Synthesis of Aqueous Blocked Polyurethane Oligomer for Pigment Ink of Inkjet Printing

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Abstract

Aqueous blocked polyurethane oligomer emulsion using as cross linking agent for pigment ink were synthesized from isophorone diisocyanate (IPDI) and polyethylene glycol (PEG), and the fixing conditions on rubbing and washing fastness were discussed. The results showed that the blocked polyurethane oligomer emulsion with small particle size and high centrifugal stability exhibited the excellent compatibility with the carbon black ink. Both rubbing and washing fastness were reached to the requirement of the customers for textiles. The optimal fixing conditions was that the amount of aqueous blocked polyurethane oligomer emulsion was 3%, and the dosage of adhesive DM-5125 was 20% and baked at 100°C for 5 minutes.

Introduction

Inkjet as a cleaner printing technology for textile has attracted lots of people's attention due to its high resolution, little pollution, and fast response to the frequent shift of cloth fashion. Unlike the dye inks, pigment inks which were suitable for all kinds of fabrics have become the most promising colorant in this technique [1, 2]. However, how to prepare the pigment ink which printed the fabrics showing the high rubbing and washing fastness is still a great challenge [3]. Adding a certain amount of fixation agents to the pigment ink is an effective method to improve the rubbing and washing fastness of the printed fabrics. At present, different kinds of fixation agents have been developed, such as polyurethane acrylate oligomers [4], cured hybrid polymers [5], emulsion [6], microemulsion [7] and so on. Among all of these fixation agents, emulsion or microemulsion have become the most commonly additives for pigment ink [8].

However, according to our pervious research, we found that the rubbing and washing fastness of the printed fabrics with the pigment ink is difficult to meet to the requirement for customers when only emulsion was used as fixation agents. The reason is that, on the one hand, the latexes will migrate from the pigment surface due to repulsive forces among the pigment and latexes for low viscosity (as shown in figure 1). On the other hand, it is not a feasible method to improve the color fastness by increasing the amount of emulsion, because the latex will absorb some energy and then change its morphology for viscoelasticity [9-13].

Aqueous blocked polyurethane acrylate oligomer has excellent stability at low temperature. The end groups of blocked aqueous polyurethane acrylate oligomer will break off and release –NCO groups at high temperature. –NCO reacted with –OH or –NH2 in emulsion or fabrics, thus can greatly improve the fastness of the printed fabrics [4]. According to this conception, in this paper, we synthesized the blocked polyurethane oligomer emulsion using the isophorone diisocyanate (IPDI) and polyethylene glycol (PEG) as the monomer, and then used as crosslinking agent for the pigment ink, and finally the effect of aqueous polyurethane dosage, curing time and temperature on fastness were discussed.

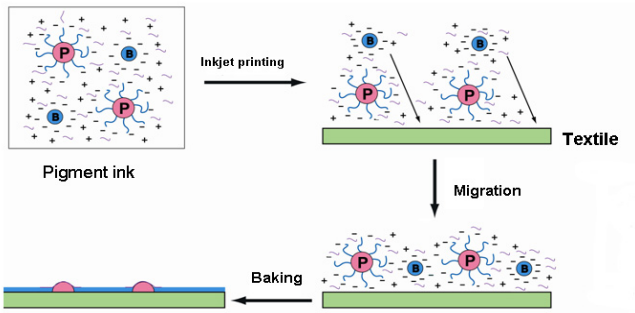

***Figure 1**. Sketch up for forming the film of pigment ink onto the fabrics, P-pigment, B-binder*

Experimental

Materials

Mill scoured, bleached and mercerized plain weave cotton fabric (29.5tex × 29.5tex) was purchased from Wujiang cotton mill of China. Isophorone diisocyanate (IPDI, CR grade) and polyethylene glycol 2000 (EG, CR grade) were purchased from Lingfeng Chemical Reagent Co. Ltd., Shanghai, China. Isopropanol (AR grade), acetone (AR grade), dibutylamine (AR grade) and sodium bisulfite (AR grade) were purchased from Guoyao Chemical Reagent Co. Ltd., Shanghai, China. Dibutyl tin dilaurate (DBTDL, AR grade) as a catalyst was supplied by Fluka Chemical Co., Switzerland. Carbon black dispersions with 10wt% solid content were prepared in our lab. All the distilled water was used in the experimental. Binder (DM-5125, solid content 35%) were commercially available and used as received from Dymatic chemicals, Inc, Wuxi, of China.

