# The Physical Properties of Aqueous Cationic–Nonionic Polyurethane with Poly(ethylene glycol methyl ether) Side Chain and Its Blend with Aqueous Cationic Polyurethane

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**ABSTRACT:** The cationic–nonionic dispersing centers with different chain lengths of poly ethylene glycol methyl ether (N-PDEA 750, N-PDEA 2000) were prepared from N-diethanol amine (NDEA), isophorone diisocyanate (IPDI), and poly(ethylene glycol methyl ether) (PEO $M_w$ = 750 and 2000), whereas aqueous cationic–nonionic polyurethane (N-PDEA PU) with different side chain lengths were prepared by N-PDEA 750 (or N-PDEA 2000), 4,4-methylene bis(isocyantocyclohexane) ($H_{12}$MDI), polytetramethylene glycol (PTMG 2000), ethylene diamine (EDA), and glycolic acid (GA) as cationic–nonionic dispersing center, hard segment, soft segment, chain extender, and quarternizing agent, respectively. The thermal and mechanical properties of PU casting film were then discussed. We also used N-methyldiethyolamine (N-MDEA) without PEO as cationic dispersing center to synthesize aqueous cationic PU (N-MDEA PU). The PU blends were blending N-PDEA 750 PU and N-MDEA PU by different weight ratios and the physical properties of casting films and coated fabric of PU and PU blends were investigated. Regarding the thermal properties, we have found out that the cationic–nonionic PU (N-PDEA 750 PU, N-PDEA 2000 PU) has lower $T_{gs}$, $T_{ms}$, $T_{mH}$, and $\Delta H_H$ than N-MDEA PU, apart from $\Delta H_s$. The N-PDEA 2000 PU with longer side-chain PEO has lower $T_{gs}$, higher $T_{ms}$ and $\Delta H$s than N-PDEA 750 PU. As for mechanical property, N-PDEA PU has lower tensile strength of casting film compared with N-MDEA PU. Regarding the comparison of side chain length of PEO, N-PDEA 2000 PU with longer side chain has higher tensile strength than N-PDEA 750 PU with shorter side chain length. In addition, N-PDEA 2000 PU group that shows hard property in stress–strain curve, whereas N-PDEA 750 PU shows soft property. The tensile strength of PU blends decreases as the content of N-PDEA 750 PU increases. When the low-blend ratio of N-PDEA 750 PU (e.g., 5%), the tensile strength of casting film only shows less influence that can improve the elongation effectively. In terms of coating-treated fabrics, cationic–nonionic PU-coated fabrics show lower waterproof capacity (WP) than those treated by cationic PU. However, the water vapor permeability (WVP) and antiyellowing of the N-PDEA 750 PU coated fabrics are significantly better than the one treated by cationic polyurethane. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2963–2974, 2006

**Key words:** water-soluble polymers; polyurethanes; blends; ionomers; thin films

## INTRODUCTION

Polyurethane (PU) is a copolymer comprising hard and soft segments. Because of its soft and hard segments, significant difference of structure leads to the thermodynamics incompatibility; it has the property of phase separation that causes the PU materials to possess some specificity such as repellent elasticity, handle, and resistance to abrasion, and so on.[1,2] In addition to the excellent membrane formation, PU can be broadly applied to breathable fabric, man-made leather, antishrink of wool, adhesives, and specialty chemicals.[3–5] Currently, considering the environmental factors, the development of aqueous PU has attracted great attention. Aqueous PU can be divided into self-emulsified type and compelling shear-force emulsified type. The former can also be classified into three types: nonionic, cationic, and anionic type. Generally speaking, nonionic PU uses ethylene oxide group as the internal-emulsifying agent, and it has less toxicity, better electrolyte stability, and resistance to shearing at low temperature than that of ionic PU, and thus are widely applied in dyeing, finishing, and cosmetics, etc. However, because of its cloud-point character, its solution possesses high temperature instability.[6] The casting films of aqueous cationic and anionic PU possess harder and stronger mechanical property, because the intermolecular columbic force is

large and the solution has higher stability against temperature. The ionic-type PU has poorer stability of electrolyte due to its ionicity. Presently, anionic PU is mostly used for foam, elastomer, coating, and so on.[7,8] Besides, cationic PU is often applied to adhesive and coagulant, etc.[9–12] Since cationic PU contains high-level of nitrogen, it tends to turn yellow and thus has restricted applications. Thus, its related literature reports or industrial application are found to be less.

