

Modified Polyurethane with Improvement of Acid Dye Dyeability

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ABSTRACT: This article concerns the modification of polyurethane using polyamide 6,6 prepolymer to improve the dyeability properties of the polyurethane copolymer with acid dye. First, the carboxyl-terminated polyamide 6,6 prepolymer was synthesized from adipic acid and 1,6-diaminohexane. The isocyanate-terminated polyurethane prepolymer was also synthesized from polytetramethylene glycol and 4,4'-diphenylmethane diisocyanate in *N,N*-dimethylformamide. The polyurethane prepolymer was then extended with a mixture of 1,4-butanediol and the polyamide 6,6 prepolymer (molar ratios of 1,4-butanediol to prepolymer being 100%, 75%, 50%, and 25%, respectively). Finally, the poly(urethane–amide) copolymers were dyed with acid dyes. The chemical, physical, and the dyeing properties of the poly(urethane–amide) copolymers are discussed. From the experimental results, it is found that the inherent viscosity of poly(urethane–amide) copolymers is increased with the increasing amount of polyamide content. The structure is proven by infrared spectra, which exhibits the absorption peaks of urethane and amide groups as we expected. From the differential scanning calorimetry mea-

surements, it is found that the poly(urethane–amide) copolymers have two-phase structures and good phase separation. There are four transition temperatures (T_{gs} , T_{gh} , T_{ms} , and T_{mh}), but only those copolymers in PTMG 2,000 series possess T_{ms} . Moreover, the T_{gs} is found to change with the length of soft segment, and the T_{gh} is increased with the increasing amount of polyamide content. Also, the dyed copolymers exhibit higher T_{gh} than those without dyeing of dye molecule, but the T_{gs} is not obviously changed. For mechanical properties, it is indicated that both the modulus and the strength of the copolymers are higher than those of unmodified polyurethane, but they are lowered after being dyed with dye molecule due to further separation of intermolecular distance of the dyed polyurethanes. For dye uptake in dyeing properties, it is found to increase with increasing amount of polyamide content. For dye fastness, the dyed copolymers exhibit higher grade of water fastness than that of unmodified polyurethane. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1397–1404, 2003

Key words: polyurethane; acid dye; poly(urethane–amide)

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 time of 50–60 min.^{9–12} It thus wastes energy and time. In this article, we try to synthesize PUs using polyamide 6,6 (PA6.6) prepolymer to improve the dyeability properties of the polyurethane copolymer with acid dye. The mechanical, thermal, and dyeing properties of the dyed PU are studied.

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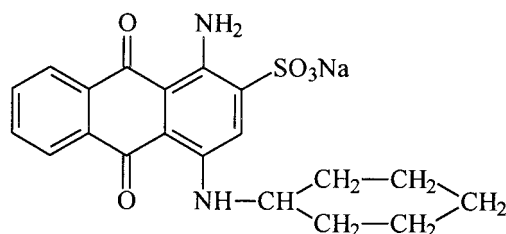
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EXPERIMENTAL

Materials

Polytertramethylene glycol (PTMG) with molecular weight of 2,000 and 1,000 from Hodotani (Tokyo, Japan) and 4,4'-diphenyl-methane diisocyanate (MDI), 1,6-diaminohexane (HD), adipic acid (AA), 1,4-butanediol (1,4-BD), and *N,N*'-dimethyl formamide (DMF; from Merck, Darmstadt, Germany) were used without further purification. Three acid dyes of C. I. Acid Blue 61, C. I. Acid Yellow 49, and C. I. Acid Red 265 (Bayer, Ludwigshafen, Germany) were used for dyeing with the modified polyurethane resin, which were also used without further purification. The chemical structure of these three acid dyes are as follows:



Scheme 1 B (blue dye): C. I. Acid Blue 61.

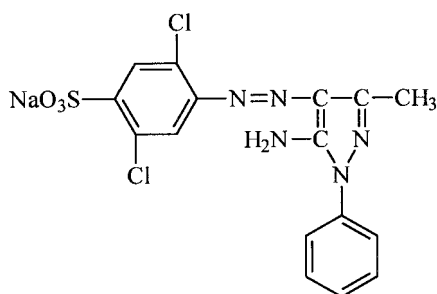
TABLE I
Code of All PU Polymer Films

Code	Composition	Molar ratios	Hard-segment content (wt %)	Soft-segment content (wt %)	PA content (wt %)
PU1	MDI/PTMG 1,000/1,4-BD	2:1:1	37.11	62.89	
PU1-PA1	MDI/PTMG 1,000/1,4-BD/PA	2:1:0.75:0.25	39.78	60.22	5.60
PU1-PA2	MDI/PTMG 1,000/1,4-BD/PA	2:1:0.50:0.50	42.23	57.77	10.75
PU1-PA3	MDI/PTMG 1,000/1,4-BD/PA	2:1:0.25:0.75	44.49	55.51	15.49
PU2	MDI/PTMG 2,000/1,4-BD	2:1:1	22.78	77.22	
PU2-PA1	MDI/PTMG 2,000/1,4-BD/PA	2:1:0.75:0.25	24.83	75.17	3.50
PU2-PA2	MDI/PTMG 2,000/1,4-BD/PA	2:1:0.50:0.50	26.77	73.23	6.81
PU2-PA3	MDI/PTMG 2,000/1,4-BD/PA	2:1:0.25:0.75	28.61	71.39	9.96

