

Preparation and Physical Properties of Nonionic Aqueous Polyurethane Coatings Containing Different Side Chain PEGME Length

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ABSTRACT: Nonionic aqueous polyurethane (NAPU) coatings were prepared by a prepolymer process using 4,4-methylene bis(isocyanatocyclohexane), poly(tetramethylene glycol) with a molecular weight of 2000 g/mol (PTMG2000), ethylenediamine and a synthesized nonionic dispersing centers of various molecular weight produced by isophorone diisocyanate, *N*-diethanol amine, and poly(ethylene glycol) monomethyl ether (PEGME) with different molecular weights. The dispersion properties of the NAPU emulsions, thermal properties of the NAPU casting films, and its tensile strength were studied. Further, the water vapor permeability (WVP) and waterproof of NAPU-coated fabric were also examined. Our results showed that the surface tension and particle size of NAPU emulsion increase with the decrease in PEGME chain length. For the thermal properties, the

melting point of soft-segment of NAPU casting films was not affected by the PEGME chain length, but the heat of fusion of the soft-segment was greatly affected. In particular, the NAPU with PEGME chain length of 2000 g/mol has two obviously crystalline endothermic peaks. The lower peak was attributed to crystallizing PTMG2000. The higher peak was attributed to the crystallizing side chain PEGME of $M_w = 2000$ g/mol. The WVP followed the order: NAPU with PEGME chain length 750 g/mol > 550 g/mol > 350 g/mol > 2000 g/mol, and the waterproof increases with increase in PEGME length. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2266–2273, 2008

Key words: polyurethanes; dispersion properties; coatings; thermal properties; water-soluble polymers

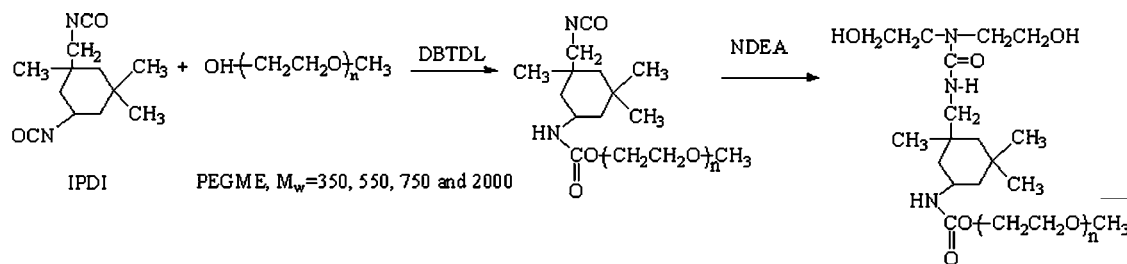
INTRODUCTION

Polyurethane (PU) material has some specificity such as film-forming ability, repellent elasticity, resistance to abrasion, and high variability of chemical structures. It has been widely applied to coatings, adhesions, paints, inks, and fiber-treated agents.^{1–6} The green chemistry revolution has provided an alternative mode for chemists and industrialists to develop polymers by the eco-friendly route, to minimize the use of toxic chemicals, particularly, volatile organic carbons (VOCs) that are hazardous to health and the environment. The development of VOCs-free aqueous PU resin has attracted great attention. The aqueous PU can be divided into three types: nonionic, cationic, and anionic. Generally speaking, the nonionic aqueous PU (NAPU) uses the hydrophilic polyether segment or ethylene oxide as internal-emulsifier. It is less toxic, and has better electrolyte stability and resistance to shearing at low temperature than

the ionic waterborne PU. However, the water-resistance and mechanical properties of PU casting film are lower than those of solvent-based PU because of introducing ionic or nonionic groups with a hydrophilic structure.^{5–8} There is still much room for improvement for soft and hard segments within the PU structure for its application on coating materials.

In past studies on solvent-based nonionic PU, the polyethylene glycol (PEG) part was almost always directly introduced into the PU backbone or the PU's side chain to help the hydrophilicity. Christina and Bengt,⁷ for example, reserved the —NCO group of hexamethylene diisocyanate in the PU side chain and then grafted the PEG into the —NCO group. This study discussed the effect of PEG content on the thermal property of PU membrane and its tensile strength, and the contact angle between water and the PU membrane. The results pointed out that the introduction of PEG into the PU side chain will effectively promote the hydrophilic nature of PU membrane, but its melting point and tensile strength will be significantly lowered. Our laboratory⁸ has synthesized cationic-nonionic PU with poly(ethylene glycol) monomethyl ether (PEGME) side chain and cationic PU without side chain. We found that the former had a higher moisture absorption; however, it had lower T_g s and

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Scheme 1 The preparation process for nonionic dispersing centers.