To improve aqueous PU of single ionic-type disadvantages, mixing-ionic aqueous PU, such as aqueous anionic–nonionic PU[13–15] and aqueous cationic–nonionic PU,[9,10,16,17] have been developed. Regarding to the research about anionic–nonionic PU, for example, Kim et al.[15] changed the kinds of soft segments (polyethylene glycol (PEG), polypropylene glycol (PPG), and polytetramethylene glycol (PTMG)) on PU backbone, and used PEG/polytetramethylene adipate glycol (PTAd) as the mixing-soft segment, dimethylol propionic acid (DMPA) as the anionic dispersing center to synthesize aqueous anionic–nonionic-type PU, and studied the emulsified particle size of solution and casting film's mechanical property. They found that the PTMG as the soft segment of PU possessed excellent mechanical properties, and swelling of casting film and the dispersing properties were improved upon increasing the PEG content. Research in our laboratory[18–21] used synthesized ester–ether type of triblock copolydiol poly(ethylene glycol)-poly(caprolactone)-poly(ethylene glycol) (PCL-PEG-PCL) as the soft segment, and 4,4-methylene bis(isocyantocyclohexane) ($H_{12}$MDI) and DMPA as hard segments and anionic dispersing center, respectively, to synthesize anionic–nonionic aqueous PU. We have found that the particle size of PU solution decreases, but water vapor permeability of the casting film as PEG content increases. However, the fixation of treated fabric declines slightly. With respect to the research of aqueous cationic–nonionic PU, for instance, Wei et al.[16] used n-butyl amine and ethylene oxide to synthesize polyoxyethylated amine (NPEO), and 4,4′-methylenediphenylene diisocyanate (MDI), N-PEO, N-methyl diethanolamine (N-MDEA) (or 1,4-butanediol (1,4BD), sodium-S-1,2-dihydroxypropyl sulfonate (SDPS)), respectively, as hard segment, soft segment, and chain-extender to synthesize aqueous cationic–ionic PU, whose main chain contains PEO. Li compound was added to improve PU's conductivity. They found that PU containing N-PEO would produce better phase-mixing property between soft and hard segments. This leads to improve elongation and conductivity of casting film. Chen et al.[17] have individually used 4,4′-diphenylmethane diisocyanate (MDI) and 1,6-hexanediisocyanate (HDI) as hard segments, PEG as the soft segment, and 1,4-bis(2-hydroethyl) piperazine and N,N-bis(2 hydroxyethyl) isonicotinamid as chain-extender to synthesize cationic–nonionic aqueous PU containing PEO in its main chain. They found that the synthesized PU possessed excellent hydrophilic property. Besides, since the chain extender is antiseptic, it has an excellent antibacterial property.
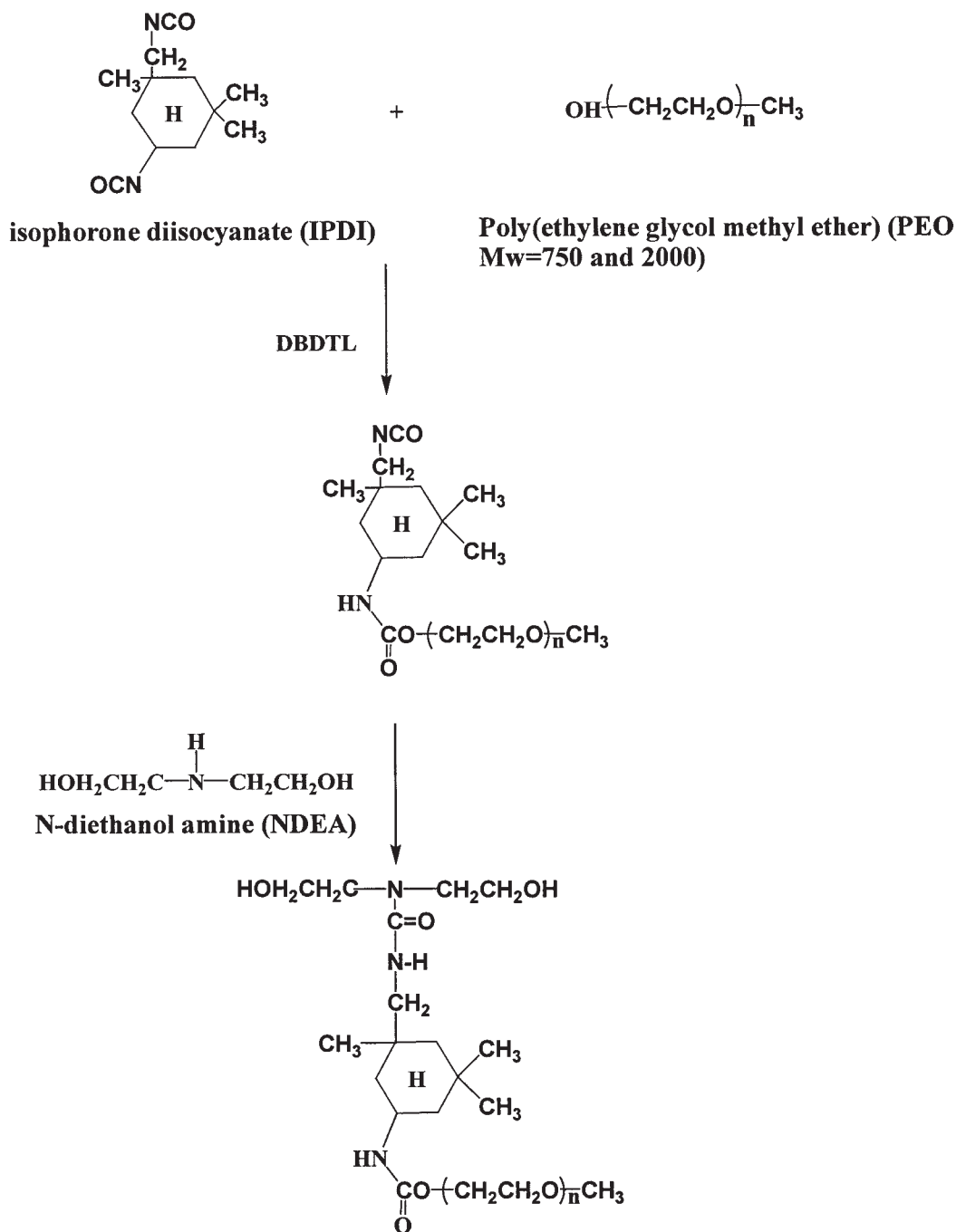
From the past researches, we have discovered that the introduction of PEO into PU could improve hydrophilic property, conductivity, and phase-mixing between soft and hard segments, as well as increasing ionic PUs shearing property at low-temperature tolerance. The method is to add PEO group to the backbone of PU for synthesizing cationic–nonionic or anionic–nonionic PU. Its application to fabric coating will affect the fixation property of coated fabrics, because nonionic functional group (PEO) is more hydrophilic and not easy to be attached on fabrics. To study the influence of placing nonionic functional group (PEO) to PU side chain, this research attached two kinds of PEO with different chain lengths to PU side chain to synthesize aqueous cationic–nonionic polyurethane. This study focuses on its influence to the thermal and mechanical properties of PU casting film, WVP, and WP of coated fabrics. We also used N-methyldiethyolamine (N-MDEA) without using PEO as cationic dispersing center to synthesize aqueous cationic polyurethane (N-MDEA PU) for comparison. The synthesis of cationic–nonionic aqueous PU begins at the synthesized nonionic dispersing center (N-PDEA 750, N-PDEA 2000), whose ends are attached to diols, with isophorone diisocyanate (IPDI), poly-(ethylene glycol methyl ether) (PEO, $M_w$ = 750 and 2000), and N-diethanol amine (NDEA). Subsequently, $H_{12}$MDI, PTMG2000, N-PDEA 750 (or N-PDEA 2000), EDA, and GA were used as hard segment, soft segment, cationic–nonionic dispersing center, chain extender, and quarternizing agent, respectively, to synthesize aqueous cationic–nonionic polyurethane (abbreviated as N-PDEA 750 PU or N-PDEA 2000 PU). We also blend N-PDEA 750 PU with N-MDEA PU by different weight ratios to study the physical properties of PU blends casting film and its effects to physical properties of coating fabric.

## EXPERIMENTAL

### Synthesis of waterborne PU

The synthesis of cationic–nonionic dispersing center

Before synthesizing cationic–nonionic aqueous PU, we had to first synthesize a cationic–nonionic dispersing center. This step was done according to the method reported by Noll et al.[22] One mole of poly-

NCO
CH₂
CH₃        CH₃
H         CH₃
OCN

**isophorone diisocyanate (IPDI)**

+

OH⁺(CH₂CH₂O)ₙCH₃

**Poly(ethylene glycol methyl ether) (PEO Mw=750 and 2000)**

**DBDTL**

NCO
CH₂
CH₃        CH₃
H         CH₃
HN
CO⁺(CH₂CH₂O)ₙCH₃
O

H
HOH₂CH₂C—N—CH₂CH₂OH
**N-diethanol amine (NDEA)**

HOH₂CH₂C—N—CH₂CH₂OH
C=O
N-H
CH₂
CH₃        CH₃
H         CH₃
HN
CO⁺(CH₂CH₂O)ₙCH₃
O

**Scheme 1**

(ethylene glycol methyl ether) (PEO, $M_w$ = 750 and 2000, reagent, Acros) in 1 mol of isophorone diiso-cyanate (IPDI, Bayer, Germany) was mixed in a four-necked reactor for dehydration. Then, we added di-*n*-butyltin dilaurate (DBDTL, TCI) of 0.05% PU solid content and reacted at 35°C under pure nitrogen ambient for 4 h. The terminal —NCO group value during the reaction was determined using standard —NCO titration method.[23] The tem-

perature was raised to 45°C. Finally, 1 mol of *N*-diethanol amine (NDEA, reagent, Acros) was added to react for 2 h, to obtain the nonionic dispersing center. The reactions involved are as Scheme 1.

