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## Enhancing ink adhesion of specialty paper using an interpenetrating polyvinyl alcohol-blocked polyurethane polymer network sizing system†

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The printing quality and strength of specialty papers such as money, maps, newspapers and bank notes have been a significance challenge in recent years. The adhesive effect between ink and paper is depend on both the secondary binding force between the molecules and the mechanical anchoring effect of the ink on the paper. Also, the porous and fibrous structures of base paper restrain its application in printed products because of the strong capillary effect leading to the diffusion of ink particles. To address the problems involved in ink diffusion and mechanical reinforcement, surface sizing is an attractive choice from the perspective of paper handling. Herein, the surface sizing system of specialty paper with an interpenetrating polyvinyl alcohol-blocked polyurethane polymer network was applied to fabricate paper of high ink adhesive properties. In the case of the same external factors (gluing temperature, drying time, etc.), the surface sizing effect of paper samples (sizing with TBPU, polyvinyl alcohol and TBPU/PVA system) were evaluated by infrared spectroscopy, X-ray photoelectron spectroscopy, water contact angle measurements and scanning electron microscopy. Some of the pure cotton pulp paper with surface sizing treatment was treated *via* adhering inks to paper by spraying, smearing and soaking. The bonding strength was tested by peel-off tape tests, soaking tests, and simulated washing tests. The results showed that the water contact angle of the sized-paper increased from 67.6° to 89.7°. The mechanical properties had been greatly improved after treatment and SEM, AFM and XPS analyses indicated an increase in surface roughness and the oxygen-containing polar groups (C=O, C-OH, -NH-COO- and COOH) enhanced the fixation of ink particles on the fiber surface. These tests indicated that the novel composite system of TBPU/PVA could endow specialty paper with superb mechanical properties and more than 90% ink retention rate. All these advantages of this composite system may contribute to its wide application in the fields of papermaking and printing.

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### 1. Introduction

Printing paper is by far the cheapest and most exploited substrate due to its environmental friendliness, recyclability and feasibility of mass production. The ink adhesion of the paper refers to the firmness of the ink and the surface of the paper, and its strength would directly affect the printing performance of the paper.<sup>1–3</sup> Generally, the adhesion effect between ink and paper could be produced by the combined action of mechanical anchoring and intermolecular secondary binding force.<sup>4–8</sup> The long-chain cyclic structure of paper cellulose with many hydroxyl groups showed asymmetric molecules similar to the main components of the ink.<sup>9–12</sup> Due to the repulsion of the same type and the attraction of the opposite

type between the intrinsic dipoles, the molecules were oriented in the state where the opposite poles were adjacent to each other in space, which successively led to the generation of orientation force, induced force and dispersion force making the ink adhere to the paper.<sup>13–17</sup> Additionally, surface morphology, porosity, surface energy and the type of chemical groups on the paper surface all affected the physical properties of the paper, thus contributing to the final printing quality.<sup>18,19</sup> Therefore, the surface sizing treatment of paper was of great significance for improving ink adhesion and printing performance.

Many efforts had been done on the improvement of ink adhesion. Liu and co-workers used three kinds of silane coupling agents  $\gamma$ -methacryloxypropyl trimethoxy silane (KH570), triethoxy vinyl silane (KH151) and 3-glycidyloxypropyl trimethoxy silane (KH560) to treat the surface of birch wood to enhance the surface adhesion strength of UV coatings.<sup>20</sup> Sónia Sousa and co-workers used surfactants and a cationic polymer [poly-(diallyldimethylammonium)chloride (PD)] for paper surface treatment {3-(*N,N*-dimethylmyristylammonio)propanesulfonate as zwitterionic surfactant hexadecyltrimethylammonium bromide as

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cationic surfactant].<sup>21</sup> Katarina Dimic-Misic and co-workers modified enzyme pretreated fibre-derived MNFC film surfaces using nitrogen plasma to enhance their amphiphilic surface affinity to polar and non-polar IP PV inks.<sup>22</sup> Nevertheless, there are few literature concerning the influence of surface sizing treatment on ink adhesion properties of paper fibers. For paper products, the common technologies are tiny droplets printing, pressureless printing, electrostatic printing and ink-jet printing.<sup>23–25</sup> In our study, we adopted the tiny droplets printing to observe the absorption of inks, ink-jet printing to obtain large-scale ink-coating on paper samples. Additionally, the peel-off scotch tape testing, soaking testing, and simulated washing testing were utilized to evaluate and ink retention of the treated paper surface.

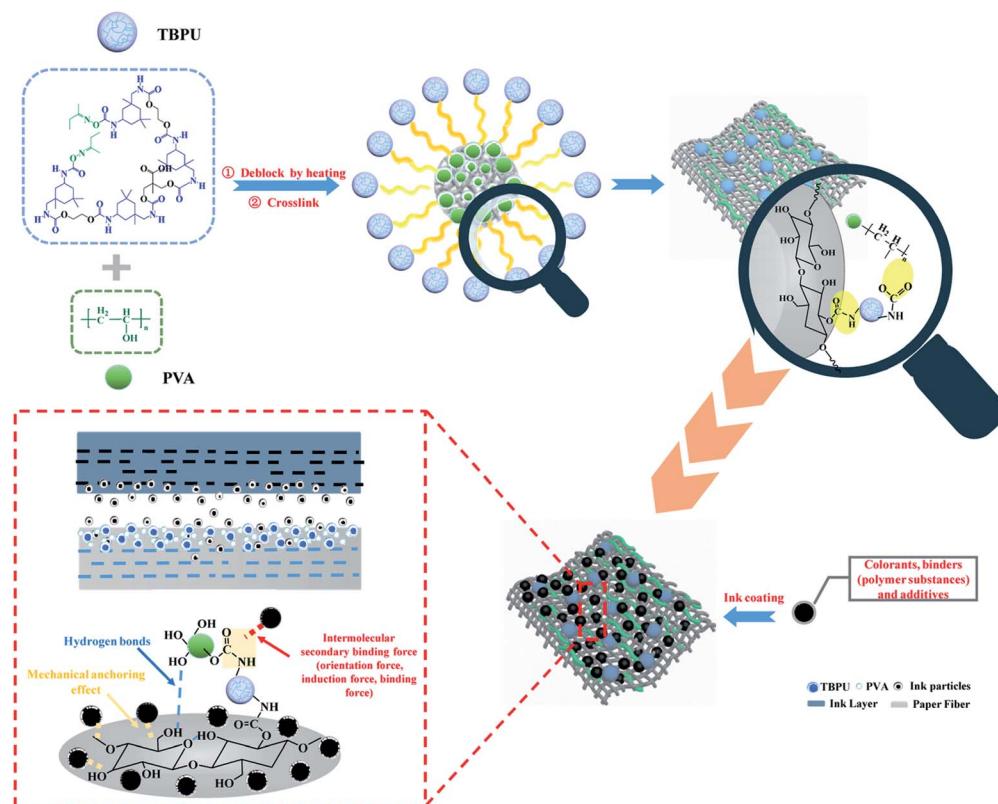
Herein, we put forward water-based end-blocked polyurethane (TBPU) functioning as a latent crosslinker in the fiber and as an adhesive at the interfaces between ink and paper fiber. The principal mechanism for the ink adhesion of sized-paper was represented in Scheme 1. Generation of the lavish polar groups (urethane) after deblocking and cross-linking progress of TBPU resulted in strong adhesion to ink particles.<sup>26</sup> Synchronously, the formation of three-dimensional network between the fibers and polymers enhanced the mechanical properties of paper.<sup>27–29</sup> Moreover, TBPU/PVA emulsion, as a new composite system, could form a good covering effect on paper fibers and form moderate crosslinks between the fibers in order to guarantee that the ink particles could enter the surface layer and form a firm bond with the

