. As a result, the crystallization of the polyurethane chain with short PEG became higher, leading to larger rigidity and higher T_m . However, BBPU-5 based on the longest soft segment PEG2000 showed T_g s for soft segment and hard segment at -60°C and 24°C , respectively, implying microphase separation between the hard and soft segments. It also presented a melting peak at 108°C . The result was in agreement with previous finding³² that the phase separation was enhanced by increasing soft segment length.

Film-Forming Property of BBPUs

Curing Rate. Film curing rate of WPU has close relations with application effect of polyurethane in fabrics. Here, the film curing rates of BBPU films varying with molecular weight of PEG were investigated at 85°C . As displayed in Figure 6, the film curing finished within 10 min as the molecular weight of PEG was below 600, while the curing time was longer than 30 min as the molecular weight of PEG was over 1000. As the molecular weight of PEG ascends, the hydrophilic ethylene oxide ($\text{CH}_2\text{—CH}_2\text{—O}$) chain segment increases, leading to stronger hydrophilicity of the obtained polyurethane. Consequently, it takes more time for the polyurethanes prepared with longer PEG to be cured. It is known that slow curing rate will result in higher curing temperature and longer curing time, which not

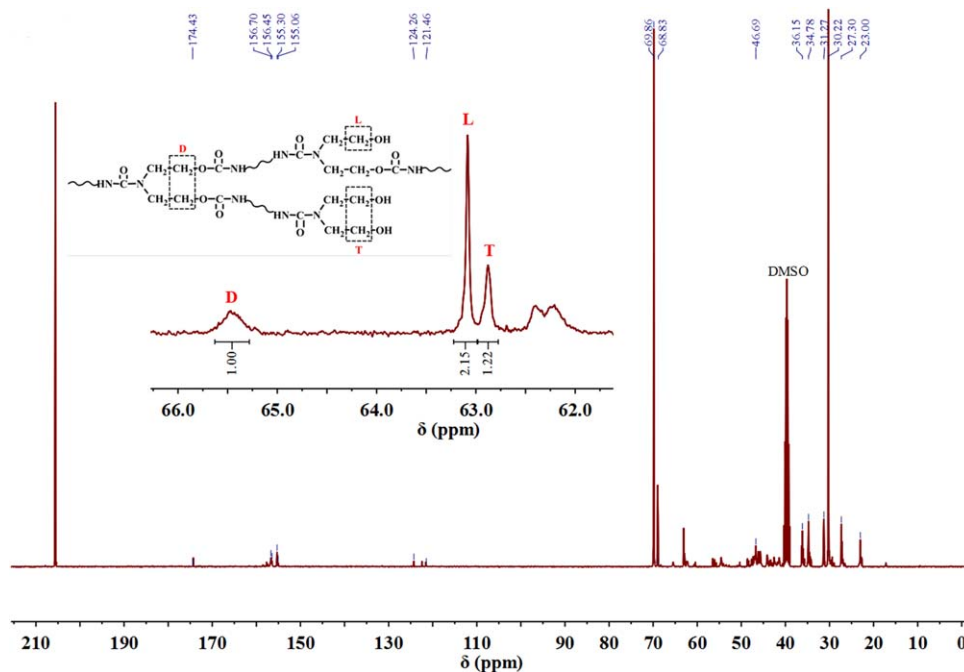


Figure 4. ^{13}C NMR of BBPU-3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

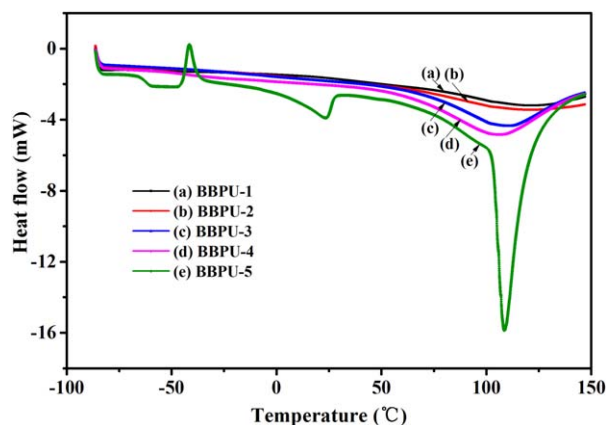


Figure 5. DSC curves of BBPUs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

only has a negative influence on the wearability of fabrics, but also decreases the production efficiency and wastes energy.

Pencil Hardness. The soft or hard segment ratio will vary with the molecular weight of soft segment, which significantly impacts on properties of textiles treated with polyurethane, such as hand-feeling, wrinkle resistance, etc. Hence, the film hardness of BBPU films based on varied molecular weight of PEG was evaluated and the results were summarized in Table II.

