Synthesis, Properties, and Dyeing Application of Nonionic Waterborne Polyurethanes with Different Chain Length of Ethyldiamines as the Chain Extender

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ABSTRACT: This study deals with the synthesis of some nonionic waterborne polyurethanes (PUs), using ethyldiamines of different chain length, such as ethylenediamine (EDA) and diethyltriamine (DETA), as the chain extender in the reaction, and examines the thermal properties, mechanical properties, and dyeing properties of the PU products and their blends. As far as each PU by itself is concerned, we found that the T_g of the one made with DETA is the highest, followed by that with EDA, and the one with 1,4-butanediol (1,4-BD) is the lowest. The PU made with 1,4-BD as the chain extender has no T_m, while the two others, using diamines as chain extenders, have a clear T_m, the one with DETA being higher than that with EDA. However, the enthalpy data are just the opposite. The tensile strengths of the two PUs, made with diamines as the chain extender, are larger than that made with 1,4-BD, but their respective elongation properties are just the opposite. A comparison within PUs made with diamines showed that the one made with EDA is greater in both strength and elongation categories than that made with DETA. However, the one made with DETA is far superior to both of those made with 1,4-BD and EDA in their dye-exhaustion ratio, color yield (K/S), fixation rate, and color fastness. In respect to the various PU mixtures that we examined, we found that both PUs synthesized with EDA or DETA as the chain extender would have their T_g's greatly increased by blending in some PU made using 1,4-BD as the chain extender. Among them, in particular, a blend of PU, made separately with DETA and 1, 4-BD as the chain extender, showed great improvements in both tensile strength and elongation and also demonstrated better dyeability. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2824–2833, 2003

Key words: thermal properties; mechanical properties

INTRODUCTION

In general, polyurethane (PU) is synthesized by first forming a prepolymer, using isocyanate as the hard segment and polyol as the soft segment, followed by a chain-extending reaction using a diamine or diol such as 1,4-butanediol (1,4-BD) and ethylenediamine (EDA). Since PU possesses various desirable properties, derived from its characteristic structure with phase separation from alternating hard and soft segments, it is widely applied in the fields of flexible fibers, paints, adhesives, artificial leather, etc. In fabric-finishing processes, it is usually used in high added-value products to improve properties such as water resistance and water-vapor permeability and to provide better texture for handling. The properties of PU products are greatly influenced by the composition of soft and hard segments and the chain extender used, the different chain extender alone making a big difference in the mechanical properties and flexibility of the end product. Furthermore, due to lack of dyeing sites, PU products are normally rather poor in their dyeing properties (dyeing ability and color fast-

ness). Therefore, to improve physical properties, especially dyeing properties, it is very important to vary the structure and composition of the polymer, whether PU is used in the membrane form or as processed artificial leather goods.

Previously, researchers tried to improve the dyeing properties of formed membrane objects by introducing dyeable functional groups into PU, directly grafting dyestuff molecules into PU, copolymerizing with dyestuff, or by fixation treatment after the dyeing process. For example, Wang and Tzun[1,2] used *N*-(2-hydroxyethyl)-ethyldiamine as the chain extender to synthesize PU with an —OH group in its side chain, then linked the resultant PU with a dispersed dyestuff containing —NH_2 groups that were pretreated with epichlorohydrin. They found that the dyeability and thermal migration value of the PU were considerably improved, but its viscosity became lower. At the same time, the formed membrane tended to have the glass transition point of the soft segment and lower strength, while its elongation increased. Jia and Yu[3] used sodium hydride to ionize the "*N*" position on the main-chain urethane of a cation-type PU, then let it react with azo dyes having terminal Br, and studied the substituting level of various dyes and their effects on the PU properties. They found that a higher substituting level of azo dyes would result in an

increase in the stereohindrance, making the molecular chain less easy to rotate; thus, the T_g's of PU increased. Chao et al.[4,5] employed a —NH$_2$ group-containing reactive dye as the chain extender to directly synthesize a dye-based PU ionomer and found that when the dye concentration increased the surface tension of the aqueous solution of the synthesized waterborne PU decreased, the particle size became larger, and the formed membrane became stronger, but elongation became smaller.

Diamine or diol is usually used as the chain extender in PU synthesis, causing many differences in terms of the requirements of synthetic reaction conditions as well as the properties of the synthesized end products. As diamines are comparatively more reactive, it is easy to form PU at lower temperatures and the synthesized PU usually has better mechanical properties. Most syntheses of waterborne PU are carried out with diamine as the chain extender. On the contrary, diols need high temperature to be reactive. It is usually necessary to add solvent to the reaction mixture to avoid gelatinizing during the synthetic process. Therefore, diol is often used in the synthesis of solvent-type PU. The end product feels soft but it is lower in strength.

In earlier research on chain extenders, Ramesh et al.[6] compared the mechanical properties of several PUs made with different diamines or diols as the chain extender and found that those made with diamines were better than those with diols in this respect. The reason is that the increased intermolecular hydrogen bonding improves the aggregating strength. Matine et al.[7] also compared the influence of various diols as chain extenders on the properties of the product and found that the chain length of the chain extender was able to affect the segment-arranged structure and the character of the PU formed. Frisch et al.[8] compared three chain extenders of different chain length, that is, hydrazine (HD), ethylenediamine (EDA), and 1,6-hexamethylenediamine (HMDA), and found that the enthalpy of their respective PU products were in the order of HMDA > EDA > HD in their thermal properties. They also found that the longer the length of the chain extender the better was the mechanical properties of the resulting PU materials. In addition, Debowski and Balas[9] tried to use a mixture of ethylene urea (EU) and 1,4-BD with various ratios as the chain extender to synthesize solvent-type PU and found that blending a small amount of EU to it would make PU with a better tensile strength and elongation and a narrower distribution of molecular weight.