matrix.<sup>30,31</sup> This new surface sizing system also had a strong toughening effect and would not cause the paper to become too brittle and hard. That was, high machine washing resistance and mechanical performance would be obtained. This study offered a facile and effective route to the gain the knowledge of surface sizing in the aspect of ink adhesion.

## 2. Experimental

### 2.1 Materials

Poly( $\epsilon$ -caprolactone) diol (PCL,  $M_n = 1000 \text{ g mol}^{-1}$ ) were dried at 120 °C for 2–3 h. 3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI, analytical grade), 2,2-dimethylol propionic acid (DMPA, 98%) were purchased from Macklin Biochemical Co. Ltd, (China). 2-Butanone oxime (MEKO, 99%) was purchased from Aladdin Biochemical Technology Co, Ltd, (China). Dibutyltin dilaurate (DBTDL, analytical grade) was supplied by Cameo Chemical Reagent Co. Ltd. (China). *N*-Methyl pyrrolidone (NMP, analytical grade) was refluxed in the presence of CaH and distilled under vacuum to remove moisture residue. PVA1799 was purchased from Guangzhou Zhong Gao Chemical Co., Ltd. Pure cotton pulp paper (basis weight of 80 g cm<sup>-2</sup>) was used for experiments and was applied by the form of dry sheets. The printing inks in our study are oil-bearing based, that means its dispersants are mostly organic solvents and have the characteristics of good fluidity, low surface tension, and strong adhesion.



Scheme 1 Schematic illustration of the surface sizing process and ink printing process used in treatments of paper fiber with PVA using TBPU latent-crosslinked sizing agent.



## 2.2 Synthesis of TBPU and composite of TBPU/PVAs

The synthesis method was demonstrated in Fig. S1† (ESI). 2,2-Dimethylol propionic acid (DMPA, 98%) was firstly dissolved in NMP solvent as a chain extender solution. Poly( $\epsilon$ -caprolactone) diol (PCL,  $M_n = 1000$  g mol $^{-1}$ ) removed moisture residue in a dried three-necked flask equipped with a mercury thermometer was cooled to 80 °C. IPDI, chain extender solution and DBTDL (0.001–0.003 wt%) were added into the flask stirring for 2 h to obtain a prepolymer. In the following step, after the system temperature reducing to 60 °C, MEKO was added for end-blocking reaction, until the –NCO ratio approaching to 0% by using toluene-di-*n*-butylamine method to measure the residual ratio of –NCO. Later, the excess *N,N*-dimethylmethanolamine was applied to neutralize the –COOH of DMPA, adjusting the pH to 7. After the neutralization, high-speed emulsification with deionized water, we obtained the end-blocked TBPU.

PVA1799 and deionized water are put into a three-necked flask and heated and diluted to 10 wt% at 90 °C for 3–5 h. TBPU was blended with PVA. And a small amount of viscosity reducer and penetrant were added into the system as well. (The blending temperature is 70 °C, and the time is 20–30 min) (Table S1,† ESI).

## 2.3 Surface treatment and ink printing process of paper samples

**2.3.1 Surface treatment.** Different TBPU/PVA composite dispersions were applied evenly onto the surface of paper at a speed of 3.0–4.0 mm s $^{-1}$  of ST-1-260 coater. A mixture of ethanol/water, a single-component TBPU aqueous dispersion and a single-component PVA aqueous dispersion were respectively coated on the surface of the paper to prepare a set of blank controls and two sets of parallel controls. After pressing roller and drying (110 °C, 15–20 min), let it stand for 24 h.

**2.3.2 Ink printing process.** All paper samples were dried at 90 °C for 3 min for pretreatment, with a humidity of 25%. After spraying with MS 205 oil-based ink, the paper sample was dried under the conditions of 130–140 °C for 3–4 h. It was found that the ink changed from a liquid to a solid coating adhering to the surface of paper samples.

## 2.4 Measurements

The chemical characteristics of paper samples before and after sizing agent treatment and ink printing process were analyzed by FTIR (VECTOR-22, Bruker) and XPS (AXIS SUPRA, UK) (FTIR parameters: scanning range = 4000–500 cm $^{-1}$ , resolution = 4 cm $^{-1}$ , number of scans = 10 s).

The JC2000A static drop contact angle measuring instrument was used to measure the water contact angle of the paper before and after surface sizing (droplets of 1–2  $\mu$ L). Moreover, surface free energy measurements (SFE) of the samples were calculated according to the eqn (1) and (2) which were described by Owens and Wendt.<sup>32</sup>

$$\gamma_{GS} = \gamma_{LS} + \gamma_L \cos \theta \quad (1)$$

$$\gamma_L(1 + \cos \theta) = 2(\gamma_S^d \times \gamma_L^d)^{1/2} + 2(\gamma_S^L \times \gamma_L^L) \quad (2)$$

where  $\gamma_{GS}$  denotes the surface energy of solid surface (saturated vapor of the liquid reaches equilibrium),  $\gamma_{LS}$  indicates the interfacial tension between liquid and solid,  $\gamma_L$  refers to the surface tension of liquid,  $\gamma_L^d$ ,  $\gamma_L^d$ ,  $\gamma_L^L$  of water and ethylene glycol were shown in Table S2† (ESI).<sup>33–35</sup>

Water absorptiveness (Cobb) and Bendtsen air permeance were determined according to ISO 535:1991, ISO 5636-3:1992, respectively.