Synthesized of the aqueous blocked polyurethane acrylate oligomer

The synthesis mechanism of blocked aqueous polyurethane obligomer was showed in figure 2. PEG was dehydrated at 80°C under vacuum conditions before using. 0.1 mole of PEG was added into a three-necked flask equipped with stirrer, thermometer, and reflux condenser under nitrogen atmosphere. 0.12 mole of IPDI containing 0.05% (w/w) DBTDL was slowly dropped into the reactor at 80°C for 1 h and the reaction mixture was stirred for an additional 1 h and then added some amount of acetone to ensure an acceptable solution without gelation.

After the reaction mixture was cooled to 0-5°C, a calculated amount of sodium bisulfite was gradually added to the reaction

mixture, and the reaction mixture was stirred for another 2 h continuously to cap the entire terminal -NCO groups. The resulting product was a clear solution of the blocked aqueous polyurethane acrylate oligomers. Deionized water was added into the kettle to form an aqueous solution of blocked aqueous polyurethane acrylate oligomer emulsion with 40% (w/w) solids content. The reaction yield was evaluated.

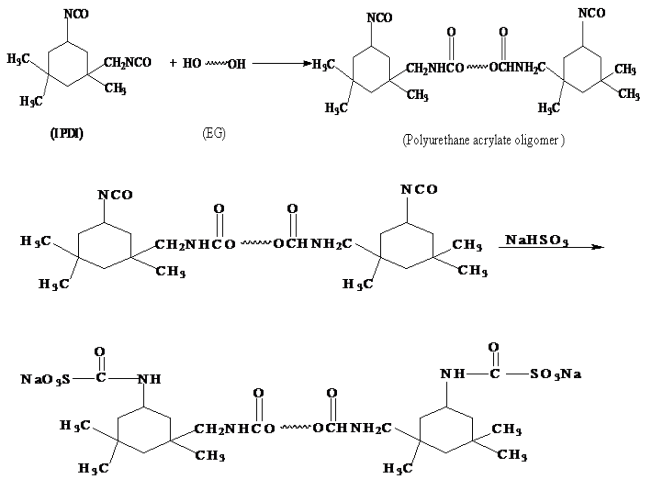

***Figure 2**. The synthesis of blocked aqueous polyurethane obligmer*

Formulation of the carbon black ink

A weight-based formulation of carbon black ink was given as follows: pigment dispersion 50%, binder DM-5125 20%, aqueous blocked polyurethane acrylate oligomer emulsion 3%, glycerol 15%, ethylene glycol mono-methyl ether 7%, urea 2%, Tween-80 1.5% and distilled water 1.5%. The above components were stirring at 300r/min until a homogeneous dispersion was obtained. After filtered through a 0.5μm pore filtering sieve, the carbon black ink was prepared.

Printing the textile

The carbon black ink was loaded on an inkjet printing machine (Mimaki JV4-180, Pizeo-electric inkjet printer, Japan). The cotton fabrics were printed under the conditions of 8 pass and 720 × 720 dpi. The printed fabrics were dried in an oven at 80 °C for 3 min and then the fabrics were subjected to bake at different temperature for some time to fix the pigment.

Measurement

FTIR spectroscopy: The aqueous blocked polyurethane acrylate oligomer was washed 3 times using methanol and subsequently washed 3 times with distilled water, and then dried at room temperature. FTIR spectra of samples (in KBr pellet) were recorded on a Nicolet Nexus 560 FTIR spectrometer.

