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Co-polymerized CMY colored polyurethane latex with high color strength and fastness for inkjet printing

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Textile digital inkjet printing suffers from substrate pretreatment, a low color fixation rate and a huge environmental cost. Covalently colored polymer latex is promising for applying in digital inkjet field, but is limited by the commercial dye structure in terms of standard color, dark color and economy. Based on the polymerizable dye library of Tsaihua Technology Company, we selected three types of structures with economical and brilliant colors, whose hues did not change after polymerization. Through PU copolymerization, we obtained three primary colors of CMY colored polyurethane with high molecular weight, and the latex after emulsified have dozens of nanometer size and excellent freezing and heat storage stability. The simple ink system prepared based on colored polyurethane latex can achieve low penetration, high precision printing, and standard, bright and brilliant color printing on unprocessed cotton fabrics and paper surfaces. The printed fabric achieves a color retention rate of over 94% after drying at 80 °C for 5 minutes, a dry friction level above 4.5, and a wet friction level above 3.5. The standard hue polymer printable latex developed in this study should inspire new advances in printable covalently colored latex and provide a greener, safer and smarter color printing material for digital inkjet printing.

Introduction

Digital inkjet printing, as an emerging, environmentally friendly, flexible, simple and efficient fabric printing method, has seen its market grow rapidly and continuously. According to data from the China Dyeing and Printing Association from 2015 to 2023, the output of digital inkjet printing of textiles in China increased from 400 million meters to 3.7 billion meters, and the total consumption of ink increased from 8300 tons to 44 350 tons, with an average annual growth rate of 23.3%.[1] Traditional inkjet inks, represented by disperse dyes and reactive dyes inks, rely on steaming or high-temperature pressing for fixation. Before printing, the fabrics need to be pretreated to enhance their fixation rate and printing accuracy. The sizing agents used in these pretreatment processes and the unfixed dyes must be removed through water washing and soaping to improve color fastness. These processes generate a significant amount of wastewater, exerting considerable pressure on the environment, and consume a large amount of energy and resources.[2–4] Although the coating of pigment ink is mild in color fixation, it has poor abrasion resistance and a poor hand feel and is prone to clogging the nozzle, causing printing accidents.[5,6] Therefore, the textile digital inkjet printing industry is striving for the development of inkjet ink that does not require pretreatment and has mild color fixation conditions, a high color fixation rate, and good color fastness.

Colored latex ink is a promising new type of ink that can solve pollution, print stability and safety issues in the inkjet printing industry.[7–10] Colored latex ink is commonly obtained by mixing waterborne polyurethane latex with dyes or pigments. The polyurethane latex generally has good direct adhesion to various substrate surfaces and can encapsulate and adsorb dyes, endowing colored polyurethane latex ink with excellent fastness performance and substrate adaptability.[11–14] As early as 2008, HP Company launched HP latex ink, in which pigment nanoparticles are stabilized through waterborne ink binders and mixed with latex particles to produce colored latex ink. When printing with latex ink, the substrate does not require surface pretreatment, and the printed latex particles are prone to form a continuous film layer that covers the pigment particles and provides good adhesion onto the dry substrate in an air environment, which results in printed patterns with good fastness performance. Although there are already colored latex inks made of different types of polymer materials, latex inks still encounter problems such as uneven color distribution and color loss during long-term storage.[10,15–17]

To solve the issues of physically mixed colored latex, covalent-colored latex inks have been developed, mainly containing co-polymerized colored polymer and graft-type colored polymer. Among them, the co-polymerized colored polymer can

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achieve a higher color concentration, better color uniformity, and better batch stability and has received more attention and research. Co-polymerized colored PU, through co-polymerization reactions between dye molecules with hydroxyl or amino groups and monomers containing NCO and other monomer extenders, can easily achieve high conversion rates, high molecular weights, and structurally customizable colored latexes,[18–22] which reveal satisfactory results in inkjet printing with fabric non pre-treatment and high-color-fastness substitution of traditional latex inks. However, up to now, copolymerized colored latexes are limited by the restricted types and quantities of commercially available dye structures, and their color hue richness, color depth, and price cannot meet the requirements of commercial use.[7,8]

Our laboratory is dedicated to the development of polymerizable dyes and co-polymerized colored PU latex for digital inkjet printing. Currently, we have obtained a PMW series of polyurethane dye latex of different colors with a dye concentration of 30%. These latexes have standard hues (CMY mode), high molecular weight and solid content. Just by mixing the common wetting agents, moisturizers and water in the ink, they can achieve high-precision and deep color printing on substrates such as cotton, linen, paper, and spandex without pretreatment. Moreover, the color fixation method is gentle. After drying at 80 °C for 5 min, the printed PMW colored PU latex ink could withstand water washing and high-temperature soaping without color fading. The dry-friction and wet-friction fastness are above level 4. However, the PMW colored PU latex ink has good printing stability, storage stability, and formulation miscibility. As a new type of textile digital ink, the promotion of its application will significantly enhance the green and intelligent level of the textile digital printing industry.

