Alkali Reduction and Reactive Dye Dyeing of T/N Nonwoven Fabrics Dipped into Silicon-Containing, Water-Borne Polyurethane

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ABSTRACT: Two series of anionic water-borne polyurethanes with alkali resistance and covalent bonds of a reactive dye were synthesized with different molar ratios of poly(tetramethylene glycol) (PTMG). They were classified with respect to PTMG 1000 and PTMG 2000. The fiber blends of polyester/nylon nonwoven fabrics were dipped into silicon-containing, water-borne polyurethane and squeezed to an 80% pickup ratio. Finally, the manmade leather was treated with alkali reduction and dyed with a reactive dye. The alkali reduction and the thermal, mechanical, and dyeing properties of the manmade leather were studied. For alkali reduction, different ratios of NaOH and Na_2CO_3 concentrations were used. Na_2CO_3 was used because of its better spreading and buffering properties. The softness and breaking load were measured and related to the weight reduction. For the dyeing properties, a reactive dye with vinyl sulfone groups was found to bond with the OH group of water-borne polyurethane by covalent bonding. On the basis of alkali reduction, a mixture of NaOH and Na_2CO_3 with a concentration ratio of $0.1N/0.2N$ could lead to better softness and alkali reduction of leather. For the mechanical properties, leather of the PTMG 1000 series showed a higher breaking load than leather of the PTMG 2000 series. However, less elongation in the PTMG 1000 series resulted. Differential scanning calorimetry showed an endothermic peak at 50–100°C. This indicated that the glass-transition temperature of the hard segment decreased with an increasing amount of the soft segment in leather; meanwhile, both the glass-transition temperature of the soft segment and the melting temperature of the hard segment also decreased as the content of the soft segment increased. For the dyeing properties, the reactive blue dye could reach up to 96.1% dye uptake in the polyurethane part of the leather. Moreover, the washing fastness could be graded as high as 4–5, and the light resistance was also graded to 4–5, in the dyed leather. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 2324–2335, 2005

Key words: dyes/pigments; polyurethanes; alkali reduction

INTRODUCTION

Polyurethane (PU) is a thermoplastic rubber that consists of repeating hard and soft segments; it therefore possesses good mechanical properties, such as medium tensile strength and high elongation. It is used widely in manmade leather, fibers, and adhesives.[1–8] Colored PU leather is mostly made of nonwoven fabrics coated with a mixture of a pigment and a PU resin. The color is dull, and there is a lack of brightness and poor rubbing resistance. In this study, we employed fine-denier nylon/polyethylene terephthalate (PET) nonwoven fabrics, which we dipped into silicon-containing, anionic, water-borne PU, as published recently,[8] then treated with an alkali-reduction agent to improve its softness,[9–11] and finally grafted with a reactive dye to form a dyed, manmade leather.[12–14] The silicon-containing, anionic, water-borne PU possessed a stable state under a basic condition and was also capable of reacting with a reactive dye to form a covalent bond with the dye molecule. The alkali reduction and the thermal, mechanical, and dyeing properties of the dye-grafted, manmade leather were studied.

EXPERIMENTAL

Materials

Poly(tetramethylene glycol)s (PTMGs) with molecular weights of 2000 and 1000 (Hodotani Co., Japan), 4,4′-methylene bis(isocyanatocyclohexane) (H_{12}-MDI) (Coating Co., Taichung, Taiwan), polydimethylsiloxane (PDMS) (Aldrich, Steinheim, Germany), ethylenediamine, N-(2-hydroxyethyl) ethylenediamine (HEDA) (Lancaster, Morecambe, UK), triethylene amide (TEA) (Tedia, Fairfield, OH), 2,2-bis(hydroxymethyl)propionic acid (DMPA) (Tedia), and N,N′-dimethylformamide (DMF) (Tedia) were used without further purification. A reactive dye (Hoechst Co., Frankfurt, Germany) from the sulfatoethyl sulfone series (C.I. Reactive Blue 222) was reacted with the alkali-reduction leather, which was also used without further purification. The chemical structure of the reactive dye was as follows:

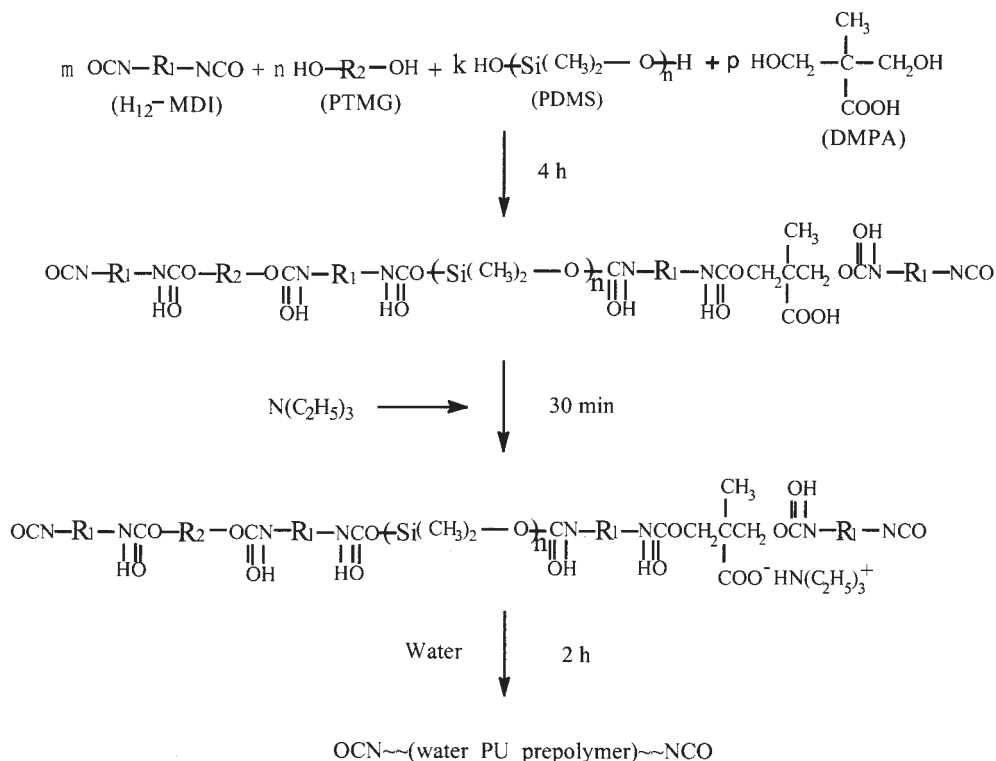*Correspondence to:* H.-H. Wang (hhwang@fcu.edu.tw).
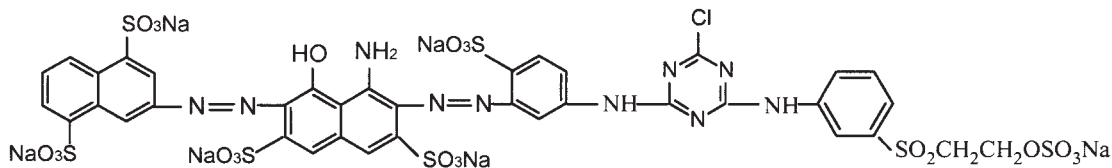
A cationic surfactant (KYL-1125) was also provided by Hoechst.