From the above-mentioned survey, clearly, the chain extender has a profound influence on the physical properties of the resulting PU through its aggregating function asserted between PU molecules. Other than that role, a chain extender can be expected to bring in certain functional groups relevant to dyeing properties. To improve the physical properties or dyeability of a PU-formed membrane, this study made use of two diamines with different chain length, that is, EDA and DETA, as the chain extender in a synthesis of nonionic waterborne PU. We tried to determine if the presence of the functional group —CH$_2$CH$_2$NH$_2$ would affect the physical properties and dyeability of the end products. We blended the resulting diamine PU with PU synthesized with 1,4-BD as the chain extender to investigate the properties of the formed PU membranes with different blending ratios.

EXPERIMENTAL

PU synthesis

Synthesis of nonionic center

Before synthesizing waterborne PU, we had to first synthesize a so-called nonionic center. This step was done according to the method reported by Noll et al.[10] It started with dissolving 1 mol of poly(ethylene oxide)monomethyl ether (PEO, molecular weight 750; Aldrich) into 1-methyl-2-pyrrolidone (NMP; Acros) with rigorous stirring and added 1 mol of isophorone diissocyanate (IPDI; Acros, GR grade) afterward. Then, we added 0.01 mol of di-n-butyltin dilaurate (DBDTL; TCI) drop by drop into the reaction mixture placed in a four-aperture reactor. It was reacted at 45°C under a pure nitrogen environment for 4 h, and then the temperature was increased to 50°C. One mole of N-diethanolamine (NDEA; Acros, GR grade) was added and reacted for 1 more h, and the nonionic center was obtained. The reactions involved are as follows:
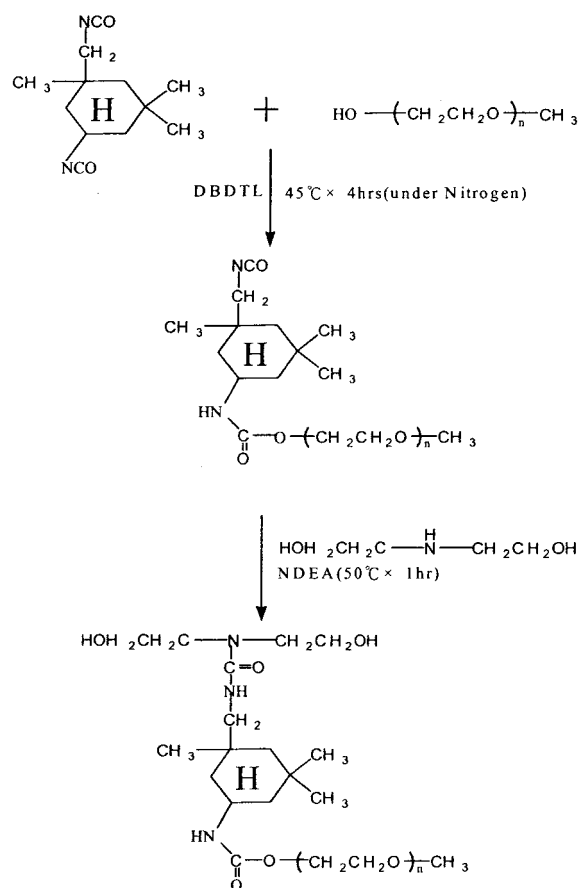
Synthesis of nonionic waterborne PU

First, we took 1 mol of polycaprolactonediol (PCL, molecular weight 530; Solvay Taiwan) and the non-ionic center, placing them in a vacuum device to get rid of the moisture content and then added to it 4 mol of 4,4′-methylenedicyclohexyl diisocyanate (H$_{12}$MDI; Bayer). The reaction was under nitrogen at 50°C initially and then the temperature was increased gradually to 80°C. The prepolymerization lasted 4 h to form the prepolymer. Before it was cooled to room temperature, water was added to let it emulsify. Finally, we separately added chain extenders 1,4-BD (Acros, GR grade), EDA (Acros, GR grade), and DETA (Acros, GR grade) to go through the chain-extending reaction and obtained the aqueous solution of those water-soluble PU made from different chain extenders. The synthetic reactions of nonionic waterborne PU are as follows:
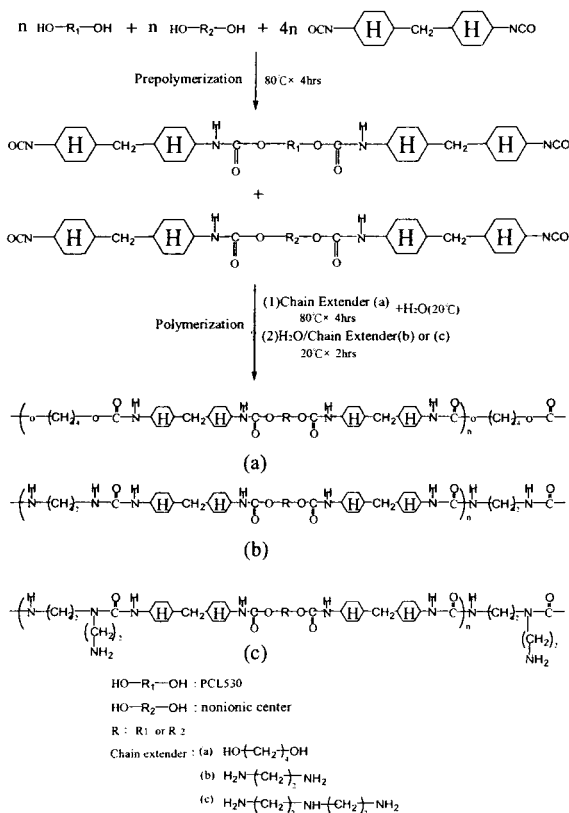
Analyses of PU structure and tests of physical properties

Analysis of PU product structure

For structural analysis of the polymer, we titrated the NCO terminal content and ran a Fourier IR spectrum analysis (FTIR). At various reaction instances during the prepolymerization reaction, the NCO terminal contents were analyzed following a method reported by David and Staley[11] using reverse titration of normal butyldiamine. The FTIR spectrum analysis was carried out by the KBr method at 25°C. The scanning range was 4000–400 nm, while the resolution was 8, and the scan, 16.