The fastness to adhere to the ink printed paper was evaluated by peel-off tape, machine wash, and soak tests. And the microstructure of the paper surface after sizing process as well as the cross sections of the substrates after ink printing were observed by a scanning electron microscope (SU8100, Japan). According to GB7975-87, ISO 105-X12:2001 and 105-C06-1994, color fastness evaluation of untreated and TBPU/PVA treated paper samples.

## 3 Results and discussion

### 3.1 Surface characterization of paper samples

The structural analysis of paper samples before and after various surface treatments was performed by FTIR and XPS for the purpose of estimating the effectiveness of surface sizing and ink printing.

**3.1.1 XPS analysis.** In order to investigate the effects of TBPU/PVA sizing treatment and ink printing process on the surface element composition of paper samples, relevant XPS spectrums were studied showing in Fig. 1. Taking Fig. 1a–c as a set of examples, the untreated paper sample only had carbon element (40.76%) and oxygen element (57.96%), a small amount of nitrogen (1.28%) as well, which was due to the presence of some chemicals in the papermaking process, such as starch and retention aids. The paper treated with TBPU/PVA showed a larger nitrogen content (10.06%), which was due to the addition of TBPU chains and the generation of urethane bonds. Remarkably, C<sub>O/C</sub> was reduced by 48% as a result of TBPU/PVA dispersion treatment, indicating that the original chemical bonds in the cellulose macromolecules were destroyed after sizing. It was symbolized a new chemical structure was born from the cross-linking reaction.

Fig. 1a and b presented the C 1s and O 1s spectra for untreated paper and TBPU/PVA sized paper. The deconvoluted peaks data corresponding to different functional groups were indicated in Tables S3 and S4† (ESI). Two weak peaks corresponding to C=O and N–C–O was noted in the C 1s and O 1s spectra of TBPU/PVA sized paper at around 288.8 eV and 532.6 eV, illustrating the appearance of new chemical bonds. And the binding energy shift of C–O–C from 534.8 eV to 533.7 eV indicated that the addition of TBPU/PVA compound sizing liquid changed the chemical state of carbon atoms and oxygen atoms on the surface of paper. Interestingly, the decrease of C–OH and the increase of C–N, C–O–C, C=O were attributed to the formation of urethane (or urea) bonds between polyurethane and the –OH groups on the paper surface. Also, due to the formation of interpenetrating three-dimensional cross-linked network structure, the presence of close-knit physical interactions was come out. This interaction provided a higher cohesive



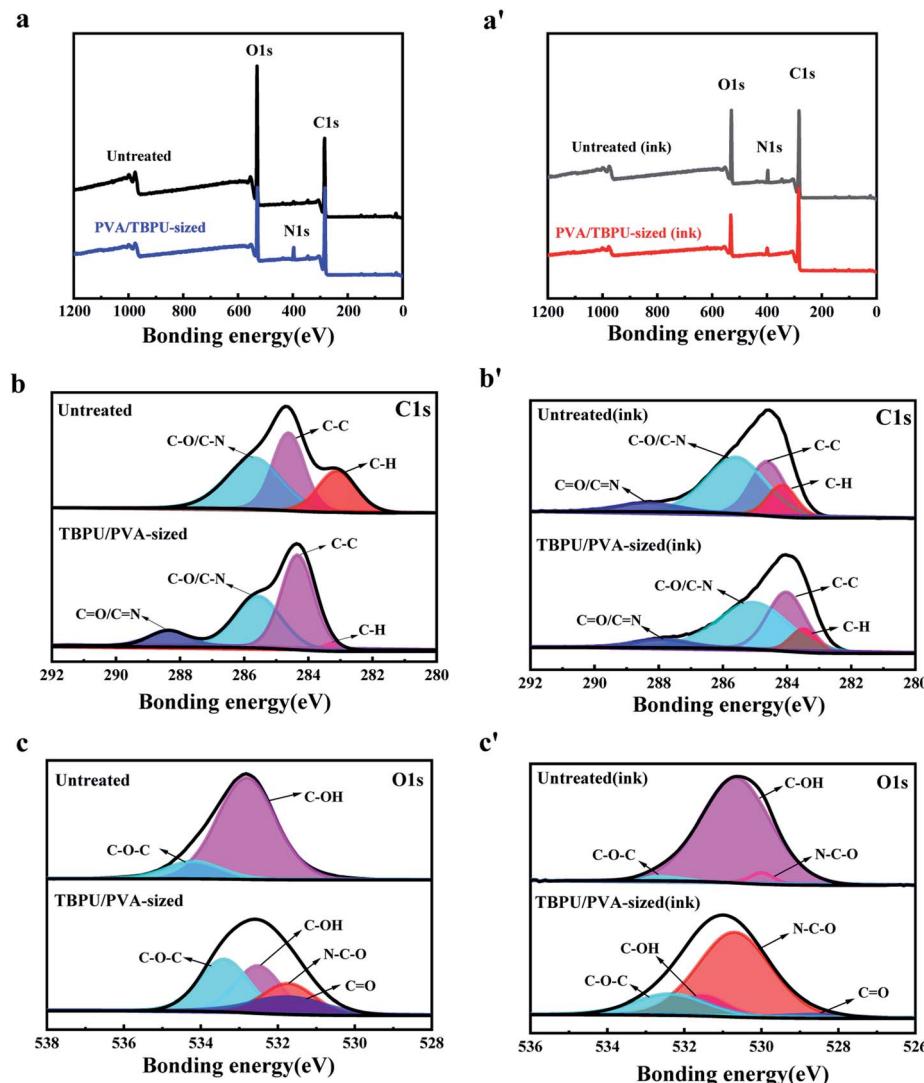


Fig. 1 XPS spectrum of paper samples before and after TBPU/PVA sizing treatment. (a and a') Broad spectrum, (b and b') C 1s, (c and c') O 1s.

force for the TBPU chains and PVA macromolecules to localize and incorporate on the surface and inside of paper fibers.