Experimental

Materials

Cotton fabric (150 g m^{-2}, bleached), commercial reactive red dye ink, and cotton fabric were obtained from Zhejiang Lanyu Digital Technology Co., Ltd. Glycerol and isotridecanol polyoxyethylene ether 10EO were obtained from Yangzhou Chenhua New Material Co., Ltd. PMW-yellow, PMW-magenta, and PMW-cyan were produced by Zhejiang Tsaihua Technology Co., Ltd.

Characterization

Molecular weight determined by GPC. The sample was dissolved in tetrahydrofuran solvent, diluted to a concentration of 0.2%, filtered through a 0.45 μm filter membrane, and then tested.

To establish the molecular weight standard curve, RID was selected as the detector, five polystyrene standard samples were tested with a narrow molecular weight distribution, 50 μL of the sample was injected with a micro-syringe, the correspondence between the peak time and the molecular weight was tested, and the standard curve was obtained. Subsequently, the samples were subjected to the same operation to measure the peak time and intensity and then fitted. Eventually, the average molecular weight and its distribution spectrum and data were obtained.

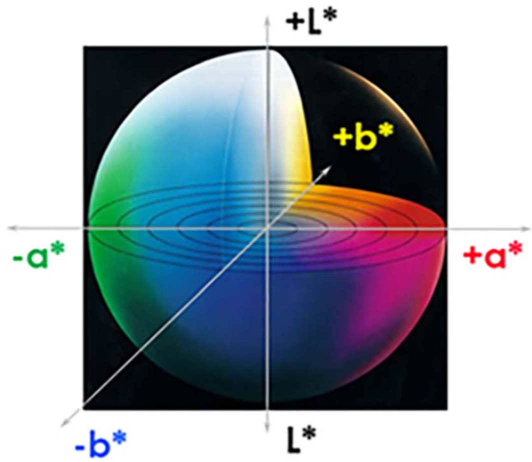


Fig. 1 Graphical representation of the CIE $L^*a^*b^*$ color space.

Color measurement. To measure color, a sample is analyzed using a spectrophotometer (CS-820P from Hangzhou CHNSpec Technology Co., Ltd.). The spectrophotometer illuminates the sample using either directional (45°/0°) or diffuse (d/8°) geometry and collects the reflected light in a standardized way to ensure accurate measurement. The spectrophotometer records the sample's reflectance (% R), or the percentage of light reflected at each wavelength of the visible spectrum (400–700 nm). These data are converted into tristimulus values, which consider standardized illuminant and observer functions. The tristimulus values are then transformed into $L^*a^*b^*$ coordinates. The CIE $L^*a^*b^*$ system is a 3D colorimetric system that includes mutually perpendicular coordinate L^* (lightness) and coordinates a^* and b^*.

As shown in Fig. 1, the $L^*a^*b^*$ values are calculated from the tristimulus values (X, Y, Z). The location of a color is defined by its location in a three dimensional, rectangular coordinate system, where

• L^* determines brightness, with high values indicating lightness and low values indicating darkness.

• a^* describes the position between red (+a) and green (−a).

• b^* describes the position between yellow (+b) and blue (−b).

• At $a^* = 0$ and $b^* = 0$, the color is neutral gray, with lightness determined solely by the L^* value.

• The vertical L* axis ranges from 0 (black) to 100 (white).

Size determined by dynamic light scattering (DLS). The sample is diluted to pure water to prepare a 0.2% ink sample. After turning on the instrument, it is preheated for 30 minutes. The test is set to be repeated three times at room temperature. The test light wavelength is 532 nm, and the scattering angle is 90°. The sample is placed in a four-way cuvette and inserted into a laser particle size analyzer for detection. The data spectrum and average molecular weight are obtained. The average of the three data points is taken as the average molecular weight.

Table 1 Molecular weight and molecular weight distribution of the PMW series colorants

	M_w	M_n	M_z	PDI	Dye content	Solid content of latex	L^*	a^*	b^*
PMW-yellow	8600	5181	12 225	1.66	31.30%	26.70%	28.43	53.73	48.65
PMW-magenta	16 203	10 681	22 686	1.517	32.50%	27.20%	0.24	0.21	−0.04
PMW-cyan	17 891	12 504	24 168	1.43	34.20%	25.60%	0.12	−0.13	−0.25

Amount of diffusion test. The line diffusion condition is observed using an optical microscope, and the ink seepage amount on the fabric is calculated using eqn (1):

$$d = d_1 - d_0, \tag{1}$$

where d represents the diffusion amount, in mm; d_1 is the measured width of the lines printed on the fabric, in mm; and d_0 represents the width designed by the printer, in mm.

