

Silicon-Containing Anionic Water-Borne Polyurethane with Covalently Bonded Reactive Dye

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ABSTRACT: A silicon-containing water-borne polyurethane (PU) polymer with hydroxyl side groups was synthesized that was stable in basic conditions and also capable of reacting with a reactive dye to form a covalently bonded dye molecule. The silicon-containing anionic water-borne PU prepolymer was synthesized from H_{12} -4,4'-diphenylmethane diisocyanate (H_{12} -MDI), polytetramethylene glycol, polydimethylsiloxane (PDMS), 2,2'-bis(hydroxymethyl) propionic acid (anionic centers), and triethylamine using the prepolymer mixing method. Water was then added to emulsify and disperse the resin to form an anionic water-borne PU prepolymer. *N*-(2-Hydroxyethyl ethylene diamine) (HEDA) was used to extend the prepolymer to form a water-borne PU polymer with a side chain of hydroxyl groups, which can further react with the reactive dye to form a dyed PU. The reactive dye of chlorosulfuric acid esters of sulfatoethyl sulfones can react with the water-borne PU polymer. Behaviors of alkali resistance and

dyeing properties were observed. In consideration of thermal properties, the dye-grafted PU polymers exhibited lower glass-transition temperatures for soft segments and hard segments than those without dye. Concerning mechanical properties, it was found that the modulus and the strength of the dyed PU polymers decreased with grafting of the dye molecule, but elongation at break was increased. The alkali resistance increased with PDMS content. For dye-uptake properties, the percentage of dye grafting was over 90%. Also, the dye-grafted PU exhibited a lower percentage of dye migration than that of polymers with ethylene diamine instead of HEDA as a chain extender, and showed greater colorfastness to light. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2045–2052, 2003

Key words: water-borne polyurethanes; dyes/pigments; covalent bonds; glass transition; mechanical properties

INTRODUCTION

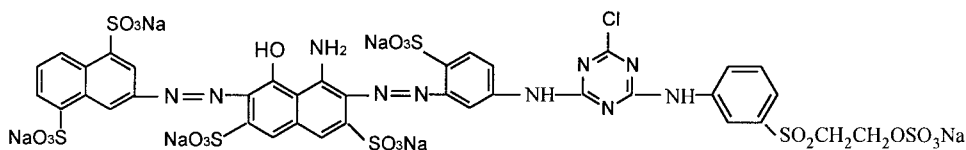
Polyurethane (PU) is a thermoplastic rubber composed of repeating hard and soft segments; it thus possesses good mechanical properties, such as medium tensile strength and high elongation. It is widely used in synthetic leather, fibers, and adhesives.^{1–8} For a colored PU leather, it is mostly made of nonwoven fabrics coated with a mixture of pigment and PU resin. Not only is the color dull, with a lack of brightness, it is also characterized by 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, at a long dyeing time of 50–60 min,^{9–13} thus wasting energy and time. In this study, we synthesized a silicon-containing anionic water-borne PU that was stable in basic conditions and also capable of reacting with a reactive dye to form a covalent bond with the dye molecule. The silicon-containing anionic water-borne PU was synthesized and grafted with the reactive dye to form a dyed PU. The

mechanical, thermal, alkali resistance, and dye migration properties of the dye-grafted PU were studied.

EXPERIMENTAL

Materials

Polytetramethylene glycol (PTMG; molecular weights of 2000 and 1000; Hodotani Co., Japan), 4,4'-methylene bis(isocyanatocyclohexane) (H_{12} -MDI), polydimethylsiloxane (PDMS), ethylenediamine (EDA), *N*-(2-hydroxyethyl) ethylene diamine (HEDA), triethylamine (TEA), 2,2-bis(hydroxymethyl)propionic acid (DMPA), and *N,N'*-dimethyl formamide (DMF) were used without further purification. The reactive dye (Hoechst, Frankfurt/Main, Germany) with sulfatoethyl sulfone series of C.I. Reactive Blue 222 was used for reacting with the modified polyurethane resin, also used without further purification. The chemical structure of the reactive dye is shown as follows:

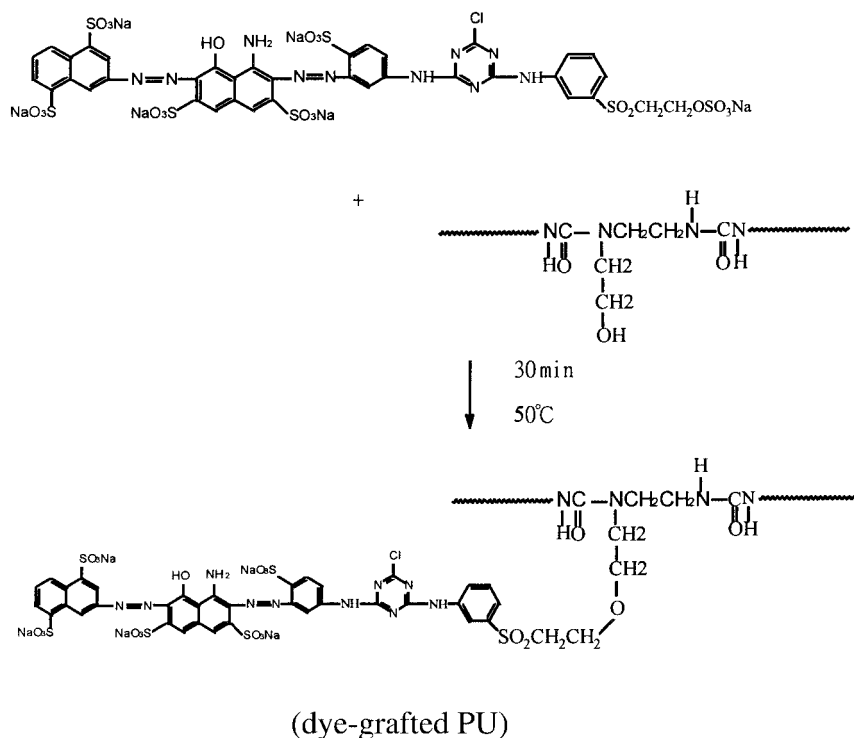


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Grafting of the dye molecule with the anionic-modified PU

The reactive dye was first added to the PU solution in a reaction flask and the temperature was raised to

50°C for 0.5 h under slightly alkaline conditions. The final solution was cast into films and washed with methanol to remove the unreacted dye, as follows:



Measurements

Infrared spectra of dyed and undyed PU were obtained using a Hitachi Model 260-50 spectrometer (Hitachi, Ibaraki, Japan), over a range of 700 to 3500 cm^{-1} . Differential scanning calorimetry (DSC) was performed with a DuPont 2200 thermal analyzer (DuPont, Boston, MA) at a heating rate of 20°C/min under nitrogen atmosphere to obtain the glass-transition temperature (T_g) and the melting point.

Mechanical properties were measured using an Instron Mode 1122 testing instrument at a crosshead speed of 20 mm/min, a chart speed of 10 mm/min (specimens: gauge length, 50 mm; width, 10 mm; thickness, 0.1–0.2 mm), and a full load of 20 kg.

To evaluate the dye migration of dyed PU, the percentage of dye migration [$M_p(\%)$] was used according to the AATCC test method.¹³ The glass plate shown in Figure 1 was coated with the dyed PU to form a film of 0.02 cm thickness, then region A was covered with a 9-cm-diameter glass cover, but region B was left uncovered. After being warmed at 60°C for 24 h, the diluted dye concentrations of regions A and B in NMP (10^{-3} M) were measured by a photometer. The percentage of dye migration was calculated as

$M_p(\%) = [(C_B - C_A)/C_A] \times 100$, where C_A and C_B are the absorbency of the A and B areas, respectively. Colorfastness to a water-cooled xenon-arc lamp light was tested according to AATCC test method 16F-1977. For the alkali resistance measurement, the PU films were vacuum dried at 100°C for 2 h, weighed, put into a 10% NaOH aqueous solution, and heated for 10 min at 90°C. After washing with water, they were neutralized with a 1% acetic acid aqueous solution and water washed again. The samples were then dried at room temperature for 1 day and further dried in an oven at 100°C for 2 h. The percentage weight loss was calculated as $\Delta w_t(\%) = [(w_{t0} - w_t)/w_{t0}] \times 100$, where w_{t0}

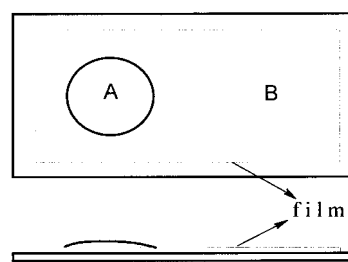


Figure 1 The glass plate for measuring dye migration.

