Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Enhancing Ink Adhesion of Specialty Paper by Interpenetrating Polyvinyl Alcohol-Blocked Polyurethane Polymer Network Sizing System

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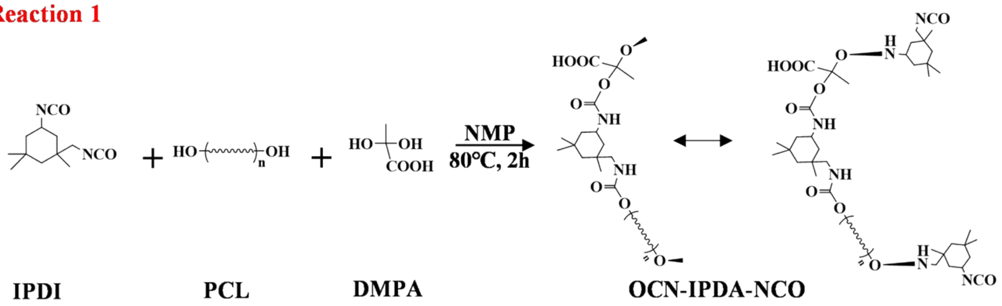
1. *Synthesis of TBPUs and composite of TBPU/PVAs*

Reaction 1



Reaction 2

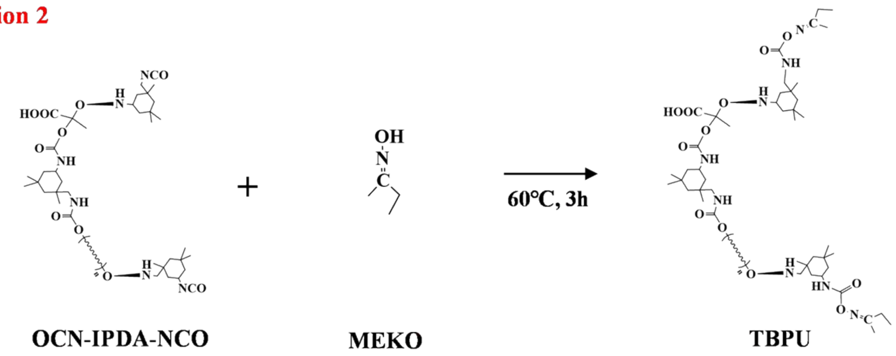


Figure S1. Synthetic route of water-based closed polyurethane TBPU.

Table S1 Formula of different sizing systems.

Surface sizing agents	**Dosage**	**content**				
		TBPU /wt%	PVA /wt%	Lubricant /wt%	Penetrant /wt%	H_2O /wt%
I	100g	——	——	——	——	100
II		3.0	——	1.0	1.0	95
III		——	40	1.0	1.0	58
IV		3.0	40	1.0	1.0	55

I: Untreated paper. II: TBPU-sized paper. III: PVA-sized paper. IV: TBPU/PVA-sized paper.
Solid content: TBPU (30%), n[(NCO)/(OH)] =1.6, w (DMPA)=9.5%; PVA1799 (10%)

2. *Owens two-liquids method for calculation of surface free energy*

Using Owens two-liquid method to calculate the surface free energy of paper samples. And the two liquids we adopted are distilled water and ethylene glycol.

Table S2 SFE components of two liquids.

SFE components	γ_l **(mJ·m⁻²)**	$\gamma^p{}_l$ **(mJ·m⁻²)**	$\gamma^d{}_l$ **(mJ·m⁻²)**	$\gamma^p{}_l/\gamma^d{}_l$
Distilled water	72.8	51.0	21.8	2.36
Ethanediol	48.3	19.0	29.3	0.65

3. *XPS analyses*

Table S3 Carbon, Nitrogen, and Oxygen Contents for paper samples

Paper samples	Wide			Ratio of O/C
	C 1s	O 1s	N 1s	
I	35.97	62.85	1.18	1.747
IV	47.18	42.76	10.06	0.906
I (ink)	62.56	31.28	6.16	——
IV (ink)	56.71	35.42	7.87	——

Table S4 C 1s assignment and O 1s assignment for paper samples

Paper samples	C 1s assignment (%)				O 1s assignment (%)			
	C−H	C−C	C−O/ C−N	C=O/ C=N	O=C	O−N−C	OH−C	C−O−C
I	35.64	41.44	22.92	——	——	——	86.49	13.51
IV	1.48	51.13	38.01	9.37	16.45	20.62	28.53	34.40
I (ink)	13.66	49.87	28.88	7.59	——	3.34	94.79	1.87
IV (ink)	9.20	49.98	34.15	6.67	2.36	69.50	16.63	11.50

