

# Preparation and Performance Study of Modified Polyurethane Based Polymer Chemical Dyestuffs

Ruisong Wei

School of Chemical and Biological, Engineering Hechi University, Hechi 546300, China  
 Wrs0905@126.com

In this paper, the chemical dyestuff AzoPU is prepared by the —OH/—NCO reaction of dihydroxyethyl azobenzene (Azo) and polyurethane and its discoloration and heterogeneity are studied. At the same time, the difference between the AzoPU and traditional chemical dyestuffs are compared in thermal performance, color performance and other parameters. The study results show that the content of Azo in AzoPU is about 4%. The polyurethane of AzoPU is not directly connected to the hydroxyl and its internal electronic transition performance is basically the same as that of Azo. The peak absorbance of AzoPU is significantly lower than that of Azo, with a decrease of approximately 72.3%. AzoPU has strong crease resistance and heat resistance, whose K/S value reaches 4.58, 2.9 times that of the K/S value. It demonstrates that AzoPU can significantly enhance the color depth of the dye. AzoPU has strong adhesive force and it is difficult to fall off during the binding process with textiles. It has high content of color body, which can have better color performance under the same amount.

## 1. Introduction

Chemical dyestuffs are one of the most widely used materials in the society and chemical dyestuffs can be found in plastics, food, textiles, machinery, construction and other fields (Tian, 2009). Traditional low-molecular dyestuffs have low utilization rate (below 70%), easy hydrolysis of molecules, difficulty in accelerating and fixing, serious environmental pollution, and it is easily to cause allergic and carcinogenic effect in humans and animals. (Wang et al., 2006). It is currently the top priority for all countries to study a safe, environmentally friendly and pollution-free polymer chemical dyestuffs.

Azobenzene-polyurethane polymer dye (AzoPU) is a new type of chemical macromolecular dyestuff developed in recent years (Briquet et al., 2006; Qiu et al., 2010; Hurt et al., 2001). The azobenzene has excellent light stability, but thermal decomposition is easily to occur at high temperature (Bandara and Burdette, 2012; Han et al., 2011; Mahimwalla et al., 2012). The azobenzene can be connected to the polyurethane polyurethane to form a stable copolymerized compound, which can effectively improve most of the defects in azobenzene (Chen et al., 2015; Chen et al., 2015; Tanaka and Ueda, 2004).

The azobenzene-polyurethane macromolecular dyestuffs have been proposed for a relatively short period of time and there lack sufficient research on their key parameters such as color performance, crease resistance and heat resistance in various fields (Lee et al., 2006; Kim et al., 2003; Zhu et al., 2008). In this paper, the chemical dyestuff AzoPU is prepared by the —H/—NCO reaction of dihydroxyethyl azobenzene (Azo) and polyurethane and its discoloration and heterogeneity are studied. At the same time, the difference between the AzoPU and traditional chemical dyestuffs are compared in thermal performance, color performance and other parameters (Shevchenko et al., 2013; Vijayakumar et al., 2011). The research conclusions can provide a theoretical reference for the preparation and application of new polymer chemical dyestuffs.

## 2. Test materials and methods

Test raw materials: diisocyanate, polycarbonate diol, dihydroxyethyl aniline, methyl diethanolamine, aniline, NaNO<sub>3</sub>, sodium acetate, HCl, HAc, C<sub>2</sub>H<sub>5</sub>OH, plain cotton cloth.

Test equipment: infrared spectrometer, spectrophotometer, color matching color instrument, digital microscope, scanning electron microscope, vacuum drying oven.

Figure 1 shows the production of dihydroxyethyl azobenzene.

On the basis of Figure 1, the azobenzene-polyurethane macromolecular dyestuff is further prepared and the preparation process of AzoPU is shown in Figure 2. It is necessary to perform preprocessing before the preparation to remove water and dry the isocyanate group and the polycarbonate diol respectively. The reactants are sequentially placed into the flask and the reaction lasts for 2.5 hours at 80°C. Finally, the reaction product was distilled and dried.