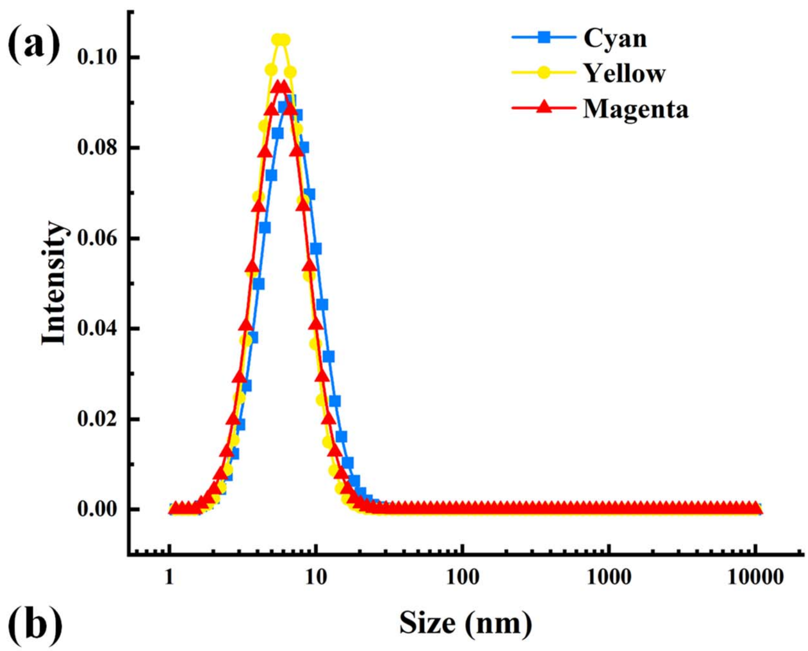
Fixation rate determination. After printing and fixing the color of the fabric sample, it is often washed with warm water. Then, it is put into a 100 ml detergent solution of pure water with 0.5 g of standard soap (detergent consistency and concentration compliance with the items of 5.1 and 5.3 in GB/T 3921 2008 according to test method D (4)) and boiled for 5 minutes. During this period, it is turned over with a glass rod every 30 seconds to simulate the washing action. After that, the fabric sample is drained of water and dried. Optical density values (OD values) before and after washing are determined. Fixation rate (%) = OD value (after washing)/OD value (before washing) × 100%. The OD value was determined by applying the EX Pro Printing Density Meter (produced by Hangzhou CHNSpec Technology Co., Ltd).

Rubbing fastness test. The dry and wet rubbing fastness of the printed fabric samples were tested in accordance with GB/T 3920-2008 “Textiles-Color Fastness Tests-Rubbing Color Fastness”.

Results and discussion

Characterization of the covalently colored polyurethane latex ink

The PMW series colorants are synthesized referred to ref. 23, by polymerizable colorant monomer (one of bright yellow, magenta, and cyan), from Tsaihua Technology Company, mixed



(b)

	Average size (nm)	D90 (nm)	D10 (nm)	PI
PMW-Yellow	7.19±0.13	8.97±0.13	3.38±0.14	0.1566
PMW-Magenta	7.62±0.15	9.56±0.15	3.19±0.16	0.199
PMW-Cyan	7.35±0.12	11.07±0.12	3.57±0.13	0.215

Fig. 2 (a) Image of the size distribution of PMW colorants measured by DLS. (b) Table of the average size and size distribution data of the PMW colorants from the DLS.

Table 2 Storage stability of the PMW ink

	Fresh sample	Storage after 60 °C, 14 days	Variety ratio	After freeze–thaw	Variety ratio
(a) PMW-yellow ink					
pH	7.62	7.59	<5%	\	\
Viscosity/mPa s	3.8	3.9	<3%	3.9	<3%
Surface tension/mN m^{-1}	35.2	35.1	<3%	35	<3%
Printing ability	Well	Well	\	Well	
(b) PMW-magenta ink					
pH	7.23	7.22	<3%		\
Viscosity/mPa s	4.5	4.7	<5%	4.6	<3%
Surface tension/mN m^{-1}	35.3	35.2	<3%	35.3	<3%
Printing ability	Well	Well	\	Well	\
(c) PMW-cyan ink					
pH	7.83	7.8	<5%	\	\
Viscosity/mPa s	4.6	4.8	<5%	4.7	<3%
Surface tension/mN m^{-1}	35	35	<3%	35.1	<3%
Printing ability	Well	Well	\	Well	\