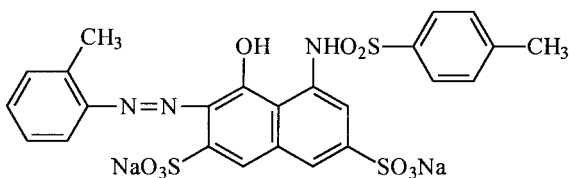
$$\text{Hard-segment content (wt \%)} = \frac{\text{MDI} + 1,4 - \text{BD} + \text{PA (weight)}}{\text{PTMG} + \text{MDI} + 1,4 - \text{BD} + \text{PA (weight)}} \times 100\%$$

$$\text{Soft-segment content (wt \%)} = 100\% - \text{hard-segment content (wt \%)}.$$

$$\text{Content of PA (wt \%)} = \frac{\text{PA (weight)}}{\text{PTMG} + \text{MDI} + 1,4 - \text{BD} + \text{PA (weight)}} \times 100\%$$



Scheme 2 Y (yellow dye): C. I. Acid Yellow 49.



Scheme 3 R (red dye): C. I. Acid Red 265.

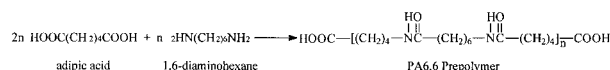
Preparation of PA6,6 salt

The diamino-hexane and the adipic acid, respectively, are warmed up and dissolved in ethyl alcohol solvent over hot water bath and cooled to room temperature. Then an equimolar amount of diamino-hexane was added into the adipic acid solution. A white crystal was precipitated and the heat was evolved due to the exothermic reaction. After being left overnight, the solution was filtered and the PA6,6 salt was collected. The salt was placed in the vacuum drying oven and dried overnight between 40 and 60°C.

Synthesis of PA6,6 prepolymer with acid group

A total of 50 wt % of PA6,6 aqueous salt solution was added with the adipic acid as stabilizing agent. It was placed in the reactor under pressure of 18 kg cm⁻³ of dry nitrogen and reacted for 1–2 h, finally reaching

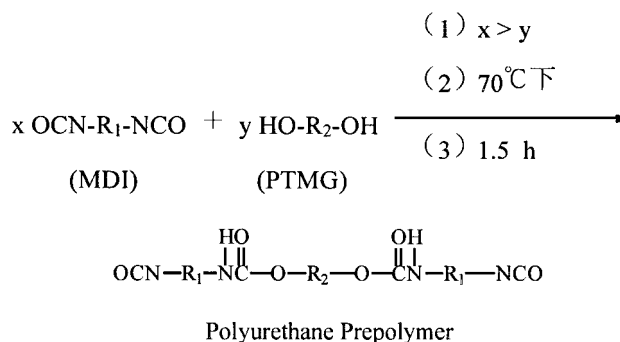
temperature of up to 250°C. Then the reactor was cooled to room temperature and ambient pressure. The solution was placed into the vacuum drying oven to dry and a PA6,6 prepolymer with terminal group of —COOH was obtained.



Scheme 4

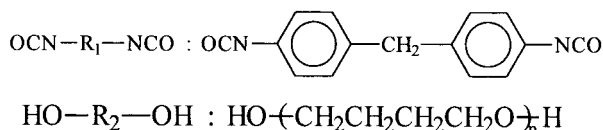
Synthesis of poly(urethane–amide) copolymer

The MDI was dissolved in DMF solvent and poured into the reaction flask, and the temperature 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 1.5 h. The polyurethane prepolymer with terminal group of —NCO was obtained. Then, cooling down the temperature to 5°C, the chain extenders were added to the mixture of 1,4-butanediol and the polyamide 6,6 prepolymer (molar ratios of 1,4-BD to prepolymer being 100%, 75%, 50%, and 25%, respectively; Table I). The reaction scheme is described as follows:



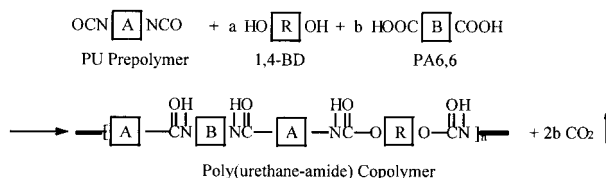
Scheme 5

where



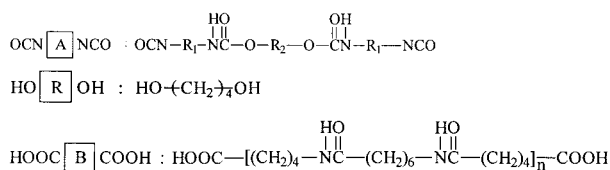
Scheme 6

then



Scheme 7

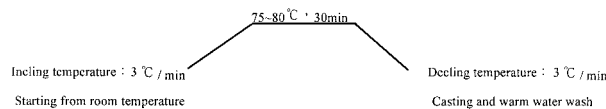
where



Scheme 8

Dyeing of modified PU with acid dyes

The dye was first dissolved in DMF and added to the PU solution in reaction flask and the temperature was raised to 80°C for 0.5 h. The final solution was cast into films and washed with warm water to remove the unreacted dye in the film.



Scheme 9

Measurements

Infrared spectra of dyed and undyed PU were obtained by Hitachi Model 260-50 Type (Hitachi, Tokyo, Japan) over a range of 700–3,500 cm⁻¹. Intrinsic viscosity was performed by a Cannon Type viscometer (Rheotec, Radeburg, Germany) in a constant-temperature water bath at 25°C. 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).

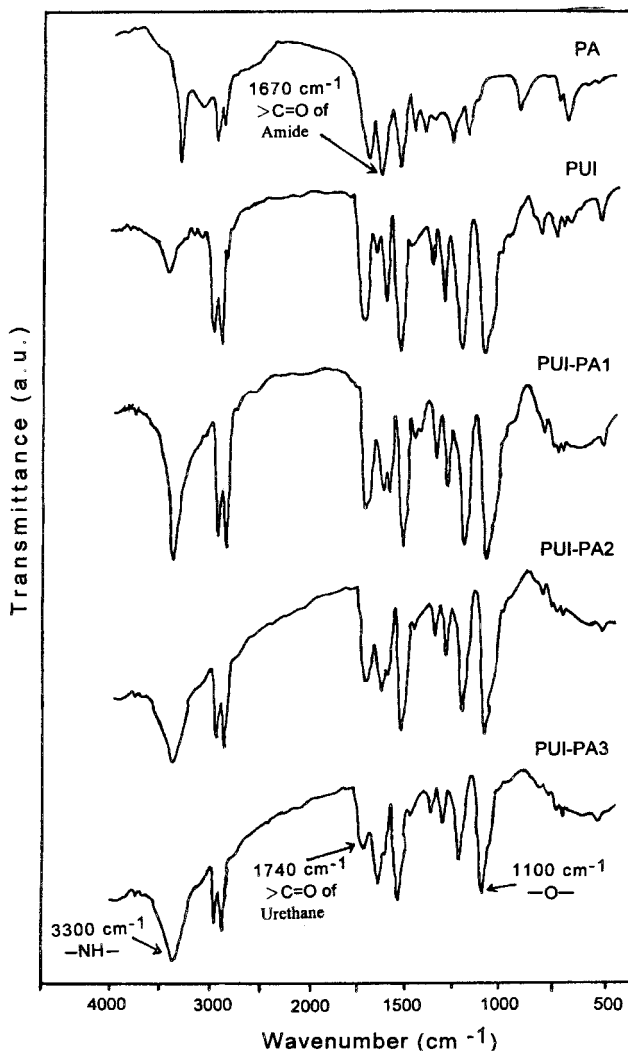


Figure 1 Infrared spectra of the PA and PU1 poly(urethane-amide) series film.

Mechanical properties were measured using an Instron Mode 1122 testing instrument (Instron, Canton, MA) at a cramp rate of 20 mm per min, a paper extension rate of 10 mm per min with the specimen of 50 mm in length, 10 mm in width, and 0.1–0.2 mm in thickness, and a full load of 20 kg.