Synthesis of nonionic waterborne PU

The cationic–nonionic waterborne PU of different chain lengths containing PEO side chain (*N*-PDEA

**Scheme 2**
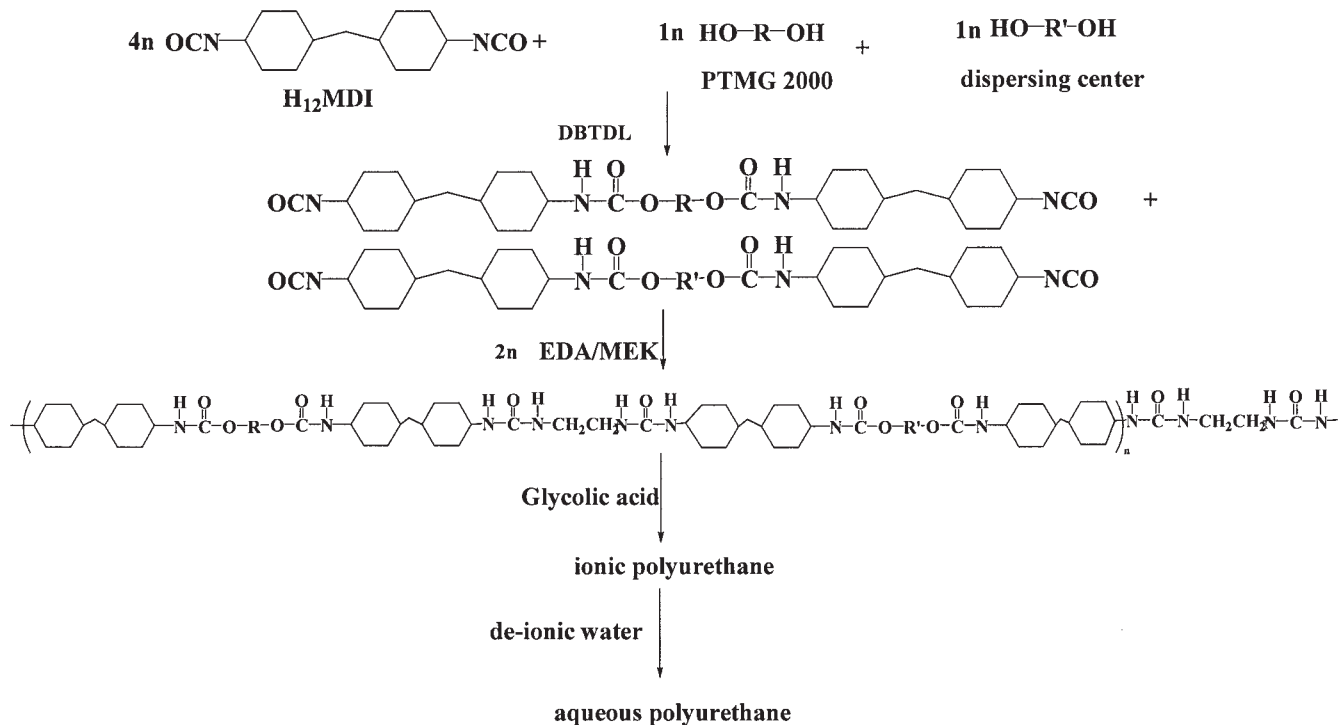
PU) was synthesized according to the acetone process method.[22] We placed 1 mol of polytetramethylene glycol, $M_n$ = 2000 (PTMG 2000, reagent, Aldrich), and 1 mol of N-PDEA, in a vacuum reactor to get rid of moisture, and then added 4 mol of 4,4'-methylenedicyclohexyl diisocyanate (H₁₂MDI, Bayer, Germany). The reaction under nitrogen was performed at 50°C initially, followed by increasing the temperature gradually to 80°C. The reaction continued until the —NCO content reached half as evidenced by titration.[23] Before it was cooled to 10°C by dissolving in methyl ethyl ketone (MEK, reagent, Acros), we separately added the ethylenediamine (EDA, reagent, Acros) to carry out the chain extending reaction. Then, it was quaterized with glycolic acid (GA, reagent, Acros) at 60°C for 30 min. Finally, deionized water was added to allow it emulsified, and then the mixture was heated to 80°C to remove MEK to obtain a PU dispersion made from different side chain lengths (N-PDEA 750 PU, or N-PDEA 2000 PU).

On other hand, we synthesized cationic waterborne PU (N-MDEA PU), in which the process was done according to the acetone process polymerization.[22] H₁₂MDI, PTMG 2000, and N-methyldiethyolamine (N-MDEA, reagent, Acros) were used as hard segment, soft segment, and cationic dispersing center, respectively, to synthesize PU prepolymer. Before it was cooled to 10°C by dissolving in MEK, we separately added EDA to carry out the

chain extending reaction. Then, it was quaternized with glycolic acid (GA) at 60°C for 30 min. Finally, deionized water was added to allow it emulsified, and then mixture was heated to 80°C to remove MEK to obtain PU dispersion. The synthesizing steps were the same as described for N-PDEA PU. The synthetic reactions of N-PDEA PU are as in Scheme 2.

### Analysis of PU structure

The FTIR spectra were recorded using Bio-Red FTIR (FTS-7) spectrometer at 25°C. The scanning range was 4000–400 nm, while resolution was 4 cm⁻¹ and scan was 64 times. Besides, the elemental analysis (EA) for cationic–nonionic dispersing center (N-PDEA 750) was conducted by a Perkin–Elmer 2400 (II) for C (%), N (%), and H (%).

### Preparations for casting film and testing physical properties

We took a PU solid content of 30% waterborne PU and coating on Teflon plate and dried at room temperature for 3 days, and then at 40°C over a week. The PU blends were blended with N-PDEA 750 PU and N-MDEA PU by different weight ratio, and the casting film was prepared as mentioned earlier. The

casting film was tested using differential scanning calorimetric (DSC) analysis, dynamic mechanical analysis (DMA), and tensile strength measurement. The DSC analysis was performed with a differential scanning calorimetric analyzer (Du-Pont Thermal analyst 2000) to measure the heat variation at a heating rate of 10°C/min in the range between −120 and 250°C. The DMA was conducted using Du-Pont Thermal analyst 2980 with the heating rate of 5°C/min, and the measurement range of this analysis was set between −120 and 150°C. Among the mechanical properties of the formed membrane by a tensile tester (Toyo Baldwin Tension UTM-3–500), membrane mechanical property test was carried out according to ASTM D 638M-93 methods. The cross-head speed was set at 50 mm/min, pinch-head pinching distance was 20 mm, and load weight was 10 kg. Each sample was measured 3–5 times.

## Measurement for the coated fabrics

For the coating of nylon fabrics study, the PU of 30% solid content dispersion was blend with 0.4% melamine resin and a 10% hydroxyethyl cellulose (HEC), and 0.01% catalyst (cat-32, Chinyee chemical company, Taiwan) was coated onto the nylon taffeta fabrics(Everest textile company, Taiwan). After coating, the fabric was predried at 100°C for 3 min and curing at 130°C for 5 min. The water vapor permeable (WVP) and waterproof capacity (WP) of the coated fabrics were preceded according to JIS-1099 $CaCl_2$ method and JIS-1092 (B) method.