with polyether diols and anionic diols monomer, react with isocyanates under anhydrous and catalyzed by stannous octoate. The relative molecular weights of the three colorant monomers are 370 for yellow, 522 for magenta, and 916 for cyan. Despite their different molecular weights, the content of colorants in the three-color polymer was controlled at 30–34 wt%. Specifically, the content of yellow polymerizable colorant in the yellow polymer is 31.30 wt%, the magenta polymer is 32.50 wt%, and the cyan polymer is 34.20 wt%. After chain extension using a chain extender, the polymerization degree of all the PMW series polymers is controlled to 99%. Then, the polymerized chain was end blocked, neutralized, and finally emulsified; thus, a stable colored polyurethane latex was obtained. The molecular weight of the polymer after end blocking was tested by GPC in tetrahydrofuran, as shown in Table 1. The molecular weights of PMW-yellow, PMW-magenta and PMW-cyan are M_w 8600, PDI = 1.66; M_w 16203, PDI = 1.52; and M_w 17891, PDI = 1.43, respectively. Among them, PMW-yellow has the lowest molecular weight and the widest molecular weight distribution. PMW-cyan shows the maximum molecular weight and the narrowest molecular weight distribution. All of them display a relatively high molecular weight and a narrow molecular weight distribution. This suggests that our dyes have excellent reactivity and that the polymerization reaction is thorough and well-controlled.

The solid content of the emulsified PMW colorants was measured by baking at 105 °C for 30 min, and the weight of the solid residual in the latex emulsion was calculated. The solid content of PMW-yellow, PMW-magenta and PMW-cyan are 26.70 wt%, 27.20 wt% and 25.60 wt%, respectively. The color presentation of the three colored latex refers to the color system of CIE $L^*a^*b^*$ and is measured through the transmission mode using a desktop spectrophotometer (CS-820P from Hangzhou CHNSpec Technology Co., Ltd). The $L^*a^*b^*$ data of the three colored latexes are displayed in Table 1. A lower L^* value means lower light transmittance and usually has a deeper color. L^* values of the PMW-yellow, PMW-magenta and PMW-cyan are 28.43, 0.24 and 0.12, respectively. This suggests the deep colors of the PMW-magenta latex and the PMW-cyan latex. The deep color of yellow tends to be orange; as a result, a much higher L^* value of the PMW-yellow is presented.

The size distribution of PMW colorants is measured by applying dynamic light scattering (DLS) in pure water at a concentration of 0.2%. The particle size distribution graph is shown in Fig. 2a. The three colorants have a single size distribution peak and are all within 10 nanometers. This indicates that PMW colorants exist in the aqueous phase in the form of spherical nanoparticles, with a relatively narrow particle size distribution. The analyzed size data in Fig. 2b reveal that the average particle size of the PMW series colorants is between 7 and 8 nm, with D90 ranging from 9 to 11 nm. PMW-cyan has a larger particle size, but it does not exceed 11 nm. The polydispersity index (PI) of the particle sizes of the three colorants is all within 0.22, indicating that the PMW colorants have good water dispersibility and storage stability.

The digital inkjet ink is prepared by mixing 30% of PMW colorants, 25% of glycerol, 0.5% isotridecanol polyoxyethylene ether 10EO and the remaining water. Glycerol is used in ink as a moisturizer and viscosity regulator, and isotridecanol 10EO is used as a wetting agent and surface tension regulator. The resulting PMW colorant ink has a pH ranging from 7 to 9, a viscosity ranging from 3.5 to 5.0 mPa s, and a surface tension ranging from 25 to 40. It should be mentioned that the proportion of glycerol is so large for general polymer latex to make the system unstable and viscous, while the PMW colorant ink still maintains low viscosity. The stability of PMW colorant ink, typically the PMW-yellow ink, is tested. The viscosity and surface tension data of the ink samples after being stored at 60 °C for two weeks and at −18 °C for 24 hours are shown in Table 2. The changes are all within 0.1 units, and the change rates are all less than 5%, indicating the excellent storage stability of PMW colorant ink.