TABLE I
Code of All PU Polymer Films

Code ^a	Component ^b	Molar ratio	Hard segment content ^c (wt %)	Soft segment content (wt %)
WPU1	H ₁₂ -MDI/PTMG(1000)/DMPA/HEDA	4:1.25:1:1.75	52.18	47.82
1A	H ₁₂ -MDI/PTMG(1000)/PDMS/DMPA/HEDA	4:1:0.25:1:1.75	52.18	47.82
1A-B	H ₁₂ -MDI/PTMG(1000)/PDMS/DMPA/HEDA/DYE-1	4:1:0.25:1:1.75:0.2	52.18	47.82
1B	H ₁₂ -MDI/PTMG(1000)/PDMS/DMPA/HEDA	4:1:0.5:1:1.5	47.15	52.85
1B-B	H ₁₂ -MDI/PTMG(1000)/PDMS/DMPA/HEDA/DYE-1	4:1:0.5:1:1.5:0.2	47.15	52.85
1C	H ₁₂ -MDI/PTMG(1000)/PDMS/DMPA/HEDA	4:1:1:1:1	39.14	60.86
1C-B	H ₁₂ -MDI/PTMG(1000)/PDMS/DMPA/HEDA/DYE-1	4:1:1:1:1:0.2	39.14	60.86
1D	H ₁₂ -MDI/PTMG(1000)/PDMS/DMPA/HEDA	4:1:1.25:1:0.75	35.90	64.10
1D-B	H ₁₂ -MDI/PTMG(1000)/PDMS/DMPA/HEDA/DYE-3	4:1:1.25:1:0.75:0.2	35.90	64.10
WPU2	H ₁₂ -MDI/PTMG(2000)/DMPA/HEDA	4:1.25:1:1.75	37.74	62.26
2A	H ₁₂ -MDI/PTMG(2000)/PDMS/DMPA/HEDA	4:1:0.25:1:1.75	37.74	62.26
2A-B	H ₁₂ -MDI/PTMG(2000)/PDMS/DMPA/HEDA/DYE-1	4:1:0.25:1:1.75:0.2	37.74	62.26
2B	H ₁₂ -MDI/PTMG(2000)/PDMS/DMPA/HEDA	4:1:0.5:1:1.5	34.86	65.14
	H ₁₂ -MDI/PTMG(2000)/PDMS/DMPA/HEDA/DYE-1	4:1:0.5:1:1.5:0.2	34.86	65.14
2C	H ₁₂ -MDI/PTMG(2000)/PDMS/DMPA/HEDA	4:1:1:1:1	30.00	70.00
2C-B	H ₁₂ -MDI/PTMG(2000)/PDMS/DMPA/HEDA/DYE-1	4:1:1:1:1:0.2	30.00	70.00
2D	H ₁₂ -MDI/PTMG(2000)/PDMS/DMPA/HEDA	4:1:1.25:1:0.75	27.94	72.06
2D-B	H ₁₂ -MDI/PTMG(2000)/PDMS/DMPA/HEDA/DYE-1	4:1:1.25:1:0.75:0.2	27.94	72.06

^a -B represents blue dye.

^b 1-A, -B, -C, -D: PTMG1000 series; 2-A, -B, -C, -D PTMG2000 series.

A series: component molal ratio of H₁₂-MDI: PTMG: PDMS: DMPA: HEDA = 4:1:0.25:1:1.75.

B series: component molal ratio of H₁₂-MDI: PTMG: PDMS: DMPA: HEDA = 4:1:0.5:1:1.5.

C series: component molal ratio of H₁₂-MDI: PTMG: PDMS: DMPA: HEDA = 4:1:1:1:1.

D series: component molal ratio of H₁₂-MDI: PTMG: PDMS: DMPA: HEDA = 4:1:1.25:1:0.75.

^c Hard segment content (wt %) =
$$\frac{\text{H}_{12}\text{-MDI} + \text{DMPA} + \text{HEDA}}{\text{H}_{12}\text{-MDI} + \text{DMPA} + \text{HEDA} + \text{PTMG}(1000 \text{ or } 2000) + \text{PDMS}(1000)}$$

and w_t are the weight of sample before and after the alkali treatment, respectively.

