Modified Polyurethane with a Covalent Bond of Dye Molecule

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ABSTRACT: In this article, we have successfully synthesized polyurethanes (PUs) with a covalent bond of dye molecule via a coupling agent of epichlorohydrin. The structure is proven by infrared (IR) spectra, which exhibits the absorption peak of dye molecule, as we expected. The dye-grafted polyurethanes were used to evaluate their inherent viscosity, mechanical, and thermal properties and, also, their dyeing behavior. For the inherent viscosity than those without grafting of the dye molecule. The tensile strength is found to decrease with the grafted PUs. But the elongation at break is increased with the grafting of the dye molecule due to the further separation of intermolecular distance of the grafted PUs. But the elongation at break is increased with the grafting of dye molecule exhibit higher T_gh than those without dye molecule. However, their T_gs and T_ms of soft segment between dyed and undyed PU seem to be similar. For dye migration property, the PUs with the grafting of dye molecule are proven to be much lower thermal migration values (Mp%) than those of simple mixing of PU and dyestuff. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 245–253, 1999

Key words: polyurethane; grafting of dye; disperse dye

INTRODUCTION

Polyurethane (PU) is a thermoplastic rubber that comprises a repeating hard and soft segments; therefore, it possesses good mechanical properties, such as medium tensile strength and high elongation. It is used widely in synthetic leather, fiber, and adhesive.^{1–8} For a colored PU leather, it is mostly made by nonwoven fabrics coated with a mixture of pigment and PU resin. The color is dull, with a lack of brightness and, also, poor rubbing resistance. In addition, the elastic PU fiber is usually dyed with an acid dye or a disperse dye at a high temperature of 90–100°C and a long time of 50–60 min.^{9–12} It wastes energy and time. In this article, we try to synthesize polyurethanes

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(PUs) with a covalent bond of dye molecule via a coupling agent of epichlorohydrin. The mechanical, thermal, and dye migration properties of the dye-grafted PU are studied.

EXPERIMENTAL

Materials

Polytertramethylene glycol (PTMG) with molecular weight of 2000 and 1000 from the Hodotani Co., Japan, and 4,4'-diphenylmethane diisocyanate (MDI), ethylenediamine (EDA), N-(2-hydroxyethyl) ethylene diamine (HEDA), epichlorohydrin, and N,N'-dimethyl formamide (DMF) were used without further purification. Three disperse dyes with amino group of C.I. Disperse Yellow 9, C.I. Disperse Red 4, and C.I. Disperse Blue 19 from Bayer were used for reacting with the modified polyurethane resin, which were also used without further purifi-

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cation. The chemical structure of these three disperse dyes are shown as follows.

Disperse dyes with — NH_2 group (Yellow, Red, and Blue).

1. Y (yellow dye): C.I. Disperse Yellow 9



2. R (red dye): C.I. Disperse Red 4



3. B (blue dye): C.I. Disperse Blue 19



Synthesis of PU Polymer with Hydroxy Side Group

The MDI was dissolved in DMF solvent and poured into the reaction flask; and the tempera-

ture was raised to 65°C under dry nitrogen. Also, the PTMG was dissolved in DMF and added to the flask dropwise. The temperature was raised to 70°C to react for 2 h. The temperature was cooled to 5°C, then EDA or HEDA was dissolved in DMF and added to the flask by drops, and the temperature was increased to 70°C for 0.5 h. The modified (undyed) PU with hydroxyl side groups was therefore synthesized. The reaction scheme is shown as follows.