As for Fig. 1a'-c', the surface composition of the TBPU/PVA sample printed with ink showed a slight increased carbon content and decreased oxygen content. This phenomenon was different from the XPS results for previous obtained samples. In the ink printing process, the synthetic resins and natural resins as binders were similarly compatible with strong polar ester groups on the surface of the TBPU/PVA composite material, resulting in the changes of paper polar and the formation of cambium on the surface of the paper. Meanwhile, the ink particles penetrated into the paper through mechanical anchoring, enhancing the adhesive strength. Thus, the physical effects accounted for the vast majority, and it was unclear whether any other chemical reaction occurred between TBPU/PVA and the ink.

**3.1.2 FTIR study.** For the purpose of investigating the chemical functional groups in the original and treated samples, FTIR analysis was carried out (Fig. 2). The main functional

groups of interest were hydroxyl ( $-\text{OH}$ ), amino ( $-\text{NH}$ ) and carbamate ( $-\text{NH}-\text{CO}-$ ). In Fig. 2a, the characteristic peak of hydroxyl stretching around  $3400\text{ cm}^{-1}$  became flat and the amino peak around  $3545\text{ cm}^{-1}$  became strong after TBPU treatment, indicating that  $-\text{OH}$  groups on the surface of the paper fiber are grafted with TBPU. A new characteristic absorption peak of urethane bond appeared at  $1727\text{ cm}^{-1}$  and  $1732\text{ cm}^{-1}$  in the samples treated with TBPU and TBPU/PVA. And  $-\text{OH}$  groups on the surface of the paper fiber and the active functional isocyanate groups released after unblocking occurred to chemical crosslinking. Compared with the paper samples treated with TBPU and PVA, relatively strong  $-\text{NH}-\text{CO}-$  absorption peaks were observed in TBPU/PVA treated samples since samples treated with TBPU/PVA had more cross-linking sites than the former two. And the enhancement of  $-\text{NH}-\text{CO}-$  peaks at  $950\text{--}1100\text{ cm}^{-1}$  and the wide and flat trends of  $-\text{OH}$  around  $3400\text{ cm}^{-1}$  in the samples treated with all three sizing agents compared with the untreated sample.



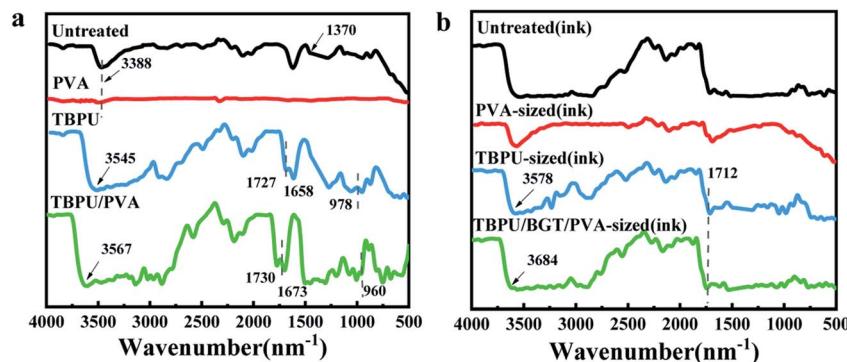


Fig. 2 FTIR spectrum of (a) the chemical characteristics of paper surface before and after sizing treatments. (b) Interactions between ink and paper samples: (I) MS 205-ink + untreated, (II) MS 205-ink + PVA-sized, (III) MS 205-ink + TPU-sized and (IV) MS 205-ink + TPU/PVA-sized.

To help understanding the paper surface-ink interactions, the inks and corresponding printed sizing samples were also characterized by FTIR spectroscopy. Similar characteristics were also observed in Fig. 2b. Taller peaks corresponding to  $\text{--NH--CO--}$  stretching vibration had been observed ( $1712\text{ cm}^{-1}$  for  $\text{C=O}$  and  $3684\text{ cm}^{-1}$  for  $\text{N--H}$ ) compared to the sample sized with TPU. Among them, part of peak effect might be the overlap with the  $\text{C=O}$  signal from the ink when the ink was printed to the treated samples. Through van der Waals force, ink particles were absorbed and penetrated into the three-dimensional interpenetrating polymer network formed by TPU, PVA and paper fibers after surface sizing, thereby firmly adhering to the paper.

### 3.2 Water wettability and apparent properties of paper

The ability of a paper substrate to adhere inks was closely related to wettability, surface energy, and crosslinking degree of sizing system.<sup>36</sup>

**3.2.1 Contact angle analysis.** Contact angles in low range ( $0 < \theta < 90^\circ$ ) indicated high surface wettability with a relative hydrophilic surface, which was also in favor of better infiltration of sizing agent and adhesion with inks.<sup>37,38</sup> The contact angle of untreated paper was  $85.5^\circ$ , showing slightly hydrophobic (Fig. 3a). All the three sizing treatments showed increases of 8.8%, 7.2% and 14.7% to the untreated sample.

Due to the high degree of alcoholysis, film-forming properties and strong intermolecular hydrogen bonding of PVA<sup>1799</sup>, paper samples are rendered more hydrophobic. Moreover, the increase hydrophobicity of other two samples indicated that the hydrophilic hydroxyl groups of the paper fibers were partially replaced by the hydrophobic strong polar carbamates.

**3.2.2 Surface energy.** Correspondingly, Fig. 3b demonstrated the Owens method results of polarity force, dispersion force, and surface energy. The introduction of the TPU/PVA composite sizing system increased the surface energy of samples from  $35.75\text{ mJ m}^{-2}$  to  $58.60\text{ mJ m}^{-2}$ , which was in basically agreement with the contact angles. In other words, the higher hydrophobicity and surface energy of sizing paper provided by TPU/PVA composite system were attributed to the functionalization of the surface with hydrophilic hydroxyl groups ( $-\text{OH}$ ) and hydrophobic carbamate groups ( $-\text{NH--COO--}$ ). (Specific calculation results were shown in Table S5,† ESI).