RESULTS AND DISCUSSION

Characteristics of anionic-modified polyurethane

The codes for all PU dyed or undyed polymer films are shown in Table I. As shown in Figures 2 and 3, the PU films of undyed WPU1, WPU2, and 1A–1D, 2A–2D and dye-grafted 1A-B, 2A-B were analyzed by IR spectrophotometry. The characteristic IR absorption peak of 3350 cm⁻¹ demonstrates the –NH stretching vibration. The characteristic absorption of C=O is observed at 1740 cm⁻¹; the C=O of the urea group is observed at 1640 cm⁻¹; the C–O–C group of PTMG is observed at 1238 cm⁻¹; and the Si–O–Si group of PDMS is observed at 1100 cm⁻¹. Moreover, the dye-grafted PU film (1A-B) shows a characteristic absorption peak at 1160 cm⁻¹, which is the sulfonyl S=O absorption. This demonstrates that the dye was grafted onto the silicon-containing modified PU to form a covalent bond.^{14,15}

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

and 5 and are listed in Table II. In Table II, it is found that the glass-transition temperatures of the soft segment (T_{gs}) of type 1B–1D or 2B–2D series with less hard segment content show a lower value than that of 1A or 2A. This suggests that a PU with longer chains of soft segment and the siloxane group can form more soft segment domains, leading to lower T_{gs} values. However, the T_{gs} is scarcely affected by the grafted dye; for example, the T_{gs} values of 1A and 1A-B are –60.3 and –1.2 °C, respectively. For the glass-transition temperature of a hard segment region (T_{gh}), it is found in Table II that the dye-grafted PU exhibits a higher T_{gh} value. This suggests that the bulkiness of the grafted dye molecule causes higher steric hindrance and, consequently, stiffer and higher T_{gh} . This result corresponds with the tensile strength, which is mainly influenced by the hard segment region. From this, we can conclude that the dye grafted into the PU is mostly situated in the hard segment region.

Also as seen in Table II, the melting temperature of the soft segments (T_{ms}) is seen only in those PUs with PTMG(2000), that is, the 2A–2D series. It is in the range of 10.2–15.2 °C and increases with increasing amounts of hard segments. Besides, it is not clearly seen in the DSC figure for the melting temperature of the hard segment (T_{mh}). It is believed that the crystallinity of the PU is low, especially in the presence of the siloxane group.

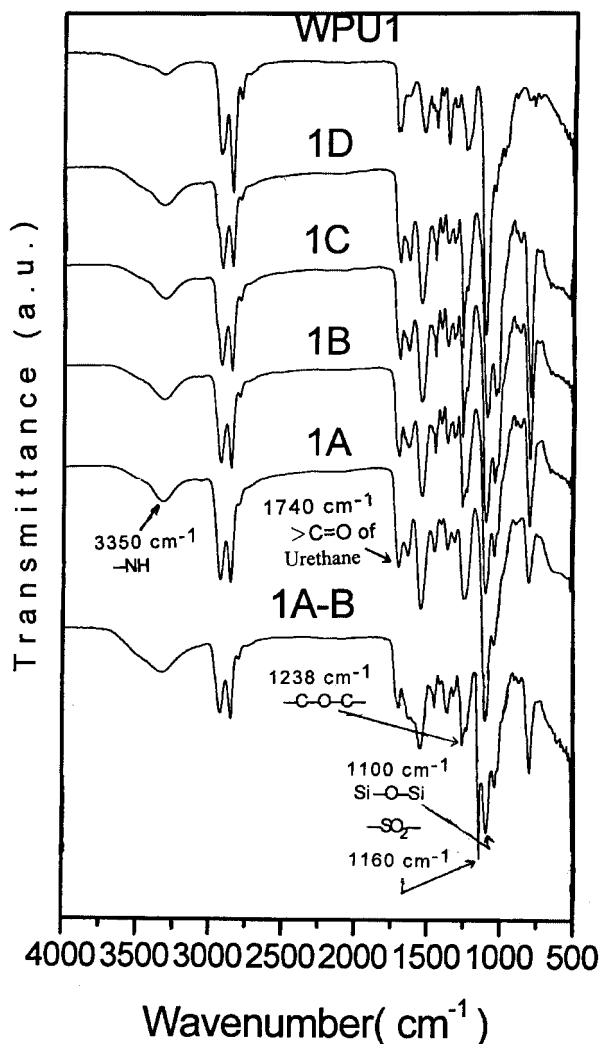


Figure 2 Infrared spectrum of PTMG(1000) series films.