The prepared PMW colorant ink samples are shown in Fig. 3a. The three colorant ink samples have a deep color but a transparent appearance without any graininess. All the inks perform well in

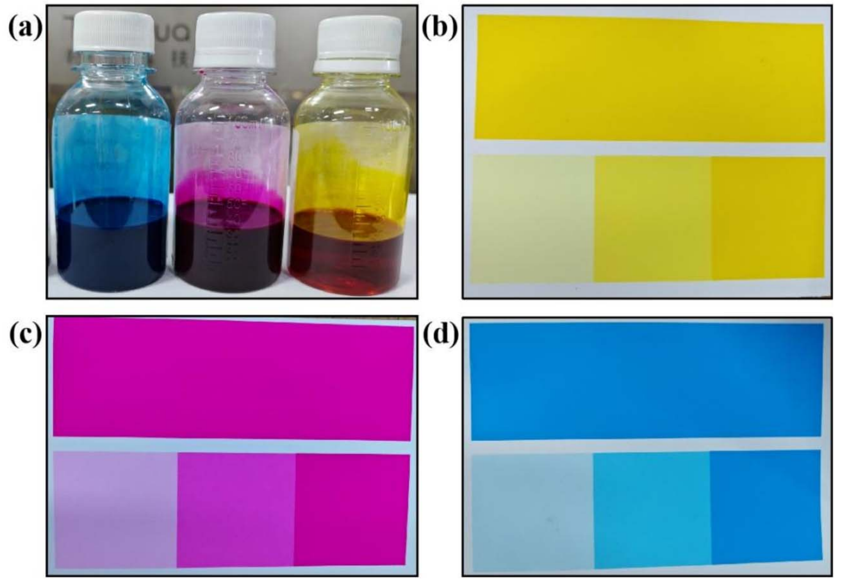


Fig. 3 Images of (a) PMW-cyan ink, PMW-magenta ink, and PMW-yellow ink from left to right; (b) PMW-yellow; (c) PMW-magenta; and (d) PMW-cyan printed gradient color blocks onto A4 paper.

the filtration through a 0.22 μm filter membrane. The filtered ink is then applied to the printer ink cartridge for printing performance testing. As shown in Fig. 3b–d, through the EPSON L310 Desktop Printer, we printed different shades of gradient color blocks onto the surface of A4 paper using the prepared digital inkjet ink of PMW-yellow, PMW-magenta, and PMW-cyan. All three colorants produce bright, continuous, and uniform colors with clear boundaries, indicating that the covalently colored polyurethane latex ink prepared by a simple formula can achieve a good effect and precision printing.

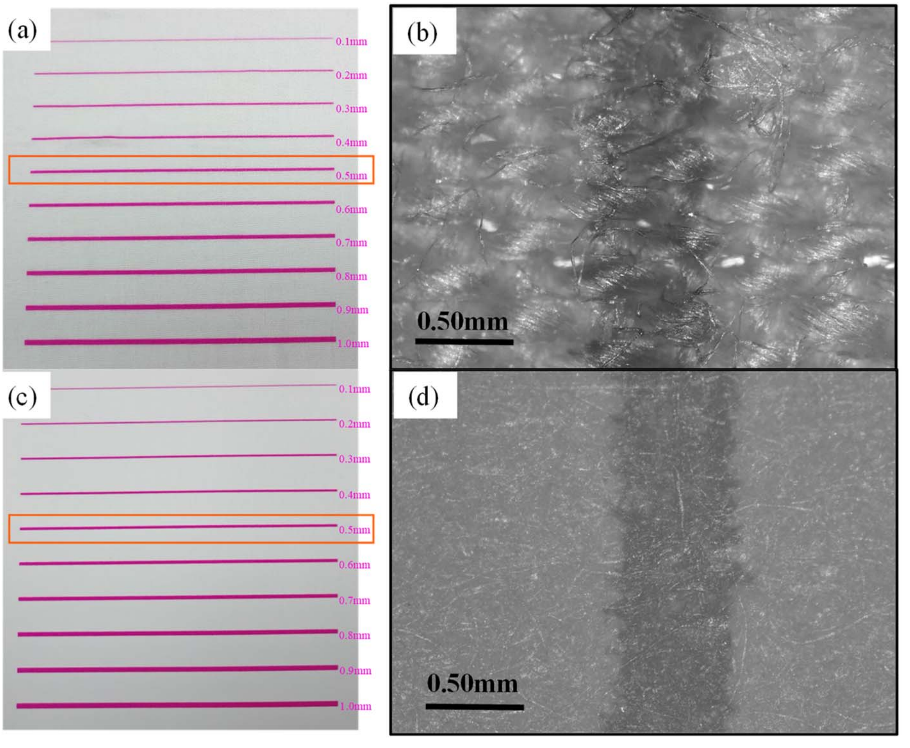


Fig. 4 Images of PMW colorant ink printed lines in sequence of 0.1 mm to 1.0 mm width into the (a) cotton fabric and (c) A4 paper surface. Microscopy images of PMW colorant ink printed as 0.5 mm wide lines on the (b) cotton fabric and (d) ordinary A4 paper. The widths of the shaded areas were 0.63 mm and 0.62 mm, respectively.