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

To evaluate the dye uptake of the dyed PU, 0.05 g of dyed PU was dissolved in 100 mL of DMF, dilute to 2×10^{-5} g/cc of concentration, measured by the photometer, and compared with the absorption value of the standard dye solution. For the dye fastness of dyed PU, the AATCC test method of 61-1985 was used.¹³

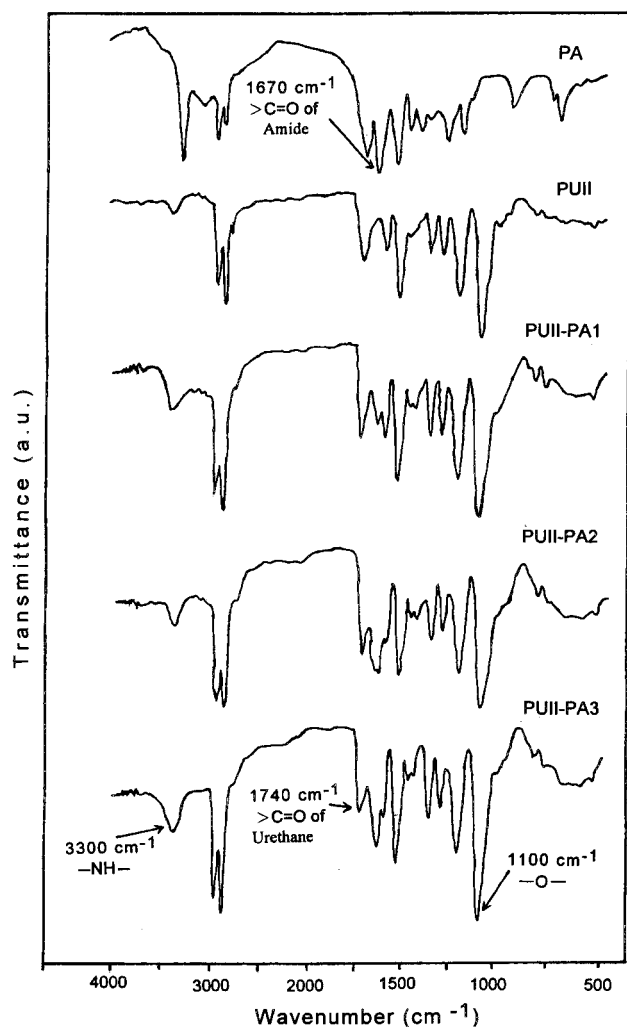


Figure 2 Infrared spectra of the PA and PU2 poly(urethane-amide) series film.

RESULTS AND DISCUSSION

Characteristics and inherent viscosity of modified polyurethane

As shown in Figures 1 and 2, the polyamide and PU films of modified and unmodified were analyzed by the infrared (IR) spectrophotometer.^{14,15} The characteristic IR absorption peak of $3,300\text{ cm}^{-1}$ demonstrates

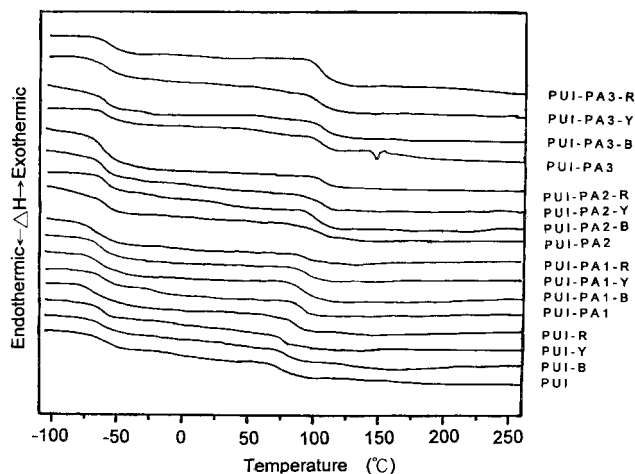


Figure 3 DSC curve of the PU1 poly(urethane-amide) series film.

the —NH— stretching vibration, and the $\text{—CH}_2\text{—}$ is observed at $2,940\text{ cm}^{-1}$. The characteristic absorption of C=O in urethane is observed at $1,740\text{ cm}^{-1}$; >C=O of the amide group is observed at $1,670\text{ cm}^{-1}$; C—O is observed at $1,230\text{ cm}^{-1}$; and C—O—C of PTMG is observed at $1,110\text{ cm}^{-1}$. Based on the above results, the modified polyurethane was successfully synthesized.

The inherent viscosity of all polymers is listed in Table II. It is found that the inherent viscosity varies with the difference in molecular weights of PTMG (molecular weights of 1,000 and 2,000) and the amide content. The modified PU exhibits a higher value of inherent viscosity than that of the unmodified PU and also increases with the amide content. It is explained that as the amide content increases, the H-bonding between the amide groups and polyurethane groups is promoted. The polarity is subsequently enhanced, so that the intrinsic viscosity is increased. The value is also found to be higher in the PU2 series. This suggests that the modified PU in the PU2 series with PTMG 2,000 as soft segment can obtain higher molecular weight than that in the PU1 series with PTMG 1,000, resulting in higher intrinsic viscosities. It is explained that with the same reactivity of —OH in

TABLE II
Intrinsic Viscosity of PU and Copoly(urethane-amide)