+ HO
$$\sim$$
 PTMG \sim OH $\xrightarrow{70^{\circ}C 2 \text{ h}}_{\text{DMF}}$
H
OCN \sim (N $\xrightarrow{\text{C}}$ O), \sim NCO

(PU prepolymer with NCO-terminated groups)





(PU polymer with hydroxyl side groups)

 $MDI : PTMG : chain extender (EDA or HEDA) \\ = 4 : 2 : 2 \qquad \dots A type$

Modification of Dye with Epichlorohydrin Coupling Agent

 $\label{eq:mdiscrete} \begin{array}{l} MDI:PTMG:chain\ extender\ (EDA\ or\ HEDA)\\ =5:3:2 \quadB\ type \end{array}$

The dye was first dissolved in DMF solvent in a flask, and then the coupling agent, epichlorohy-

drin, was added dropwise and heated to 50°C for 0.5 h to form a modified dye. The reaction scheme is shown as follows.

$$Dye - NH_2 + \underbrace{O}_{Cl} \xrightarrow{50^{\circ}C \ 0.5 \ h}_{DMF} \\ Dye - NHCH_2CHCH_2Cl \\ | \\OH$$

Dye-NHCH₂CHCH₂Cl

Grafting of the Dye Molecule with the Modified PU

The modified dye solution was first added into the PU solution in reaction flask and the temperature was raised to 60°C for 2 h. The final solution was casted into films and washed with methanol to remove the unreacted dye in film, as follows:



dye-grafted PU

Measurements

Infrared spectra of dyed and undyed PU were obtained by Hitachi Model 260-50 Type, over a range of 700 to 3500 cm⁻¹. Intrinsic viscosity was performed by a Connon Type in a constant temperature water bath at 25°C. And, the value of intrinsic viscosity (η_{inh}) was calculated as $\eta_{inh} = (\ln(t/t_0))/C$, where t_0 is the flowing time of pure solvent; t, the flowing time of polymer solution; and C, a constant (g dL).

Mechanical properties was measured using an Instron Mode 1122 testing instrument at a cramp rate of 20 mm min; a paper extension rate of 10 mm min with the specimen of 50 mm length, 10 mm width, and 0.1-0.2 mm thickness; and a full load of 20 kg.

Differential scanning calorimetry (DSC) was performed by a Du Pont 2200 at a heating rate of 20°C min under a nitrogen atmosphere to obtain the glass transition temperature (T_g) and the melting point.

To evaluate the dye migration of dyed PU, the percentage of migration (Mp%) was used accord-



Figure 1 The glass plate for measuring the dye migration.

ing to the AATCC test method.¹³ The glass plate shown as in Figure 1 was coated with the dyed PU to form a film of thickness of 0.02 cm, then region A is covered with a 9-cm-diameter glass cover, but region B is left uncovered. After being warmed at 60°C for 24 h, the diluted dye concentrations of region A and B in NMP ($10^{-3}M$) were measured by a photometer. The percentage of dye migration $[Mp \ (\%)]$ is calculated as $Mp \ (\%) = [(C_B - C_A)/C_A] \times 100$, where C_A and C_B are the absorbency of the A and B areas, respectively.

RESULTS AND DISCUSSION

Characteristics of Modified Polyurethane

The codes for all PU dyed or undyed polymer films is shown in Table I. Those with an apostrophe (') mean the polymer film dyed in acetone solution at 60°C for 3 h in oven; those with a quotation mark (") indicate a simple mixture of dye and the modified PU in solution.

As shown in Figures 2 and 3, the PU films of undyed A10 and dye grafted A1B were analyzed by the IR spectrophotometer. The characteristic IR absorption peak of 3300 cm^{-1} demonstrates the --- NH stretching vibration, and the --- CH== of stretching vibration of benzyl is observed at 3030 cm^{-1} ; the --CH₂-- is observed at 2940 cm⁻¹. The characteristic absorption of C=O is observed at 1700 cm⁻¹;)C=O of the urea group is observed at 1640 $\,\mathrm{cm^{-1}};$ the aromatic —NH is observed at 1600 cm⁻¹; C—O is observed at 1230 cm⁻¹; and C—O—C of PTMG is observed at 1110 cm⁻¹. Moreover, the dye-grafted PU film (A1B-PU) shows a characteristic absorption peak at 1191- 1150 cm^{-1} . Although the peak is an overlap of -O-CHOH- and CH-NH-C absorptions, but it demonstrates that the dye was grafted onto the modified PU to form a covalent bond.^{14,15}