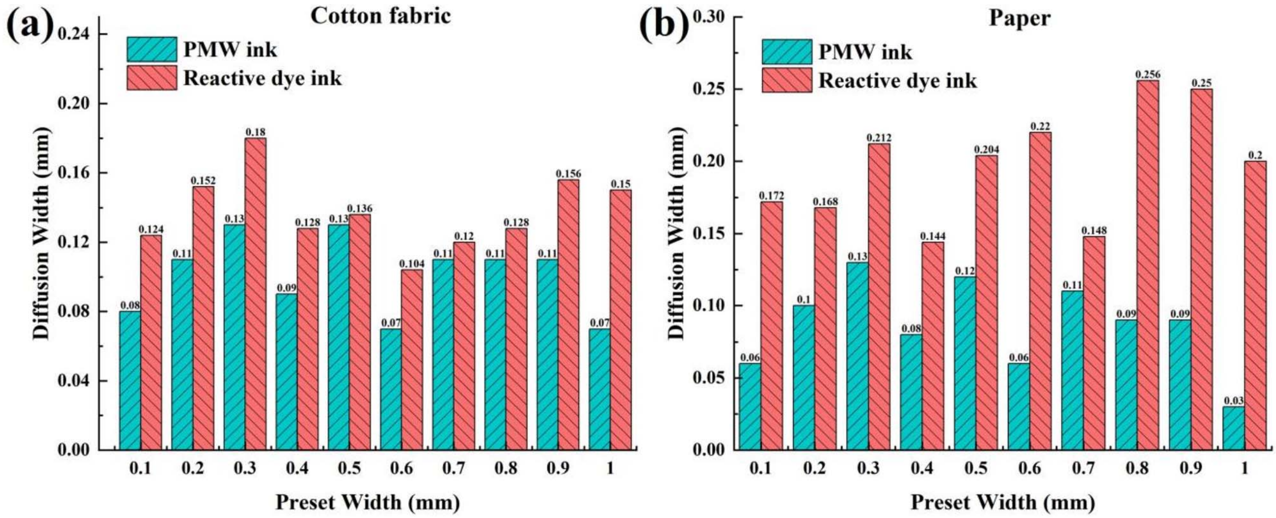


Fig. 5 Diffusion width of PMW colorant ink compared with traditional reactive dye ink printed lines onto (a) clean cotton fabric and (b) paper with preset-width.

We further conducted tests on the printing accuracy of the ink. Using the ink PMW-magenta, the printing program set ten lines ranging from 0.1 mm to 1.0 mm and printed them onto the surface of A4 paper and a clean, unbleached cotton fabric sample. As shown in Fig. 4a and c, when the print width is 0.1 mm, the printer supplies less ink, and there are clear and continuous ink marks on the surfaces of both substrates. As the print width gradually increases, the printer supplies more ink, and the color strength and contrast of the ink mark images also gradually increase. By observing the penetration amount of the lines under a microscope, as shown in Fig. 4b and d, the main body of the PMW-magenta ink spreads in straight lines on the surfaces of the fabric fibers and pulp fibers, with clear boundaries. The main body shows no white areas; there is a certain but limited branching diffusion phenomenon at the ink edges, and there are areas with non-branched ink marks. Generally, the imprints of poor-quality printing inks on the substrate surface appear as circular sputtering patterns, and sputtered ink dots often appear at the edges of adjacent printed ink marks. However, no sputtered ink dots are observed in the imprints of the PMW colorant, and it has good printing uniformity. This indicates that the diffusion and penetration of PMW-magenta ink are weak, suggesting that PMW colorants have good single-sided printing performance and clarity on both non-sizing cotton fabric surfaces and paper surfaces.

Table 4 Migration resistance performance of the PMW colorant ink compared with the reactive red dye ink after fixation on a clean cotton fabric using different methods

Items	Color fixing condition	Rubbing fastness	
		Dry rubbing	Wet rubbing
PMW-yellow	Steaming	4.5	3.5
	Blanching	5	4
	Bake at 80 °C	5	4
Reactive red	Steaming	4	4
PMW-magenta	Steaming	5	3.5
	Blanching	5	4
	Bake at 80 °C	5	4
PMW-cyan	Steaming	5	3.5
	Blanching	5	4
	Bake at 80 °C	5	4