T_m s. We also found that the soft segment composition greatly influences the physical properties of NAPU.⁹ However, an investigation on the effect of side chain PEGME length of NAPU on the physical properties is scarce in the literature.

This study examined the effect of side chain PEGME length of NAPU for their solution, thermal, and mechanical properties. The waterproofing and water vapor permeability (WVP) of NAPU-coated fabric were also examined. First, the nonionic dispersing centers with different PEGME chain lengths were prepared by isophorone diisocyanate, *N*-diethanol amine (NDEA), and poly (ethylene glycol) monomethyl ether (PEGME) with different molecular weights; and the NAPUs were synthesized by using the PTMG2000, H12MDI, and different kinds of dispersing centers as the soft segment, hard chain, and internal-emulsifier, respectively.

EXPERIMENTAL

Material

The poly (ethylene glycol) methyl ether of various molecular weights (PEGME, $M_w = 350, 550, 750,$ and 2000 g/mol, Acros, Belgium, reagent), NDEA and isophorone diisocyanate (IPDI, Bayer, Germany) were dried at 45°C and 1–2 mmHg for 3 h before use for synthesizing the nonionic dispersing center (Abbreviated as N-PDEA350, N-PDEA550, N-PDEA750, and N-PDEA2000). Polytetramethylene glycol (PTMG, $M_w = 2000$ g/mol, reagent, Acros) used as the soft part was dried at 90°C and 1–2 mmHg for 4 h before use. 4,4'-Methylenedicyclohexyl diisocyanate (H_{12} MDI, Bayer, Germany) used as hard segments was vacuum dried at 30°C for 4 h. Ethylene diamine (EDA, Acros chemical, reagent grade, Belgium) used as neutralizer, chain extender, respectively, were immersed in 4 Å molecular sieves for more than a week before use. The di-*n*-butyltin dilaurate (DBTDL, $[\text{CH}_3(\text{CH}_2)_3]_2 \text{Sn}[\text{O}-\text{CO}(\text{CH}_2)_{10}\text{CH}_3]_2$, reagent, TCI) was used as a catalyst. The nylon taffeta fabric (the warp and woof specifications are $70^D/24^F$, the warp and woof density are 110 ends/in. \times 76 picks/in., was provided from Lipeng textile company (Yang-Mei, Taiwan).

Preparation of NAPUs

Preparation of nonionic dispersing centers

The preparation of the nonionic dispersing center followed the method of Noll.¹⁰ Each PEGME mole was added into vacuum to remove moisture. Then each mole of PEGME was added to IPDI (1 mol) and DBTDL (0.01 mol) to react for 4 h at 35°C under surrounding nitrogen. The residual $-\text{NCO}$ content during the reaction was determined using the standard $-\text{NCO}$ titration method.¹⁰ Increasing the temperature to 50°C , NDEA 1 mol was added for 4 h to gain four kinds of dispersing center. The formative products were confirmed by Fourier transform infrared and elemental analysis. The preparation processes of nonionic dispersing centers with different PEGME chain length are shown in Scheme 1.