Physical property tests of PU

Some 30% waterborne PU was spread evenly on top of a Teflon sheet and let dry in open air for 3 days and then in a 50°C circulating hot-air oven for another 3 days to completely get rid of the moisture and any residual solvent for the formation of a thin membrane. The resulting membrane was tested for differential scanning calorimetric (DSC) analysis and membrane tensile–elongation measurement. The DSC analysis was performed with a differential scanning calorimeter (Perkin–Elmer) to measure the heat variation at an increasing temperature rate of 10°C/min. The measuring range of this analysis was set between −100 and 100°C. The membrane tensile–elongation test was carried out according to the ASTM D 638M-93 method. The crosshead speed was set at 300 mm/min, the pinch-head pinching distance was 20 mm, and the pinch-head load weighed 10 kg.

Dyeing method and dyes property test

For studies on coating nylon fabrics, a 30% WBPU dispersion blended with 0.4% melamine resin, 0.5% of the thickening agent [NH$_4$OH(aq)], and 0.01% of the catalyst was coated onto nylon taffeta fabrics. The coated nylon fabric was dyed with an acidic dye (C.I. Acid Blue 40, 3% owf). The pH of the dye bath was adjusted to 2.85; the bath ratio, to 1:30; and the temperature, to 90°C; under such conditions, the fabric was dyed for 30 min. After that, the dyed fabric was washed with Marseilles soap at 60 °C × 10 min. The dye-exhaustion ratio was calculated from the difference of dye concentration in the dye bath before and after the dyeing session. The dye concentration was calculated by taking the UV light absorbency of the dye solution with a Shimadzu UV-240 spectroscope and comparing the data with a standard concentration curve. The dye exhaustion ratio was $E \% = 1 - A_2/A_1 \times 100\%$, where A_1 and A_2 are the dye concentrations before and after the dyeing session, respectively. Color yield, shown as the K/S reflection value of the PU-coated surface of the test fabric, was measured with an ACS color-measuring instrument. Fastness to washing and fastness to friction were determined by the CNS-8149 and CNS-3843B methods, respectively.

RESULTS AND DISCUSSION

Synthesis and identification

Figure 1 illustrates the residual NCO value (weight percent) analysis of the waterborne PU prepolymer-
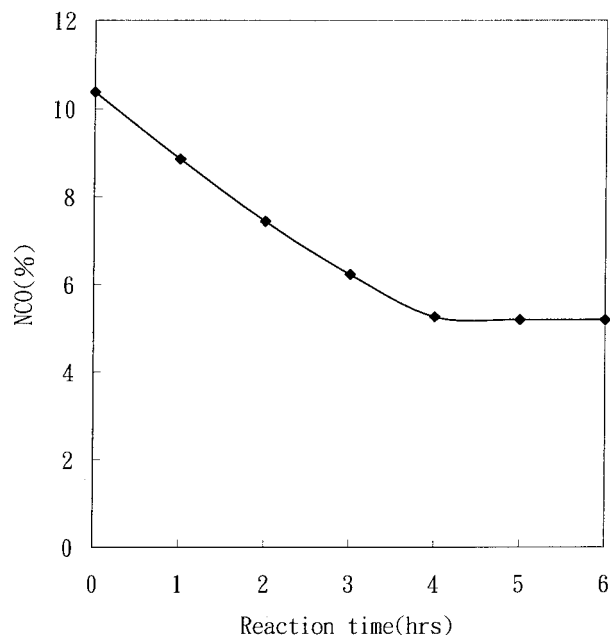
Figure 1 Residual NCO value (wt %) analysis of the waterborne PU prepolymerization after different periods of reaction time.

ization after different reaction times. It shows that the resulting PU prepolymer, after 4 h of reaction, gives a residual NCO value equivalent to half of that before the reaction started, an indication of the completion of the PU prepolymerization and the reason why the prepolymerization proceeded for 4 h to form the waterborne PU.

Figure 2 shows FTIR spectroscopic analyses of the synthesized waterborne PU. (a) is the FTIR spectrum for the prepolymer before the chain-extending reaction; (b), (c), and (d) are FTIR spectra for the synthesized waterborne PU polymers, each made with 1,4-BD, EDA, or DETA, respectively, as the chain extender. From this figure, we can see that the absorption peak of NCO at 2250–2270 cm^{-1} is very prominent before the chain-extending reaction, but this peak disappeared in all PU products after the chain-extending reaction. Instead, there are absorption peaks in all three spectra of the PU products at 3327, 1730, 1530, and 1450 cm^{-1} corresponding to functional groups of —NH—, —C=O, —COO—, and —CNH, respectively. These prove the formation of urethane groups in the nonionic waterborne PU. Besides, we can see that, in (c) and (d), an obvious absorption peak also shows up at a frequency of 1658–1640 cm^{-1} typical for C=O in a urea group. This is due to the fact that (c) and (d) are the spectra of PU made with ethyldiamines used as the chain extender and there are urethane and urea groups coexisting in those PU products.