Dynamic light scattering (DLS): The particle size distribution of aqueous blocked polyurethane acrylate oligomer in emulsion was determined by DLS method using a Malvern Zetasizer Nano ZS90 instrument at 25 °C with a fixed angle of 90 degree.

Transmission electron microscope (TEM): The sample was diluted with distilled water until the latex was no longer opaque. One drop of the diluted sample was placed on a copper grid, the excess liquid was removed with a tissue, and the grid was left to dry. The morphology was observed using A Phillips CM12.

Performance of the carbon black ink: The mean particle size of the emulsion was measured by DLS method. The centrifugal stability and freeze-thaw stability was investigated according to the reference [14]. The viscosity at 25°C was measured by the Brookfield DV-III. The printing performance of the inks was tested by Mimaki JV4-160, and the clogging nozzle rate (B) was calculated according to eq. (1),

$$B = \frac{C_1}{S} \times 100 \quad \% \qquad (1)$$

where C_1 is the amount of clogged nozzle, S is the sum of the nozzle on the print head. The cotton fabrics (24 cm×24 cm) were printed by Mimaki JV4-180.

Color performance of the printed fabrics: The rub and washing fastness were tested according to AATCC standard 8-2001, 61.

Results and discussion

Synthesis of the blocked polyurethane acrylate oligomer

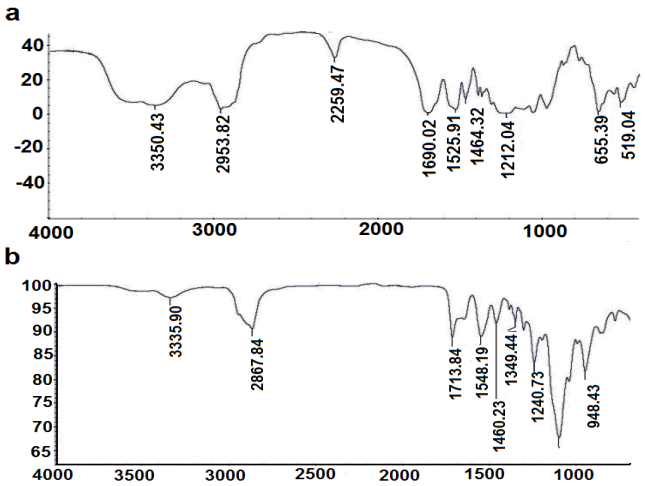

***Figure 3**. FTIR spectra of (a) un-blocked polyurethane acrylate oligomer and (b) blocked polyurethane acrylate oligomer*

Figure 3a shows that some strong absorption bands appeared at 1212.04cm^{-1} (C-O), 1464.32cm^{-1} (C-N-C), 1525.91cm^{-1} (N-CO), l690.02cm^{-1} (C=O) and 2259.47cm^{-1} (NCO), which all are the characteristic adsorption of polyurethane acrylate oligomer, these results indicate that the un-blocked polyurethane acrylate oligomer was successfully synthesized. Moreover, it is also clear from FTIR spectra of Figure 1b that there is no absorption band at 2274 cm^{-1} which corresponds to -NCO group, which indicates that the entire amount of isophorone diisocyanate enters into the reaction and the end product is free from isocyanate.

Morphology of the blocked polyurethane acrylate oligomer

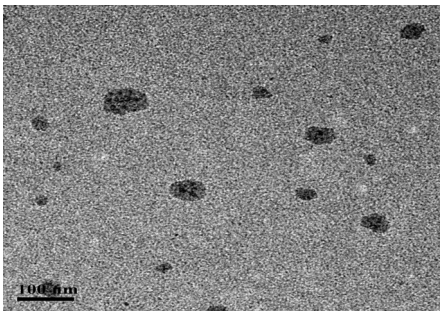

***Figure 4**. TEM photo of the blocked aqueous polyurethane acrylate oligomer in the emulsion*

Figure 4 shows the morphology of the blocked polyurethane acrylate oligomer. It can be seen that the particles of the blocked polyurethane acrylate oligomer are spherical and uniformly distributed in the emulsion, and the mean particle size was about 80 nm, which was far smaller than that of the pigment particles (150 nm) and the binder particle (115 nm) in the carbon black ink.