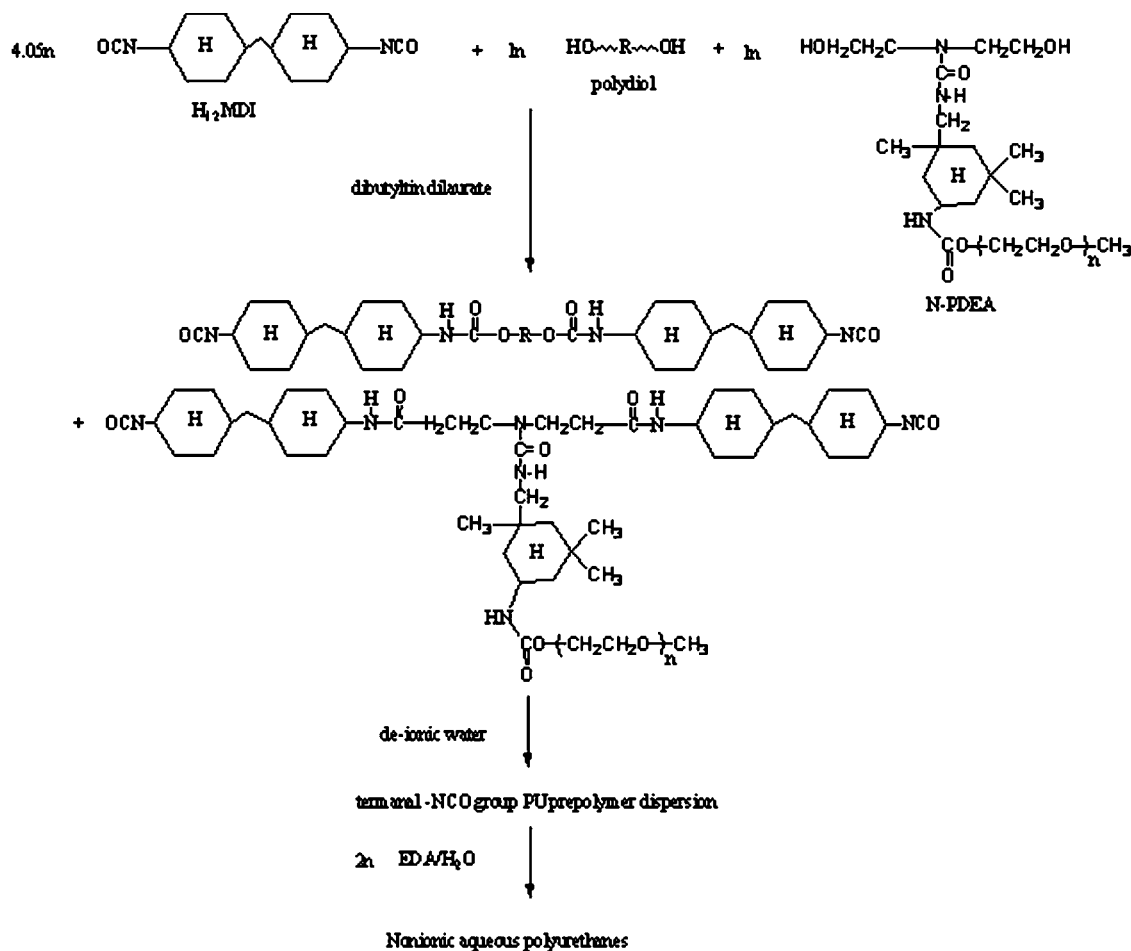
Preparation of NAPUs

The NAPU was prepared by the prepolymer process method.⁹ The PTMG2000 (1 mol) and dispersing center (1 mol) were put in a vacuum reactor to produce a mixture, followed by dehydration, and then H_{12} MDI (4.05 mol) was added. The reaction under pure surrounding nitrogen was performed at 50°C initially and gradually increased to 80°C . The reaction continued until the $-\text{NCO}$ residual value reached a half of the reactant as shown by titration.¹¹ Followed by cooling to 10°C , the deionized water was added to emulsify the prepolymer and EDA for the chain extending reaction. Finally, the solid content of NAPU was adjusted to a 30% aqueous solution. The preparation process is shown in Scheme 2.

Identification and analysis of NAPUs

Fourier transform infrared

The Fourier transform infrared (FT-IR) spectrums were analyzed using BIO-RAD FTS-7 spectrometer at 25°C . The scanning range was $4000\text{--}400$ cm^{-1} with a resolution of 4 cm^{-1} for 64 times. Figure 1 depicted the FT-IR spectrum for NAPUs. The $-\text{N}=\text{C}=\text{O}$ group absorption peaks (2270 cm^{-1}) of these synthetic compounds disappeared, indicating



Scheme 2 The preparation process for NAPUs.

that the $-N=C=O$ end group of the synthetic compounds must have reacted completely. The absorption peaks of $-NH$, $-COO$, and $-RCNH-$ groups occurred at 3330 , 1708 , and 1531 cm^{-1} , respectively. The formation of $-NHCOO$ (urethane) group in the structure of synthetic compounds was confirmed by these three groups. Further, the absorption peaks at 1112 cm^{-1} , and 2850 cm^{-1} and 2940 cm^{-1} belong to $-O-$, and $-CH_2-$ or $-CH_3$ groups, respectively.

Elemental analysis

The elemental analyses (EA) for the dispersing centers were conducted by a Perkin-Elmer 2400 (II) for C (%), N (%), and H (%). The measured data are given in Table I. The data are close to the theoretical values, pointing out that the synthesized dispersing centers have excellent purity.