We also found, in (c) and (d), that the —C=O absorption peak seems to be split. The two peaks

located at 1730 and 1712 cm^{-1} represent the free and bonded C=O absorption of urethane groups, respectively, while peaks at 1658 and 1640 cm^{-1} represent the free and bonded C=O absorption of urea groups, respectively. This indicates that, in the case of PU synthesized using diamine as the chain extender, the existence of urea groups would increase the opportunity of hydrogen-bond formation in PU molecules. Copper et al.[12–14] studied the effects of the urea segment on intermolecular hydrogen bonding and found that the strength of intermolecular bonding increased along with the content of the urea group. Furthermore, in Figure 2(d), we find that the bonded C=O at 1640 cm^{-1} is apparently enhanced. It indicates that, in comparison of the intermolecular hydrogen bonding strength in PU made with DETA to that in PU made with EDA, the former is slightly stronger than is the latter.

PU thermal property test

To analyze all nonionic waterborne PUs and their mixtures with DSC, we listed the relevant glass transition temperatures (T_g's) of the soft segments, the melt point of the soft segments (T_m), and the enthalpy (ΔH) data in Table I and graphed T_g against the blending ratio in Figure 3. From the T_g and T_m listed in Table I, we can see that, among pure PUs, the T_g of the one made with DETA is the highest, followed by that with EDA, and the one with 1,4-BD is the lowest. The PU made with 1,4-BD as the chain extender has no T_m, while the two others using diamines as chain extenders show a clear T_m, and the one with DETA is higher than that with EDA.

However, the enthalpy data are just the opposite. In other words, as far as the T_g of PU is concerned, DETA > EDA > 1,4-BD, which clearly shows that both PUs synthesized with the diamines have a larger restricting force toward the internal soft segment than has the one with 1,4-BD. The reason for the T_g of PU derived from DETA being larger than that from EDA is that the former has another —CH$_2$CH$_2$NH$_2$ group, which is able to hydrogen bond with PCL. As to the T_m, because we used PCL530 as the soft segment in this study and its molecular weight was rather low, the PU thus formed does not easily form crystals between its main chains.[15] PU formed with 1,4-BD has lower hydrogen bonding between its hard segment. In the case of 1,4-BD as the chain extender, there is no T_m formed as a result. However, in the case of diamine used as the chain extender, the urea group becomes part of the PU molecule, enhancing the opportunity of hydrogen bonding between its hard segments. As a result, the restriction between those hard chains becomes greater, which may make the side-chain PEO on the hard segment or the soft segment easier to gather. In the meantime, there is a repellent force between PCL and
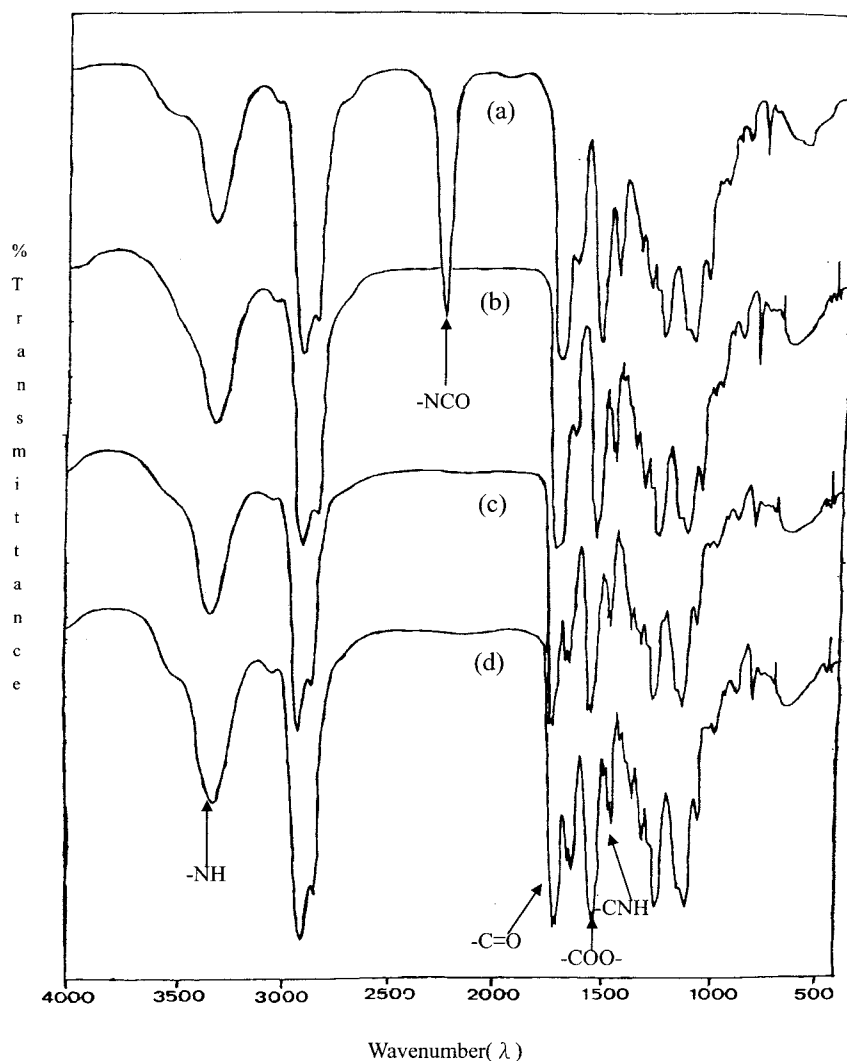
Figure 2 FTIR spectroscopic analyses of the synthesized waterborne PUs: (a) prepolymer; (b) with 1,4-BD as chain extender; (c) with EDA as chain extender; (d) with DETA as chain extender.