Synthesis of silicon-containing, anionic, waterborne PU with hydroxy side groups

H_{12}-MDI was dissolved in the *N*-methyl-2-pyrrolidone (NMP) solvent and poured into a reaction flask; the temperature was raised to 65°C under dry nitrogen. Also, PTMG and PDMS were dissolved in NMP separately and added to the flask dropwise. The temperature was raised to 90°C for 4 h of reaction. The temperature was cooled to 30°C, DMPA was dissolved in NMP and added to the flask by drops, and the temperature was increased to 90°C for 0.5 h. The temperature was then lowered to 30°C again, $N(C_2H_5)_3$ was added, the mixture was stirred for 30

(A)

(silicon containing PU prepolymer with NCO-terminated groups)

where:

$-R_1-$: (cyclohexyl)$-CH_2-$(cyclohexyl)

$-R_2-$: $-(CH_2CH_2CH_2CH_2-O-)_n-$

Scheme 1 Synthesis of the silicon-containing PU prepolymer.

OCN~~(water PU prepolymer)~~NCO

$$\text{HNCH}_2\text{CH}_2\,\text{NH}_2$$
$$\text{CH}_2\text{CH}_2\text{OH}$$
(HEDA)   30 min   30°C

(silicon containing PU polymer with hydroxyl side groups)

Scheme 2 Chain extension of the silicon-containing PU prepolymer.

min, pure water was added, and the mixture was stirred for 2 h. Finally, the extender HEDA in NMP was added at 30°C for 30 min. A modified (undyed) PU with hydroxyl side groups was therefore synthesized. The reaction is shown in Schemes 1 and 2.
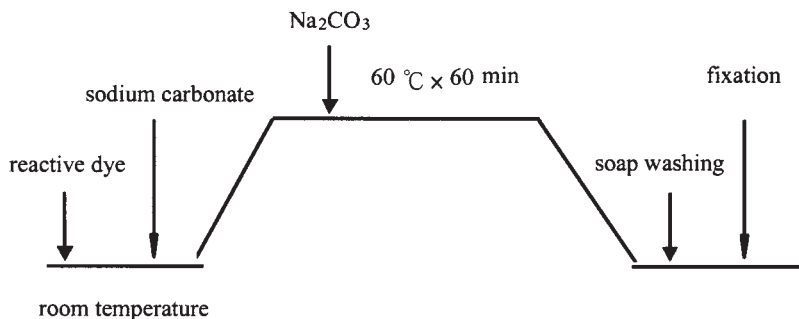
Alkali reduction of PET and leather

The theoretical alkali reduction of PET, as shown in Scheme 3, required 2 mol of NaOH to degrade 1 mol of polyester repeat units. Therefore, the relationship between the theoretical reduction percentage of PET and the amount of sodium hydroxide consumed was $192 \times$ consumed NaOH (% on weight of fiber)/80, where 192 and 40 are the weight of the polyester repeating unit and the molecular weight of sodium hydroxide, respectively. However, this theoretical equation could not be employed in calculating the reduction percentage of PET in leather because the combined reduction agents of NaOH and Na_2CO_3 were used in the alkali-reduction experiments. However, the actual reduction percentage of PET could be

calculated from the reduction percentages of leather and PU, as described later in this article.

The actual reduction percentage of leather was evaluated as follows: [(leather weight before alkali reduction − leather weight after alkali reduction)/leather weight before alkali reduction] × 100%.

Grafting of the dye molecule to alkali-reduced leather

The leather, after being treated with $0.1N$ NaOH/$0.2N$ Na_2CO_3 (the better combined concentration), was dyed with the reactive dye, as shown in Scheme 4. The dyeing mechanism was ascribed to the OH side groups in the water-borne PU molecular chain, which bonded covalently with the reactive dye, as shown in Scheme 5. The mechanism is discussed in a previous article[11] in detail.

Measurements

Differential scanning calorimetry (DSC) was performed with a DuPont 2200 thermal analyzer

Scheme 3

bath ratio 1 ∶ 20; dye concentration 6 ％ O.W.F.;   pH=7

Scheme 4

(DuPont, Wilmington, DE). The DSC measurements proceeded at a heating rate of 20°C/min under a nitrogen atmosphere, and the glass-transition temperature (T_g) and melting temperature (T_m) were obtained. The softness of the leather was measured according to CNS 12915 with a specimen size of 2.54 cm × 15 cm. The experimental value was calculated from the average value of five specimens tested in one side and also in the other side.

The mechanical properties were measured with an Instron 1122 testing instrument (Instron Corp., Canton, MA) according to ASTM D 1682 at a crosshead speed of 300 mm/min; the gauge length was 7.62 cm, and the specimen size was 6 × 1 in.