Gel permeation chromatography

The gel permeation chromatography (Water RI-6000) test uses polystyrene as the standard. Then, the sample was injected into the apparatus at a concentration of

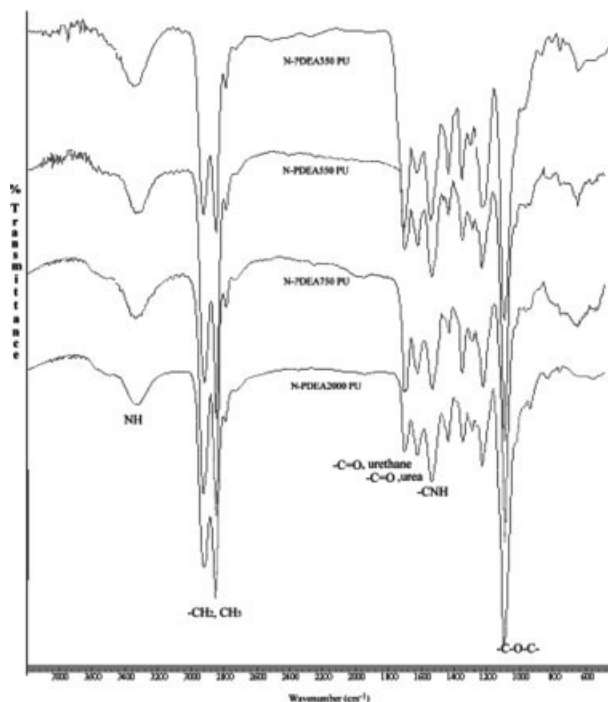


Figure 1 The FT-IR analyses of NAPUs.

TABLE I
Element Analysis for Nonionic Dispersing Centers and Molecular Weight of NAPUs

Symbol	Element analysis for dispersing centers						Molecular weight, measured by GPC ^a		
	C (%)		N (%)		H (%)		$M_w \times 10^4$	$M_n \times 10^4$	M_w/M_n
	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental			
N-PDEA350 PU	55.55	55.61	6.20	6.31	9.18	9.43	3.21	1.52	2.11
N-PDEA550 PU	55.28	55.43	4.79	4.30	9.19	9.40	3.98	1.92	2.07
N-PDEA750 PU	56.15	55.75	3.90	3.92	9.24	9.51	4.67	2.02	2.31
N-PDEA2000 PU	54.42	55.57	1.80	1.92	9.18	9.00	6.21	2.46	2.52

^a M_w , weight-average molecular weight; M_n , number-average molecular weight.

7–8 mg/mL (Water RI-6000 at a speed of 1 mL/min), which determined the molecular weight and the distribution of NAPUs, these data are also given in Table I.

Dispersion properties of NAPU

The particle size was measured by the laser light scattering method (He-Ne laser, 633 nm, Malvern). The sample was first diluted in deionized water to 0.5%, followed by ultrasonic treatment, and the dispersion was homogenized. The surface tension of diluted 2% NAPU emulsion was measured by CBVP-A3 (Kyowa Kaimenagaku Co., Japan). The contact angle between NAPU emulsion to untreated nylon fabric surface was tested by FACE CA-4 150 (Kyowa Kaimenagaku Co.). The testing method of contact angle was dropping the NAPU emulsion with low concentration (2 wt %) onto the surface of the nylon fabric.

Preparation and testing of casting films

The solid content of 30% NAPU coating on a teflon plate was dried at room temperature for 3 days, and then at 40°C over a week. Differential scanning calorimetry (DSC, Du-Pont Thermal analyst 2000) was used to study the thermal properties of NAPU casting films with a heating rate of 10°C/min under nitrogen purge of 60 mL/min. The dynamic mechanical analysis (DMA) was conducted by using Du-Pont thermal analyst 2980 with a heating rate of 5°C/min, from –120 to 150°C. The thermogravimetric analysis was measured by TGA-Q600 with a heating rate of 10°C/min from 30 to 600°C. Among the mechanical properties of the NAPU membrane performed by a tensile tester (Toyo Baldwin Tension UTM-3500), it was carried out according to the ASTM D 638M-93 methods. The crosshead speed was set at 50 mm/min, and the distance of the two pinch-heads was 20 mm.

Measurement of coated fabrics

About 30% solid content NAPU blended with 0.4% melamine resin and 10% hydroxyl ethyl cellulose

was coated onto the nylon taffeta fabrics. It was pre-dried at 100°C for 3 min and cured at 130°C for 5 min. The contact angle between pure water and NAPU-coated fabric was tested by FACE CA-4 150 (Kyowa Kaimenagaku Co.), which drops pure water on the NAPU-coated fabric. The WVP of the coated fabrics was measured based on the JIS-1099 CaC1 method at 40°C with a 90% relative humidity, and the waterproof capacity was preceded according to the JIS-1092 (B) method.