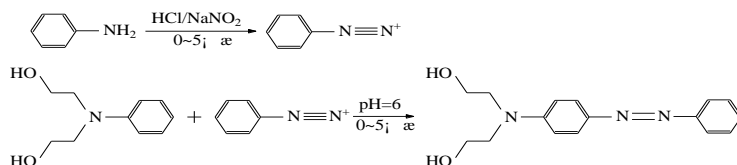


Figure 1: Preparation process of dihydroxyethyl azobenzene

The performance test method for the polymer chemical dyestuff is as follows:

Infrared spectrum and visible spectrum analysis: the prepared AzoPU is analyzed using the infrared spectrometer and the test range is 3500-5000/cm. The visible spectrum test uses the spectrophotometer with a test range of 150-800 nm.

The color performance is determined using the color measurement value; the crease resistance uses the fabric crease elasticity to measure the fold rate of the dyestuff under quick and slow shot.

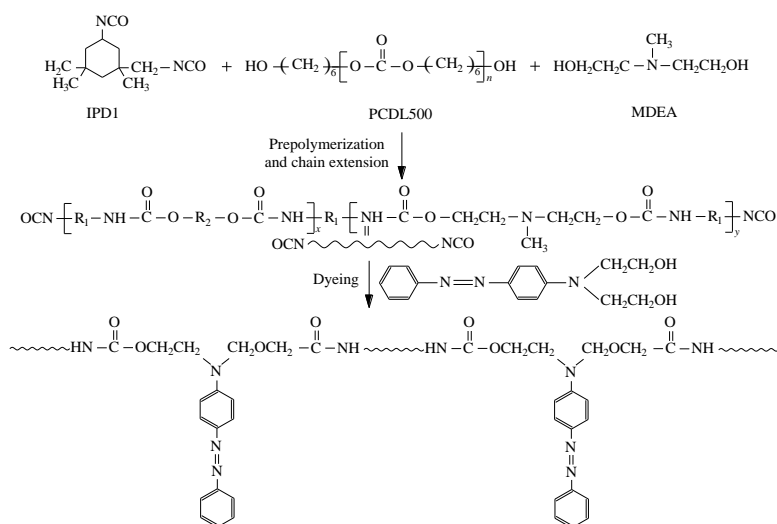


Figure 2: Preparation process of AzoPU

### 3. Test results and analysis

#### 3.1 Structural characterization of azobenzene-polyurethane polymer dyestuff

Figure 3 shows the infrared characterization of azobenzene-polyurethane polymer dyestuff (shown in figure b) while a is the infrared spectrum of azobenzene. It can be seen from the a curve in the figure that the stretching vibration peaks of -CH<sub>2</sub> and -OH occur at 2890/cm and 3448/cm respectively; the stretching peaks of dinitrogen and benzene ring occur at the 1519/cm and 1596/cm respectively. From the b curve, the stretching vibration peaks of C—O and N—H occur at 1248/cm and 3319/cm respectively, and the dinitrogen and benzene ring stretching vibration peaks occur at the same position as azobenzene at 1521/cm and 1597/cm respectively. This shows that azobenzene-polyurethane macromolecular dyestuff has been completely prepared.

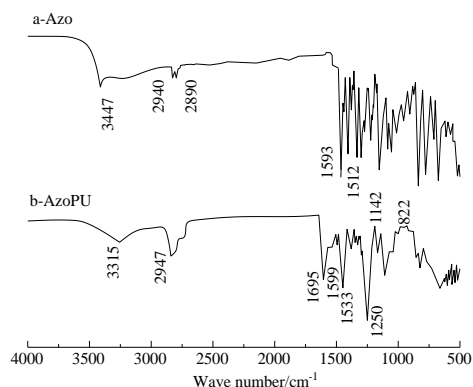


Figure 3: Infrared characterization of azobenzene-polyurethane polymer dyestuff

Figure 4 shows the NMR characterization curves of Azo and AzoPU. It can be seen from the figure that the shift peak at 7 ppm in AzoPU represents the benzene ring proton in Azo; the shift peak at 2.21 ppm is the chemical shift associated with polycarbonate diol; the shift peak at 1.46 ppm represents the chemical shift related to isophorone diisocyanate. The NMR results also indicate that AzoPU has been successfully prepared.