## RESULTS AND DISCUSSION

### Identification and analysis of the synthetic compound

The cationic–nonionic dispersing center (N-PDEA750) was found be chemically shifted by $^1$H-NMR analysis at 4.14, 4.08, 2.70, 2.87, 2.86, 4.9, 3.34, 3.6, 1.32, and 0.8–1.6 ppm, which represents the hydrogen atom from the groups of CON$H$C$H_2$, NHC$H_2$, N—C$H_2$C$H_2$OH, N$H$COO, (C$H_2$C$H_2$O), OC$H_3$, —C$H_3$, and —C$H_2$, respectively. In addition, the element analysis of the dispersing center (N-PDEA 750) suggests that the element contents of C, N and H% are 55.75, 3.92 and 9.51%, respectively. These data are very close to the theoretical values of 56.15, 3.90, and 9.24%, indicating that the synthesized dispersing center N-PDEA 750 has excellent purity.

Figure 1 shows the FTIR analyses of cationic–nonionic dispersing center (N-PDEA750), aqueous cationic PU (N-MDEA PU), and aqueous cationic–nonionic PU (N-PDEA 750 PU and N-PDEA 2000 PU). The isocyanate (—N=C=O) absorbion peak of the dispersing center (N-PDEA) [as in Fig. 1(a)] at 2270 cm$^{-1}$



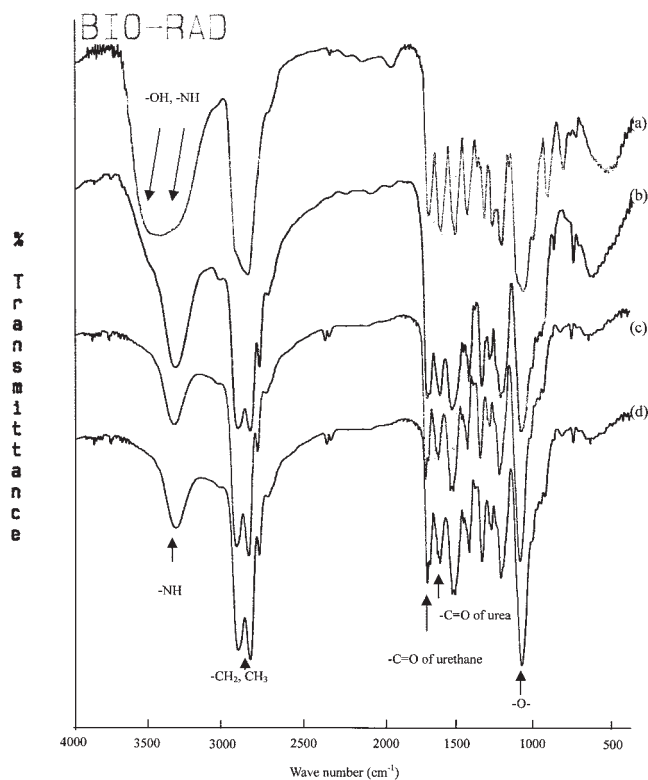**Figure 1** The FTIR spectra of PU synthesized (a) N-PDEA dispersing center, (b) N-MDEA PU, (c) N-PDEA 750 PU, and (d) N-PDEA 2000 PU.

has disappeared, indicating that the —N=C=O group of IPDI terminal of the synthetic compound is completely reacted. Moreover, there are, respectively, the absorption peaks of —OH, —NH—, —C=O, and —CNH at 3450, 3333, 1712, and 1530 cm$^{-1}$, respectively, and there is a clear absorption peak of ether group (—O—) at 1111 cm$^{-1}$. It shows that the synthetics are ether compounds whose ends possess an OH group. Besides, from FTIR spectrum of N-MDEA PU [Fig. 1(b)], N-PDEA 750 PU [Fig. 1(c)], and N-PDEA 2000 PU [Fig. 1(d)], it can be found that the —N=C=O (2270 cm$^{-1}$) absorption peaks of these three synthetic compounds have been disappeared, indicating that the —N=C=O group at the ends of synthetic compounds have reacted completely. The absorption peaks of —NH, —COO, and —NHCO— group occurred at 3330, 1708, and 1531 cm$^{-1}$. The formation of —NHCOO (urethane) group in the structure of synthetic compounds is confirmed by the three groups. Furthermore, the absorption peaks at 1112 cm$^{-1}$, and 2850–2940 cm$^{-1}$ belong to —O—, and —CH$_2$— and —CH$_3$ group, respectively. The peak of 1630 cm$^{-1}$ is the absorption peak of —C=O of —NH-CONH (urea group) that indicates the synthetics have the structure of polyurethane–urea. From the figure, the —C=O absorption peak of N-PDEA 750 PU ap-
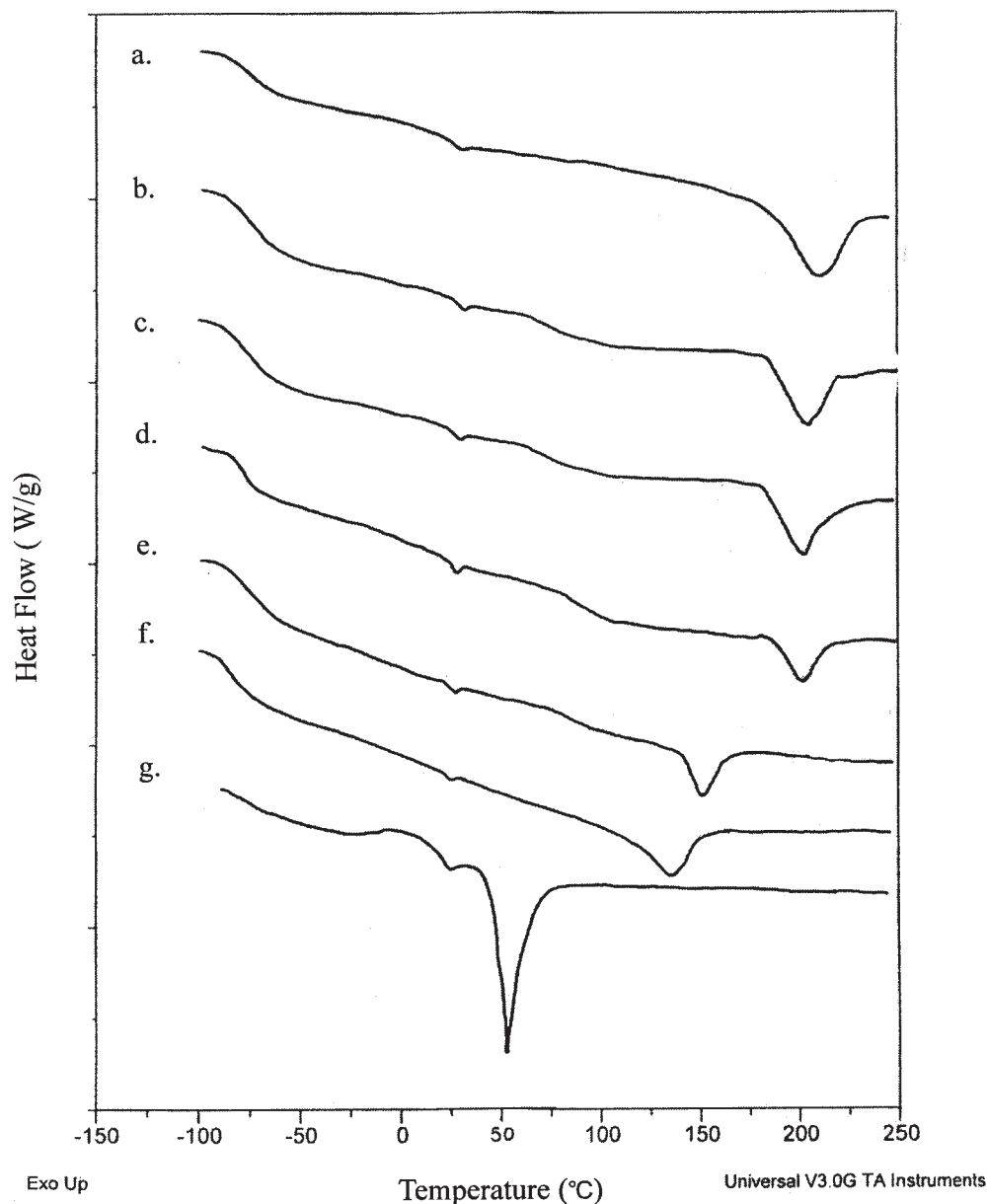
**Figure 2** The DSC spectra of PU and PU blends (a) *N*-MDEA PU, (b) *N*-PDEA 5%, (c) *N*-PDEA 25%, (d) *N*-PDEA 50%, (e) *N*-PDEA75%, (f) *N*-PDEA 750 PU, and (g) *N*-PDEA 2000 PU.