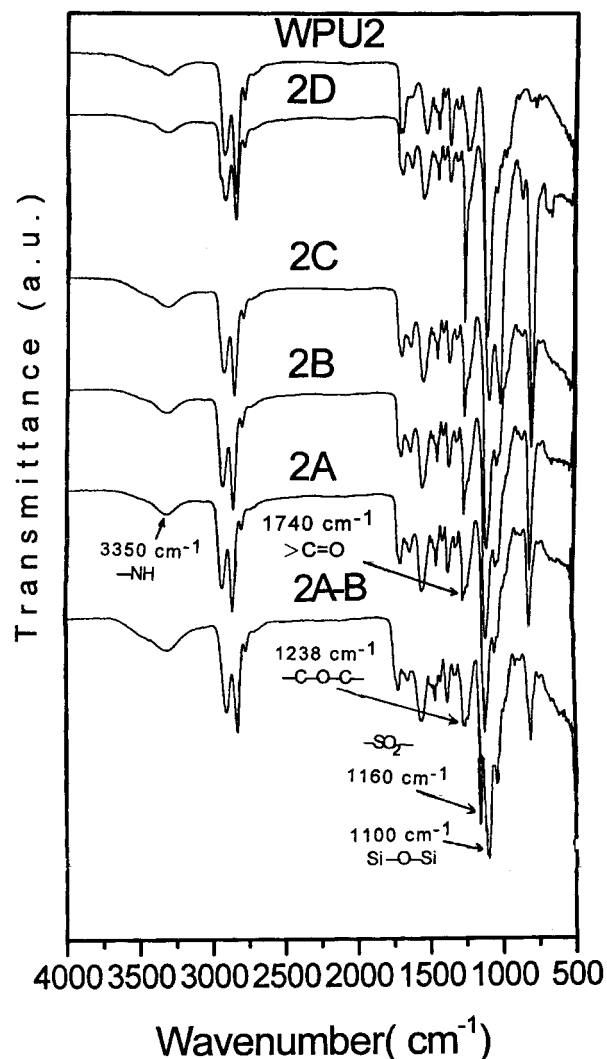


Figure 3 Infrared spectrum of PTMG(2000) series films.

Mechanical properties of dye-grafted anionic polyurethane

The mechanical properties of all polymers are listed in Table III. 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 increasing dye content. This demonstrates that as the dye molecules are grafted into the PU, the domain of hard segments with 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 the other hand, because the amount of amorphous content in the dye-grafted PU is increased, the breaking elongation increases. Moreover, as shown in Table III, all the mechanical properties are improved with increases in the amount of hard segments; for example, the strengths of 1A and 1D are 17.69 and 14.95 MPa, respectively. The higher value of 1A is attrib-

uted to its greater hard segment content (52.18%) than that in 1B (35.90%) and also fewer siloxane groups. Similarly, the tensile strength of 1A with PTMG(1000) exhibits higher strength than that of 2A

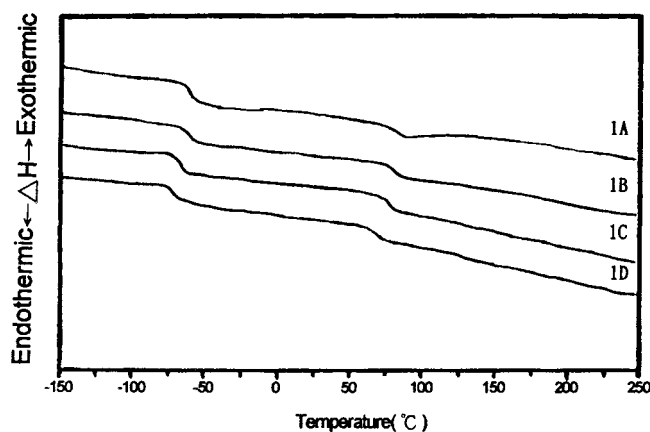


Figure 4 DSC curves of PTMG(1000) series PU.