Zeta potentials

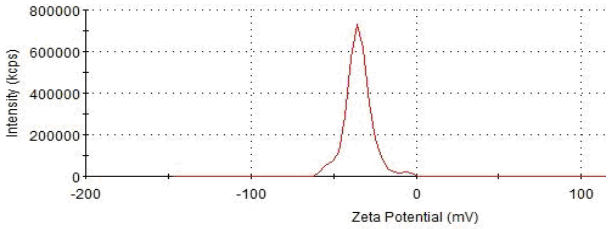

***Figure 5**. Zeta potentials distribution of the aqueous blocked polyurethane acrylate oligomer in the emulsion*

Figure 5 show that the zeta potential distribution of the blocked polyurethane acrylate oligomer in emulsion fit in with the normal distribution, and the mean zeta potentials is -36.64 mV. Commonly, the higher zeta potential is, and the stronger repulsive forces among the particles are, which resulted in an excellent stability. Figure 6 show that the particle distribution changed small after centrifugal treatment except with the deposition of some large particles in the emulsion. These results indicate that the prepared emulsion has excellent centrifugal stability, and meanwhile, the large particles can be effectively eliminated by centrifugal method.

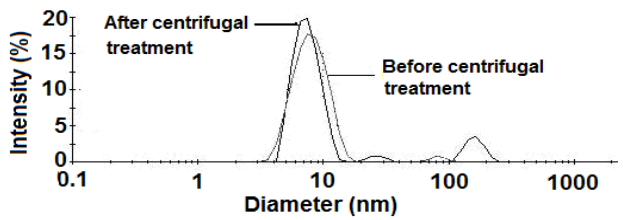

***Figure 6**. Centrifugal stability of the blocked polyurethane acrylate oligomer*

Fixing performance of carbon black ink

Table1 Effect of the fixing temperature on the rubbing and washing fastness of the printed cotton fabrics using the carbon black ink [a].

Temperature (°C)	Rubbing fastness (grade)		Washing fastness (grade)	Handle feeling
	Dry	Wet		
80	2-3	1-2	1-2	Very soft
90	2-3	1-2	2	Very soft
100	3	2	2	Soft
110	3	2	2-3	hard

[a]Note: amount of the blocked polyurethane acrylate oligomer 3%, baking time 5 min.

Table 1 shows that the rubbing and washing fastness of the printed cotton fabrics is improved with an increase of the baking temperature, and reached to the maximum when the baking temperature was higher than 100°C. The reason was that the end groups of the blocked polyurethane acrylate oligomer can not leave and produce –NCO at low temperature, and therefore, no cross linking was taken place, which resulted in a poor color fastness. On the contrary, the cross linking will occur for –NCO groups producing from the blocked polyurethane acrylate oligomer at high temperature.

Table2 Effect of the baking time on rubbing and washing fastness of the printed cotton fabrics using the pigment ink[a].

Time (min)	Rubbing fastness (grade)		Washing fastness (grade)	Handle feeling
	Dry	Wet		
2	2-3	1-2	1-2	Very soft
3	2-3	1-2	1-2	Soft
4	2-3	1-2	2	Soft
5	3	2	2	Soft
6	3	2	2	Hard

[a]Note: amount of the blocked polyurethane acrylate oligomer 3%, baking temperature 100°C.

