Preparation of Cationic Polyurethane Dispersion and Its Effectiveness as Denim Dye Fixing Agent

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Abstract. The issue encountered by the textile industry is that the colours are fading off, particularly in denim fabric, by constant washing, so fixing agent is needed to enhance the colour fastness of the denim fabric. Polyurethane is one of the promising types of non-formaldehyde dye fixing agents. It has good film covering properties and allows air permeability. In this study, cationic polyurethane dispersions (CPU) were synthesized and applied as fixing agent for sulphur dye denim fabric. Different formulation of CPU were synthesized using isophorone diisocyanate, different molecular weight of polyols, and tertiary amine. Formulated CPU were then analysed using FTIR, zeta potential analyser and viscometer. Zeta potential obtained was in the range of +8.1 mV to +41.7 mV indicates that some of the CPU particles tend to agglomerate and some are stable. After fixing treatment, colour fastness to crocking of the treated fabric has improved. Surface morphology changes were determined by SEM and it shows that smooth finishing fibre surface was obtained in treated black denim fabric.

Introduction
Denim garmen is always a leading segment in textile industry. It has been widely used fabric and most fashionable in the world since mid-19th century. In general, it is made of cotton and coloured using sulfur dye to produce black color. However, this type of dye has low affinity to the cotton fabric. In order to increase the affection of the dye to the denim fabric, dye fixing agent is needed during the finishing stage of the denim production process. In textile industry, color fastness to crocking of the fabric is one of the criteria for quality control. It refers to the fabric resistance to all kinds of forces in the process of processing and use (Fan, et. al, 2016). Black denim fabric famous for poor colour fastness especially at full depths of shade (Giannoulis, et al., 2016).

At present, many types of dye fixing agent has been formulated and commercialized in the market. At the beginning, commercially available dye fixing agent is formaldehyde based. Due to the environmental concern, current research is now moving towards the non formaldehyde dye fixing agent such as polyamine (Jamadhar, et al., 2017) quaternary ammonium cation (Liu, 2015) and commercialized cationic fixing agent (Burkinshaw, et al., 1997; Blackburn, et al., 1998; Sharif, et al., 2008). However, it is still very difficult to promote the wet crocking fastness up to three or above for normal non-formaldehyde fixing agent. Therefore, the research and development of new and high-efficiency dye fixing agents continues to be a thriving study area among textile industrial researchers. In this study, fixing agent for black-dye denim fabric has been developed by preparing cationic polyurethane dispersion because it has unique properties such as water dispersibility, excellent adhesion to many polymers including fabric (Elsayed, et al., 2010).
Methodology

Materials
Polyethylene glycol (PEG: $M_n = 400 \text{ g/mol}, 600 \text{ g/mol}, \text{ and } 1000 \text{ g/mol}$) was supplied by Merck. The diisocyanate used was isophorone diisocyanate (IPDI, mixture of cis- and trans-isomer) was also provided by Merck (Germany). N-methyl diethanolamine and triethanolamine were used as cationomer (internal emulsifier). Acetic acid and bromobutane were used as quartenizing agent. Propylene glycol methyl ether acetate (PGMEA) was used as solvent and DBTDL as catalyst. All chemicals were used as received without further purification.

Synthesis of cationic polyurethane dispersion

Cationic polyurethane were synthesized by reaction of PEG and IPDI. DBTDL (0.02% based on the total reaction was added to the reactor to catalyse the reaction. The prepolymer was synthesised and then extended with N-alkyldiethanolamine and followed by the addition of quartenizing agent. The reaction was carried out in a four necked flask fitted with a reflux condenser, a mechanical stirrer, a thermometer, and solvent. The reaction mixture was stirred for 170 mins at 65-70°C. At the end of the reaction, water was added with vigorous stirring for complete emulsification. The chemical compositions in the preparation of cationic polyurethane shown in table 1. Suggested synthesis route of CPU 42B illustrated in figure 1.

Table 1: shows the chemical compositions of cationic polyurethane

| Sample no. | Type of polyol | Type of tertiary amine | Type of quartenizing agent |
|------------|----------------|------------------------|----------------------------|
| CPU 43B    | PEG 400        | TEOA                   | Bromobutane                |
| CPU 42B    | PEG 400        | NMDEA                  | Bromobutane                |
| CPU 62B    | PEG 600        | NMDEA                  | Bromobutane                |
| CPU 43A    | PEG 400        | TEOA                   | Acetic acid                |
| CPU 42A    | PEG 400        | NMDEA                  | Acetic acid                |
| CPU 103B   | PEG 1000       | TEOA                   | Bromobutane                |

Application of Cationic Polyurethane Dispersion as Fixing Agent

The denim fabrics were subjected to fixation process (Standard crocking). 5 g of denim fabric were treated with 0.2% of CPU solution at 50°C for 20 mins. The treated fabric were then undergo color fastness to crocking test by employing white test cloth squares and follow the AATCC-TM8-2016 standard.

Identification of CPU using Infrared Spectroscopy

The IR spectra of CPU, polyol and IPDI were obtained using a Perkin Elmer Spectrum 100 spectrometer (Quest ATR Diamond 45°). The samples were placed directly on the ATR sampling accessory and all measurements were recorded in the range of 4000 to 400 cm$^{-1}$ with a nominal resolution of 4 cm$^{-1}$.