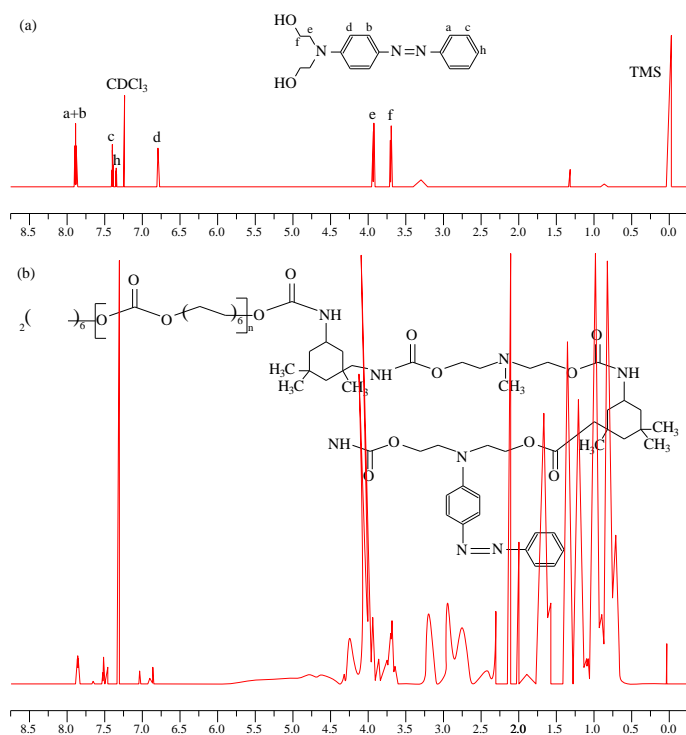


Figure 4: NMR characterization of Azo and AzoPU

### 3.2 Thermogravimetric analysis of azobenzene-polyurethane polymer dyestuff

The thermogravimetric change of azobenzene, azobenzene-polyurethane polymer and blank polyurethane is further analyzed and the results are shown in Figure 5. Figure 5(a) shows the thermal weight loss of three substances and Figure 5(b) analyzes the percentage of weight loss.

It can be seen from the figure that there is thermal decomposition in Azo only at 200-400°C throughout the process and the weight loss rate reaches 80%, corresponding to the temperature of 300°C. Blank polyurethane loses about 5% of its mass before 200°C. The main weight loss stage of AzoPU and blank polyurethane is between 250-450°C and the reason for the weight loss of AzoPU at this stage is mainly caused by the breakage of the azo group on the polyurethane.

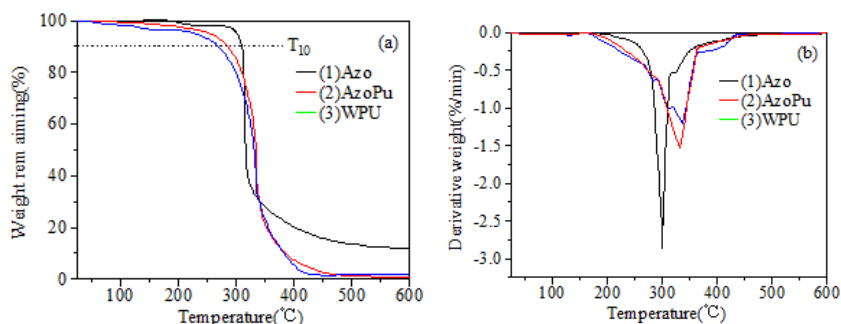


Figure 5: Thermogravimetric analysis of Azo, Azopu and blank polyurethane

### 3.3 Color performance of azobenzene-polyurethane macromolecular dyestuff

Figure 6 shows the absorbance curve of the azobenzene solution and the corresponding fitting equation is obtained through the test of the absorbance of the azobenzene solution. As it can be seen from the figure that the content of Azo in the azobenzene-polyurethane macromolecular dyestuff is about 4%.