To evaluate the dye uptake of the dyed leather, we partially dissolved 10 g of the dyed leather in a small amount of formic acid to dissolve the PU and nylon parts of the dyed leather. We then solidified the leather with water, redissolved the solid in 100 mL of a formic/DMF (20 : 80) solution, measured the absorption value with a photometer, and compared it to that of the standard dye solution. For the dye fastness of the dyed leather, the AATCC 61-1985 IIIA and AATCC 16-1993 Option E test standards were used to measure the water fastness and light fastness, respectively.[13]

RESULTS AND DISCUSSION

Effect of the combined alkali concentration of NaOH/Na$_2$CO$_3$ on the weight-loss percentage of water-borne PU, leather, and PET

Table I shows the compositions and molar ratios of all the PU polymers. Eight PU copolymers were synthesized with two kinds of PTMGs and different molar ratios of each component.
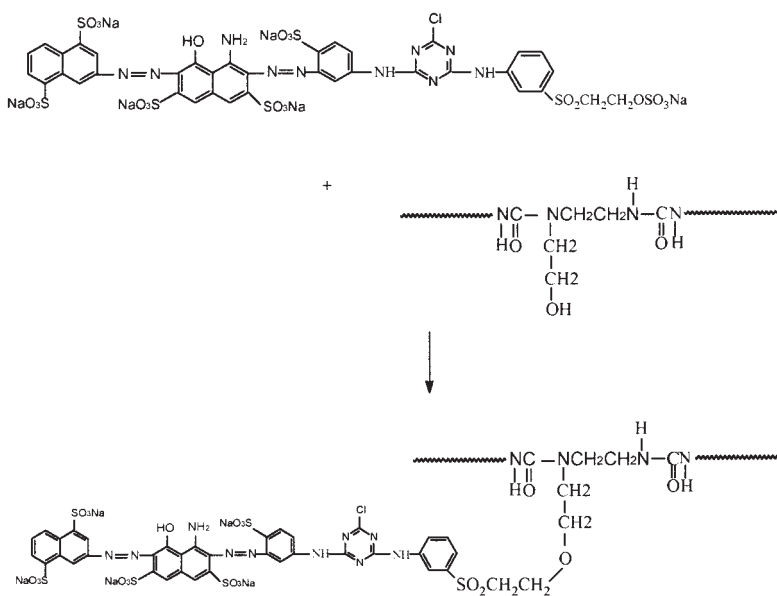
Scheme 5

TABLE I
Compositions and Molar Ratios of All the PU Polymers

Code	Composition	Molar ratio	Hard-segment content (wt %)[a]	Soft-segment content (wt %)[b]	Molar content of PDMS (%)	Molar content of HEDA (%)
1A	H_{12}-MDI/PTMG 1000/PDMS/DMPA/HEDA	4:1:0.25:1:1.75	25.18	47.82	3.12	21.87
1B	H_{12}-MDI/PTMG 1000/PDMS/DMPA/HEDA	4:1:0.5:1:1.5	47.15	52.85	6.25	18.75
1C	H_{12}-MDI/PTMG 1000/PDMS/DMPA/HEDA	4:1:1:1:1	39.14	60.86	12.5	12.5
1D	H_{12}-MDI/PTMG 1000/PDMS/DMPA/HEDA	4:1:1.25:1:0.75	35.90	64.10	15.62	9.38
2A	H_{12}-MDI/PTMG 2000/PDMS/DMPA/HEDA	4:1:0.25:1:1.75	37.74	62.26	3.12	21.87
2B	H_{12}-MDI/PTMG 2000/PDMS/DMPA/HEDA	4:1:0.5:1:1.5	34.86	65.14	6.25	18.75
2C	H_{12}-MDI/PTMG 2000/PDMS/DMPA/HEDA	4:1:1:1:1	30.00	70.00	12.5	12.5
2D	H_{12}-MDI/PTMG 2000/PDMS/DMPA/HEDA	4:1:1.25:1:0.75	27.94	72.06	15.62	9.38

1A, 1B, 1C, and 1D represent the PTMG 1000 series. 2A, 2B, 2C, and 2D represent the PTMG 2000 series. A-H_{12}-MDI/PTMG/PDMS/DMPA/HEDA = 4:1:0.25:1:1.75; B-H_{12}-MDI/PTMG/PDMS/DMPA/HEDA = 4:1:0.5:1:1.5; C-H_{12}-MDI/PTMG/PDMS/DMPA/HEDA = 4:1:1:1:1; D-H_{12}-MDI/PTMG/PDMS/DMPA/HEDA = 4:1:1.25:1:0.75.

[a] Hard-segment content (wt %) =

$$\frac{H_{12}\text{-MDI} + \text{DMPA} + \text{HEDA (weight)}}{H_{12}\text{-MDI} + \text{DMPA} + \text{HEDA} + \text{PTMG (1000 or 2000)} + \text{PDMS1000} \times \text{(weight)}} \times 100$$

[b] Soft-segment content (wt %) = 100% hard-segment content (%)

Table II shows the alkali resistance of dry, thin PU films treated with different concentrations of NaOH/Na_2CO_3 at 100°C for 1 h. The weight-loss percentage of the water-borne PU films was less than 3% and decreased with an increasing concentration of PDMS (from 1A to 1D or from 2A to 2D). This demonstrated that the PU films had a certain resistance to alkaline solutions. Moreover, because the PDMS behaved hydrophobically and had low surface energy, it easily migrated to the surface of the PU polymer and exhibited good alkali resistance. Therefore, the reduction PU percentage was only 2.91–2.96%. This demonstrated that increasing the concentration of Na_2CO_3 did not promote the reduction percentage of PU much; that is, the variation of the weight-loss percentage of PU was only ±0.05%. Besides, increasing the Na_2CO_3 concentration did not degrade PU much as the PDMS concentration remained constant in the solution.