Inherent Viscosity Analysis

The inherent viscosity of all polymers is listed in Table II. It is found that the inherent viscosity decreases with the presence of grafted dye in PU. The decrement of inherent viscosity in dyegrafted PU (intrinsic viscosity of A10 = 0.78 and A1Y = 0.63) is attributed to two factors. First, the extender in extension reaction of A1Y is HEDA instead of EDA in A10. The reactivity of HEDA is believed to be less than that of EDA; thus, the molecular weight of HEDA-extended PU is low-

Table I Code of All PU Polymer Films

Code	Component Molar Ratio (MDI : PTMG1000 : PTMG2000 : EDA : HEDA)	Dye Used
A10	4:2:0:2:0	None
A1Y	4:2:0:0:2	Yellow
A1R	4:2:0:0:2	Red
A1B	4:2:0:0:2	Blue
A20	4:0:2:2:0	None
A2Y	4:0:2:0:2	Yellow
A2R	4:0:2:0:2	Red
A2B	4:0:2:0:2	Blue
B10	5:3:0:2:0	None
B1Y	5:3:0:0:2	Yellow
B1R	5:3:0:0:2	Red
B1B	5:3:0:0:2	Blue
B20	5:0:3:2:0	None
B2Y	5:0:3:0:2	Yellow
B2R	5:0:3:0:2	Red
B2B	5:0:3:0:2	Blue
A1Y′	4:2:0:0:2	Yellow
A1R′	4:2:0:0:2	Red
A1B′	4:2:0:0:2	Blue
A2Y′	4:0:2:0:2	Yellow
A2R'	4:0:2:0:2	Red
A2B'	4:0:2:0:2	Blue
A1Y″	4:2:0:2:0	Yellow
A1R″	4:2:0:2:0	Red
A1B″	4:2:0:2:0	Blue
A2Y″	4:0:2:2:0	Yellow
A2R″	4:0:2:2:0	Red
A2B″	4:0:2:2:0	Blue

An ' indicates modified PU dyed in an acetone solution at 60° C, 3 h in an oven.

 $^{\prime\prime}$ indicates a simple mixture of dye and the modified PU in solution.

ered. Secondly, the decrease of hydrogen bonding (less polar group) and, also, the bulkiness of dye molecule, can separate the dye-grafted PU molecule apart further. Thus, the intrinsic viscosity of the dye-grafted PU (A1Y) is much dropped. On the other hand, the inherent viscosities of A10 and A20 are 0.78 and 1.03, respectively. The value is higher in A20. This suggests that the PU in the A2 series with the PTMG 2000 as soft segment can obtain a higher molecular weight than that in the A1 series with PTMG 1000, resulting in higher intrinsic viscosities. Also from Table II, the hard segment does not affect the intrinsic viscosity of PU much, for instance, with the value of A10 and B10 being 0.78 and 0.75, respectively.



Figure 2 Infrared spectrum of A10 polyurethane film.

Thermal Properties of Dye Grafted Polyurethane

The thermal properties of all types of PU polymers, which were measured by DSC are shown in Figures 4–7 and are listed in Table III. In Table III, it is found that the glass transition temperature of soft segment $(T_g s)$ of type B1 or B2 series with less hard segment contents show a lower

Table II Intrinsic Viscosity of All PU Polymers Code Extender HSC (%)^a $\eta_{\rm inh}$ A10 HEDA 35.9 0.78 A1Y EDA 37.7 0.63 A1R EDA 37.7 0.65A1B EDA 37.7 0.57B10 HEDA 0.75 31.4B1Y EDA 32.7 0.73B1R EDA 32.7 0.74B1B EDA 32.70.70A20 HEDA 21.91.03A2Y EDA 23.20.78 A2R EDA 23.20.81 A2B EDA 23.20.77 B20 HEDA 18.60.98 B2Y EDA 19.6 0.75B2R EDA 19.6 0.78B2B EDA 19.6 0.82