Code	Composition	Molar ratios	PA content (wt %)	η_{inh} (dL g ⁻¹)
PU1	MDI/PTMG 1,000/1,4-BD	2:1:1		0.43
PU1-PA1	MDI/PTMG 1,000/1,4-BD/PA	2:1:0.75:0.25	5.60	0.55
PU1-PA2	MDI/PTMG 1,000/1,4-BD/PA	2:1:0.50:0.50	10.75	0.59
PU1-PA3	MDI/PTMG 1,000/1,4-BD/PA	2:1:0.25:0.75	15.49	0.62
PU2	MDI/PTMG 2,000/1,4-BD	2:1:1		0.54
PU2-PA1	MDI/PTMG 2,000/1,4-BD/PA	2:1:0.75:0.25	3.50	0.64
PU2-PA2	MDI/PTMG 2,000/1,4-BD/PA	2:1:0.50:0.50	6.81	0.66
PU2-PA3	MDI/PTMG 2,000/1,4-BD/PA	2:1:0.25:0.75	9.96	0.70

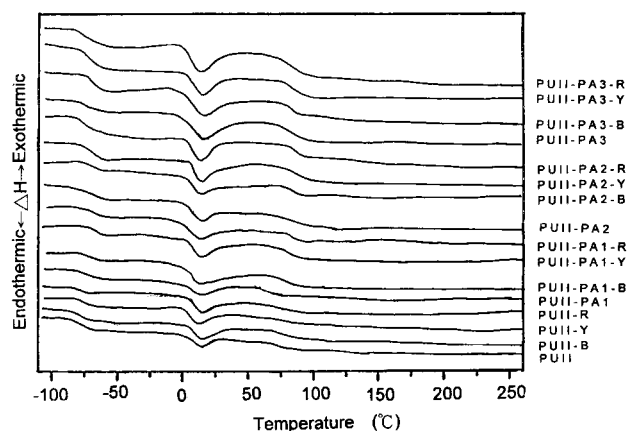


Figure 4 DSC curve of the PU2 poly(urethane-amide) series film.

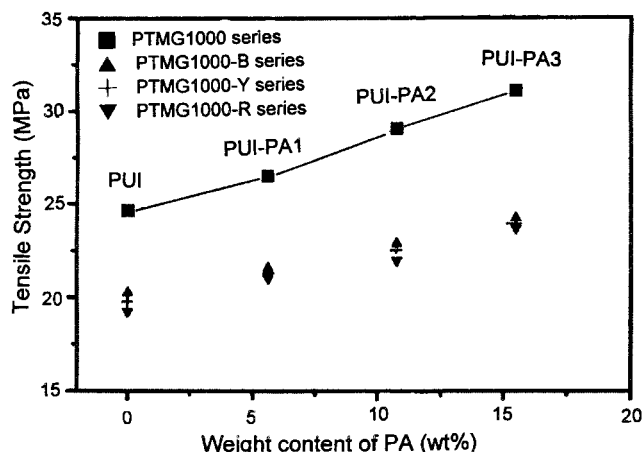


Figure 5 Effect of PA segment content on the tensile strength of the PU1 series film.

PTMG, a higher molecular weight of PTMG 2,000 would end up a higher molecular weight prepolymer than that of PTMG 1,000 as they reacted with MDI. Consequently, a higher molecular weight PTMG 2,000 polymer could be obtained.

Thermal properties of modified polyurethane

The thermal properties of all types of PU polymers measured by DSC are shown in Figures 3 and 4 and listed in Table III. In Table III, it is shown that the