pears at a higher wave number in comparison with *N*-PDEA 2000 PU and *N*-MDEA PU in the FTIR analysis. This result suggests that the hydrogen bonds in intermolecules of *N*-PDEA 750 PU are weaker.

## Thermal properties of PU and PU blends

Figure 2 displays the DSC analysis of cationic–nonionic PU with different side chains lengths (*N*-PDEA 750 PU and *N*-PDEA 2000 PU), cationic PU (*N*-MDEA PU), and the PU blends. In this figure, the temperature area at −70 to 80°C is the glass-transition temperature ($T_{gs}$) of soft segment (PTMG), and the temperature, at

20–40°C, is the melting point of the soft segment ($T_{ms}$), whereas 135–210°C is the melting point of the hard segment ($T_{mH}$).[9] First of all, by comparing *N*-PDEA PU and *N*-MDEA PU, we can find that *N*-PDEA PU has lower $T_{gs}$, $T_{ms}$, $T_{mH}$, and $\Delta H_H$ than *N*-MDEA PU, but the $\Delta H_s$ was opposite. In addition, *N*-PDEA 2000 PU has two endothermic peaks of $T_{ms}$, but no $T_{mH}$, and both $T_{ms}$ and $\Delta H_s$ were higher than *N*-PDEA 750 PU. The *N*-PDEA PU has lower $T_{gs}$, $T_{ms}$, $T_{mH}$, and $\Delta H_H$ because its side chain PEO, which exists in PU hard domain, possesses flexible property. This tends to interfere the hydrogen bonding of interhard segments, and influence the molecular chains' stacking of hard

TABLE I
Thermal Properties of Cast Film of N-PDEA 750 PU and Its Blends

| | Polymer blend, by weight ratio | | DSC analysis | | | | | DMA | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Symbol | N-MDEA PU | N-PDEA750 $\varphi$U | $T_{gs}$ (°C) | $T_{ms}$ (°C) | $\Delta H_s$ (J/g) | $T_{mH}$ (°C) | $\Delta H_H$ (J/g) | $\beta$ peak ($T_{gs}$, °C) | $\alpha$ peak ($T_{gH}$, °C) | $\Delta T_g$ (°C) |
| N-MDEA PU | 100 | – | −74.1 | 28.6 | 0.4 | 213.1 | 34.2 | −60.9 | 57.7 | 118.6 |
| N-PDEA PU 5% | 95 | 5 | −74.55 | 28.5 | 0.45 | 213 | 30.5 | −61.2 | 52.9 | 114.1 |
| N-PDEA PU 25% | 75 | 25 | −75.3 | 28.2 | 0.6 | 209.6 | 28.7 | −61.8 | 52.3 | 113.8 |
| N-PDEA PU 50% | 50 | 50 | −75.9 | 27.5 | 0.8 | 205.7 | 24.2 | −62.0 | 49.8 | 111.7 |
| N-PDEA PU 75% | 25 | 75 | −76 | 25.5 | 1.2 | 149.8 | 21.3 | −62.6 | 48.2 | 110.8 |
| N-PDEA 750 PU | – | 100 | −76.2 | 23.3 | 1.3 | 134.9 | 11.2 | −62.9 | 45.6 | 108.5 |
| N-PDEA 2000 PU | – | – | −77.07 | 24.6, 53.10 | 2.57, 34.47 | – | – | −62.3 | 53.82 | 116.12 |

N-PDEA (%) was calculated by weight ratio from $N-PDEAPU N-PDEAPU + N - MDEAPU \times 100$; $\Delta T_g = T_{gH} - T_{gs}$; respectability that the microphase separation between hard segment and soft segment.

segment from of PU. The molecular chains are difficult to array tightly, causing an increase of free volume and decrease of $T_{gs}$. Furthermore, the soft segment (PTMG) is slight different from side-chain PEO, in terms of structure. When the side-chain PEO content increases, these tend to form large amount of crystalline with bad quality, and thus $\Delta H_s$ proportionally increases. On the other, the N-PDEA 2000 PU has two $T_{ms}$, but no $T_{mH}$. Of which, the lower $T_{ms}$ (24.6°C) of the endothermic peak of N-PDEA 2000 PU is caused by the melting point of soft segment PTMG 2000, similarly for N-PDEA 750 PU and the higher $T_{ms}$ (53.1°C) comes from the melting point of side chain PEO 2000. Besides, N-PDEA 2000 has no $T_{mH}$ since the crystallite of side-chain PEO 2000 prevents from the crystallization of the hard segment. N-PDEA 750 PU possesses no endothermic peak at 50°C because it's not easy to form crystalline as side-chain PEO length with an $M_w$ of 750. The former statement of FTIR analysis as the carbonyl absorption (—C=O, 1716 cm$^{-1}$) of N-PDEA 750 PU is coincident with the result that appears at higher wave number than the carbonyl absorption (—C=O, 1702 cm$^{-1}$) of N-MDEA PU and the carbonyl absorption (—C=O, 1708 cm$^{-1}$) of N-PDEA 2000 PU in the FTIR analysis. About the thermal properties data of individual PU and PU blends, the crystalline melting enthalpy ($\Delta H_H$) of hard segment, and the crystalline melting enthalpy ($\Delta H_s$) of soft segment are concluded in Table I and illustrated in Figure 3.

Figure 3 shows the effect of the N-PDEA 750 PU content on the thermal properties of casting film of PU blends. It can be found that the $T_{gs}$ of PU blends dramatically drops 2°C, when a small quantity of N-PDEA 750 PU is added (from 0% up to 25%), whereas it gradually declines after exceeding 25%. $T_{ms}$ and $T_{mH}$ have no significant change upon adding as small quantity (5%), but begin to rapidly decline, respectively, at blending ratios of 25 and

50%. $\Delta H_s$ is proportionally increased along with the adding amount, but $\Delta H_H$ was opposite. Upon the addition of a small quantity of PU with side chain PEO, because the free volume of PU amorphous region increases, the amorphous region of the soft segment is likely easy to move; therefore, adding a small quantity of PU with side-chain PEO leads to rapid decrease of $T_{gs}$. However, as exceeding 50%, soft segment has sufficient space to free motion, so $T_{gs}$ is not changed much. Additionally, the small amount of blending N-PDEA PU (N-PDEA PU 25%) cannot affect the hydrogen bonding in PU crystal region; hence $T_{ms}$, $T_{mH}$, and $\Delta H_H$ were not influenced. Yet, when the addition of N-PDEA PU exceeds 50%, the side-chain PEO of N-PDEA 750 PU tends to interfere with the hydrogen bonds in the crystallizing region, leading to the increase of mixing degree between hard and soft segments.[13] Therefore, $T_{ms}$, $T_{mH}$, and $\Delta H_H$ dramatically drop down. The soft segments of PTMG are similar to the side-chain PEO in structure, and while the content of side-chain PEO increases; they can easily form a large quantity of crystallites to increase the $\Delta H_s$ proportionally.

