

Polyurethane having Dye Structure in its Backbone

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1. INTRODUCTION

Polyurethane (PU) has been widely used in textile industry, especially in manufacturing artificial leather because of its good chemical and physical properties[1]. But, artificial leather dyed with disperse dyes often exhibits poor wash fastness probably due to migration of disperse dye from PU. When PU is used as a resin for artificial leather, PET fabric is impregnated with PU solution and then it is dyed with disperse dyes. PU is so hydrophobic that it has affinity to the hydrophobic disperse dye. Hence, disperse dye molecules are absorbed not only on PET but also on PU during dyeing process. The disperse dyes staining PU have been recognized as the main reason for low wash fastness of the dyed artificial leather[2,3]. Careful selection of disperse dye and appropriate reduction clearing can improve the wash fastness of artificial leather. Coloration of PU with pigment whose color is very similar to a disperse dye for PET is frequently adopted in dye-house to secure high level of wash fastness.

The purpose of this study is to synthesize PU having dye structure in its backbone and to characterize its various properties.

2. EXPERIMENTAL

All chemicals used in the synthesis and analysis were laboratory grade reagents. Three dyes, whose chemical structures are shown in Figure 1, were synthesized and purified by the standard procedures.

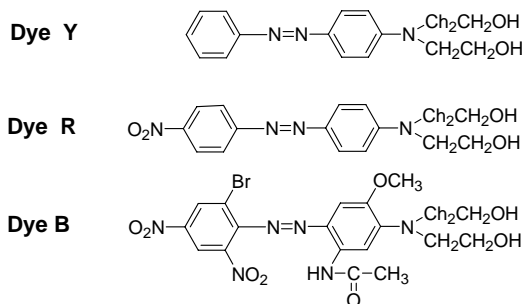


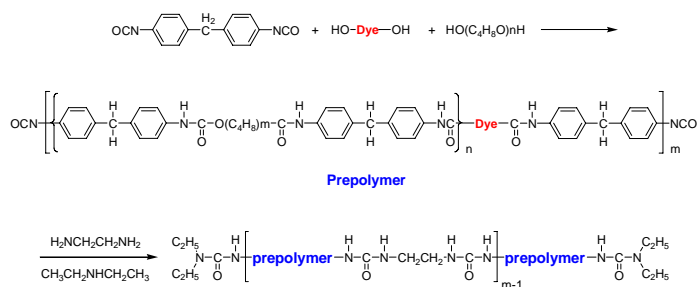
Figure 1. Chemical structure of dyes

The colored prepolymers were prepared by the reaction of 4,4'-methylene-bis(phenyl isocyanate) (MDI) with poly(oxytetramethylene) oxide (PTMG) and dyes having two hydroxyl groups at 80 °C for two hr. The colored PU was obtained by the addition of ethylene diamine (EDA, chain extender) and diethylamine (DEA, chain terminator) at 50 °C into the colored prepolymer diluted with dimethyl acetamide. Synthetic method for preparing colored PU is described in Scheme 1.

Table 1. Composition of the colored PU

PU	PTMG	Dye	MDI
Standard	75.00mmol	-	127.50mmol
PU-R1	73.75mmol	1.25mmol	127.50mmol
PU-R2	72.50mmol	2.50mmol	127.50mmol
PU-Y2	72.50mmol	2.50mmol	127.50mmol
PU-B2	72.50mmol	2.50mmol	127.50mmol
PU-R3	70.00mmol	5.00mmol	127.50mmol
PU-R4	65.00mmol	10.00mmol	127.50mmol

The colored prepolymer and PU were analyzed on FTIR (Jasco 300E), DSC (Du Pont, DSC-2010), tensile property tester (UTM Lloyd LR50K), and Spectrophotometer (Color-Eye 3100).



Scheme 1. Synthetic route of the colored PU.

3. RESULTS AND DISCUSSION

Chemical structure of the synthesized PU were confirmed by the extinction of NCO peak at 2420 cm^{-1} , and by the existence of -NH-, -C=O, -COO-, -CNH- peaks at 3325, 1730, 1530, 1450 cm^{-1} respectively, as shown in Figure 2.