Table S5 SFE data of sizing samples

Samples	Contact angle /°		γ^p_S (mJ·m^{-2})	γ^d_S (mJ·m^{-2})	γ_S (mJ·m^{-2})	γ^p_S/γ^d_S
	θ_1	θ_2				
I	85.5	64.2	0.30	35.45	35.75	0.0085
II	93.1	57.3	0.42	40.22	40.64	0.0104
III	91.7	30.1	1.30	85.31	86.62	0.0152
IV	98.1	58.6	2.12	31.35	58.60	0.0676

I: Untreated paper. II: TBPU-sized paper. III: PVA-sized paper. IV: TBPU/PVA-sized paper.

4. *Ink absorption behavior on sizing surface*

Figure S2 were obtained after a same condition (contact time, dosage of ink, temperature etc.). When the ink was dropped on the surfaces of sized paper, it left gamut area of different sizes on the untreated and sizing surfaces. Unsurprisingly, gamut area on the TBPU/PVA sizing surface had a biggest size. This ability to adhere ink particles could be attributed to the strong polarity of the sizing layer and the high compactness of TBPU/PVA sized paper. As a result, the utilization of this composite surface sizing could adhere 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 bonds and van der Waals forces, etc.) that determined the ink particles fixations, spreading or absorption.

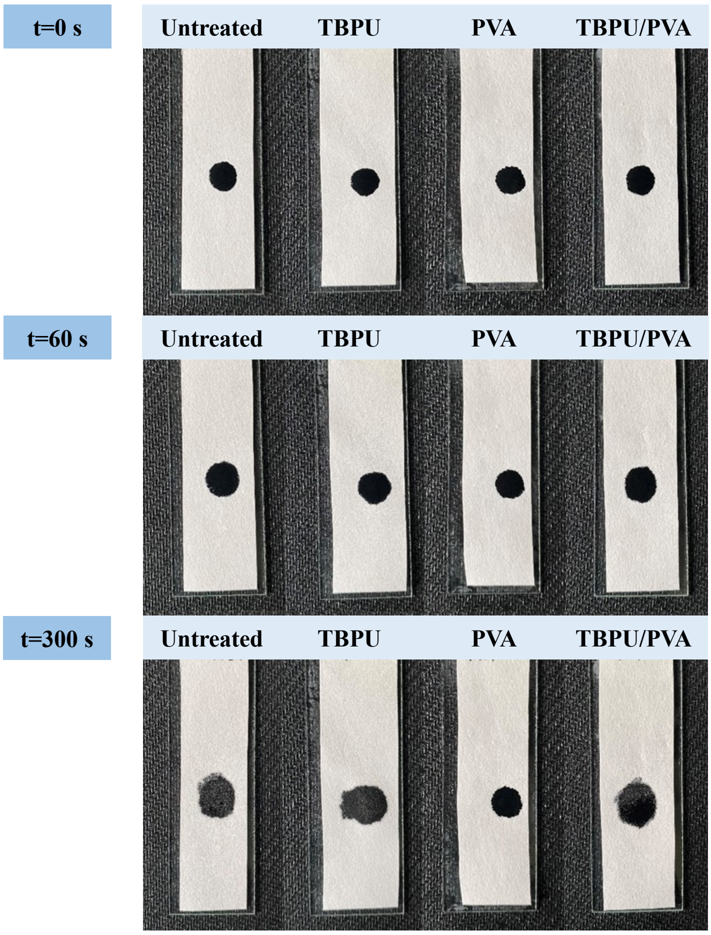


Figure S2. Status of ink penetration left by the ink on the untreated surface, TBPU sizing surface, PVA sizing surface and TBPU/PVA sizing surfaces.

Table S6 Ink adhesion of samples

Sizing agents	Ink peeling rate/%	Peel resistance grade
Untreated	66	D
PVA	44	C
TBPU	27	B
SAE	18	B
PU(SJ-28)/PVA	9	A
TBPU/PVA	6	A

A: less than 10%; **B**: 10%-35%; **C**: 35-65%; **D**: more than 65%

5. Rating criteria of color fastnesses (ink retention class)

The rating criteria presented below are the five arbitrary levels of evaluation rating set after our visual inspection of the samples on the 5 rating system. Class 5 is for no staining/color change, 4 for slightly staining/color change, 3 for noticeable staining/color change, 2 for considerable staining/color change and 1 for excessive staining/color change.