The DMA of casting film for N-PDEA 750 PU, N-MDEA PU, and their blends are illustrated in Figure 4. The data are shown in Table II. Because PU structure derived from soft and hard segments cause two phase structures, and two peaks, $\alpha$ (40–60°C) and $\beta$ (−80 to 70°C), appear on tan δ curve of DMA. The $\beta$ and $\alpha$ peak indicate the glass transition temperature of the soft segment ($T_{gs}$) and glass transition temperature of the hard segment ($T_{gH}$).[24] From Figure 4, the $\alpha$ ($T_{gH}$) and $\beta$ peak ($T_{gs}$) of N-PDEA 750 PU were both lower than that of N-MDEA PU. The $\alpha$ and $\beta$ peak of PU blends decrease followed by the increase of N-PDEA 750 PU content. The decrease of $T_{gs}$ corresponded with the DSC result. In the rubber plateaus between $\alpha$ and $\beta$ peak,
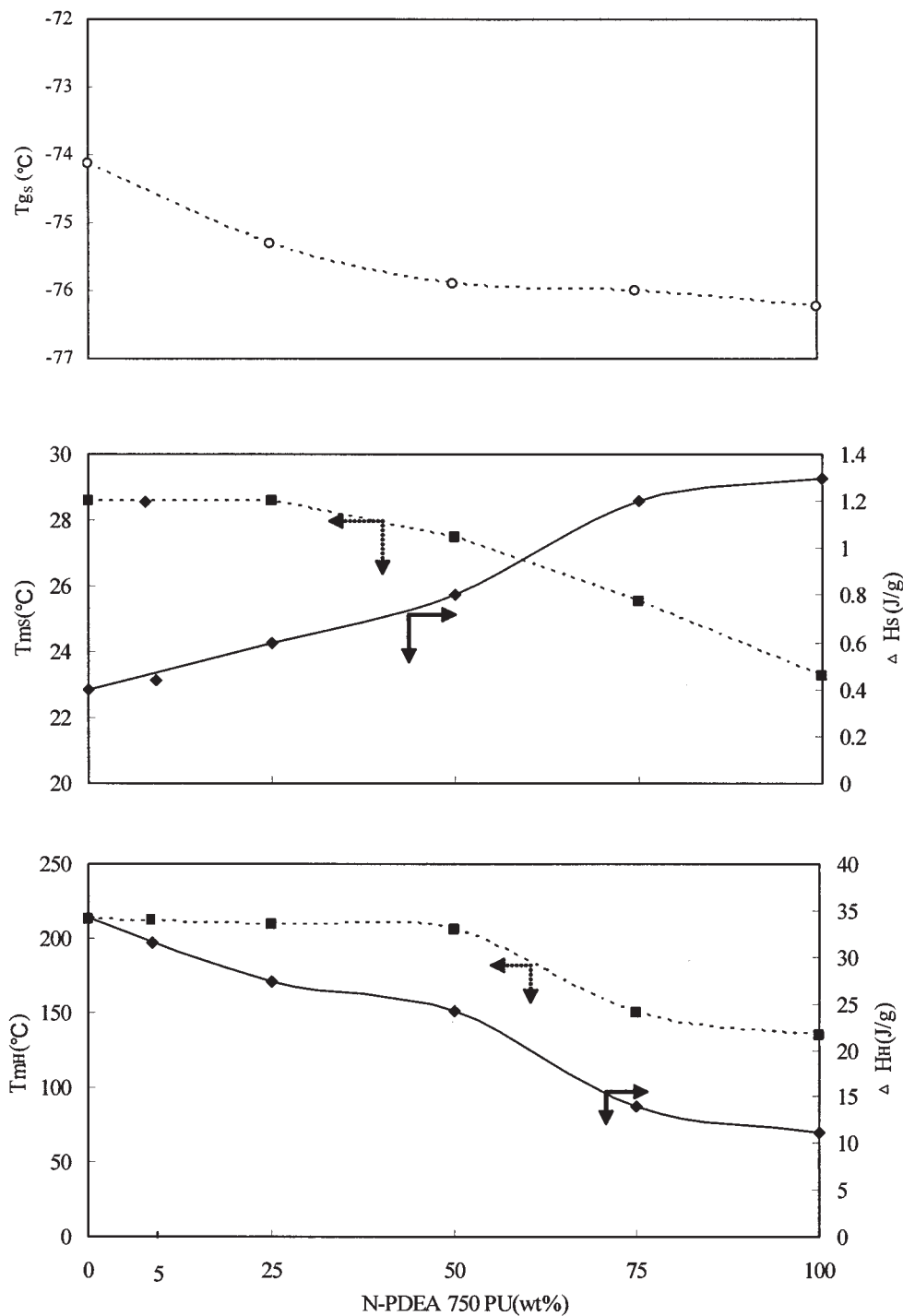
**Figure 3**  Effect of *N*-PDEA 750 content on thermal properties of PU synthesized and its blends.

*N*-PDEA 750 PU has higher tan δ than *N*-MDEA PU, because the side-chain PEO of *N*-PDEA 750 PU is more flexible and rotatable than *N*-MDEA PU; the PU blends shows the increase of tan δ along with the increase of *N*-PDEA 750 PU content, and this indicates that the casting film of PU blend in high *N*-PDEA 750 PU content is softer. In Table I, there are