Tables III and IV show the experimental alkali-reduction percentages of leather, water-borne PU, and PET. The PET alkali-reduction percentage was calculated from the alkali-reduction percentage of

leather and PU. For example, as shown in 1A, the concentration of NaOH/Na_2CO_3 remained 0.1N/0.05N, and the alkali-reduction percentages were 3.49 and 2.84% in leather and PU, respectively. Then, the PET alkali-reduction percentage was calculated to be 13.36% [(3.49–2.84)/(0.3 × total weight of nonwoven fabrics), where 0.3 is the weight fraction of PET in the fabrics]. In addition, as shown in Tables III and IV, the reduction percentage of PET increased with an increasing concentration of Na_2CO_3. This was attributed to Na_2CO_3, which made it easier for NaOH to permeate the fabrics, and so a higher alkali reduction of PET resulted.

Relationship between the alkali reduction of leather and its softness

The Na_2CO_3 concentration was varied from 0.05 to 0.2N, but the NaOH concentration was fixed at 0.1 N; because the surface-active agent (KYL-1125) was added to the alkali solution, Na_2CO_3 had a good spreading and buffering effect. Tables V and VI show the relationship between the percentage reduction of leather in the PTMG

TABLE II
Weight-Loss Percentage of Thin PU Films Treated with Different NaOH/Na_2CO_3 Alkali Ratios at 100°C

Alkali ratio of NaOH/Na_2CO_3 (N)	Weight loss percentage of PU Film							
	1A	1B	1C	1D	2A	2B	2C	2D
0.1	2.84	2.66	2.53	2.30	2.94	2.68	2.52	2.36
0.1:0.05	2.84	2.64	2.53	2.27	2.91	2.68	2.53	2.33
0.1:0.1	2.83	2.65	2.56	2.31	2.95	2.73	2.48	2.38
0.1:0.15	2.83	2.67	2.58	2.28	2.93	2.71	2.51	2.36
0.1:0.2	2.83	2.69	2.56	2.31	2.94	2.65	2.55	2.38
0.1:0.25	2.84	2.69	2.54	2.28	2.96	2.68	2.56	2.37

TABLE III
Experimental Reduction Percentages of Leather, Waterborne PU, and PET at Different NaOH/Na$_2$CO$_3$ Alkali Ratios in the PU 1000 Series

Code	NaOH/Na$_2$CO$_3$ (N)	Reduction percentage of leather (%)	Reduction percentage of waterborne PU (%)	Reduction percentage of PET (%)[a]
1A	0.1	3.49	2.84	13.36
1A-0.05	0.1:0.05	3.49	2.84	13.36
1A-0.1	0.1:0.1	3.55	2.83	13.75
1A-0.15	0.1:0.15	3.65	2.83	14.35
1A-0.2	0.1:0.2	3.86	2.83	15.61
1A-0.25	0.1:0.25	3.86	2.84	15.61
1B	0.1	3.08	2.66	11.38
1B-0.05	0.1:0.05	3.10	2.64	11.56
1B-0.1	0.1:0.1	3.20	2.65	12.13
1B-0.15	0.1:0.15	3.29	2.67	12.62
1B-0.2	0.1:0.2	3.42	2.69	13.34
1B-0.25	0.1:0.25	3.43	2.69	13.40
1C	0.1	2.80	2.53	10.05
1C-0.05	0.1:0.05	2.85	2.53	10.35
1C-0.1	0.1:0.1	2.91	2.56	10.63
1C-0.15	0.1:0.15	2.98	2.58	10.99
1C-0.2	0.1:0.2	3.01	2.56	11.23
1C-0.25	0.1:0.25	3.02	2.54	11.34
1D	0.1	2.63	2.30	9.54
1D-0.05	0.1:0.05	2.69	2.27	10.08
1D-0.1	0.1:0.1	2.73	2.31	10.21
1D-0.15	0.1:0.15	2.76	2.28	10.47
1D-0.2	0.1:0.2	2.82	2.31	10.75
1D-0.25	0.1:0.25	2.81	2.28	10.78

[a] PET-30% of weight in non woven material.

TABLE IV
Experimental Reduction Percentages of Leather, Waterborne PU, and PET at Different NaOH/Na$_2$CO$_3$ Alkali Ratios in the PU 2000 Series

Code	NaOH/Na$_2$CO$_3$ (N)	Reduction percentage of leather (%)	Reduction percentage of waterborne PU (%)	Reduction percentage of PET (%)[a]
2A	0.1	3.63	2.94	13.94
2A-0.05	0.1:0.05	3.65	2.91	14.14
2A-0.1	0.1:0.1	3.72	2.95	14.45
2A-0.15	0.1:0.15	3.78	2.93	14.86
2A-0.2	0.1:0.2	3.89	2.94	15.50
2A-0.25	0.1:0.25	3.90	2.96	15.51
2B	0.1	3.53	2.68	14.03
2B-0.05	0.1:0.05	3.58	2.68	14.33
2B-0.1	0.1:0.1	3.60	2.73	14.61
2B-0.15	0.1:0.15	3.65	2.71	14.67
2B-0.2	0.1:0.2	3.72	2.65	15.25
2B-0.25	0.1:0.25	3.73	2.68	15.23
2C	0.1	3.38	2.52	13.56
2C-0.05	0.1:0.05	3.45	2.53	13.95
2C-0.1	0.1:0.1	3.49	2.48	14.32
2C-0.15	0.1:0.15	3.53	2.51	14.49
2C-0.2	0.1:0.2	3.62	2.55	14.92
2C-0.25	0.1:0.25	3.64	2.56	15.01
2D	0.1	3.27	2.36	13.32
2D-0.05	0.1:0.05	3.31	2.33	13.65
2D-0.1	0.1:0.1	3.38	2.38	13.93
2D-0.15	0.1:0.15	3.40	2.36	14.11
2D-0.2	0.1:0.2	3.45	2.38	14.35
2D-0.25	0.1:0.25	3.47	2.37	14.49

[a] PET-30% of weight in non woven material.