TABLE III
Thermal Properties of Various PU

Code	Hard-segment content (wt %)	PA content (wt %)	$T_{g,s}$	$T_{m,s}$	$T_{g,h}$	$T_{m,h}$	$T_{g,h}-T_{g,s}$
PU1	37.11		-62.0		80.1		142.1
PU1-B	37.11		-61.5		82.4		143.9
PU1-Y	37.11		-61.4		83.1		144.5
PU1-R	37.11		-61.1		85.3		146.4
PU1-PA1	39.78	5.60	-60.5		90.2		150.7
PU1-PA1-B	39.78	5.60	-60.2		93.5		153.7
PU1-PA1-Y	39.78	5.60	-60.0		93.7		153.7
PU1-PA1-R	39.78	5.60	-59.6		94.9		154.5
PU1-PA2	42.23	10.75	-59.9		98.0		157.9
PU1-PA2-B	42.23	10.75	-59.7		101.7		161.4
PU1-PA2-Y	42.23	10.75	-59.7		102.4		162.1
PU1-PA2-R	42.23	10.75	-59.2		104.6		163.7
PU1-PA3	44.49	15.49	-59.1		104.7	160.5	163.9
PU1-PA3-B	44.49	15.49	-58.9		106.6		165.5
PU1-PA3-Y	44.49	15.49	-59.0		106.5		165.5
PU1-PA3-R	44.49	15.49	-58.4		107.3		165.7
PU2	22.78		-75.0		73.1		148.1
PU2-B	22.78		-74.5	13.4	74.8		149.3
PU2-Y	22.78		-74.6	13.3	75.0		149.6
PU2-R	22.78		-74.1	13.1	76.6		150.7
PU2-PA1	24.83	3.50	-70.4	13.6	78.5		148.9
PU2-PA1-B	24.83	3.50	-69.9	13.5	79.8		149.7
PU2-PA1-Y	24.83	3.50	-69.7	13.4	80.1		149.8
PU2-PA1-R	24.83	3.50	-69.4	13.2	82.0		151.4
PU2-PA2	26.77	6.81	-69.8	13.8	80.9		150.7
PU2-PA2-B	26.77	6.81	-69.6	13.7	83.1		152.7
PU2-PA2-Y	26.77	6.81	-69.5	13.6	83.5		153.0
PU2-PA2-R	26.77	6.81	-69.2	13.3	84.1		153.3
PU2-PA3	28.61	9.96	-69.1	14.1	83.2		152.3
PU2-PA3-B	28.61	9.96	-68.8	14.0	84.5		153.3
PU2-PA3-Y	28.61	9.96	-68.5	13.8	84.8		153.3
PU2-PA3-R	28.61	9.96	-68.3	13.7	85.6		153.9

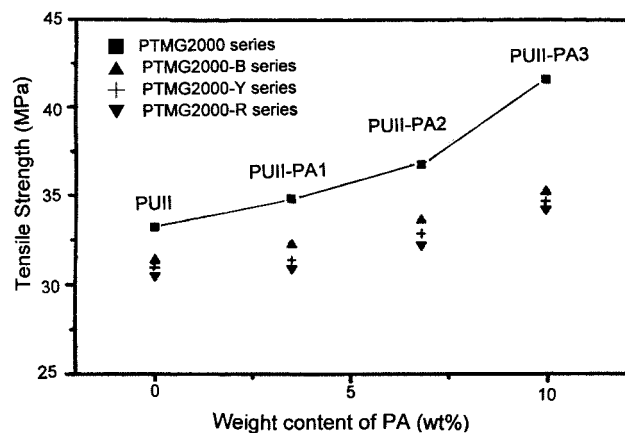


Figure 6 Effect of PA segment content on the tensile elongation of the PU2 series film.

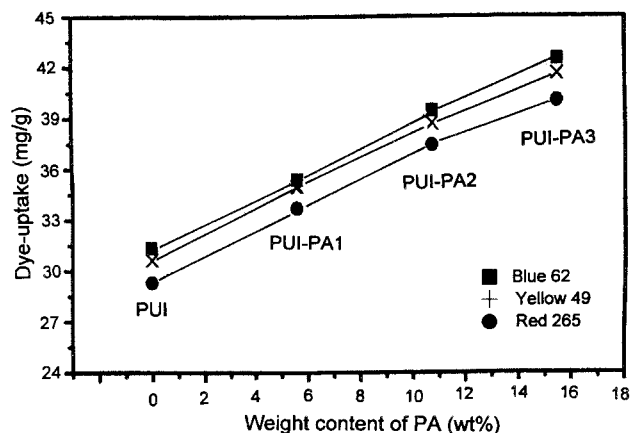


Figure 7 Effect of PA segment content on the dye uptake of the PU1 series film.

glass-transition temperature of soft segment (T_g^s) of type PU1-PA1 or PU2-PA1 with less hard-segment contents show a lower value than that of PU1-PA3 or PU2-PA3. 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 is not much affected after being dyed; for example, the T_g^s of PU1-PA1 and PU1-PA1-Y are -60.5 and -60.0°C , respectively. For the glass-transition temperature at a hard-segment region (T_g^h), it is