Figure 7 shows the visible spectrum of Azo and AzoPU. It can be seen from the figure that the peak absorbance of AzoPU and Azo is between 400-430 nm, indicating that there is no color change in the AzoPU synthesized in this paper. This is due to the fact that the polyurethane of AzoPU is not directly connected to the hydroxyl and the electronic transition within the AzoPU is not substantially affected. However, the peak absorbance of AzoPU is significantly lower than that of Azo, which reduces by about 72.3%.

Figure 8 shows the application of Azo and AzoPU to cotton fabrics to compare their color parameters. As it can be seen from Figure that the K/S value of the original azobenzene on the maximal absorption wave on the textile is 1.56 while the corresponding K/S value of the AzoPU prepared in this paper reaches 4.58, which is 2.9 times that of azobenzene, indicating that the AzoPU prepared in this paper can significantly enhance the color depth of the dyestuff and the dyestuff color is also more abundant. This is due to the fact that the AzoPU prepared has a strong binding force and thus it is difficult to fall off during the binding process of the textile. It also has large amount of color body and can thus have better color performance under the same amount.

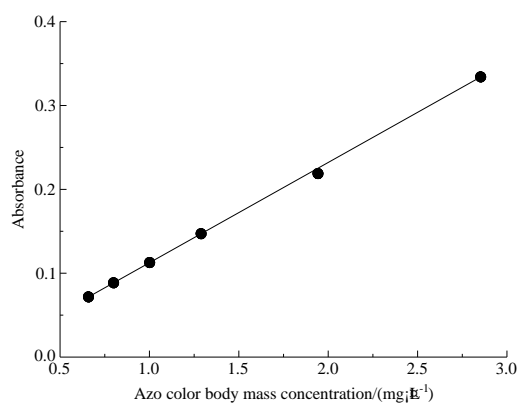


Figure 6: Absorbance curve of Azo solution

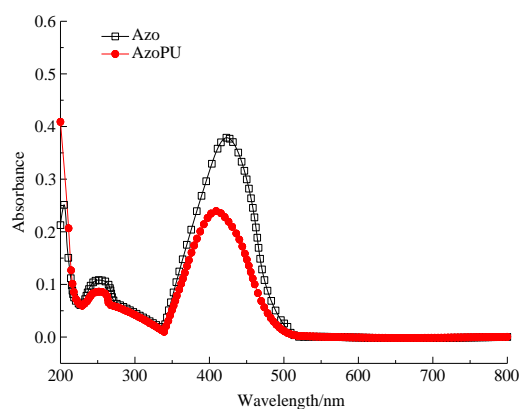


Figure 7: Visible spectrum curve of Azo and AzoPU

### 3.4 Crease resistance and heat resistance of azobenzene-polyurethane polymer dyestuff

Figure 9 shows the crease resistance analysis of Azo and AzoPU and in this figure, a blank textile is set as a comparison. It can be seen from the Figure that the crease angle of the quick and slow shot of the blank textile fabric is  $110^\circ$  and  $136^\circ$  respectively. The two indexes of the Azo textile fabrics increase by about 35% compared to the blank textile fabrics and the two indexes of AzoPU textile fabrics increase by approximately 69% compared to blank textile fabrics. The calculation results of Figure 9 demonstrate the strong crease resistance performance of the azobenzene-polyurethane polymeric dyestuff prepared in this paper. For the combination of the original azobenzene and polyurethane, the intermolecular force between the two is very strong, which is very difficult to fall off after filming on the fiber surface, so that the resilience of the cotton fabric is significantly enhanced.

Figure 10 shows the heat resistance of the Azo and AzoPU coating and the blank cotton fabrics are selected for comparison. As it can be seen from the figure that the thermal mobility of the Azo and AzoPU coating is 11% and 5% respectively. After applying the AzoPU prepared in this paper on the textile, the staining phenomenon has been significantly improved compared to the blank cotton. The combination of azobenzene and polyurethane can effectively limit the mobility of the dyestuff. The AzoPU reacts with the hydroxyl contained on the cotton cloth to generate hydrogen bonds, which can effectively enhance the heat resistance of the dyestuff.