TABLE V
Relationship Between the Reduction Percentage of Leather, Softness, and NaOH/Na$_2$CO$_3$ Alkali Ratios in the PU 1000 Series

Code	NaOH/Na$_2$CO$_3$ (N)	Reduction percentage of leather (%)	Softness (mm)	Code	NaOH/Na$_2$CO$_3$ (N)	Reduction percentage of leather (%)	Softness (mm)
1A	0.1	3.49	35.8	1C	0.1	2.80	42.2
1A-0.05	0.1:0.05	3.49	36	1C-0.05	0.1:0.05	2.85	41
1A-0.1	0.1:0.1	3.55	35	1C-0.1	0.1:0.1	2.91	39
1A-0.15	0.1:0.15	3.65	34.2	1C-0.15	0.1:0.15	2.98	38
1A-0.2	0.1:0.2	3.86	32.6	1C-0.2	0.1:0.2	3.01	36.8
1A-0.25	0.1:0.25	3.86	32.4	1C-0.25	0.1:0.25	3.02	36.2
1B	0.1	3.08	36.3	1D	0.1	2.63	44.3
1B-0.05	0.1:0.05	3.10	38	1D-0.05	0.1:0.05	2.69	42
1B-0.1	0.1:0.1	3.20	37	1D-0.1	0.1:0.1	2.73	41.4
1B-0.15	0.1:0.15	3.29	36.8	1D-0.15	0.1:0.15	2.76	41
1B-0.2	0.1:0.2	3.42	35.4	1D-0.2	0.1:0.2	2.82	39.8
1B-0.25	0.1:0.25	3.43	35	1D-0.25	0.1:0.25	2.81	39.2

1000 and 2000 series, respectively, and also their softness and alkali ratios. Figures 1 and 2 also show a typical relationship between the alkali-reduction percentage of leather and its concentration of Na$_2$CO$_3$. The alkali-reduction percentage and the softness of leather increased with an increasing concentration of Na$_2$CO$_3$ (from 0.05 to 0.25N). Nevertheless, as the concentration of Na$_2$CO$_3$ was greater than 0.2N, the alkali-reduction percentage only increased slightly. The reason was possibly the dissociation of Na$^+$ ions of NaOH and Na$_2$CO$_3$ being excessive in the solution. This caused the OH$^-$ concentration to decrease and resulted in a decrease in the surface alkali reduction of PU and PET. Moreover, the reduction percentage of leather decreased with an increasing content of PDMS (e.g., 1A–1D). This demonstrated that the addition of PDMS had a good alkali-resistance effect.

Figure 3 and Tables VII and VIII show a typical relationship between the softness and alkali-reduction percentage of leather with alkali-reduction solutions of the same concentration. For example, in the PTMG 1000 series, when the NaOH/Na$_2$CO$_3$ concentration was 0.1N/0.05N, there were five points of softness (1A, 0.05; 1B, 0.05; 1C, 0.05; and 1D, 0.05). The leather softness increased with an increasing reduction percentage because increasing the reduction percentage of the leather led to more microvoids in the leather, and so the softness increased.

Moreover, the relationship between the alkali-reduction percentage and softness of leather with the variation of the Na$_2$CO$_3$ concentration (Figs. 1 and 2) indicated that 0.1N NaOH/0.2N Na$_2$CO$_3$ led to better results for the alkali-reduction percentage and softness. Thus, the

TABLE VI
Relationship Between the Reduction Percentage of Leather, Softness, and NaOH/Na$_2$CO$_3$ Alkali Ratios in the PU 2000 Series

| Code	NaOH/Na$_2$CO$_3$ (N)	Reduction percentage of leather (%)	Softness (mm)	Code	NaOH/Na$_2$CO (N)	Reduction percentage of leather (%)	Softness (mm)
2A	0.1	3.63	34.8	2C	0.1	3.38	42.3
2A-0.05	0.1:0.05	3.65	35.5	2C-0.05	0.1:0.05	3.45	41.8
2A-0.1	0.1:0.1	3.72	35	2C-0.1	0.1:0.1	3.49	41.4
2A-0.15	0.1:0.15	3.78	34.8	2C-0.15	0.1:0.15	3.53	40.1
2A-0.2	0.1:0.2	3.89	33.4	2C-0.2	0.1:0.2	3.62	39.2
2A-0.25	0.1:0.25	3.90	33.2	2C-0.25	0.1:0.25	3.64	39.1
2B	0.1	3.53	36.5	2D	0.1	3.27	45.1
2B-0.05	0.1:0.05	3.58	38.6	2D-0.05	0.1:0.05	3.31	44.6
2B-0.1	0.1:0.1	3.60	38.2	2D-0.1	0.1:0.1	3.38	44
2B-0.15	0.1:0.15	3.65	37.8	2D-0.15	0.1:0.15	3.40	43.2
2B-0.2	0.1:0.2	3.72	36.2	2D-0.2	0.1:0.2	3.45	42.8
2B-0.25	0.1:0.25	3.73	36	2D-0.25	0.1:0.25	3.47	42.8
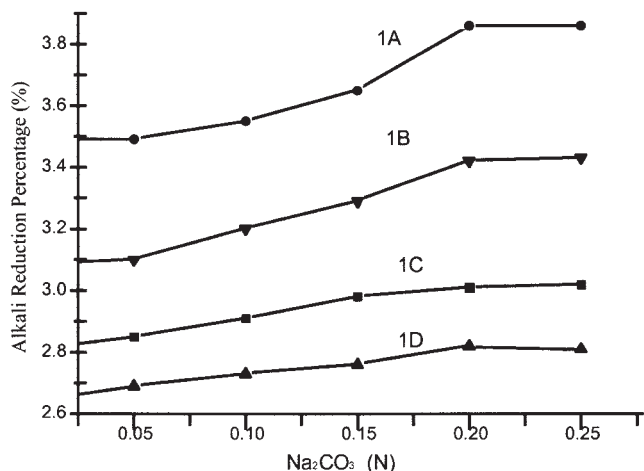
Figure 1 Relationship between the alkali-reduction percentage and the concentration of Na_2CO_3 in the leather for the PU 1000 series.