It is found that the pencil hardness of the films decreases from 4H to 5B as the molecular weight of the PEG soft segment increases from 200 to 2000. The polyurethane film based on low molecular weight PEG shows high hardness and yet fragility. This is because low molecular weight PEG usually shows poor flexibility. In addition, the increasing molecular weight of the soft segment leads to the relative increase of the soft segment ratio in the polyurethane chains, improving the flexibility but reducing the hardness of polyurethane films. This finding is in agreement with previous results that an increase in the soft segments content decreased the elastic modulus and the extent of cross-linking of the polyurethanes.³³

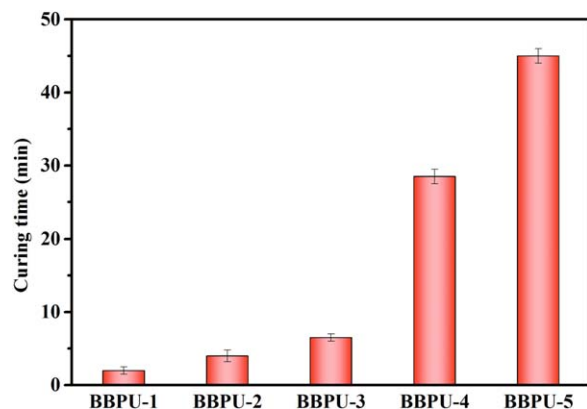


Figure 6. Curing rate of BBPU films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Pencil Hardness of BBPU Films

Film samples	Pencil hardness
BBPU-1	4H
BBPU-2	2H
BBPU-3	H
BBPU-4	B
BBPU-5	5B

Chemical Resistances. The chemical resistances for BBPUs based on different molecular weight PEG were assessed, as summarized in Table III. The moisture rate of the films distinctly increased from 18.1% to 49.2% as the molecular weight of PEG varied from 200 to 2000, suggesting that water resistance of the film became poor with increasing the molecular weight of PEG. This is because the increasing PEG chain resulted in growing polar groups which can combine with water molecules to form hydrogen bond. On account of the effect of hydrogen bond, it is apt for water to absorb and further enter into the polyurethane film, making the moisture rate rising. Additionally, the acid resistance of the polyurethane films is unchanged (3 grade) while the alkali resistance is improved by one grade with increasing the molecular weight of PEG. Excellent chemical resistance was obtained due to branched structure that enhanced the cross-linking density.

Color Fastness of Printed Cotton Fabrics

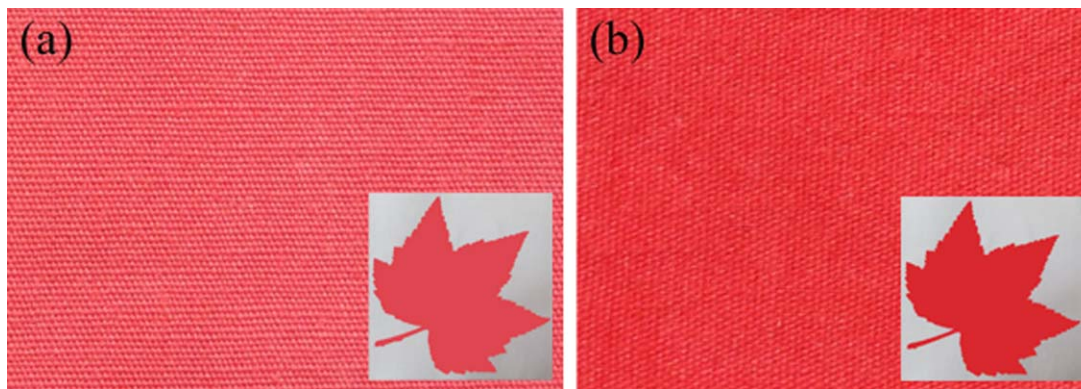
The synthetic BBPU-3 was chosen to treat the printed cotton. The colorfastness of cotton treated by BBPUs with different usages and cured at 85°C for 6 min was investigated. As listed Table IV, the untreated printed cotton fabrics show washing, dry and wet rubbing, and light rating 2–3, 2, 1, and 5 grade, respectively. However, the treated fabrics offer washing fastness in the range of 4–5, dry and wet rubbing rating in the range of 3–4 to 5 and 3 to 4–5, respectively. It is clearly revealed that the treatment with BBPUs has pronounced effect on the colorfastness properties of the treated fabric samples, especially washing and rubbing fastness. The —NCO groups regenerated after deblocking and then covalently bonded with —OH groups in cellulosic fibers. As a result, network structure films formed on the fabric surface, preventing pigments from falling off the fabrics. Nevertheless, as the BBPU amount increases above 15%, all the colorfastness of treated fabrics remains unchanged due to