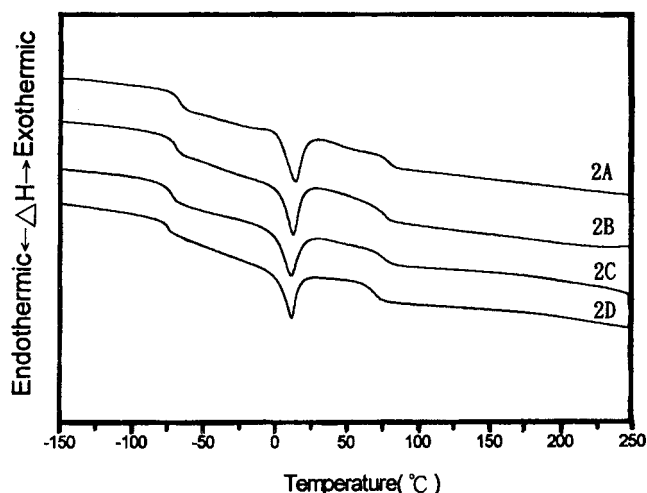


Figure 5 DSC curve of PTMG(2000) series PU.

with PTMG(2000), with values of 17.69 and 16.66 MPa, respectively. Also, as seen in Table III, the initial modulus of all PU polymers is found to increase with hard segment content.

Alkali resistance property of silicon-containing dye-grafted polyurethane

The alkali resistance of the dye-grafted PU film is presented in Table IV, which shows that the percentage weight loss decreases with the presence of the siloxane group. The PU films without the siloxane group (WPU1 and WPU2) show poor alkali resistance, the percentage weight loss values of which were 13.3 and 11.9, respectively. On the contrary, the PU films containing the siloxane group (1A–1D and 2A–2D) show better alkali resistance with percentage weight

TABLE II
Thermal Properties of Various PU Polymers

Code	T_g for soft segment (T_{gs}) (°C)	T_m for soft segment (T_{ms}) (°C)	T_g for hard segment (T_{gh}) (°C)	T_m for hard segment (T_{mh}) (°C)
1A	-60.3	—	84.0	—
1A-B	-61.2	—	94.1	—
1B	-61.0	—	83.1	—
1B-B	-61.3	—	91.7	—
1C	-63.4	—	80.5	—
1C-B	-64.0	—	86.3	—
1D	-64.1	—	78.9	—
1D-B	-64.4	—	84.1	—
2A	-67.7	15.2	77.2	—
2A-B	-68.2	14.3	88.4	—
2B	-68.6	13.8	76.6	—
2B-B	-68.3	14.3	84.6	—
2C	-71.4	12.0	74.1	—
2C-B	-72.5	11.5	79.9	—
2D	-72.5	11.9	73.4	—
2D-B	-72.9	10.3	78.2	—

TABLE III
Mechanical Properties of Various PU Polymers

Code	Initial modulus (MPa)		Tensile strength (MPa)	Elongation at break (%)
	at 300%	at M600%		
1A	5.49	—	17.69	334
1A-B	4.27	—	14.42	395
1B	5.14	—	16.65	363
1B-B	4.43	—	15.31	405
1C	4.57	—	15.20	370
1C-B	4.08	—	14.18	409
1D	4.17	—	14.95	387
1D-B	3.55	—	12.58	433
2A	3.62	—	16.66	543
2A-B	3.01	2.21	13.58	614
2B	3.25	—	13.66	568
2B-B	2.70	1.88	11.52	607
2C	2.54	1.81	10.97	605
2C-B	2.20	1.27	7.85	653
2D	2.22	1.72	10.90	638
2D-B	1.94	1.15	9.18	692

loss values between 1.5 and 2.8. This suggests that the PU polymer with siloxane groups has less surface energy, thus providing the polymer with good water repellancy and preventing the alkali molecule from penetrating into the film, resulting in a better alkali resistance.

Thermal migration and dyeing property of dye-grafted polyurethane

The dye uptake of the dye-grafted PU film was measured by photometer and results are presented

TABLE IV
Alkali Resistance of Various PU Polymers

Code	Before alkali resistance test (g)	After alkali resistance test (g)	Weight loss percentage (%)
WPU1	3.15	2.73	13.3
WPU2	3.27	2.88	11.9
1A	3.07	3.00	2.3
1A-B	3.11	3.02	2.8
1B	3.02	2.94	2.6
1B-B	3.10	3.03	2.2
1C	3.11	3.06	1.6
1C-B	3.15	3.09	1.9
1D	3.10	3.06	1.2
1D-B	3.08	3.03	1.6
2A	3.20	3.12	2.5
2A-B	3.07	2.99	2.6
2B	3.08	3.01	2.2
2B-B	3.09	3.01	2.5
2C	3.11	3.05	1.9
2C-B	3.14	3.07	2.2
2D	3.13	3.08	1.5
2D-B	3.11	3.06	1.6