TABLE IV
Mechanical Properties of Various PU Polymers

Code	Hard-segment content (wt %)	PA content (wt %)	$M_{300\%}$ (MPa)	$M_{600\%}$ (MPa)	$M_{900\%}$ (MPa)	Tensile strength (MPa)	Elongation at break (%)
PU1	37.11		3.70	2.60		24.64	788
PU1-B	37.11		2.99	1.95		20.28	828
PU1-Y	37.11		2.92	1.90		19.78	836
PU1-R	37.11		2.82	1.83		19.24	857
PU1-PA1	39.78	5.60	4.29	2.94		26.50	738
PU1-PA1-B	39.78	5.60	3.51	2.30		21.59	806
PU1-PA1-Y	39.78	5.60	3.62	2.26		21.30	818
PU1-PA1-R	39.78	5.60	3.39	2.20		21.03	831
PU1-PA2	42.23	10.75	4.90	3.49		29.06	711
PU1-PA2-B	42.23	10.75	3.89	2.66		22.91	775
PU1-PA2-Y	42.23	10.75	3.86	2.57		22.89	786
PU1-PA2-R	42.23	10.75	3.83	2.57		22.00	806
PU1-PA3	44.49	15.49	5.48	4.27		31.07	663
PU1-PA3-B	44.49	15.49	4.15	2.80		24.25	744
PU1-PA3-Y	44.49	15.49	4.10	2.73		24.13	756
PU1-PA3-R	44.49	15.49	4.04	2.60		23.70	773
PU2	22.78		3.25	1.98	2.79	33.22	1146
PU2-B	22.78		2.78	1.68	2.31	31.38	1174
PU2-Y	22.78		2.83	1.76	2.38	31.19	1181
PU2-R	22.78		2.71	1.62	2.15	30.50	1230
PU2-PA1	24.83	3.50	3.74	2.41	3.23	34.82	1088
PU2-PA1-B	24.83	3.50	3.07	1.81	2.56	32.25	1154
PU2-PA1-Y	24.83	3.50	3.01	1.79	2.48	31.38	1173
PU2-PA1-R	24.83	3.50	2.86	1.72	2.14	30.91	1207
PU2-PA2	26.77	6.81	4.29	2.80	3.63	36.77	1020
PU2-PA2-B	26.77	6.81	3.33	2.02	2.84	33.63	1110
PU2-PA2-Y	26.77	6.81	3.47	2.00	2.77	32.87	1124
PU2-PA2-R	26.77	6.81	3.21	1.91	2.53	32.23	1160
PU2-PA3	28.61	9.96	4.89	3.24	4.44	41.58	939
PU2-PA3-B	28.61	9.96	3.77	2.34	3.19	35.24	1062
PU2-PA3-Y	28.61	9.96	3.66	2.25	3.30	34.70	1079
PU2-PA3-R	28.61	9.96	3.51	2.14	2.96	34.24	1095

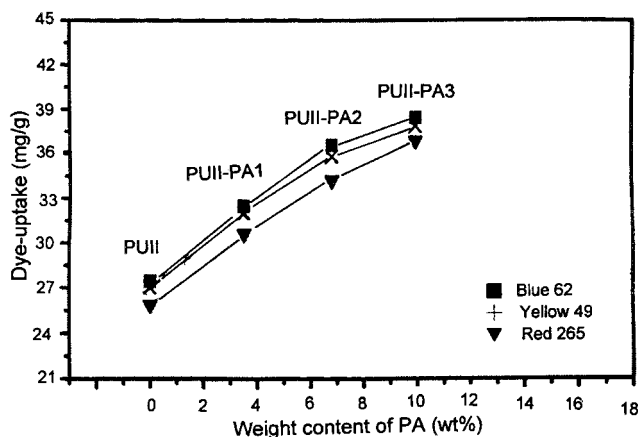


Figure 8 Effect of PA segment content on the dye uptake of the PU2 series film.

found that the T_g increases with more amount of hard-segment content and also the dyed PU. The reason is believed to be that the bulkiness of dye molecule causes higher steric hindrance and consequently stiffer and higher T_g . This result corresponds with the tensile property, which is mainly influenced by the hard-segment region. From this we can conclude that the dye in PU is mostly situated in the hard-segment region.

Also shown in Table III, the melting temperature of soft segment (T_m) is only seen in those PUs with

PTMG 2,000, that is, the PU2 series. It is in the range of 13.1–14.1°C and seems irregular with the kind of dye dyed. Besides, it is not clearly seen in the DSC figure for the melting temperature of the hard segment (T_m) except for PU1-PA3 with high amount of hard-segment content (44.49%). It is believed that the crystallinity region in the PU is not much. As the hard-segment content is less than 44%, the T_m is not manifested.

Mechanical properties of dye-modified polyurethane

The mechanical properties of all polymers are shown in Figures 5 and 6 and listed in Table IV. It is found that both the initial modulus and the breaking strength decrease with the presence of dye molecules in dyed PU, especially the strength. On the other hand, the breaking elongation increases with the dye molecule. This demonstrates that as the dye molecule is dyed 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 the other hand, since the amount of amorphousness in dyed PU is increased, the breaking elongation is promoted. Moreover, as shown in Figures 5 and 6, the tensile strength