**3.2.3 Cobb value and apparent properties.** The changes in Cobb<sub>60</sub> value (Fig. 4a), apparent density and air permeability (Fig. 4b) can be responsible for changes in the wettability of sized paper surfaces. The lowest water absorption ( $28.3\text{ g m}^{-2}$ ) had been found for TPU/PVA-sized paper. And the curves of apparent density and air permeability revealed that the introduction of TPU increased the crosslinking density of sizing system to some extent, decreasing the porosity of paper. The

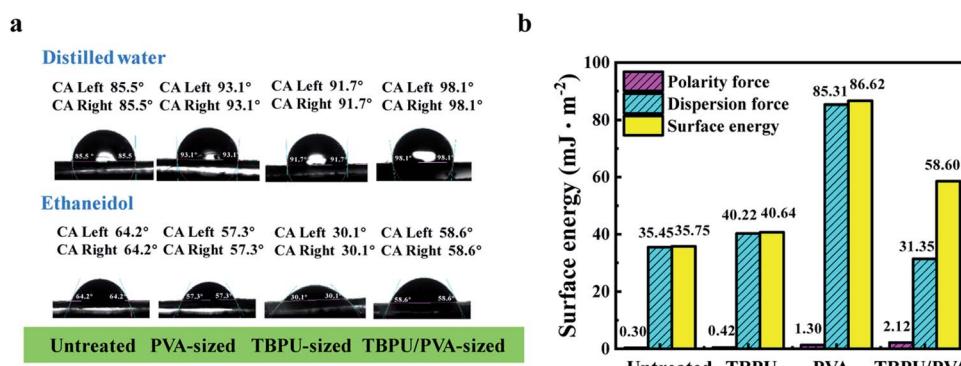


Fig. 3 (a) Water contact angles of paper surfaces before and after surface treatments at  $100\text{ g m}^{-2}$ . (b) Surface energy of the paper samples.



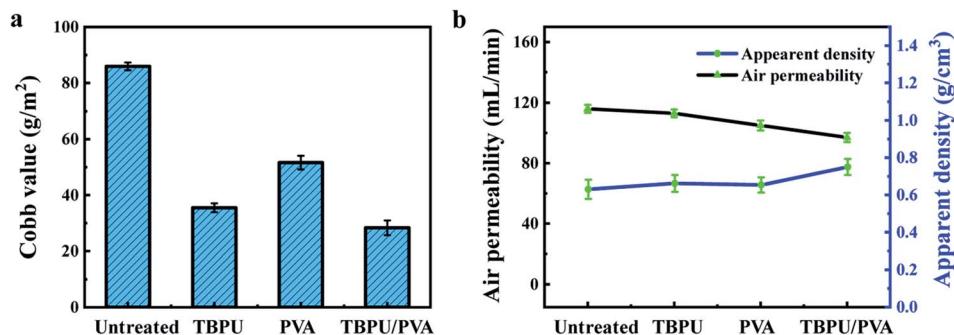


Fig. 4 (a) Water absorptiveness (Cobb<sub>60</sub> values) for paper samples with different sizing agents. (b) Apparent density and air permeability of paper samples.

interpenetrating network structure of lavish urethane groups generated from crosslinking reaction was conducive to the formation of chain entanglement, hydrogen bonding and Coulomb force between rigid segments, which enhancing the intermolecular interaction and further decreasing the water wettability and the air permeability. Consequently, paper sized with TBPU/PVA showed less wettability but higher hydrophobic property than other surface treatments.

Unlike the wettability analysis above, it was found that TBPU/PVA sizing papers possessed a fairly smooth surface, as obtained *via* roughness parameters by PPS tester (Table 1). From a macro perspective, untreated paper displayed a rough surface with obvious depression caused by the existence of several pores. Nevertheless, treated paper showed a homogeneous surface topography without pores. This noteworthy phenomenon demonstrated the transition from a rough surface with large pores to a dense surface with pores filled.

### 3.3 Morphology analysis

Taking into account the looseness of the fiber and sizing effects directly affecting the subsequent penetration behavior of ink particles, the morphology of paper samples was illustrated by SEM and AFM images (Fig. 5).<sup>39,40</sup> The SEM images of treated paper (a<sub>1</sub>-d<sub>1</sub>) revealed much smoother surface; its degree of gap-filling effect between paper fibers and the accumulation became denser than the original paper. From the cross-section SEM morphology (a<sub>2</sub>-d<sub>2</sub>), the burred characteristic was observed on the surface of fibers after the process of brittle fracture of sizing paper by liquid nitrogen. And the TBPU/PVA compound system showed optimal surface aggregation and filling-crosslinking effects on paper samples. These results indicated that TBPU/PVA compound system was capable of

penetrating into paper fibers and bridging the fibers together to form interpenetrating cross-linked network structure, which prompted much greater bond strength between fibers than the specific strength of the fibers.

After confirming the inner filling and crosslinking behaviors, the microscopic roughness of the TBPU/PVA interpenetrating cross-linked networked structure surface had also studied by AFM (a<sub>3</sub>-d<sub>3</sub> and a<sub>4</sub>-d<sub>4</sub>). We found that paper samples showed varying degrees of undulation from the side. To compare these microscopic surfaces, in a quantitative way, the root-mean-square roughness ( $R_q$ ) was used to evaluate the subtle deviation of the imaged surface from a flat plane. The  $R_q$  of the sizing surface increased from 7.2 to 52.9 nm (on the basis of untreated paper) after interpenetration of TBPU/PVA cross-linked with paper fibers. A preliminary conclusion can be drawn that the introduction of TBPU polymer increased the microscopic surface roughness and the number of hydrophobic porous structure to some extent; its rough surface could supply much more surface ability for the paper fibers to grab abundant water molecules or ink particles and also accelerated the penetration of ink faster into the fiber in collaboration with the capillary effect of fibers, which will be studied in the follow-up work.

### 3.4 Ink adhesion of the sizing surface *via* rubbing and washing

Generally, the ink absorption behavior of the paper itself mainly depended on three factors: surface energy, roughness and size of the polar chemical bond force with ink.<sup>38</sup> In other words, paper with high surface energy, strong polarity, and high roughness might have outstanding ability of ink absorption.<sup>41</sup> The ink absorption behavior of different sizing paper samples from a visual evaluation had studied to verify this conjecture about the ink absorption characteristics of the sizing surface (Fig. S2,† ESI). As a result, the utilization of this composite could capture ink particles and facilitate ink penetration. It could be explained that the interaction of paper surface physical properties and paper surface chemistry (such as coulombic forces, hydrogen bonding and van der Waals forces, *etc.*) that determined the ink particles fixations, spreading or absorption.