^a HSC (%) is the hard segment content (%).

value than those of A1 or A2. This suggests that a PU with more content of a longer chain of soft segment can form a more soft segment domain, leading to lower T_g s. However, the T_g s are not much affected by the dye grafted; for example, the T_g s of A10 and A1Y are 59.5 and -60.8°C, respec-



Figure 3 Infrared spectrum of A1B polyurethane film.



Figure 4 DSC curve of A1-PU.



Figure 5 DSC curve of B1-PU.

tively. For the glass transition temperature at a hard segment region (T_gh) , it is found that the dye-grafted PU exhibits a higher T_gh . The reason





Figure 7 DSC curve of B2-PU.

believed is that the bulkiness of grafted dye molecule causes higher steric hindrance and, consequently, stiffer and higher T_gh . This result corresponds with the tensile property, which is mainly influenced by the hard segment region. From this, we can conclude that the dye grafted in PU is mostly situated in the hard segment region.

Table III Thermal Properties of Various PU

	HSC	T_{a} s	$T_{\rm m} { m s}$	$T_{r}h$
Code	(%)	(°C)	(°C)	(°C)
A10	35.9	-59.5	_	72.5
A1Y	37.7	-60.8		95.4
A1R	37.7	-59.1	_	
A1B	37.7	-60.6	_	78.1
B10	31.4	-62.6	_	80.1
B1Y	32.7	-60.1	_	88.3
B1R	32.7	-65.4	_	98.5
B1B	32.7	-62.4	_	82.5
A20	21.9	-49.5	5.1	61.0
A2Y	23.2	-50.2	7.6	71.5
A2R	23.2	-48.9	9.8	_
A2B	23.2	-51.3	12.6	61.4
B20	18.6	-53.4	10.1	71.5
B2Y	19.6	-51.7	9.3	
B2R	19.6	-54.0	10.2	77.4
B2B	19.6	-52.8	8.5	79.1



Figure 8 Effect of hard segment content on the tensile strength of all PU polymers.

Also as seen in Table III, the melting temperature of soft segment $(T_m s)$ is only seen in those PU with PTMG 2000, that is, the A2 and B2 series. It is in the range of 5–13°C and decreases with the increasing amount of hard segment, but it seems irregular with the kind of dye grafted. The results of decreasing of T_m s with the amount of hard segment can be explained by the Flory melting temperature equation of copolymer. The PU can be regarded as a copolymer with the hard and the soft segment. The melting temperature of copolymer decreases with the increase of hard segment content as a second component. Besides, it is not clearly seen in the DSC figure for the melting temperature of the hard segment $(T_m h)$. It is believed that the crystallinity region in the PU is not much. As the hard segment content is less than 38%, the $T_m h$ is not manifested.

Mechanical Properties of Dye Grafted Polyurethane

The mechanical properties of all polymers are shown in Figures 8–10 and listed in Table IV. It is found that both the initial modulus and the breaking strength decrease with the presence of grafted dye molecules, especially the strength. On the contrary, the breaking elongation increases with the dye molecule. This demonstrates that as the dye molecule grafted in PU, the domain of hard segment with the hydrogen bonding is partially destroyed, and the crystallinity in the hard segment region is consequently decreased. Thus, both the initial modulus and the breaking strength are decreased. On another hand, since the amount of amorphous in dye-grafted PU is



Figure 9 Effect of hard segment content on the tensile elongation of all PU polymers.

increased, the breaking elongation is promoted. Moreover, as shown in Figure 8, all of the mechanical properties are increased with the amount of hard segment. For example, the strength of A10 and B10 are 36.4 and 25.5 MPa, respectively. The higher value of A10 is owing to its harder segment content (35.9%) than that of B10 (31.4%). Similarly, the tensile strength of A10 with PTMG 1000 also exhibits higher strength than that of A20 with PTMG 2000; they are 36.4 and 31.0 MPa, respectively. Also, as seen in Figure 10, the initial modulus of all PU polymer is also found to increase with the hard segment content.