$0.1N$ NaOH/$0.2N$ Na_2CO_3 concentration ratio was chosen for further study of other properties.

DSC thermal analysis

The thermal properties of manmade leather were measured with DSC and are shown in Figures 4 and 5. For leather with hard and soft segments, the glass-transition temperatures of the soft and hard segments (T_{gs} and T_{gh}, respectively) and the melting temperatures of the soft segment and hard segments (T_{ms} and T_{mh}, respectively) should have appeared. However, some might have overlapped and not appeared. For example, leather in the PTMG 1000 series did not show T_{ms} because the molecular weight of PU was too small.

T_g's and T_m's of all the leather samples are shown in Table IX and Figures 4 and 5. T_m's of nylon 6,6 and PET were 225 and 255°C, respectively. In addition, an endothermic peak absorption appeared at 50–100°C,
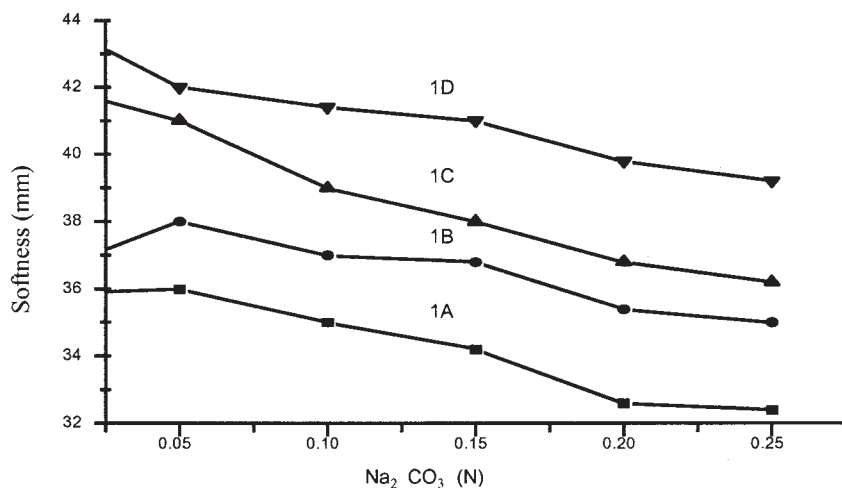

Figure 2 Relationship between the softness and the concentration of Na_2CO_3 in the leather for the PU 1000 series.
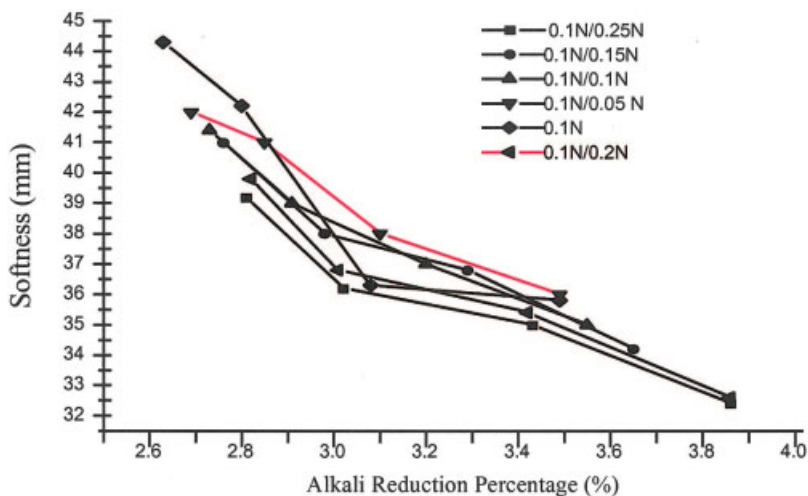

Figure 3 Relationship between the softness and reduction percentage of the leather for the PU 1000 series.

TABLE VII
Relationship Between the Reduction Percentage of Leather and Softness in the PU 1000 Series

Code	Reduction percentage of leather (%)	Softness (mm)	Code	Reduction percentage of leather (%)	Softness (mm)
1A	3.49	35.8	1A-0.15	3.65	34.2
1B	3.08	36.3	1B-0.15	3.29	36.8
1C	2.80	42.2	1C-0.15	2.98	38
1D	2.63	44.3	1C-0.15	2.76	41
1A-0.05	3.49	36	1A-0.2	3.86	32.6
1B-0.05	3.10	38	1B-0.2	3.42	35.4
1C-0.05	2.85	41	1C-0.2	3.01	36.8
1D-0.05	2.69	42	1C-0.2	2.82	39.8
1A-0.1	3.55	35	1A-0.25	3.86	32.4
1B-0.1	3.20	37	1B-0.25	2.43	35
1C-0.1	2.91	39	1C-0.25	3.02	36.2
1D-0.1	2.73	41.4	1C-0.25	2.81	39.2

which might have been T_{gh}'s of nylon 6,6, PET, and PU overlapping in this region. As the leather was heated quickly nearly to T_{gh}, the segmental relaxation time dropped rapidly, and this made the free volume increase suddenly and create an endothermic peak of T_{gh}. T_{gh} shifted toward a low-temperature region with a decreasing concentration of hard segments. Also, T_{ms} for the leather of the 2000 series shifted toward a low-temperature region as the soft segment increased.