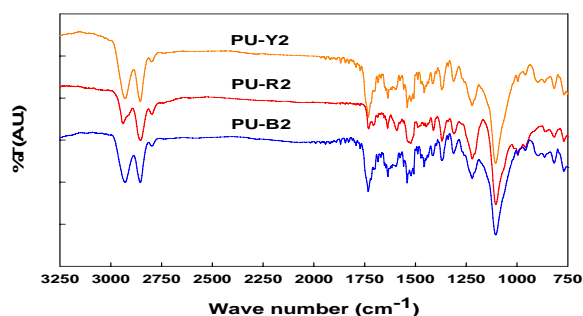


Figure 2. IR spectra of the colored PU.

The crystallization temperature, heat of crystallization, melting point, and heat of melting were measured and listed in Table 2. The crystallization temperature increased in the order of PU-B2 > PU-R2 > PU-Y2. These results indicated that as the molecular weight of the dye increased the tendency of crystallization decreased due to steric hindrance caused by the dye molecule.

Table 2. Thermal properties of the colored PU

PU	Tc(°C)	ΔH_c (J/g)	Tm(°C)	ΔH_m (J/g)
PU-Y2	-17.18	24.62	20.53	34.34
PU-R2	-18.80	23.50	20.23	33.38
PU-B2	-19.84	23.88	20.94	33.99

Mechanical properties of the colored PU were measured to elucidate effect of the amount of dye molecule, and listed in Table 3. As the amount of added dye increased, the tensile strength and elongation at break decreased, but modulus increased. It is generally accepted that the addition of the third component during polymerization results in the deterioration of mechanical properties. The dye molecule might hinder the formation of compact micro structure of the polymer.

Table 3. Mechanical properties of the colored PU

PU	Tensile strength(MPa)	Modulus	Elongation at break(%)
Standard	55.97	125.35	558
PU-R1	55.45	128.06	541
PU-R2	55.20	131.74	523
PU-R3	55.17	137.38	502
PU-R4	54.29	141.53	477

Figure 3 shows color coordinates of PU films. They were made by mixing three component colored PU such as PU-R2, PU-Y2, PU-B2. Value of L* decreased because of the subtractive color mixing. Values of a* and b* changed according to mixing ratio of the three component colored PU. The color

gamut, which is achieved by mixing the three component colored PU, is designated as the triangle in Figure 3.

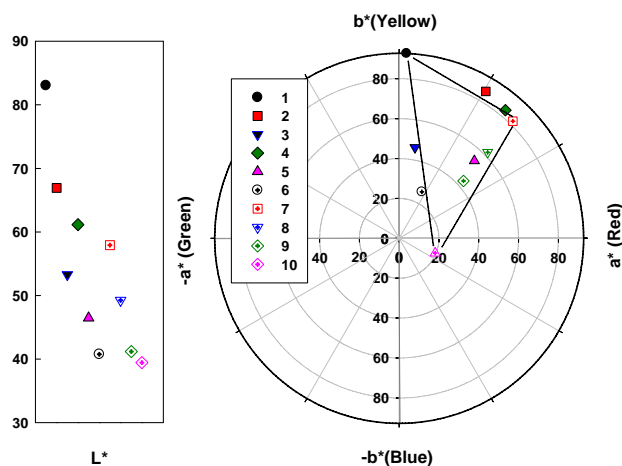


Figure 3. Color coordinate of PUs prepared by mixing the three component colored PU.

4. CONCLUSIONS

It was possible to produce the colored PU by introducing dye molecules which had two hydroxyl groups into the backbone of PU. Thermal and mechanical properties of the colored PU did not change significantly. It was also possible to produce new color by combining three component colored PU at appropriate ratios.

5. REFERENCES

- [1] D. Y. Kim, "Polyurethanes: PU Science & Technology", The Polyurethane Society of Korea, 2006.
- [2] H. F. Qian and X. Y. Song, *Dyes and Pigments*, 74, 672-676(2007).
- [3] J. H. Park and S. D. Kim, *Textile Science and Engineering*, 45(3), 186-191(2008).