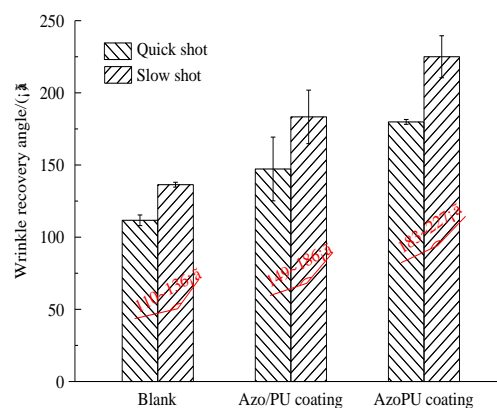
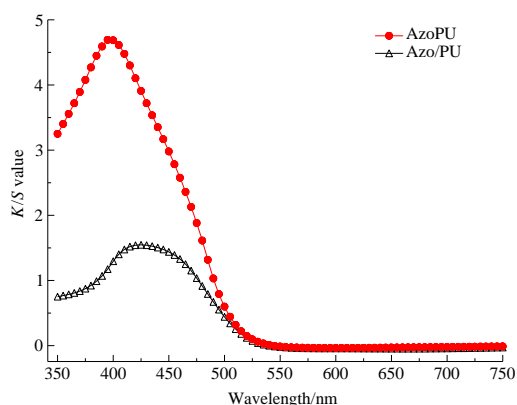


Figure 8: K/S curve of the wave absorption of coated fabrics of Azo and AzoPU

Figure 9: Analysis of the crease angle of coated fabrics of Azo and AzoPU

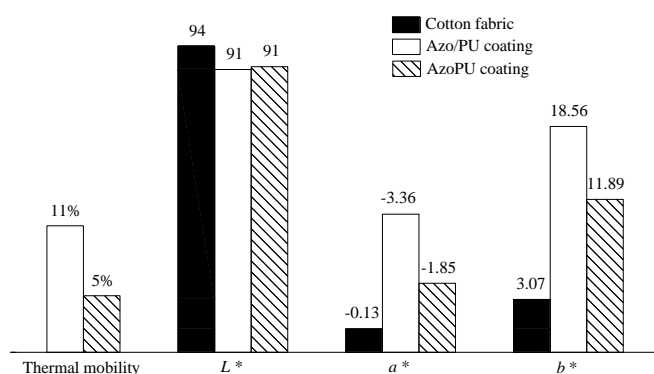


Figure 10: Heat resistance of Azo and AzoPU coating

#### 4. Conclusion

In this paper, the chemical dyestuff AzoPU is prepared by the —OH/—NCO reaction of dihydroxyethyl azobenzene (Azo) and polyurethane and its discoloration and heterogeneity are studied. At the same time, the difference between the AzoPU and traditional chemical dyestuffs are compared in thermal performance, color performance and other parameters. The findings are as follows:

(1) The main weight loss stage of AzoPU is 250-450°C. The weight loss is due to the breakage of azo groups on the polyurethane. The content of Azo in AzoPU is about 4% and the hydroxyl of AzoPU is not directly connected to the polyurethane, so the electronic transition in AzoPU is not substantially affected. However, the peak absorbance of AzoPU is significantly lower than that of Azo, which reduces by about 72.3%.

(2) Azobenzene-polyurethane polymer dyestuff has strong crease resistance and heat resistance. The K/S value of AzoPU reaches 4.58, which is 2.9 times higher than that of azobenzene, indicating that the AzoPU can significantly enhance the color depth of the dyestuff. AzoPU has strong adhesive force and it is difficult to fall off during the binding process of textile fabrics. It also has large amount of color body and can thus have better color performance under the same amount.