TABLE V
Apparent Dye Uptake of Dye-Modified PU Films

Code	Hard-segment content (wt %)	PA content (wt %)	Dye added (mg g ⁻¹) ^a	Absorbency after dilution	Apparent dye uptake (mg g ⁻¹)
PU1-B	37.11		50.00	0.255	31.35
PU1-PA1-B	39.78	5.60	50.00	0.288	35.35
PU1-PA2-B	42.23	10.75	50.00	0.321	39.45
PU1-PA3-B	44.49	15.49	50.00	0.346	42.47
PU2-B	22.78		50.00	0.224	27.45
PU2-PA1-B	24.83	3.50	50.00	0.265	32.47
PU2-PA2-B	26.77	6.81	50.00	0.298	36.53
PU2-PA3-B	28.61	9.96	50.00	0.313	38.40
PU1-Y	37.11		50.00	0.065	30.90
PU1-PA1-Y	39.78	5.60	50.00	0.073	34.84
PU1-PA2-Y	42.23	10.75	50.00	0.082	38.89
PU1-PA3-Y	44.49	15.49	50.00	0.088	41.86
PU2-Y	22.78		50.00	0.057	27.06
PU2-PA1-Y	24.83	3.50	50.00	0.067	32.02
PU2-PA2-Y	26.77	6.81	50.00	0.076	36.01
PU2-PA3-Y	28.61	9.96	50.00	0.080	37.85
PU1-R	37.11		50.00	0.014	29.54
PU1-PA1-R	39.78	5.60	50.00	0.016	33.31
PU1-PA2-R	42.23	10.75	50.00	0.018	37.18
PU1-PA3-R	44.49	15.49	50.00	0.019	40.02
PU2-R	22.78		50.00	0.012	25.87
PU2-PA1-R	24.83	3.50	50.00	0.014	30.60
PU2-PA2-R	26.77	6.81	50.00	0.016	34.43
PU2-PA3-R	28.61	9.96	50.00	0.017	36.19

^a Amount of dye added (mg g⁻²) = dye/(MDI + PTMG + 1,4-BD + PA).

TABLE VI
Water Fastness of All PU Polymers

Code	C. I. Acid Blue 62	C. I. Acid Yellow 49	C. I. Acid Red 265
PU1	2-3	2-3	3
PU1-PA1	3	3	3-4
PU1-PA2	3-4	3-4	4
PU1-PA3	4	4	4-5
PU2	2	1-2	2-3
PU2-PA1	2-3	2-3	3
PU2-PA2	3-4	3	3-4
PU2-PA3	3-4	3-4	4

Grade of water fastness: 5, highest; 1, lowest.

is increased with the amount of hard segment. For example, the strength of PU1-PA3 and PU1-PA1 are 31.1 and 26.5 MPa, respectively. The higher value of PU1-PA3 can be attributed to its more hard-segment content (44.5%) than that in PU1-PA1 (39.8%). Also, the modulus of PU1 (at 300% elongation) with PTMG 1,000 also exhibits higher modulus than that of PU1 with PTMG 2,000, which are 3.70 and 3.25 MPa, respectively. Therefore, the initial modulus of all PU polymers increases with the content of hard-segment content.

Dye uptake and dye fastness of dye-modified polyurethane

The dye uptake of the dyed PU film was measured by the photometer and shown in Figures 7 and 8 and also listed in Table V. As seen in Table V, The dye uptake of modified polyurethane shows an increase in tendency as the amide content increases. This is attributed to the increase of the dye sites in the amide segment of the copolymer. Besides, when comparing PU1 with the PTMG 1,000 and PU2 with the PTMG 2,000 series, the former shows a higher dye uptake than the latter because of higher amide content in the PU1 series.

The dye-modified polyurethane was also measured by water fastness test and the results are listed in Table VI. It is found that water fastness is increased with increasing amount of amide content. Besides, the copolymer with more hydrophilic long-chain structure ($-\text{CH}_2-$) also enhances the dye uptake. This is attributed to the increase in affinity between the polymer and the dye stuff. Therefore, the water fastness of

copolymer can be up to 4-5 grade with higher PA content.

CONCLUSIONS

In this study, the copoly(urethane-amide) was synthesized with two different molecular weights of PTMG (1,000, 2,000), MDI, and extended with mixture of 1,4-butanediol and the polyamide 6,6 prepolymer. These modified PUs could promote the dyeability of acid dye. From the experimental results, the intrinsic viscosity of dyed PU is decreased, the tensile strength is lowered, but elongation is enhanced. Also, dyed PU exhibits greater $T_g h$ of the hard segment, but almost no effect on $T_g s$ and $T_m s$ of the soft segment. This indicates that the dye was dyed mainly in the hard-segment region of PU. For the dyeing properties, the dyed PU does show a higher dye uptake and water fastness, indicating that the presence of amide segment in the modified polyurethane can increase the affinity between the dye molecule and the modified polyurethane.

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