data about the degree of phase separation from $\Delta T_g$ ($\Delta T_g = (T_{gH} - T_{gs})$) of DMA. PU has smaller $\Delta T_g$ indicating that the phase-mixing between soft segment and head segment. *N*-PDEA PU has larger phase-mixing than *N*-MDEA PU, and the phase-mixing degree of PU blends increases along with the increase of *N*-PDEA mixing content. The results cor-
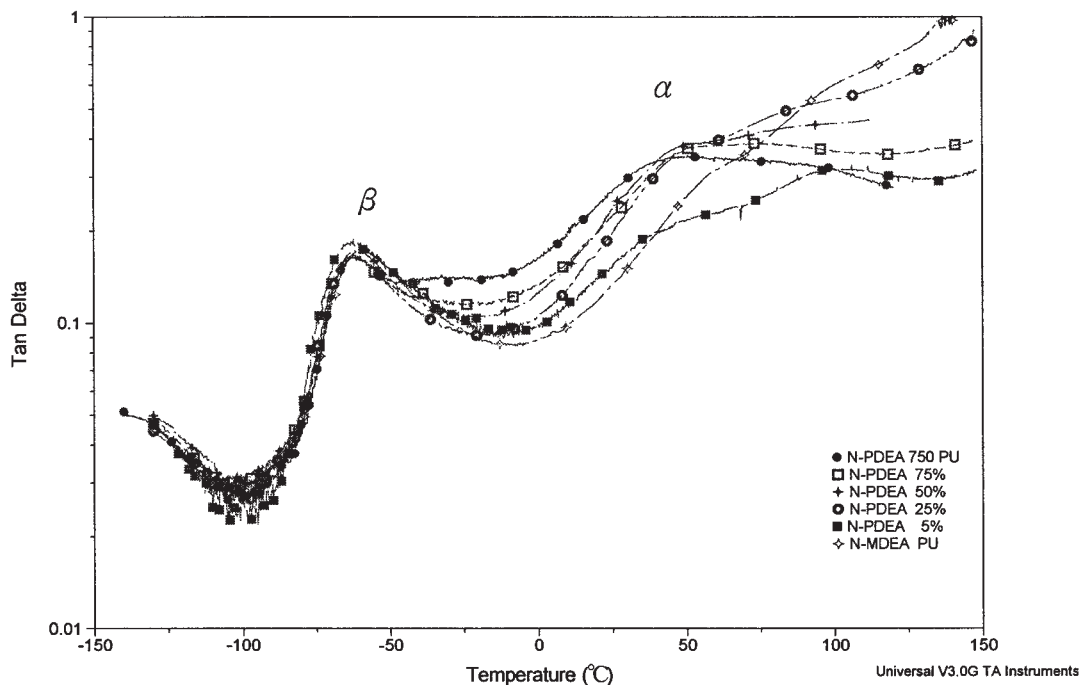
**Figure 4** The DMA spectra of PU and PU blends synthesized and its blends.

respond to that of Wei et al.,[16] which showed cationic–nonionic aqueous PU introducing PEO in backbone increased the phenomenon of phase mixing.

## Mechanical property of PU and its blends

Figure 5 shows the stress–strain curve of aqueous cationic–nonionic PU (N-PDEA 750 PU, N-PDEA 2000 PU) with different lengths of side-chain PEO (N-MDEA PU) and casting film from their blends with N-MDEA PU. The data of mechanical property are shown in Table II. From the figure, we find that tensile strength of casting film from N-PDEA PU is far lower

than that of N-MDEA PU. The reason is that the side-chain PEO of N-PEDA 750 PU has larger steric hindrance, which weakens the intermolecular force of the main chain, and N-MDEA PU has larger intermolecular coulombic force. Regarding the comparison of different side chain length of PEO, N-PDEA 2000 PU with longer side chain has more tensile strength than N-PDEA 750 PU with shorter side chain lengths. In addition, N-PDEA 2000 PU shows the curve of hard character and N-PDEA 750 PU appears the curve of soft character because N-PDEA 2000 PU's side-chain PEO tends to form partial crystal. The mechanical property of PU blends is depicted in Figure 6. From the figure, we can see the tensile strength of the PU blends casting film is not affected obvious in N-PDEA750 content of minute, but the tensile strength dramatically decline when it exceeds 75%. In general, N-PDEA 750 PU mixing into N-MDEA PU should have proportional decline of mechanical properties. However, Table I shows that $\Delta H_s$ increases as the mixing amount increases. Therefore, the strength does not largely decrease following the increase of mixing amount, which could be due to the fact that side chain PEO can lower the stress-concentration of casting film. Besides, the elongation of PU blends' casting film is significantly increased by adding 5% N-PEDA 750 PU, and addition of 25% does not affect the elongation; however, when it exceeds 75%, the elongation decline dramatically.
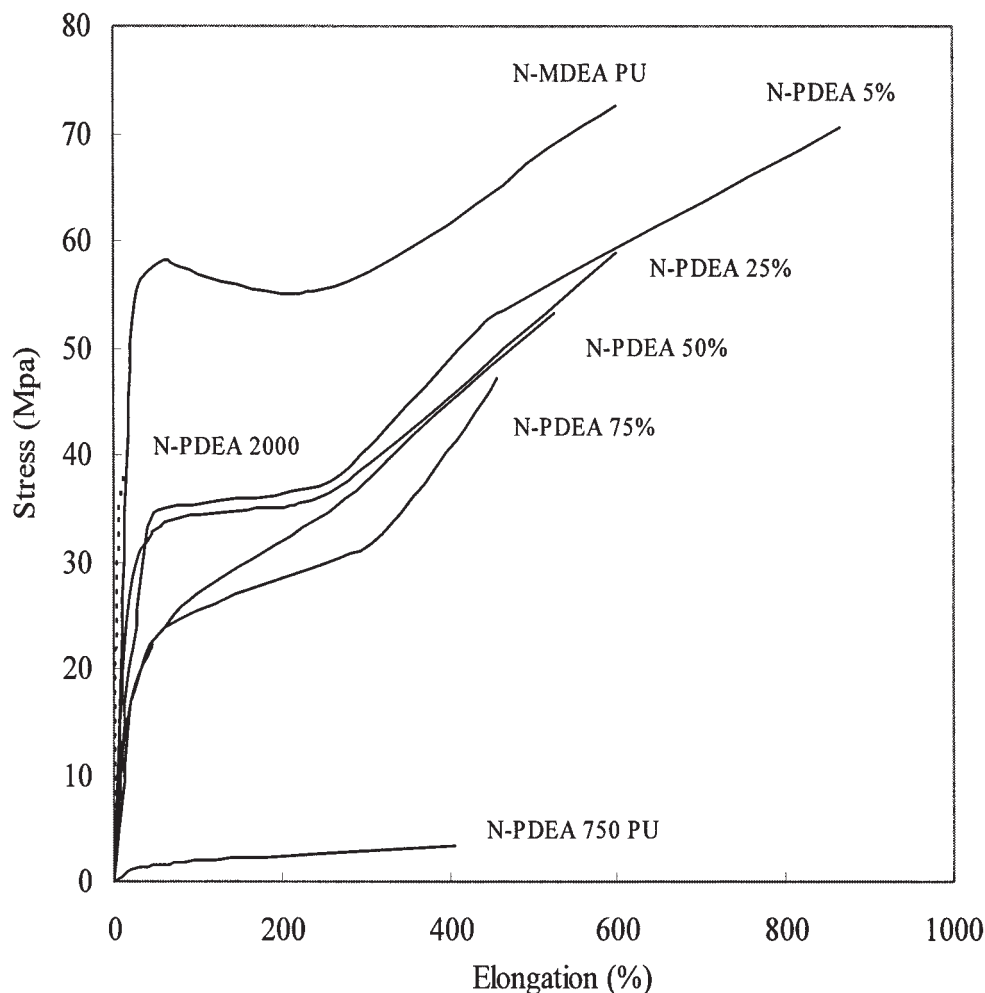
**TABLE II**
**Mechanical Properties of Cast Film of N-PDEA 750 PU and Its Blends**

| Symbol | Content, weight ratio (%) | | Tensile strength (MPa) | Elongation (%) |
|---|---|---|---|---|
| | Hard segment | Soft segment | | |
| N-MDEA PU | 39.18 | 60.82 | 72.6 | 600 |
| N-PDEA PU 5% | 35.04 | 64.96 | 70.5 | 865 |
| N-PDEA PU25% | 28.75 | 71.25 | 58.9 | 595 |
| N-PDEA PU 50% | 31.03 | 68.97 | 53.2 | 525 |
| N-PDEA PU 75% | 33.14 | 66.86 | 47.1 | 458 |
| N-PDEA 750 PU | 27.53 | 72.47 | 3.4 | 405 |
| N-PDEA 2000 PU | 21.27 | 78.73 | 39.8 | 20 |

**Figure 5** The stress–strain curve of cast film of various PU synthesized and its blends.

## Physical property of coated fabrics

The physical properties of coated fabrics, such as appearance, contact angle with water, WVP, WP, and tensile strength are listed in Table III. From the table, regarding the appearance of coated fabric, N-PDEA 750 PU, N-PDEA 2000 PU, and PU blends do not have yellowing condition except for the N-MDEA PU, indicating the N-MDEA PU blending into N-PDEA 750 PU confers the resistance against yellowing.