Considering the above behavior and the factors affecting ink adhesion ability, the strength of the physical action between the polar bond of the sizing matrix and the ink was regarded as

Table 1 PPS roughness parameters for paper samples depending on the type of sizing agents<sup>a</sup>

Samples	I	II	III	IV
Roughness (mL min <sup>-1</sup> )	607	587	562	519

<sup>a</sup> I: untreated paper. II: TBPU-sized paper. III: PVA-sized paper. IV: TBPU/PVA-sized paper. Under the same solid concentration: TBPU (30%),  $n[(\text{NCO})/(\text{OH})] = 1.6$ ,  $w(\text{DMPA}) = 9.5\%$ ; PVA1799 (10%).



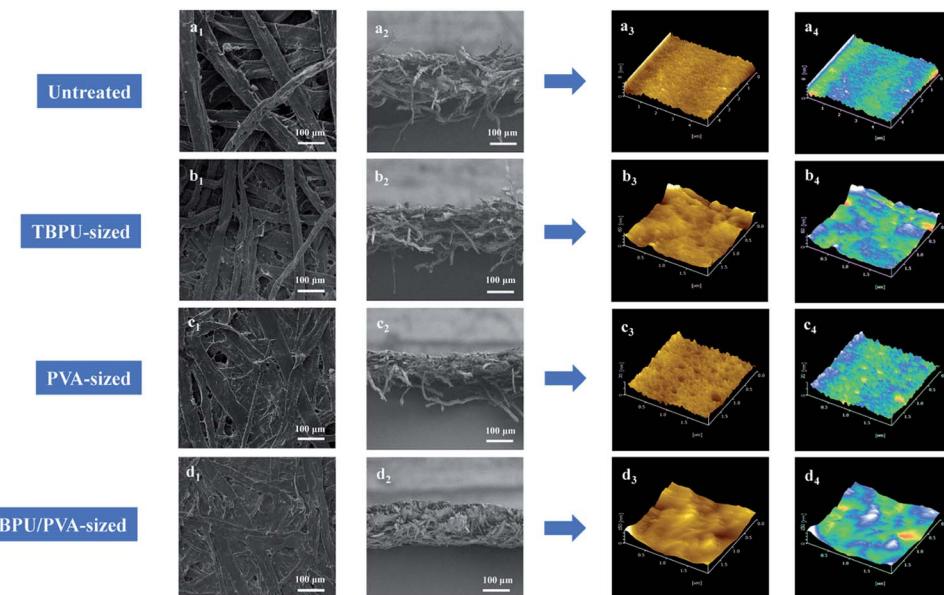


Fig. 5 Surface morphologies and cross-sectional fiber porosity images: (a<sub>1</sub>–d<sub>1</sub> and a<sub>2</sub>–d<sub>2</sub>) SEM images (Scale bars: 100  $\mu$ m), (a<sub>3</sub>–d<sub>3</sub> and a<sub>4</sub>–d<sub>4</sub>) AFM 3D topography images of paper samples.

main object of our study.<sup>42,43</sup> Through the chemical reaction between TBPU/PVA composite sizing system and the paper fiber, the ability to adhere the ink on the sizing paper surface was more challenging than simple sizing treatment, which required more cross-linking sites and a large number of polar bonds. Due to the blocked isocyanate end of TBPU was covalently attached to hydroxyl of PVA and cellulose, the obtained high polar carbamate chains could be tightly bound to the ink coating thereby forming a high-energy surface (higher than the surface tension of the ink) and firmly grabbing ink particles. To investigate the adhesion between the surfaces of the paper sized with TBPU/PVA composite sizing solution and ink layer, the ink adhesive tests was carried out on several sized papers. Moreover, the base-paper and paper sized with PVA were used to be parallels. All tests were intended to observe the adhesion effect between the ink and the paper surface which subjected to the conditions of different sizing agents.

**3.4.1 Preparation of ink printed samples.** The ink printing procedure was carried out to evaluate the effect of the surface sizing modification on adhesion performance. Color blocks and lines were printed with black and blue ink on the papers and these images captured by digital camera. Fig. 6a–d demonstrated three simple ink printing processes of paper samples, including ink spraying, directly writing and 100 grid method. All the obtained samples were performed to do a series adhesion tests.<sup>44–46</sup>

**3.4.1.1 Samples I of directly writing.** “SUST” logos of two colors are directly written on the surface of the base paper and the surface-sized paper.

**3.4.1.2 Samples II of ink spraying.** The sized paper was pre-treated by water and the ink is applied to the surface of the paper by spraying, and it is placed for 7 days after drying.

**3.4.1.3 Samples III of 100 grid method.** Firstly, a 1 cm  $\times$  1 cm grid was drawn on the based paper. After surface sizing respectively with two single component sizing agent (TBPU, PVA) and one compounded agent (TBPU/PVA) with dosage of 100 g, printing process was carried out immediately to make full use of the surface treatment with better bonding. The paper coated with the ink was put in an oven at 150 °C for 20 min.

### 3.4.2 Ink adhesion properties of sizing paper

**3.4.2.1 3 M scotch tape testing.** The paper was taken out and allowed to stand overnight for the latter tap adhesive test. During the tape test, 3 M Scotch tape was attached to the surface and peeled off in different directions randomly. The specific operations were as follows: clean the surface of the inked paper sample, stick 3 M Scotch tape on the surface, and peel it off randomly from different directions. The tape peeling test was considered to have passed if the ink surface did not peel off after 30 visual inspections. Peeling times less than 10 times was regarded as failing the experiment. Its experimental results were presented in Table 2. It can be seen from Table 2 that the untreated paper and the PVA-treated paper failed the tape peeling test, while the paper chemically cross-linked with the sizing solution and the paper fibers passed the test.