TABLE V
Grafting Efficiency of Various PU Polymers

Code	Theoretical dye uptake ^a (10 ⁻³ g/wg)	Experimental dye uptake (10 ⁻³ g/wg)	Grafting efficiency ^b (%)
1A-B	90.9	83.1	91.4
1B-B	84.5	78.3	92.7
1C-B	74.2	67.4	90.8
1D-B	69.9	63.7	91.1
2A-B	68.1	61.7	90.6
2B-B	64.5	60.2	93.3
2C-B	58.3	53.1	91.1
2D-B	55.6	50.4	90.6

DYE

$$^a \text{Theoretical dye uptake (g/wg)} = \frac{\text{DYE}}{(\text{H}_{12}\text{-MDI} + \text{PTMG} + \text{PDMS} + \text{DMPA} + \text{TEA} + \text{HEDA} + \text{DYE})}$$

$$^b \text{Grafting efficiency (\%)} = (\text{Experimental dye uptake} / \text{Theoretical dye uptake}) \times 100\%$$

in Table V, which shows that the grafting efficiency (the ratio of experimental dye uptake to theoretical dye uptake) is over 90%. The reason for its inability to reach 100% efficiency is attributed to the steric hindrance of the -OH group in the side chain of the PU polymer. The results of dye migration in all dyed PUs are shown in Table VI. It was found that PUs grafted with reactive dye have better thermal migration than that of ungrafted PUs. Furthermore, the modified PUs dyed with reactive dye (e.g., 1A-B) exhibit better thermal migration than those with EDA instead of HEDA as a chain extender (e.g., 1A-B').¹⁶ This indicates that the PU with covalent bonded dye molecules can contribute to the thermal migration. Moreover, for the light fastness of the dye-grafted PU, as presented in Table VII, it has been found that those using EDA as a chain extender are characterized by poor light fastness of grades 1 and 2.¹⁶ However, the dye-grafted PU with HEDA as a chain extender can reach grades 5 to 6,

indicating that the dye molecule in dye-grafted PU can transfer its energy in the excited state to PU by its covalent bonding with the PU main chain, thus reducing the possibility of dye degradation.

CONCLUSIONS

In this study, two different molecular weights of PTMG (1000 and 2000), PMDS, MDI, and HEDA were employed to synthesize silicon-containing PU copolymers. Those modified with HEDA as a chain extender could be grafted with a reactive dye. The tensile strength was lowered, but elongation increased. Also, the dye-grafted PU exhibited greater T_{gh} of the hard segment, but almost no effect on T_{gs} or T_{ms} of the soft segment. This indicates that the dye was grafted mainly in the hard segment region of the PU. For the alkali resistance and dyeing properties, the dye-grafted PU showed better alkali resistance as the content of siloxane group was increased. The dye-grafted PU also showed low thermal migration, indicating that the presence of covalent bonding between dye and PU can prevent the thermal migration of the dye in dyed PU.

TABLE VI
Migration Properties of Dye-Grafted PU Films

Code ^a	C_A (10 ⁻³ g/wg)	C_B (10 ⁻³ g/wg)	M_p (%) ^b
1A-B	1.003	1.027	2.3
1A-B'	0.989	1.076	8.7
1B-B	0.949	0.967	1.8
1B-B'	0.725	0.785	8.2
1C-B	0.810	0.842	3.9
1D-B	0.759	0.785	3.4
2A-B	0.739	0.767	3.7
2A-B'	0.986	1.129	14.5
2B-B	0.723	0.755	4.4
2B-B'	0.703	0.819	16.5
2C-B	0.640	0.657	2.6
2D-B	0.610	0.624	2.2
2D-Y	0.600	0.619	3.1

^a Represents dye-grafted PU with EDA instead of HEDA as extender (without -OH groups).
^b $M_p(\%) = (C_B - C_A) / C_A \times 100\%$.

TABLE VII
Colorfastness Property of Dye-Grafted PU Films

Code ^a	Light Fastness
1A-B	5-6
1A-B'	2
1B-B	6
1C-B	6
1D-B	6
2A-B	5
2A-B'	1
2B-B	6
2C-B	5-6
2D-B	6

^a 1, using EDA as a chain extender.

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