Mechanical property analysis

The mechanical properties, such as the maximum breaking load and elongation, are shown in Table X. Figure 6 also shows typical load–elongation curves for undyed and dyed leathers of the PU 1000 series. The PU 1000 series had a higher breaking load, but the PU 2000 series had a higher elongation, because the soft segment in the PU 2000 series behaved more softly than that in the PU 1000 series. Moreover, there was a shoulder in the elongation region of 20–40 mm. This

indicated that the leather exhibited plastic deformation after the shoulder. This suggested that the entire load was sustained only by water-borne PU after this point was passed. Thus, the load increased more slowly. Moreover, as shown in Table X, the maximum breaking load and elongation dropped after dyeing. This might have been due to the dye molecules entering the spaces along the molecular chain; this destroyed the crosslinks of water-borne PU, and so a lower breaking load resulted. Besides, from 1A to 1D, as the concentration of PDMS increased, the reduction percentage of leather also decreased. Meanwhile, as the concentration of HEDA was decreased (the covalent bonds with dye molecules being fewer), the amount of dye entering the molecular chain became less. The difference in the breaking loads of the dyed and undyed leather samples was subsequently smaller. Similarly, for the PU 2000 series, the maximum breaking load also decreased after dyeing, but the difference between the dyed and undyed leather samples gradually narrowed from 2A to 2D.

TABLE VIII
Relationship Between the Reduction Percentage of Leather and Softness in the PU 2000 Series

| Code	Reduction percentage of leather (%)	Softness (mm)	Code	Reduction percentage of leather (%)	Softness (mm)
2A	3.63	34.8	2A-0.15	3.78	34.8
2B	3.53	36.5	2B-0.15	3.65	37.8
2C	3.38	42.3	2C-0.15	3.53	40.1
2D	3.27	45.1	2C-0.15	3.40	43.2
2A-0.05	3.65	35.5	2A-0.2	3.89	33.4
2B-0.05	3.58	38.6	2B-0.2	3.72	36.2
2C-0.05	3.45	41.8	2C-0.2	3.62	39.2
2D-0.05	3.31	44.6	2C-0.2	3.45	42.8
2A-0.1	3.72	35	2A-0.25	3.90	33.2
2B-0.1	3.60	38.2	2B-0.25	3.73	36
2C-0.1	3.49	41.4	2C-0.25	3.64	39.1
2D-0.1	3.38	44	2C-0.25	3.47	42.8
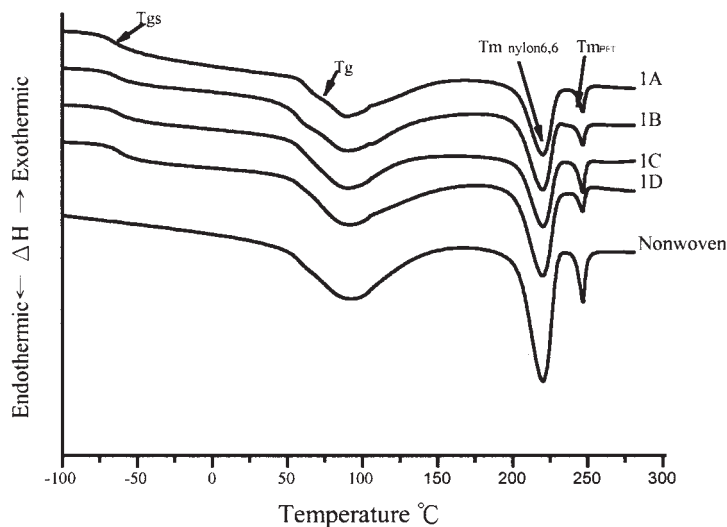
Figure 4 DSC curve of the leather for the PTMG 1000 series.

Dyeing and fastness properties of dye-grafted leather

The dye was dissolved in a formic acid/DMF mixed solution, and the dye concentration was kept at 10–50 ppm. Ultraviolet spectroscopy was used to obtain the maximum wavelength absorbance of the dye and to evaluate the dye uptake of the dyed leather.

Table XI shows the dye uptake of the dyed leather. The dye uptake of the dyed leather decreased with a decreasing concentration of HEDA. This was due to fewer OH groups (dye sites) in water-borne PU. Thus, leathers in the PU 1000 series had higher dye uptake than those in the PU 2000 series. Also, according to a

comparison of the repeat units of the PU 2000 and 1000 series, the PU 2000 series had higher molecular weights than the PU 1000 series; that is, there were more OH groups in the PU 1000 series and thus better dyeing properties.

Moreover, as shown in Table XII, the light fastness of the dyed leather was graded 4 or 4–5. This could be explained as follows. The reactivity dye formed a covalent bond with PU, which caused the light excitation energy to be absorbed by the polymer. Thus, the dye molecules were not easily oxidized, reduced, or decomposed to fade away. Moreover, because PDMS
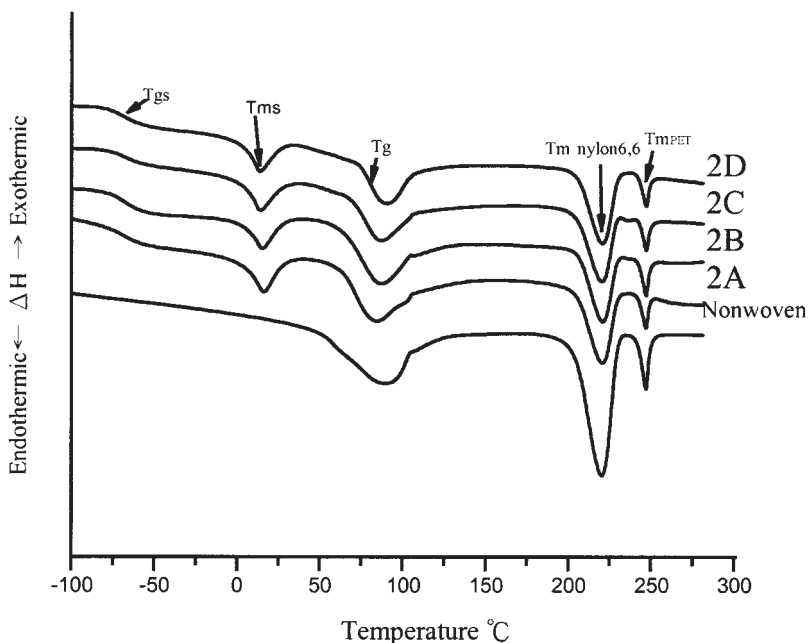

Figure 5 DSC curve of the leather for the PTMG 2000 series.