**3.4.2.2 Alcohol scrubbing testing.** The steps of the alcohol wiping experiment were as follows: squeeze a cotton pad soaked in a 75% ethanol aqueous solution until there are no water droplets. Scrub back and forth on the surface of the paper sample with horizontal force. One reciprocating scrub was regarded as 1 s. Wipe repeatedly until the degree of ink peeling is greater than 50%, then record the number of wipes. The results were exhibited in Fig. 7a and b. It can be seen from Fig. 7a that the performance of ink peeling condition from sizing agents of one-component (PVA, TBPU) to multi-component (TBPU/PVA) are gradually better. It also can be

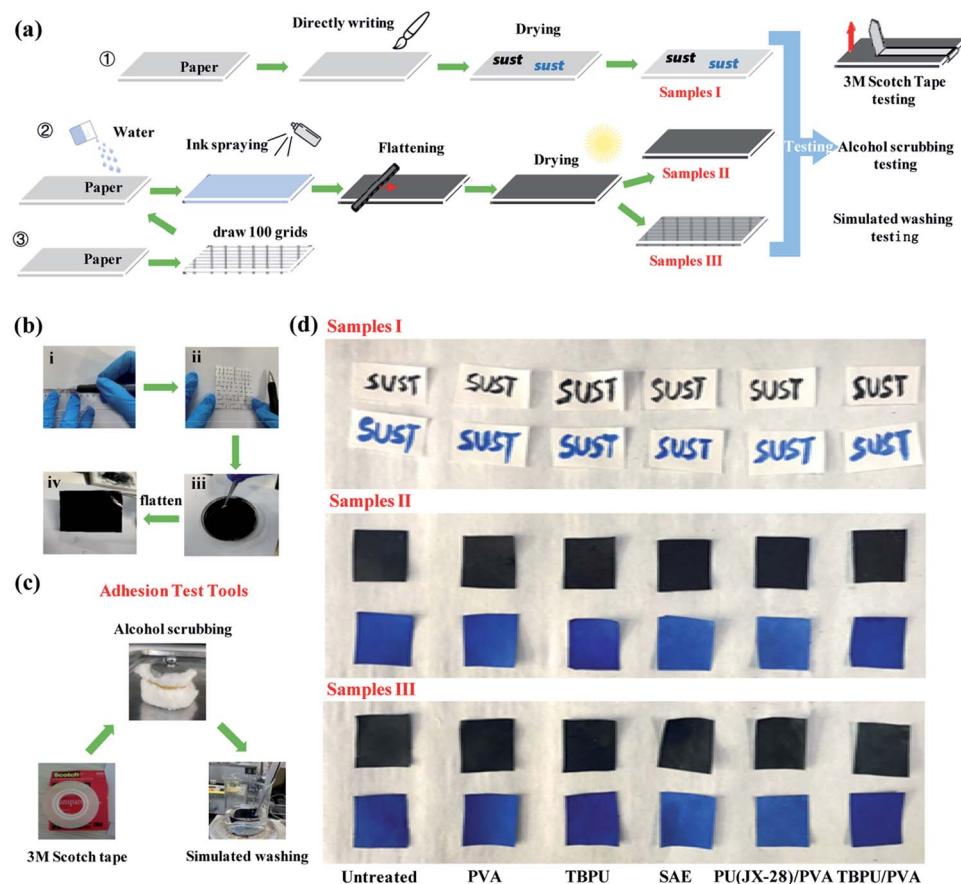


Fig. 6 (a) Schematic illustration of sized-paper inkjet printing; (b) photos of the process of ink printed samples (100 grid method); (c) adhesion testing tools; (d) all the printed paper samples.

found from Fig. 7b that the number of alcohol scrubbing of Samples II are 0, 11, 18, 26, 36 and 50, respectively. These results indicated that the increase of chemical cross-linking density of paper is propitious to improve their ink peeling resistance.

**3.4.2.3 Simulated washing testing.** The adhesion of the paper surface to the ink was evaluated under simulated wash test conditions. The simulated washing experiments involved stirring the inked paper samples in an aqueous solution containing 0.1 wt% Libai (liquid) brand dishwashing liquid at 300 rpm for 15 min at room temperature. The paper samples were then rinsed with distilled water. The washed paper samples were placed on a laboratory bench and allowed to air dry naturally in the air for 24 h. The resulting paper samples were then observed for ink retention. These results were demonstrated in Fig. 8a and b. And the specific results of ink adhesion were shown in Table S6† (ESI).

From Fig. 8a and b, there was less residual ink on the surface of untreated paper (D level). Around 30% of the ink remained on the surface of the paper sizing by PVA (C level) and TBPU (B level). TBPU/PVA-treated paper had the best ink retention (A level), which was better than commercially available sizing agents (SAE and PU<sub>JX-28</sub>). It indicated that sizing with single PVA or single TBPU was not enough to obtain paper with strong ink adhesion. The excellent ink adhesion could be ascribed to the high cross-linking density of the composite sizing system and abounded in polar carbamate groups ( $-\text{NH}-\text{COO}-$ ) and reinforced the ink adhesion to fibers. Overall, the composite strategy of interpenetrating cross-linked TBPU/PVA network was particularly important, which had a promoting effect on the increase of adhesion.

**3.4.3 The color fastness and ink peel resistance grade of sizing paper.** Color fastness is regarded as an important parameter to measure the printed quality of paper. Besides,

Table 2 Results of tape peel testing for paper samples<sup>a</sup>

Sizing treatment	Untreated	PVA	TBPU	SAE	PU(SJ-28)/PVA	TBPU/PVA
Ink adhesion	✗	✗	✓	✓	✓	✓

<sup>a</sup> The samples used in the tape peeling test were Samples I.



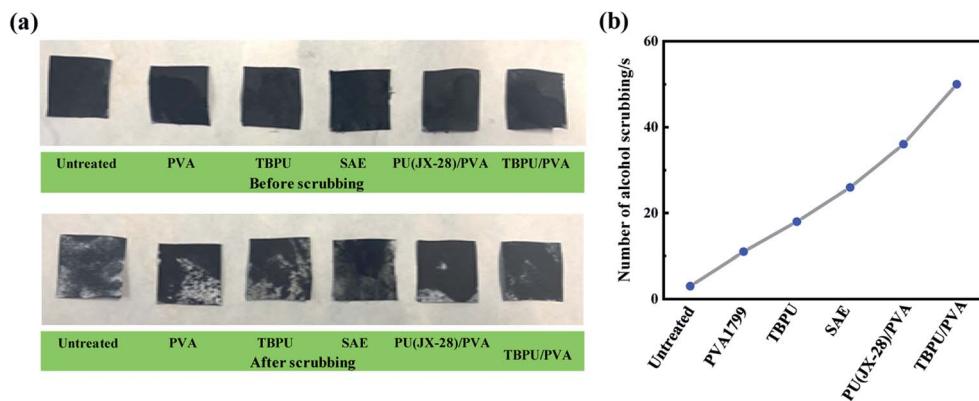


Fig. 7 (a) Photos showing the alcohol scrubbing testing results for untreated, PVA, TBPU/PVA treated papers; (b) number of alcohol scrubbing of different paper samples treated with different sizing agents.