## References

- Bandara H.M., Burdette S.C., 2012, Photoisomerization in Different Classes of Azobenzene, *Chemical Society Reviews*, 41(5), 1809-1825, DOI: 10.1039/c1cs15179g
- Briquet L., Vercauteren D.P., Perpète E.A., Jacquemin D., 2006, Is Solvated Trans -Azobenzene Twisted or Planar, *Chemical Physics Letters*, 417(1), 190-195, DOI: 10.1016/j.cplett.2005.09.119
- Caihong C., Yang Z.N., Qiu F.X., Ye F.Y., Cao G.R., Guan Y.J., 2015, Novel Three Chiral Azobenzene Polyurethanes: Preparation, Optical Properties and Simulation Comparisons of Two Different Polymeric Thermo-optic Switches, *Journal of Nonlinear Optical Physics & Materials*, 24(03), DOI: 10.1142/s0218863515500289
- Chen C., Yang Z., Da Z., Qiu F., Ye F., Cao G., 2015, Novel Chiral Azobenzene-containing Polyurethanes: Synthesis, Optical Properties and Simulation Comparison of Two Kind of Polymeric Thermo-optic Switches, *Journal of Polymer Research*, 22(10), 1-11, DOI: 10.1007/s10965-015-0831-2,
- Han M., Honda T., Ishikawa D., Ito E., Hara M., Norikane Y., 2011, Realization of Highly Photoresponsive Azobenzene-functionalized Monolayers, *Journal of Materials Chemistry*, 21(12), 4696-4702, DOI: 10.1039/c0jm03697h
- Hurt C., Thomas B., Burn D., Hindle J., Landau S., Samuel M., 2001, Synthesis and Characterization of Some Azobenzene Polyurethane Cationomers, *Acta Scientiarum Human & Social Sciences*, 18(1), 97-102.
- Kim M.R., Kim P.S., Kang E.H., Ha C.S., Lee J.K., 2003, Syntheses and Properties of Polyurethanes Containing Side-chain Azobenzene Groups, *Polymer International*, 52(5), 658-663, DOI: 10.1002/pi.931,
- Lee J.K., Park S.W., Lee J.W., Kim M.R., 2006, Synthesis, Molecular and Optical Characterization of Polycarbonates Containing Azobenzene Side-chains, *Polymer International*, 55(8), 849-853, DOI: 10.1002/pi.2019
- Mahimwalla Z., Yager K.G., Mamiya J.I., Shishido A., Priimagi A., Barrett C.J., 2012, Azobenzene Photomechanics: Prospects and Potential Applications, *Polymer Bulletin*, 69(8), 967-1006, DOI:10.1007/s00289-012-0792-0
- Qiu F., Zhang W., Yang D., Zhao M., Cao G., Li P., 2010, Synthesis, Characterization, and Thermo-optical Properties of Azobenzene Polyurethane Containing Chiral Units, *Journal of Applied Polymer Science*, 115(1), 146-151, DOI: 10.1002/app.30948
- Shevchenko V.V., Sidorenko A.V., Bliznyuk V.N., Tkachenko I.M., Shekera O.V., Smirnov N.N., 2013, Synthesis and Properties of Hydroxylated Core-fluorinated Diamines and Polyurethanes Based on Them with Azobenzene Nonlinear Optical Chromophores in the Backbone, *Polymer*, 54(24), 6516-6525, DOI: 10.1016/j.polymer.2013.09.053
- Tanaka M., Ueda S., 2004, Synthesis, Thermal and Optical Properties of Polyurethanes Containing the Azobenzene Derivatives in the Side Chains, *Kōbunshi Ronbun Shū*, 61(5), 289-294, DOI: 10.1295/koron.61.289
- Tian L., 2009, Review and Prospects of Dyestuffs and Organic Pigments Sector, *China Chemical Reporter*, (9), 17-19.
- Vijayakumar C., Balan B., Kim M.J., Takeuchi M., 2011, Noncovalent Functionalization of Swnts with Azobenzene-containing Polymers: Solubility, Stability, and Enhancement of Photoresponsive Properties, *Journal of Physical Chemistry C*, 115, 4533-4539, DOI: 10.1021/jp111248r
- Wang J.X., Zhang S.F., Tang B.T., Yang J.Z., 2006, Application of Polymeric Dyes in Textile Fields, *Dyestuffs & Coloration*, 899-906.
- Zhu Z., Li Q., Zeng Q., Li Z., Li Z., Qin J., 2008, New Azobenzene-containing Polyurethanes: Post-functional Strategy and Second-order Nonlinear Optical Properties, *Dyes & Pigments*, 78(3), 199-206, DOI: 10.1016/j.dyepig.2007.11.006