TABLE IX
T_g **and** T_m **Values of All of the Polymers**

Code	Hard-segment content (wt %)	Soft-segment content (wt %)	T_{gs} of soft segment (°C)	T_{ms} of soft segment (°C)	T_{gh} of hard segment (°C)	T_m of nylon-6,6 (°C)	T_m of PET (°C)
1A	52.18	47.82	−60.3	—	53.5	225.0	250.0
1B	47.15	52.85	−61.0	—	52.3	225.0	250.0
1C	39.14	60.86	−63.4	—	52.0	225.0	250.0
1D	35.90	64.10	−64.1	—	51.8	225.0	250.0
2A	37.74	62.26	−67.7	15.2	63.2	225.0	250.0
2B	34.86	65.14	−68.6	13.8	62.8	225.0	250.0
2C	30.00	70.00	−71.4	12.0	62.5	225.0	250.0
2D	27.94	72.06	−72.5	11.9	62.0	225.0	250.0

TABLE X
Relationship Between the Maximum Breaking Load and Elongation to the Reduction Percentage of Leather

Code[a]	Reduction percentage of leather (%)	Maximum breaking load (kgf)	Elongation (%)
T/N nonwoven	0	23.12	65
1A	3.86	43.23	198
1A-b	3.86	37.83	183
1B	3.42	45.21	209
1B-b	3.42	40.38	190
1C	3.01	47.68	215
1C-b	3.01	41.85	200
1D	2.82	49.23	215
1D-b	2.82	47.1	207
2A	3.89	34.55	242
2A-b	3.89	28.34	183
2B	3.72	36.33	259
2B-b	3.72	31.56	216
2C	3.62	38.51	249
2C-b	3.62	32	216
2D	3.45	40.56	275
2D-b	3.45	35.56	249

[a] b = blue dye.

possessed better thermostability and oxidation properties against weathering, the dyed leather had better light fastness as the PDMS content increased.

CONCLUSIONS

In this study, PTMGs of two molecular weights (1000 and 2000), PDMS, H_{12}-MDI, and HEDA were employed to synthesize silicon-containing PU copolymers. Those modified with HEDA as a chain extender were grafted with a reactive dye via the dipping of nonwoven leather in a PU solution. On the basis of the relationship between the leather softness and the alkali-reduction percentage, the $0.1N$ NaOH/$0.2N$ Na_2CO_3 alkali concentration ratio was chosen for the posttreatment.

According to DSC thermal analysis, T_{gs}, T_{gh}, and T_{ms} of the leather shifted toward a low-temperature region as the concentration of soft segments in PU increased. In addition, a heat absorption peak at 50–100°C appeared; this was overlapping T_{gh} values of nylon 6,6,
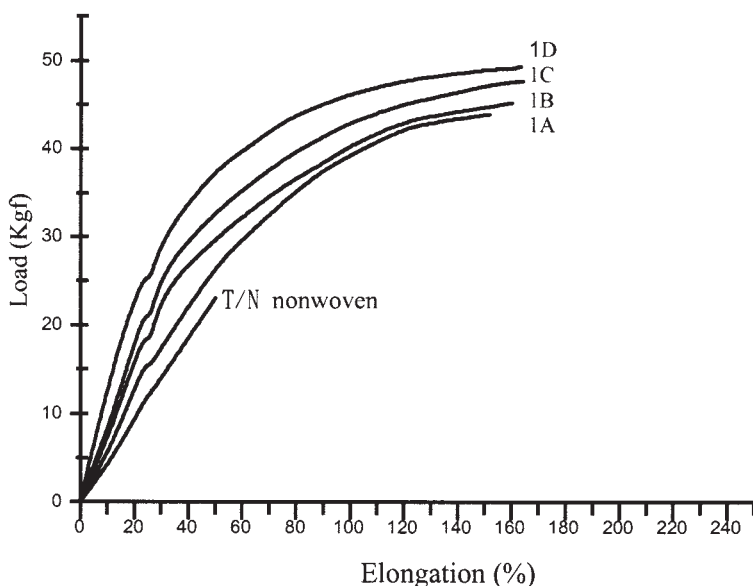

Figure 6 Relationship between the load and elongation of the leather for the PU 1000 series.

TABLE XI
Dye Uptake of Dyed Leather

Code[a]	Dye uptake (g/gf)	Efficiency of the dye uptake (%)[b]
1A-b	0.0577	96.1
1B-b	0.0563	93.8
1C-b	0.05430	90.5
1D-b	0.0523	87.1
2A-b	0.0502	83.7
2B-b	0.0491	81.8
2C-b	0.0485	80.8
2D-b	0.0472	78.6

The dye concentration was 6% OWF.
[a] b = blue dye.
[b] Efficiency of dye uptake = dye uptake/(Weight of leather × 6% OWF)

TABLE XII
Dye Fastness of Dyed Leather

Code[a]	Water Fastness	Light Fastness	Code[a]	Water Fastness	Light Fastness
1A-b	4–5	4	2A-b	4–5	4
1B-b	4–5	4	2B-b	4–5	4
1C-b	4–5	4	2C-b	4–5	4
1D-b	4–5	4	2D-b	4–5	4

[a] b = blue dye.

PET, and water-borne PU in the leather. As for the mechanical properties, the leather of the PTMG 1000 series showed a higher breaking load than the leather of the PTMG 2000 series. Nevertheless, the leather of the PTMG 2000 series exhibited better elongation. After dyeing, the breaking load and elongation decreased. However, the breaking load increased with PDMS.

As for the dyeing properties, the dye showed good reactivity with OH groups of PU. The dye uptake was as high as 96.1% in the PU part of the leather. This was possibly due to the blue color dye being a straight structure. For the dyeing fastness, the washing fastness could reach up to a grade of 4–5, and light resistance also reached a grade of 4–5 in leather dyeing. This was due to the dye being covalently bonded with the OH groups of PU.

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