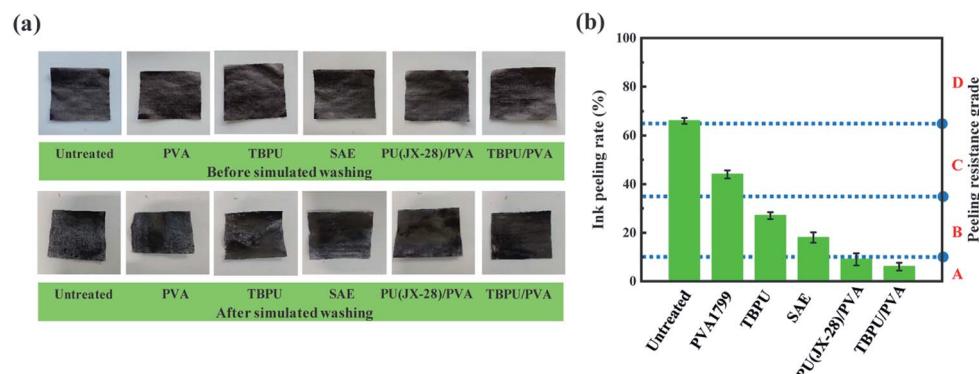


Fig. 8 (a) Photos showing the simulated washing testing results for untreated, PVA, TBPU/PVA treated papers; (b) the ink peeling rate of paper samples treated with different sizing agents.

after simulated machine washing test, ink peel resistance grade of paper surface are also an important indicator for ink retention (see ESI† for rating criteria). The relevant results for the untreated paper and the TBPU/PVA sizing paper are listed in Table 3. As shown in Table 3, the significantly increased color fastness class symbolized the enhancement of the chromaticity of TBPU/PVA surface-modified paper samples. This result can be supported by previous ink adhesion studies. Thus, compared to untreated paper (level 1), samples treated with composite TBPU/PVA sizing system (>level 4) enhanced the amount of ink colorants stayed on per area of the paper surface, which can retain more ink and show higher color strength.

### 3.5 Mechanical properties of the sizing paper

Due to the highly crosslinked structure of our composite sizing system, the resultant sizing samples had higher cross-linking density and was expected to exhibit better mechanical performance, which was also essential factor of ink adhesion for specialty paper.<sup>47-49</sup> The basic mechanical properties in terms of tensile index, tearing index and folding resistance were tested (Fig. 9). The dry tensile index of TBPU single sizing samples was increased by 27.0% (compared with untreated paper) and 17.1% (compared with control PU<sub>JX-28</sub>). Impressively, TBPU/PVA

composite sizing system could increase the dry tensile index by 55.0% (compared to untreated paper) and 5.9% higher than the control group (PU<sub>JX-28</sub>/PVA). Similar results were obtained for the wet tensile index and tearing index parameter. More strikingly, the folding resistance (Fig. 9b) of the TBPU/PVA composite sizing system could reach to 4453 s. The brilliant folding resistance could be attributed to the latent cross-linking property of the end-blocked polyurethane (TBPU), and its unblocked -NCO groups could tightly bound to paper fibers and PVA -OH chains *via* covalent bonding. These results implied that the TBPU/PVA composite sizing paper samples bonded tightly with paper surface and displayed superior mechanical performance.

Table 3 Ink peel resistance grade results of untreated and sizing paper treated with different agents

Sizing samples	Color fastness grade (wet)		Ink peel resistance grade	
	Black	Blue	Black	Blue
Untreated	2-3	2-3	1-2	1
TBPU/PVA	4	4	4-5	4-5

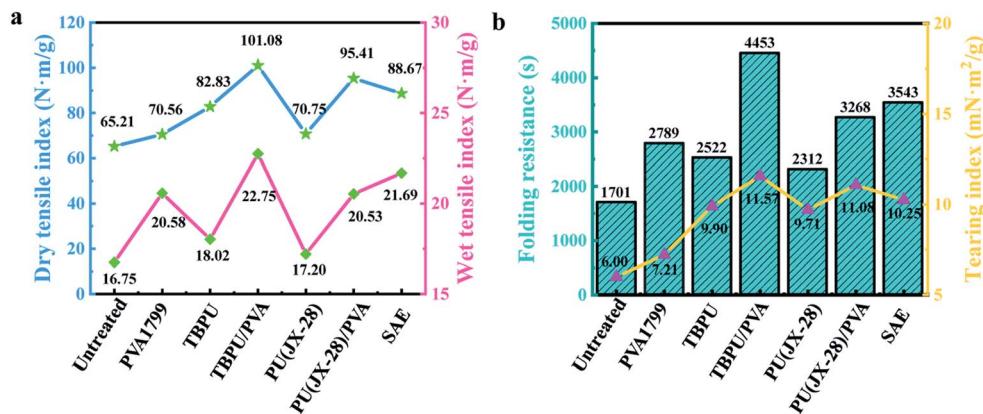


Fig. 9 Mechanical properties of the surface sizing paper, (a) dry tensile index and wet tensile index, (b) folding resistance and tearing index (PU<sub>JX-28</sub>, TBPU = 3.0 wt%, PVA = 4.0 wt%; sizing temperature = 70 °C; sizing liquid dosage is 5 g m<sup>-2</sup>).

## 4. Conclusion

In conclusion, we developed and evaluated a surface sizing system of interpenetrating polyvinyl alcohol-blocked polyurethane polymer network with strong ink adhesion. Functional NCO groups were deblocked through increasing the temperature. Deblocking of NCO groups of end-blocked polyurethane (TBPU) was almost proceeded synchronously to the crosslinking with hydroxyl groups of PVA and cellulose forming an interpenetrating polymer network that bridged the paper fiber. The sizing paper with a surface energy of 58.60 mJ m<sup>-2</sup> was obtained upon the addition of only 3.0 wt% TBPU and 4.0 wt% PVA1799. And its sized paper displayed favorable hydrophobicity and superb ink adhesion. Oil-based ink (MS205) was penetrated into smaller range on the TBPU/PVA sizing surface. And the TBPU/PVA composite sizing system produced abundant strongly polar carbamate groups (–NH–COO–) on the paper surface and results in better ink adhesive ability. Furthermore, the composite sizing liquid of TBPU/PVA sized on paper surfaces exhibited superior mechanical performance. Therefore, this high ink-adhesion, robust mechanical performance composite sizing system along with its facile preparation process demonstrated more attractive advantages for broad application in green coatings and ink printing.

## Conflicts of interest

The authors declare that there is no conflict of interest regarding publication of this paper.

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