PEO, which might facilitate the alignment of PEO to form crystals. So, the two PUs using diamines as chain extenders have clear T_m's.

Earlier studies[16-19] compared urea with urethane by their influence on polymer properties and found that an increase in the urea group content would enhance

TABLE I
Thermal Property of Nonionic Waterborne PUs and Their Blends

Code[a]	PU composition		T_g (°C)	T_m (°C)	ΔH (J/g)
	Chain extender	Blending ratio			
B100	1,4-BD	—	−47	—	—
E100	EDA	—	−39	22	4.5
D100	DETA	—	−27	33	2.7
B75-E	1,4-BD/EDA	75/25	−30	—	—
B50-E	1,4-BD/EDA	50/50	−27	—	—
B25-E	1,4-BD/EDA	25/75	−25	—	—
B75-D	1,4-BD/DETA	75/25	−20	—	—
B50-D	1,4-BD/DETA	50/50	−15	—	—
B25-D	1,4-BD/DETA	25/75	−12	—	—

[a] B, E, and D of the code indicates 1,4-BD, EDA, and DETA as the chain extender, respectively. The number of the code shows the blending ratio of the waterborne PU.
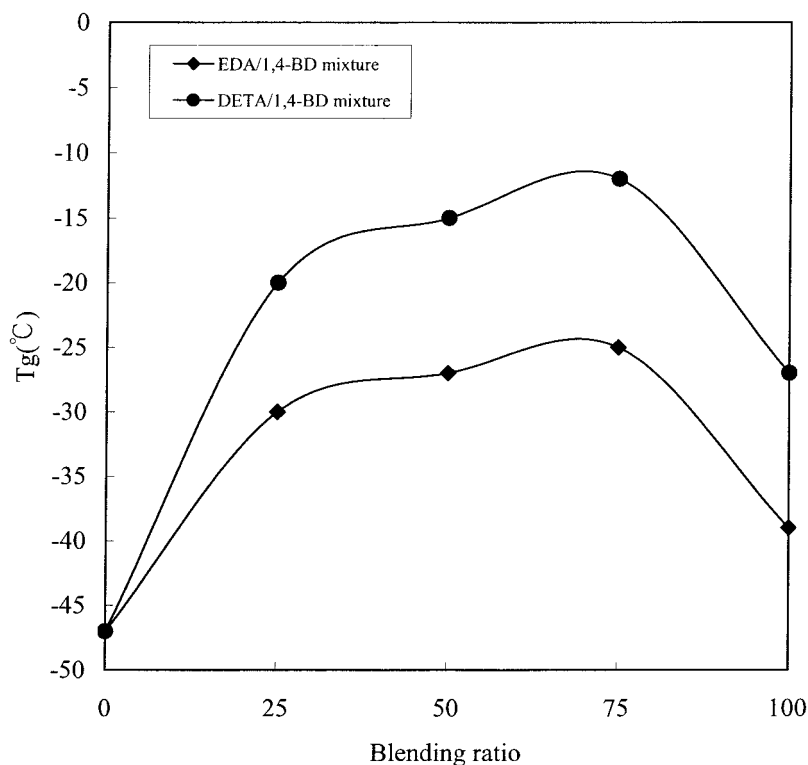
Figure 3 Effect of blending ratio against T_g of nonionic waterborne PU with different chain extenders.

the extent of hydrogen bonding between hard segments to result in phase segregation. Other than that, PU formed with DETA as the chain extender has a higher T_m but lower ΔH than those of the PU with EDA. The reason lies in the fact that DETA has —$CH_2CH_2NH_2$ and can form stronger hydrogen bonding to result in a higher T_m. It is also due to the presence of —$CH_2CH_2NH_2$ that its increased stereo-hindrance causes reduced crystallinity and, hence, a smaller ΔH. PU formed with diamine as the chain extender would have a greater hydrogen-bonding force, which is amply demonstrated in the FTIR analyses shown in Figure 2.

Figure 3 shows the effect of the blending ratio on the T_g of blended PUs formed from different chain extenders. We can see that, whenever we blend PU formed with EDA or DETA into PU formed with 1,4-BD, we always end up with a much higher T_g than those of pure PU by themselves, and it reaches a maximum at a blending ratio of 75/25. Blending probably increases the extent of phase mixing between hard and soft segments. Furthermore, this kind of phase mixing also causes chaotic results in the arrangement of PEO side chains and prevents them from forming crystals (see Table I).

Mechanical property test of PU membrane

Figure 4 shows stress–strain curves of various PUs formed using different chain extenders and their