Table 2 shows that the rubbing and washing fastness of the printed cotton fabrics improved with an increase of the baking time, and reached to the maximum when baking time was higher than 5 min. It is clear that some –NCO may not be released in short time, that is to say, not all the –NCO was taken part in the cross-linking, and therefore, the poor fastness was obtained.

Table3 Effect of amount of the blocked polyurethane acrylate oligomer on rubbing and washing fastness of the printed cotton fabrics using the pigment ink [a].

Amount of the blocked polyurethane acrylate oligomer (%)	Rubbing fastness (grade)		Washing fastness (grade)	Handle feeling
	Dry	Wet		
0	2	1	1	Very soft
3	3	2	2	Soft
6	3	2	2	Soft
12	3	2	2-3	Hard
18	3	2	2-3	Hard

[a] *Note: baking time 5 min, baking temperature 100°C.*

Table 3 shows that the overall fastness of the printed cotton fabrics improved 1 grade when 3% amount of blocked polyurethane acrylate oligomer was added into the carbon black ink. The overall fastness did not increase with further increasing the amount of blocked polyurethane acrylate oligomer. Furthermore, the handle feeling will be damaged for high cross linking when more amount of blocked polyurethane acrylate oligomer was added into the carbon black ink.

Table4 the fastness properties of the colored cotton fabrics with different pigmented black ink [a].

Carbon black ink [a]	Rubbing fastness (grade)		Washing fastness (grade)	Handle feeling
	Dry	Wet		
A	3	2	2	Soft
B	4	4	5	Soft
C	4	3	3~4	Soft

[a] *Note: A refers to pigment carbon black ink; B refers to pigment carbon black ink containing 20% binder; C refers to pigment carbon black ink containing 20% binder and 3% blocked polyurethane acrylate oligomer emulsion.*

In order to further improve the rubbing and washing fastness of the printed cotton fabrics, we also added some binder into the carbon black ink, and the color fastness of the printed cotton fabrics was shown in table 4. It can be seen that the excellent rubbing and washing fastness of the colored cotton fabrics will be obtained when the carbon black ink was prepared with 20% amount of binder and 3% amount of blocked polyurethane acrylate oligomer emulsion. The reason was that the blocked polyurethane acrylate oligomer will release some –NCO groups at high temperature, and the–NCO was rapidly reacted with the –OH in the binder and the cotton fabrics, thus greatly improve the fastness of the colored cotton fabrics.

Table 5 shows that the performance of the carbon black ink containing 20% binder was more close to the carbon black ink containing 20% binder and 3% blocked polyurethane acrylate oligomer emulsion, which indicates that the performance of the black ink was not destroyed when 3% amount of blocked polyurethane acrylate oligomer emulsion was added into the carbon black ink.

Table5 the performance of the pigmented ink containing 3% blocked polyurethane acrylate oligomer emulsion.

Pigmented black ink [a]	η (mpa .s)	σ (N/m)	D (nm)	Stability (%)		B (%)
				R	*FT*	
A	4.76	29.12	168	82	2.1	2.1
B	5.32	28.93	154	81	4.3	4.2
C	5.74	29.06	149	87	4.3	4.2

[a] *Note: A refers to pigment carbon black ink; B refers to pigment carbon black ink containing 20% binder; C refers to pigment carbon black ink containing 20% binder and 3% blocked polyurethane acrylate oligomer emulsion.*

Conclusions

Aqueous blocked polyurethane oligomer emulsion as an effective cross linking agent can be synthesized from isophorone diisocyanate (IPDI) and polyethylene glycol (PEG) using sodium bisulfite as blocking agent. The carbon black ink prepared with 3% amount of aqueous blocked polyurethane oligomer emulsion and 20% amount of binder can effectively improve the rubbing and washing fastness without influence its printing performance.

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Author Biography

Guan Yu received her BE in Light Chemical Engineering from Jiangnan University (2012).Since then she has focused on the development of pigment ink for digital inkjet printing and she will soon study for Master's Degree in Textile Engineering at Jiangnan University