RESULTS AND DISCUSSION

Dispersion properties

The effect of side chain PEGME length on the surface tension of NAPUs are given in Figure 2, where the surface tension increased with increasing PEGME chain length. This is because the longer PEGME chain length could produce more hydrogen bonding with moisture resulting in a higher hydro-

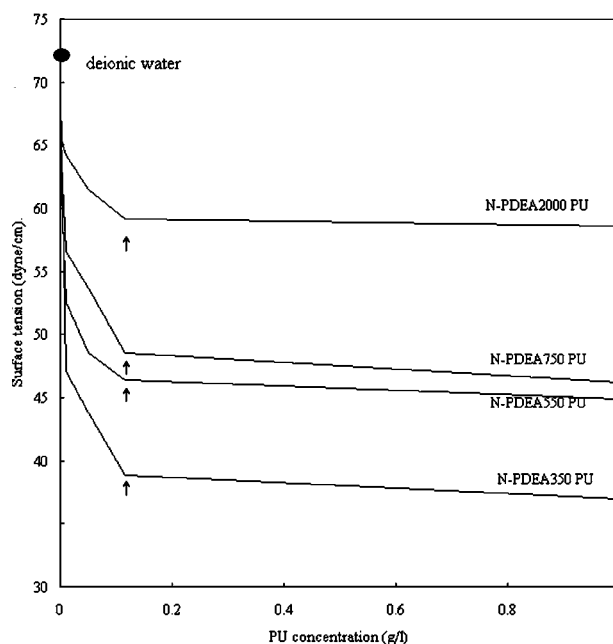


Figure 2 The surface tension of NAPU dispersions.

TABLE II
Solution Properties of NAPUs

Symbol	PU composition, weight ratio (%)			Solution properties		
	Hard segment	Soft segment	PEGME content	Surface tension	Contact angle (°)	Particle size (μm)
Pure water	–	–	–	72.3	128	–
N-PDEA350 PU	30.39	51.99	17.62	37.5	118	1.42
N-PDEA550 PU	28.88	49.41	21.71	45.3	116	1.61
N-PDEA750 PU	27.53	47.09	25.38	46.25	113	1.81
N-PDEA2000 PU	21.27	36.38	42.35	59.7	109	80.79

philic nature in NAPU. Therefore, the polymer chain of NAPU was not easy to arrange at the air–water contact on the NAPU solution, causing a higher surface tension value.

The affinity between NAPU emulsion and substrate (nylon fabric) is an important issue in textile coating. It was evaluated by measuring the contact angle between diluted 2% NAPU solution with nylon fabrics. The results are listed in Table II. The lower contact angle represents a larger interaction between NAPU and nylon fabric. The contact angle decreases with an increase in the M_w of PEGME (shown in Table II). There are three reasons for this: first, the longer pendant PEGME chain length has a higher hydrophilic characteristics,⁹ therefore, the NAPU with higher hydrophilicity cannot easily produce an interaction force on the hydrophobic nylon fabric. Second, the hard segment content of NAPU becomes lower on increasing the M_w of PEGME, and this would decrease their interaction force. Third, the dispersing center is found in the hard segment's pendant group. Thus, it causes greater steric hindrance as the PEGME molecule chain becomes longer, resulting in the lower affinity between intermolecules.

The average particle size of NAPU dispersion is given in Table II, where the particle size from 1.42 μm substantially increases to 80.79 μm as the molecular weight of PEGME increases from 350 to 2000 g/mol. In general, the particle size is mainly affected by its molecular weight, polymer chain extending property, and the intermolecular interaction in the solution. Here, the emulsification mechanism of NAPU is extending the long alkyl with ethylene oxide group toward water phase for forming a stable colloid structure resulting in a larger particle size as the PEGME becomes longer.