Thermal Migration Property of Dye Grafted Polyurethane

The results of dye migration in all dyed PU is listed in Table V, it is found that the PU grafted



Figure 10 Effect of hard segment content on the initial modulus of all PU polymers.

with dye molecule via epichlorohydrin as a coupling agent does have a better thermal migration property than that without it. Furthermore, those modified PU dyed with epichlorohydrin modified dye (for example, A1Y') exhibit a better migration property than those with a simple mixture of dye and PU (for example, A1Y''). Thus, it indicates that the PU with a covalent bond of dye molecule can contribute to the best thermal migration property.

CONCLUSIONS

In this study, two different molecular weight of PTMG (1000, 2000), MDI, and EDA or HEDA were employed to synthesize PU copolymers. Those modified PU with HEDA as chain extender could be grafted with the dye molecule via the epichlorohydrin as a coupling agent. From the experimental results, the intrinsic viscosity of dye grafted PU is decreased, and the tensile strength is lowered, but elongation is promoted. Also, the dye-grafted PU exhibits greater T_gh of the hard segment but almost no effect on T_gs and T_ms of the soft segment. This indicates that the dye was grafted mainly in the hard segment region of PU. For the dyeing properties, the dye-grafted PU

Table IVMechanical Properties of Various PUPolymers

Code	HSC (%)	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (MPa)
A10	35.9	36.4	590	18.6
A1Y	37.7	19.0	685	17.0
A1R	37.7	20.1	652	18.4
A1B	37.7	15.7	704	16.7
B10	31.4	25.5	659	17.0
B1Y	32.7	21.3	710	16.5
B1R	32.7	16.2	712	16.2
B1B	32.7	20.8	702	16.3
A20	21.9	31.0	635	15.7
A2Y	23.2	13.9	818	14.0
A2R	23.2	15.7	731	15.4
A2B	23.2	13.2	761	12.9
B20	18.6	21.7	614	11.6
B2Y	19.6	17.4	777	10.0
B2R	19.6	16.2	864	9.0
B2B	19.6	21.3	659	10.9

Table VThe Migration Propertiesof Dye-Grafted PU Films

Code	C_A	C_B	<i>Mp</i> (%)
A1Y	0.540	0.556	3.01
A1R	0.805	0.828	2.88
A1B	0.428	0.441	3.13
A2Y	0.511	0.533	4.29
A2R	0.856	0.889	3.89
A2B	0.455	0.474	4.15
B1Y	0.562	0.569	1.12
B1R	0.851	0.853	0.27
B1B	0.468	0.508	0.85
B2Y	0.534	0.548	2.53
B2R	0.901	0.920	2.08
B2B	0.447	0.458	2.37
A1Y'	0.556	0.594	6.80
A1R'	0.799	0.848	6.14
A1B'	0.409	0.432	5.74
A2Y'	0.543	0.585	7.78
A2R'	0.832	0.882	6.06
A2B'	0.424	0.455	7.23
A1Y″	0.527	0.589	11.85
A1R″	0.872	0.986	13.05
A1B"	0.413	0.454	10.03
A2Y″	0.530	0.604	13.89
A2R''	0.893	0.993	11.20
A2B''	0.438	0.492	12.36

An ' indicates modified PU dyed in an acetone solution at 60° C, 3 h in an oven.

 $^{\prime\prime}$ indicates a simple mixture of dye and the modified PU in solution.

does show a low thermal migration property, indicating that the presence of covalent bond between dye and PU can prevent the thermal migration of dye in dyed PU.

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