blended mixtures. Their corresponding tensile strength, elongation, and modulus are listed in Table II. As to the individual PUs, PU formed with diamine as the chain extender has a higher tensile strength than that formed with 1,4-BD, but for elongation, the result is the opposite. When EDA is used as the chain extender, the formed PU contains a urea group in its hard segment and the group has greater hydrogen bonding to improve the restricting force of the hard segment toward the soft ones, which is why its strength is greater than that of PU from 1,4-BD, but its elongation lower. However, in comparison of PUs made from the two diamines, we find that the one from EDA has greater tensile strength and elongation than has the one from DETA. The situation is different from that of T_m and ΔH. As we mentioned earlier, the one derived from DETA has an extra —$CH_2CH_2NH_2$ side chain that would facilitate intermolecular reaction through hydrogen bonding and the tensile strength should to be larger than that with EDA. However, also because of the presence of —$CH_2CH_2NH_2$ groups, the increase in stereohindrance influences the arrangement of the main chains in the molecule, plus the larger local stress caused by side-chain crystallinity results in the fact that PU made from DETA has lower tensile strength than that of the one from EDA: The former has almost no elongation and appears brittle. Minoura et al.[20] investigated the effect of the side chain on the mechanical properties and found that
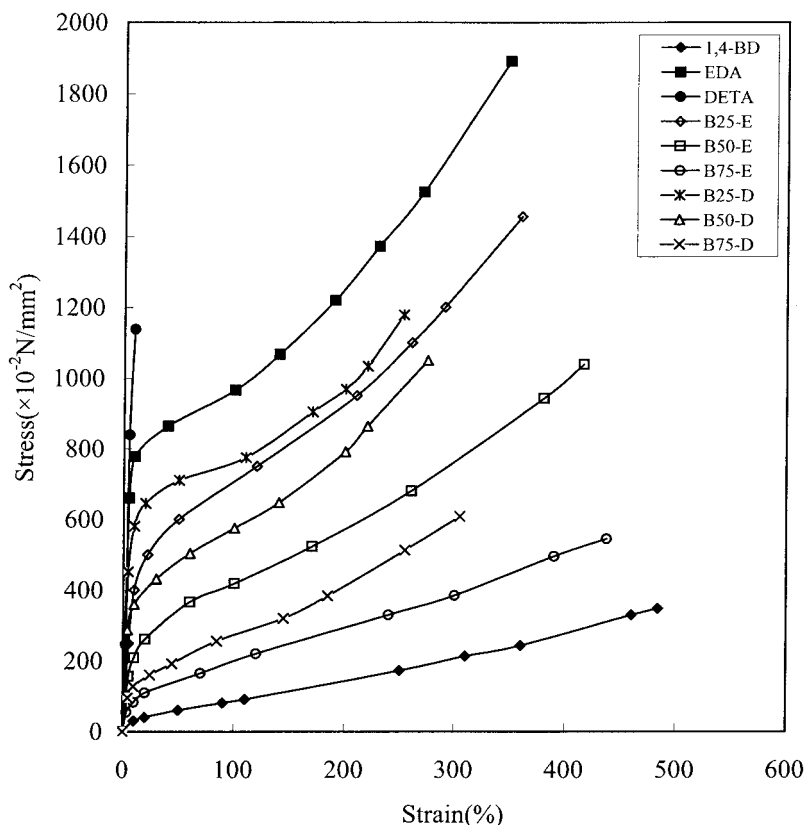
Figure 4 Stress–strain curves of various PUs formed used different chain extenders and their blended mixtures.

mechanical properties of the elastomers derived from the chain extenders having a methyl side group or double bonds were poor because of the disturbance in orientation.
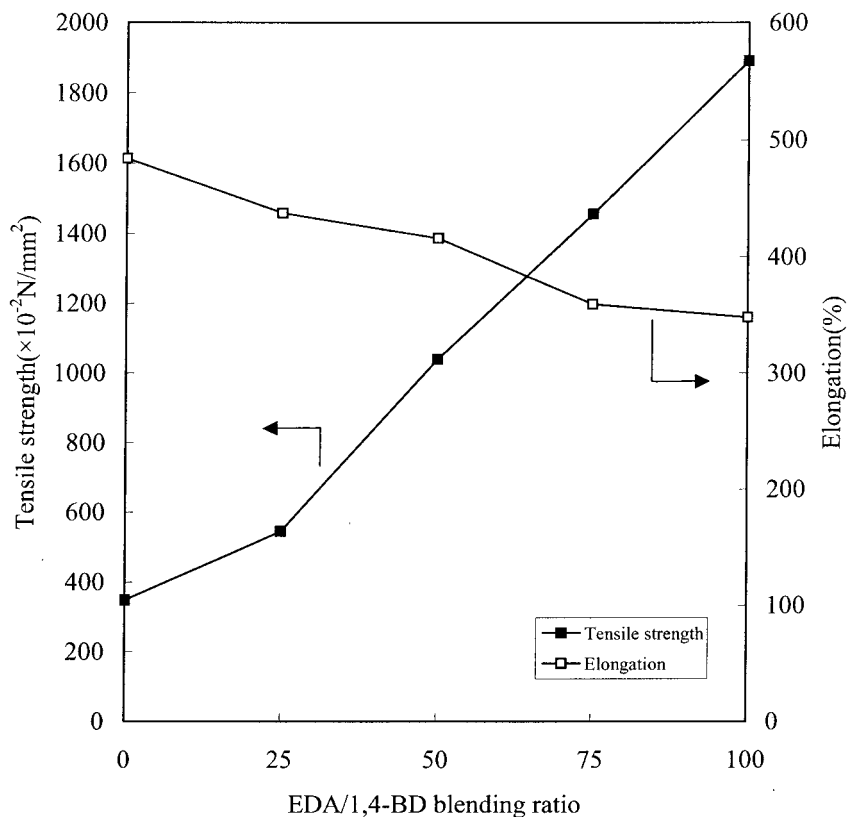
Figures 5 and 6 show the tensile strength and elongation of fabricated membranes made by blending PU formed with EDA and DETA, respectively, into PU formed with 1,4-BD. We found that the tensile strength of blended PU increases but elongation decreases with the blend ratio of EDA–PU stoichiometrically. However, when DETA is involved

instead of EDA, the increases in both tensile strength and elongation are significant and there is a significant improvement in the physical strength of the membrane. Among those blended mixtures, the improvement seems to reach a maximum with a combination of D75B25. This might be because, of the two PU that are more compatible in the mixture (greater T_g), the flexible chains in the 1,4-BD–PU can better fit into the side-chain stereohindrance effects of the DETA–PU, so that local crystallinity disappears and higher elongation is obtained.