In terms of contact angle of water to coated fabric, the film-casting by PU with side-chain PEO has smaller contact angle than the one without side chain PEO. The contact angle of PU blends decreases when the mixing amount of N-PDEA 750 PU increases; because the N-PDEA 750 PU side chain is the hydrophilic PEO group, and the increase of free volume between hard and soft segment molecules. On the basis of the above result, we recommend that the attachment of PEO into PU side chain can improve hydrophilic properties of treated fabrics.

Regarding WVP and WP of coated fabric, cationic–nonionic PU-coated fabrics have lower WR than those treated by N-MDEA PU (N-MDEA PU > N-PDEA 750 PU > N-PDEA 2000PU), but the influence of WVP has opposite trend. The WVP of N-PDEA 750 PU is 46% higher than that of N-MDEA PU, exceeding with only 20% decline of WP than untreated fabrics. This result is related to PU's crystallite and side chain of PU that contains hydrophilic PEO functional group. The WVP of PU blends significantly increases as the mixing amount of N-PDEA750 PU increases with only slight decline of waterproof capacity. Table III also indicates the influence of N-PDEA 750 PU and its blends with N-MDEA PU to mechanical property of coated fabrics. Following the increase of N-PDEA 750 PU content, the tensile strength of treated fabric tends to decline. With the consideration of treated fabric of physical balance, the application of coated fabrics should be better by using PU blends. For example, the addition of N-PDEA 750 PU 25% in PU blends can obtain excellent physical properties balance.
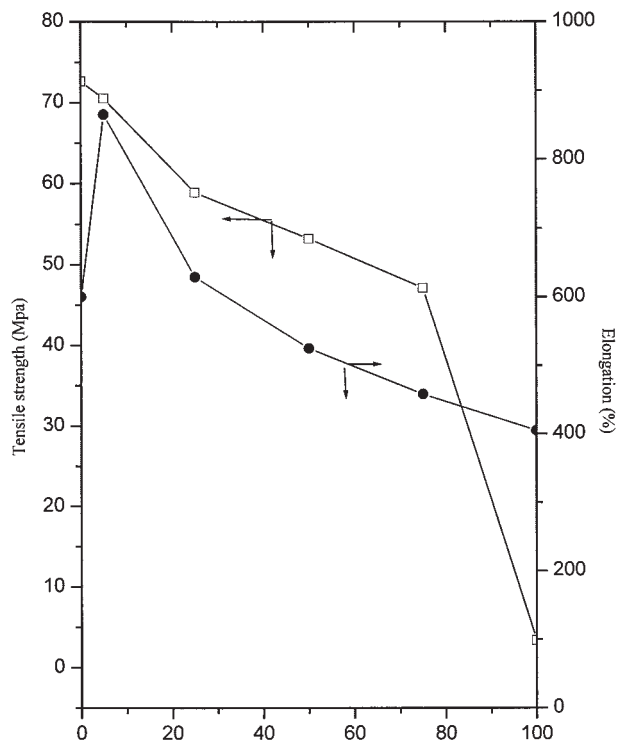
**Figure 6** Effect of N-PDEA 750 PU content on mechanical properties of PU synthesized and its blend.

## CONCLUSIONS

In this study, the cationic–nonionic PU containing side-chain PEO with different chain lengths was synthesized. The physical properties of different PEO chain lengths synthesized on PU cast film and the applications on nylon-coated fabrics were investigated. We also used N-methyldiethyolamine (N-MDEA) as the cationic dispersing center (without PEO) and synthesized cationic PU (called N-MDEA PU), which blended with N-PDEA 750 PU by different weight ratios. The physical properties of PU

blends and its application on nylon-coated fabrics were also investigated. The results give rise to the following observations:

1. In terms of thermal properties of PU casting film, we have found out that N-PDEA PU have lower $T_{gs}$, $T_{ms}$, $T_{mH}$, and $\Delta H_H$ than N-MDEA PU, expect $\Delta H_s$. The N-PDEA PU with longer side chain PEO has lower $T_{gs}$, and higher $T_{gH}$, indicating larger degree of phase separation between soft and hard segments. Regarding the PU blends, slight addition of N-PDEA 750 PU into N-MDEA PU does not affect $T_{ms}$ and $T_{mH}$ much. Nevertheless, when the addition exceeds 50%, they rapidly decline. In addition, $T_{gS}$ and $T_{mS}$ both decrease, followed by the increase of N-PDEA 750 PU content, but $\Delta H_s$ have an increasing tendency. The degree of phase-mixing between soft and hard segments also increases along with the content of N-PDEA 750 PU.
2. With respect to the mechanical property, N-PDEA 750 PU and N-PDEA 2000 PU have lower strength of casting film, in comparison with N-MDEA PU. The strength of PU blend also decreases as the addition of N-PDEA 750 increases. Only the little mixing of N-PDEA 750 PU (e.g., 5%) does not influence casting film strength, and can effectively improve the extensibility of casting film.
3. In terms of nylon-coated fabric, N-PDEA PU-treated fabrics have slightly lower waterproof capacity than that treated by N-MDEA PU. However, the antiyellowing property and water vapor permeability of the N-PDEA PU-treated fabrics are significantly better than the one treated by N-MDEA PU. To consider the physical properties of treated fabrics, the application of coated fabrics should be better by using PU blends, especially the addition of N-

### TABLE III
### The Physical Properties of Nylon-Coated Fabric of N-PDEA 750 PU and Its Blends

| Symbol | Water proof (mm $H_2O$) | Water vapor permeability (g/m²/day) | Tensile strength (kgf/cm²) | Contact angle with water (2Θ) | Appearance of coated fabric |
|---|---|---|---|---|---|
| Untreated | 0 | 7634 | 22 | 114 | – |
| N-MDEA PU | 5000 | 5264 | 37 | 102 | Slight yellow, limpid |
| N-PDEA-5% | 4900 | 5400 | 36.3 | 98 | White, limpid |
| N-PDEA-25% | 4400 | 5500 | 36 | 80 | White, limpid |
| N-PDEA-50% | 4250 | 6100 | 35 | 76 | White, limpid |
| N-PDEA-75% | 4050 | 7000 | 34 | 75 | White, limpid |
| N-PDEA 750 PU | 4000 | 7700 | 32.6 | 70 | White, limpid |
| N-PDEA 2000 PU | 3000 | 3357 | 35 | 76 | White, limpid |

Textile finishing process: coating-predrying (100°C×5 min)-curing (130°C × 3 min)

PDEA 750 PU 25% in PU blends can obtain excellent physical properties balance.

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