Subsequently, we measured the diffusion amount of PMW-magenta ink, in comparison with traditional reactive red dye ink, on the fabric surface and paper surface under different printing widths. As shown in Fig. 5, the diffusion amount of PMW-magenta ink is much smaller than that of the traditional reactive dye ink, both on cotton fabric and paper substrate. The diffusion amount of PMW magenta ink fluctuated from 0.07 mm to 0.13 mm on the cotton fabric surface and fluctuated from 0.03 mm to 0.13 mm on the paper surface, while the diffusion amount of the traditional reactive red dye ink fluctuated from 0.104 mm to 0.18 mm on the cotton fabric surface and fluctuated from 0.144 mm to 0.256 mm on the paper surface. As a result, PMW colorant ink have smaller diffusion amount and smaller fluctuation degree of diffusion amount than traditional dye on paper surface. However, the overall diffusion amount of the PMW-magenta ink on the paper surface was smaller than that on the cotton fabric, which could be ascribed to the even paper leading to easier and faster ink diffusion than uneven cotton fabric. The uneven cotton surface led to ink splash and drift, resulting in a smaller difference of the uneven surface than the even surface for weak diffusion ink but a larger difference in the even surface than the uneven surface. Therefore, we can obtain a much lower diffusion ability and higher printing accuracy and resolution for PMW colorant ink than for traditional reactive dye ink. There is a significant difference in the amount of ink diffusion on the two surfaces at different printing widths. The amount of ink diffusion on the paper surface varies more distinctly with widths. However, there are also many printing widths where the amount of ink diffusion is the same or similar, with the same changing trend, and all of them have a lower amount of ink diffusion between 0.4 mm and 0.6 mm. This indicates that the amount of ink diffusion is directly related to the printing accuracy of the printer, while the material influence is minor, that is, the PMW colorant ink has superior printability. Overall, PMW colorant ink can achieve good printing accuracy on fabric without sizing.

Characterization of the color fixation rate on the surface of cotton fabrics

After the PMW colorant ink is packed into the box, the ink output is adjusted to ensure that the optical density (OD) value of the printed color blocks is around 0.9. Then, the color blocks are printed onto the unprocessed cotton fabric and steamed (at 103 °C and 75% humidity for 15 minutes, respectively). The traditional reactive red dye ink conducts the printing and steaming work on a sized cotton fabric as a comparison. Moreover, the PMW colorant ink adopts the blanching process (150 °C, hot pressing for 1 minute) and the drying process (80 °C, drying for 5 minutes) for color fixation. After the color fixation procedure, the printed cotton fabric is washed with water at room temperature for 1 minute, followed by washing with soap at 95 °C for 3–5 minutes, and then washing twice with clean water. After drying, the OD and $L^*a^*b^*$ values of the processed printed color blocks were tested, and the results are shown in Table 3. The OD value of the reactive red dye fixed color block was distinctly reduced to 0.77 from the initial value of 1.13 after washing, and the fixation rate was calculated to be 68.14%. Remarkably, the color hue of the PMW colorant-processed fabric samples obtained by different fixation processes did not change significantly, and the OD values of the processed fabric were similar to the initial OD values. The lowest fixation rate is 94.2% for PMW-cyan, and the highest is 97.8% for PMW-magenta, while the remaining color strengths of PMW-bright yellow and PMW-magenta display higher OD values. The hot-stamping process generally produces a superior color-fixing effect, and the steaming is comparable to drying processes. However, there is a higher color-fixing rate of PMW-yellow when the drying process is used than when the steaming process is used. Steam distillation is generally the preferred process for reactive dye inks. It can open the internal gaps of fibers through high-temperature and humid steam and at the same time drive the reactive dyes to enter the internal fiber surface for reaction, thereby achieving a high dyeing rate on the fiber surface and a high fixation rate of reactive dyes. However, during the process, when reactive dyes react on the fiber surface, they undergo hydrolysis under the action of steam, resulting in a loss of fixation rate. As a result, the evaporation process fixation rate of general reactive dye inks is less than 70%, and only high-end brands and a few species can achieve a fixation rate of 80%.

PMW colorant latex is a physical aggregate composed of anionic covalently colored polymer and is stable in the aqueous phase due to electrostatic repulsion. When water is evaporated and absorbed by cellulose fibers, the latex loses stability, and its structure collapses after it contacts the matrix. After the collapse of PMW colorant latex, it becomes a water non-dispersible colored nanosized glue. Under the effect of heat, the collapsed colorant latex collides with the fabric fiber surface, seeps into the fiber gaps, and achieves tight contact with the fibers. Relying on hydrogen bonds and van der Waals forces, firm adhesion and soaping fastness are achieved. However, the presence of moisture may disrupt the hydrogen bond between PMW colorants and cellulose. Since it is a purely thermal process, the hot baking process may present a better color fixation effect compared to steaming.