TABLE II
Mechanical Properties of Nonionic Waterborne PU-formed Membrane

| Code[a]	Tensile strength ($\times 10^{-2}$ N/mm^2)	Elongation (%)	Young's modulus at 100% elongation ($\times 10^{-2}$ N/mm^2)	Young's modulus at 200% elongation ($\times 10^{-2}$ N/mm^2)	Young's modulus at 300% elongation ($\times 10^{-2}$ N/mm^2)
B100	348.48	484.00	86.42	68.63	68.97
E100	1891.10	348.00	965.88	632.91	552.41
D100	1138.70	9.50	—	—	—
B75-E	545.51	437.50	193.41	173.57	128.57
B50-E	1039.26	416.00	418.85	285.34	253.05
B25-E	1455.84	359.50	710.41	470.27	415.24
B75-D	573.60	304.50	272.26	208.2	197.52
B50-D	1050.60	274.50	575.67	395.78	—
B25-D	1178.70	252.50	762.12	484.40	—

[a] See footnote a to Table I.

Figure 5 Tensile strength and elongation of nonionic waterborne PU-formed membrane made with 1,4-BD and EDA as chain extenders and their blends.

Dyeability of PU-coated nylon fabrics

Table III shows the dyeability results of nylon fabrics coated with various PUs and their mixtures with
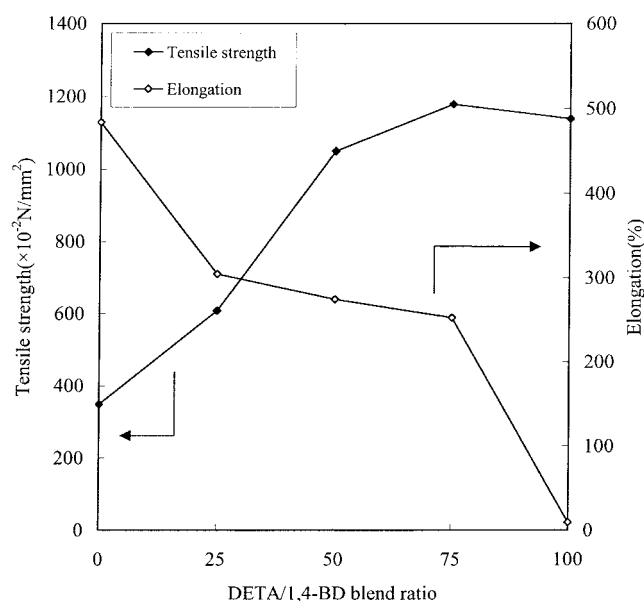
Figure 6 Tensile strength and elongation of nonionic waterborne PU-formed membranes made with 1,4-BD and DETA as chain extenders and their blends.

acidic dyestuff. We found from the data presented that the dye-exhaustion ratio, color yield (K/S), and color fastness of fabrics coated with PU made with diamines (EDA and DETA) are all higher than those for fabric coated with 1,4-BD–PU and that DETA–PU is the better of the former two. The addition of DETA–PU into 1,4-BD–PU not only enhances the color yield, but also has better fastness to washing as the content of the former increases. Figure 7 shows the effect of the blending ratio on the complete adsorption rate, in which we can clearly see that the EDA–PU in the blending with 1,4-BD–PU can only moderately improve the dye-exhaustion ratio of its coated nylon fabric, whereas the one replaced with DETA–PU gives tremendous enhancement to the dye-exhaustion ratio. The ratio approaches 100% when the blending ratio reaches 75%. In this study, we realize that, in this experiment, part of the adsorption comes from the nylon fabric itself, but the difference shown in the figure is surely due to the various adsorptions by the PU used. Figure 8 is the result of K/S. K/S represents the reflection measurement of the PU-coated nylon fabric surface. This figure shows that the DETA–PU blended with 1,4-BD–PU has higher dyeability. When the blending ratio reaches 50%, the K/S value is significantly enhanced. Again, the diamine chain extender adds a urea group into the PU structure, while

TABLE III
Dyeability Results of Nylon-coated with Various PUs and Their Blends with Acidic Dyestuff

Code[a]	Color yield (K/S)	Dye-exhanstion ratio ($E\%$)	Fastness to washing (degree)	Fastness to friction (degree)
B100	14.17	37.40	1–2	4
E100	37.47	87.23	2–3	5
D100	39.75	99.63	4–5	5
B75-E	26.66	40.00	1–2	5
B50-E	30.40	51.64	1–2	5
B25-E	31.02	73.31	1–2	5
B75-D	31.61	61.00	1–2	5
B50-D	37.84	90.97	2–3	5
B25-D	40.35	98.52	3–4	5

[a] See footnote a to Table I.

the diol chain extender adds an urethane group instead. The former has relatively more dye affinity from the —NH— group, so its dyeability tends to be better. Both fabrics coated with DETA–PU or DETA–PU blended with 1,4-BD–PU have the best dye-exhaustion ratio as well as fastness. This is due mainly to the existence of side-chain —CH$_2$CH$_2$NH$_2$, as the —NH$_2$ in it would form stronger ionic bonding with the dyestuff, which causes the increase in fixation between the dye and PU as well as in the color fastness of the PU-coated fabrics to washing.