Table III. Chemical Resistance of BBPU Films

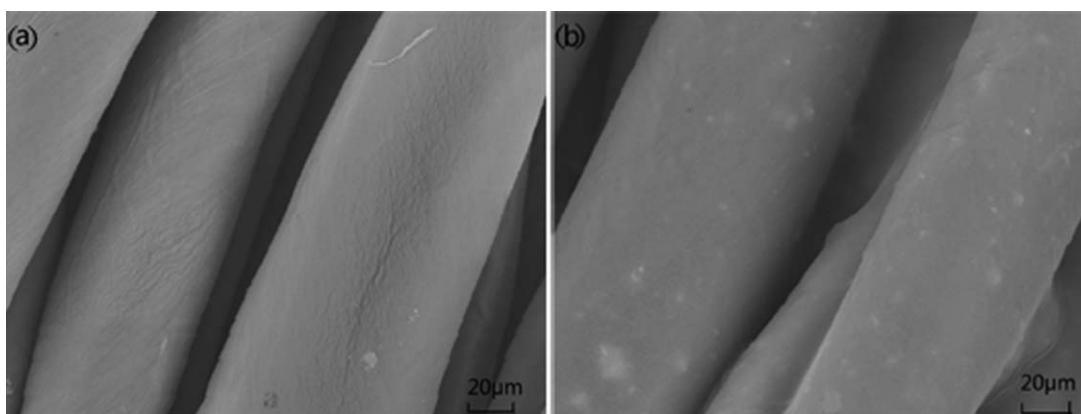
Film samples	BBPU-1	BBPU-2	BBPU-3	BBPU-4	BBPU-5
Moisture rate (%)	18.1	23.5	27.3	36.5	49.2
10% H ₂ SO ₄ (grade)	3	3	3	3	3
10% NaOH (grade)	2	2	3	3	3

Table IV. Color Fastness of Printed Cotton with Varied Amount of BBPU-3

BBPU-3 amount (%)	Washing fastness		Rubbing fastness		Light fastness (grade)
	Discoloring (grade)	Staining (grade)	Dry (grade)	Wet (grade)	
0	2-3	2-3	2	1	5
5	4	4	3-4	3	5-6
10	4-5	5	4-5	4	5-6
15	4-5	5	5	4-5	6
20	4-5	5	5	4-5	6

**Figure 7.** Printed cotton fabrics with BBPU-3 (a) 0% and (b) 10% after washing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Table V.** Color Fastness of Printed Cotton Treated with BBPU-3 at Different Curing Conditions

Conditions	Washing fastness		Rubbing fastness		Light fastness (grade)
	Discoloring (grade)	Staining (grade)	Dry (grade)	Wet (grade)	
70°C/3 min	4	4-5	4-5	2-3	5
85°C/3 min	4	4-5	4-5	3	5
100°C/3 min	4	4-5	4-5	3	5
70°C/6 min	4-5	5	4-5	3-4	5-6
85°C/6 min	4-5	5	4-5	4	5-6
100°C/6 min	4-5	5	4-5	4	5-6

**Figure 8.** SEM of cotton fabrics (a) control sample, and (b) printed sample with BBPU-3.

the complete reaction of —OH groups in cellulosic fibers. Figure 7 presents the printed cotton fabrics with 0% and 10% BBPU after washing.

Furthermore, the influences of curing temperature and time on the color fastness of printed cotton treated by BBPU-3 (10 wt %) were also discussed, and relevant results were shown in Table V. It is found that the wet rubbing fastness of the printed cotton fabrics can be improved by 1/2 grade as the curing temperature was increased from 70°C to 100°C for the same curing time. Besides, the resistances to washing, rubbing and light were able to be enhanced by 1/2 or 1 grade via prolonging the curing time to 6 min at the same curing temperature. It was because more —NCO groups regenerated and more complete polyurethane films on the fiber surface formed under the condition of higher curing temperature and longer time, leading to stronger combination of the polyurethane films, pigments, and fibers. Taking energy-saving into consideration, the BBPU treated cotton fabrics were suit to be cured at 85°C for 6 min to obtain good color fastness.

SEM of Printed Cotton Fabrics

The surface morphology of cotton fabrics before and after printing was displayed in Figure 8. The untreated cotton fibers exhibit distinctly natural grooves and characteristic parallel ridges. After treated with BBPU-3, the natural features on cellulose fiber surface were invisible. Instead, BBPU formed dense and smooth film, which effectively prevented pigments dropping from the fiber surface.

CONCLUSIONS

BBPUs were prepared using diisocyanate prepolymer and diethanol amine to obtain highly branched structure, followed by end-capping with hydrosulphite. Taking both reaction efficiency and energy saving into consideration, the appropriate conditions for prepolymerization, chain extending, and blocking reaction were at 70°C for 90 min, 80°C for another 90 min, and 0°C–5°C for 40 min, respectively. FTIR spectra confirmed that the tailored blocked polyurethane structure and the number-average molecular weight of the BBPU based on PEG600 was about 12,451. T_m of the BBPUs decreased with increasing molecular weight of PEG soft segment. The curing rate, pencil hardness, and water resistance of the BBPU films were dramatically reduced with increasing the molecular weight of PEG soft segments. The resistances to acid and alkali of the BBPU films were 3 grade. The color fastnesses of printed cotton fabrics, including washing, rubbing and light fastness were able to be significantly enhanced after the treatment with 10% BBPU based on PEG600. The printed cotton fabrics showed good color fastness after curing at 85°C for 6 min. In summary, the WPU with blocked and branched structures is a promising candidate for application in textile pigment printing.

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