Dry and wet rubbing fastness

The dry and wet rubbing fastness of the fabric samples fixed with the PMW colorant ink and reactive red dye ink were tested, and the data are shown in Table 4. All the dry friction levels of the PMW-yellow, PMW-magenta and PMW-cyan colorant inks are at grade 4.5, and all their wet friction levels are above grade 3.5. In terms of the reactive red dye fixed cotton fabric with steaming, both the dry rubbing fastness and wet rubbing fastness are at grade 4. Though the dry rubbing fastness for PMW-yellow, which has the problem of uneven coloring during the steaming process, resulting in a dry rubbing fastness of 4.5 grade, all the other products have full grade dry rubbing fastness and non-color sticky performance using the three fixation methods. Wet rubbing fastness shows fastness grade 4 for all the PMW colorants with blanching and bake processes, similar to the reactive dye, but fastness grade 3.5 for the steaming process, relatively lower than traditional reactive dye. As

Table 3 The color hue, color concentration (OD value) and fixation rate of the printed PMW-yellow, PMW-pink, and PMW-cyan colorants inks (initial color density (OD value = 0.90 ± 0.10)) compared with the reactive red dye ink (initial OD value of 1.13) after fixation on a clean cotton fabric using different methods

Items	Color fixing condition	OD	L^*	a^*	b^*	Color fixation rate
PMW-yellow (initial OD = 0.90)	Steaming	0.85	88.5	−3.9	79.8	95.5%
	Blanching	0.87	87.4	−3.0	80.0	97.7%
	Baked at 80 °C	0.86	88.6	−3.6	80.1	96.6%
Reactive red ink (initial OD = 1.13)	Steaming	0.77	48.3	42.5	5.6	68.14%
PMW-magenta (initial OD = 0.93)	Steaming	0.89	57.2	79.2	−19.5	95.7%
	Blanching	0.91	57.7	80.3	−19.3	97.8%
	Bake at 80 °C	0.89	57.3	80.1	−19.5	95.7%
PMW-cyan (initial OD = 0.87)	Steaming	0.82	62.6	−15.9	−73.1	94.2%
	Blanching	0.84	61.9	−16.3	−73.5	96.5%
	Baked at 80 °C	0.82	62.8	−16.1	−73.3	94.2%

a result, there is superior dry rubbing fastness but comparable wet rubbing fastness for the PMW series colorants to the traditional reactive dye under the majority of fixation methods.

The wet rubbing fastness of the three PMW colorant inks fixed on the cotton fabric by the steaming process was generally inferior to that of the blanching process and the drying process, which was consistent with the results of the previous high-temperature soaping. Although the drying process has a low processing temperature, the dry and wet rubbing fastness achieved is of a relatively high grade. The superior dry and wet friction performance of the PMW series products may be because the covalently colored polyurethane, as a nanosized glue, can form a very thin film layer on the fiber surface. Meanwhile, their large molecular weight can provide strong van der Waals forces, coupled with the hydrogen bond effect in the molecular chain; their bonding to the fiber surface is firm, and they exhibit superior anti-friction strength.

Conclusion

We launched three primary color (CMY) inkjet inks made by covalently coloring anionic polyurethane latex named PMW series inkjet inks. The PMW series inkjet inks possess excellent storage stability with a simple formula composed of a large proportion of glycerol. PMW-type inks can be used for high-precision inkjet printing on cellulose-based materials, such as cotton fabric, office paper, and corrugated paper, without pretreatment, and the color fixation process condition is mild, where the color is firmly fixed after drying at a mild temperature. Fabrics printed with PMW colorant inks have excellent resistance to hot water and soap washing without color fading and have superior dry rubbing performance and good wet rubbing performance. In summary, the PMW series of covalently colored anionic polyurethane latex inks is a type of digital inkjet ink product that can effectively improve the problems of high energy consumption, high pollution, and low efficiency of reactive dye inkjet inks and can provide a feasible solution for the subsequent development of inkjet ink systems with broader fabric and other substrate adaptability and higher wet rubbing fastness.

Author contributions

Bin Liu synthesized the colored polyurethane latex and wrote the manuscript. Jun Chen and Xibin He synthesized the polymerizable dyes. Shuxu Chen conducted measurements. Junpei Li provided guidance in the entire process of the project. Fucai Liu guided the program framework and revised the manuscript.

Conflicts of interest

The authors declare no competing interests.

Data availability

The authors declare that any raw data files be needed in another format, they are available from the corresponding author upon reasonable request. Source data are provided with this paper.

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