CONCLUSIONS

This study dealt with the synthesis of nonionic waterborne PU using two ethyldiamines of different chain length as the chain extender in the reaction and investigated some physical properties and dyeability of the fabricated membranes of the PU products as well as its blends with the PU formed with 1,4-BD as the chain extender. The results can be summarized as follows:

1. With respect to the thermal properties, between individual PUs, the T_g of DETA–PU is the largest of the three, followed by EDA–PU, and that of 1,4-BD–PU is the lowest. 1,4-BD–PU has no T_m at all while the two PU formed with diamines as chain extenders show obvious T_m. The T_m of DETA–PU is higher than that of EDA–PU; however, their enthalpies are in the opposite order. In the cases of PU formed with diamines but blended in with 1,4-BD–PU, the fabricated ob-
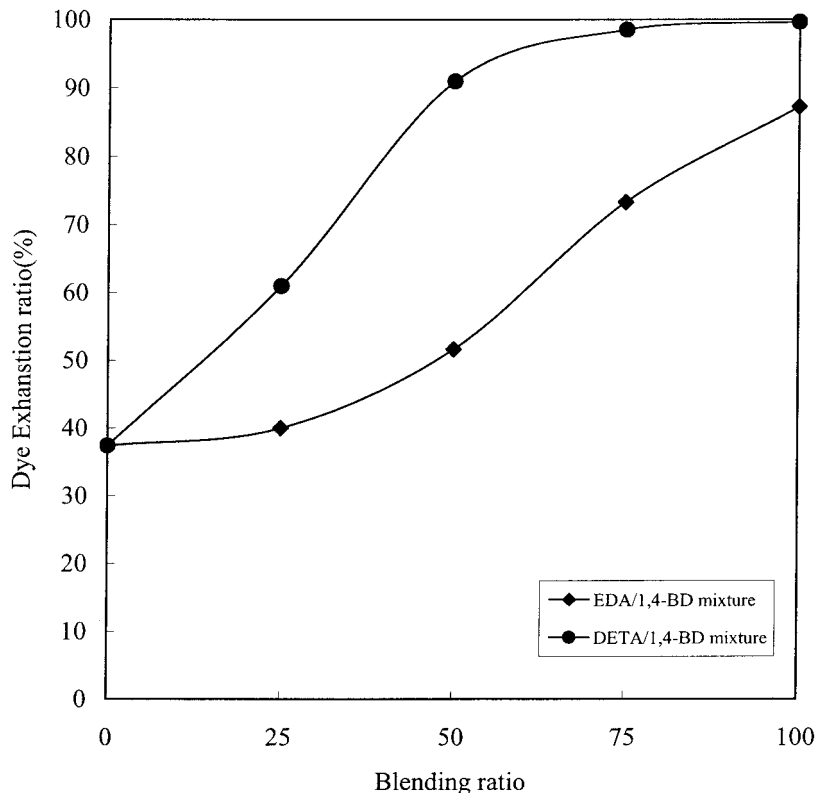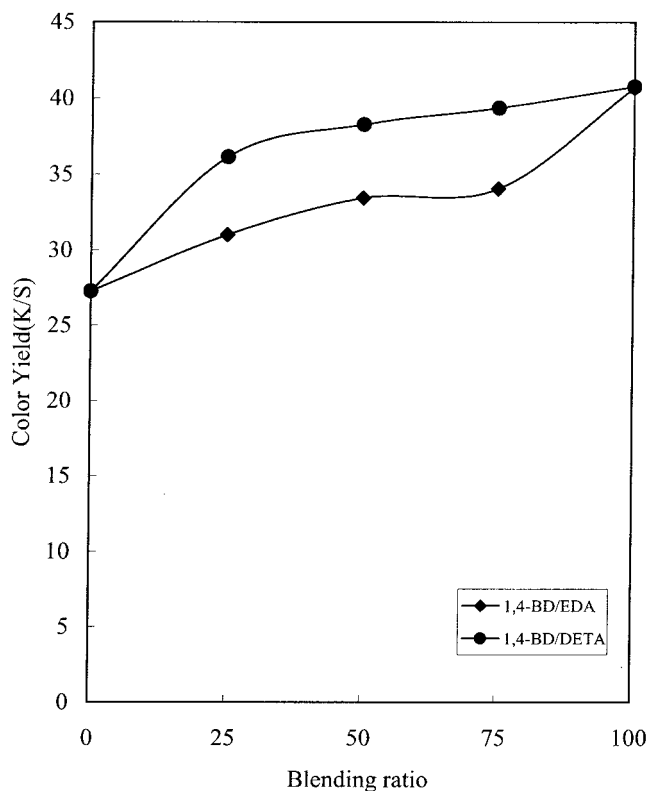

Figure 7 Effect of blending ratio on dye-exhanstion ratio of nonionic waterborne PU with different chain extenders.

Figure 8 Effect of blending ratio on color yield (*K/S*) of nonionic waterborne PU.

jects show no T_m. However, the T_g of both PUs with 1,4-BD–PU added are enhanced significantly and become far greater than those of the pure PU. Both reach their maximum at a blending ratio of 75/25.

2. With respect to mechanical properties, again as far as individual PU are concerned, PU formed with diamine as the chain extender has higher tensile strength than that of the 1,4-BD–PU, but the elongation is just the opposite. As the data of the two diamine–PUs were compared, we found that EDA–PU is higher than DETA–PU in both categories. For the mixture of the diamine–PU and the diol–PU, we found that the addition of DETA–PU into 1,4-BD–PU led to great improve-

ment both in tensile strength and elongation, reaching its maximum in a composition of D75–B25.

3. With respect to dye properties, fabrics coated with PU formed with diamines (EDA and DETA) as chain extenders are better than PU formed with 1,4-BD in terms of the dye-exhaustion ratio, color yield (*K/S*), and color fastness, and DETA–PU performed considerably better than did EDA–PU. In the case of blending DETA–PU into 1,4-BD–PU, the mixture not only gave a greater fixation rate, but the fabric also had better fastness to washing with the higher blending rate of DETA–PU.

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