Zeta Potential Measurement

Zeta potential was determined using a Zetasizer Nano-ZS (Malvern Instruments) via dynamic light scattering principles. It was measured using the electrophoresis principle. 0.1 g of each formulation was diluted with 5 mL of distilled water and measured at 25 °C. The mean zeta potential were obtained from the average of three measurements for each sample.
Viscosity determination

The viscosity of the CPU was determined using NDJ-1 100000mPas Portable Viscometer. The CPU was poured into the sample cup and the viscosity was determined through the measurement of the torque on a vertical shaft that rotates a spindle.

Analysis of Surface Morphology of fabric

Surface morphology of treated and untreated fabric were performed on a Scanning Electron Microscope, Hitachi. The fabric was coated with gold prior to analysis.

Result and Discussion

Preparation of cationic polyurethane dispersion was achieved via different molecular weight of polyethylene glycol and isophorone diisocyanate. Tertiary amine containing diol (triol), have been used to form water-dispersible urethane prepolymer without any significant reaction between the amine and isocyanate groups. The final step involved neutralization and dispersion in water where polyurethane backbones was quartenized by the addition of quartenizing agent.

Identification of Cationic Polyurethane using Infrared Spectroscopy

Figure 2a, b shows that absorption band of NCO at 2247 cm⁻¹ disappeared illustrating the free NCO groups from IPDI completely participated in the reaction. The structure of synthesized CPU was confirmed by FTIR spectra analysis as presented in Figure 3 a, b. The formation of an absorbance peak at 33 46 cm⁻¹ confirmed the formation of urethane by the reaction of polyol and IPDI. An absorbance
peak at 1708 cm\(^{-1}\) corresponded with carbonyl group stretching and the \(-\text{NH}\) bending observed at 1536 cm\(^{-1}\) demonstrating the existence of polyurethane formation.

![IR spectra of IPDI, PEG and CPU](image)

**Figure 2a, b: IR spectra of IPDI, PEG and CPU**

![Surface Morphology of denim fabric](image)

**Figure 3 a, b**

*Surface Morphology of denim fabric*

Surface morphologies of sulfur black denim fabric untreated and treated with CPU were investigated using SEM technique to determine the difference in the denim fiber surface. It is clear that the diameter of the denim became uniform after the treatment. Figure 4(a) shows, crack and blemishes were present on the surface of untreated dyed denim fabric, indicating that the surface of the fiber is coarse and uneven. However, the coarse surface of the untreated dyed cotton fabric is obviously improved after being fixed with CPU. Figure 4 (b) shows that the morphology of the denim fabric is smooth and its seems to be a coating film formed on the surface of the denim fibers.
Colour fastness to crocking

Colour fastness is a term used in the textile industry to describe the resistance of a fabric against colour fading or colour transfer. The colour fastness to crocking is categorised from 1 to 5. The ideal fastness is 5. However in denim industry, the colour fastness to crocking should be at least level 3 for dry crocking and at least level 3-4 for dry crocking (Nilsson & Linstam, 2012). Table 2 shows the colour fastness to crocking of black denim fabric by undergo fixing process with different formulation of CPU on the fabric. It clearly shows that colour fastness to crocking improvement is dependent on the formulation of CPU.

Table 2: Colour fastness to crocking of black denim fabric

| Sample         | Blank | CPU 43B | CPU 42B | CPU 62B | CPU 43A | CPU 42A | CPU 103B |
|----------------|-------|---------|---------|---------|---------|---------|----------|
| Wet crocking   |       |         |         |         |         |         |          |
| fastness Level | 1     | 1       | 3       | 1-2     | 4       | 2-3     | 1        |

In order to determine the effect of the characteristic of CPU formulated to the colour fastness, viscosity and zeta potential of CPU formulated were measured. Figure 5 (a) shows the effect of different molecular weight of polyols to the colour fastness to crocking. From the figure, it is clearly indicate that the shorter the molecular weight of polyols, the higher the level of colour fastness to crocking. Therefore, PEG 400 were selected to be used to formulate CPU for black denim fixing agent.

Colloidal properties of CPU were determined via zeta potential and viscosity determination. The stability of CPU determined by forces among the CPU particles. When the repulsive force is higher than attractive force, the CPU particles will stably disperse into the media. Otherwise, the CPU particles will aggregate together.

Figure 5-7 shows the correlation between colour fastness to crocking improvements to the viscosity and zeta potential of CPU formulated. The higher the viscosity of formulated CPU, the higher the effectiveness it is as fixing agent for black denim fabric. Effectiveness of CPU as fixing agent is varied by varying the cationic compound in the backbone of prepolymer. As demonstrated in figure 6, it shows that triethanol amine produce more effective fixing agent as compared to diethanol amine possibly because it produce branching on polymer chain. Effect of quartenizing agent to the effectiveness as fixing agent is demonstrated in figure 7. It shows that acetic acid is more effective as compared to bromobutane in the preparation of CPU.
Figure 5(a) Level of color fastness to crocking of treated black denim fabric CPU 42B, CPU 62B and CPU 102B and (b) its colloidal properties

Figure 6(a) Level of color fastness to crocking of treated black denim fabric CPU 42B and CPU 43B and (b) its colloidal properties

Figure 7(a) Level of color fastness to crocking of treated black denim fabric CPU 43A and CPU 43B and (b) its colloidal properties
Conclusions

Cationic polyurethane was successfully synthesised via reaction of polyethylene glycol and isophorone diisocyanate incorporated with tertiary amine. Colour fastness to crocking of black dye denim fabric were obviously improved by treating it using CPU 42A and CPU 43B as fixing agent. Zeta potential of CPU synthesised were in the range of +8.1 mV to +41.7 mV. As a conclusion, cationic polyurethane dispersion synthesised in this work is a promising alternative for formaldehyde based dye fixing agent which is harmful to environment as well as human health.

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