Thermal properties

Differential scanning calorimetric (DSC) analysis

The DSC curves of NAPUs are shown in Figure 3. It was found that all samples show a significant endothermic melting peak at 23°C, which was attributed to the crystallization of the soft segment phase (T_{m_s}). The N-PDEA 2000 PU shows another obviously crys-

talline endothermic peak at 48.9°C, which was attributed to the crystallizing side chain PEGME with a molecular weight of 2000 g/mol. The heat of fusion of the soft segment (ΔH_s) of NAPU are also listed in Table III, where the ΔH_s increases with increasing PEGME chain length, but decreases as the chain length at 2000 g/mol (N-PDEA2000 PU). The ΔH_s of N-PDEA750 PU (40.2 J/g) is larger than the N-PDEA350 PU (38.2 J/g) and N-PDEA 550 PU (38.7 J/g), because of the soft segment content of N-PDEA750 PU being more than the other two. Therefore, the cohesive energy of the soft segment chain of N-PDEA750 PU was less affected by the hard segment (shown in Table II). In addition, the PEGME and PTMG both have an ether-type structure; therefore, the longer PEGME molecule chain could produce more hydrogen bonding with PTMG easily resulting in the cohesive force increasing. Besides, the ΔH_s of N-PDEA2000 PU (17.6 J/g) was lower than the N-PDEA750 PU because of the N-PDEA2000 PU forming self-crystallization in PEGME as the M_w of PEGME is 2000 g/mol, therefore, the crystallinity cohesive of soft segment of N-PDEA2000 PU may be affected by PEGME. Generally, the PEGME chain length is less influential to T_{m_s} , but significantly to ΔH_s .

Dynamic mechanical analysis (DMA)

The DMA curves of NAPUs are shown in Figure 4. Because the NAPU structure drawn from soft and

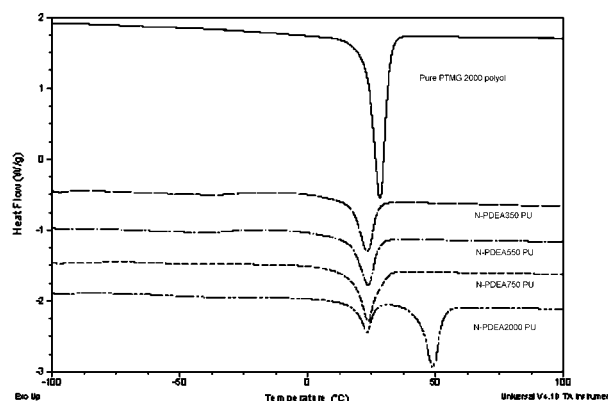


Figure 3 The DSC curves of NAPU casting films.

TABLE III
Thermal Properties of NAPU Casting Films

Symbol	DSC analysis			DMA			TGA		
	T _{g_s} (°C)	T _{m_s} (°C)	ΔH _s (J/g)	β peak (°C)	α peak (°C)	ΔT _g (°C)	Td ₅ (°C)	Td ₁₀ (°C)	Td ₁₅ (°C)
N-PDEA350 PU	-66.80	23.17	38.2	NA	NA	NA	145	178	199
N-PDEA550 PU	-67.45	23.62	38.7	-71.31	39.32	110.6	170	232	272
N-PDEA750 PU	-65.78	23.67	40.2	-68.23	46.17	114.4	243	284	303
N-PDEA2000 PU	-74.84	23.19	17.6	-71.69	61.86	133.6	203	266	304
		48.86	36.8						

hard segments cause two-phase structures,¹² two peaks, α peak (40–60°C) and β peak (-80 to -70°C) appear on tan δ curve of DMA. The β peak and α peak were defined as the glass transition temperatures of the soft segment (T_{g_s}) and hard segment (T_{g_H}), respectively. The temperature of β peak increases with increasing PEGME chain length, then decreases at 2000 g/mol. This is because the PEGME and the PTMG soft segment both have an ether-type structure. Thus, the longer PEGME chain could produce hydrogen bonding with PTMG easily as the chain length increases from 350 to 750 g/mol, leading to the PTMG molecular chain being restrained, resulting in an increase in its T_{g_s} value. However, the PEGME could produce self-crystalline as its chain length at 2000 g/mol resulting in the molecular motion of PTMG not being affected by PEGME. The β peak appeared at a low temperature. Besides, the microphase separation degree between the hard and soft segments can be represented by ΔT_g (ΔT_g = T_{g_H} - T_{g_s}) of DMA analysis that found the microphase separation degree increases with the increase in PEGME length. The phase separation improves the mechanical properties of NAPU, but reduces the flexibility and solubility.¹³ The thermostability properties measured by thermogravimetric analysis are shown in Figure 5. The trend of TGA followed the order: N-PDEA750 PU > N-PDEA2000 PU > N-PDEA550 PU > N-PDEA350 PU.

Tensile strength of NAPU film

The Tensile strength of NAPU films and its elongation are given in Table IV, where the N-PDEA350

PU cannot form to film; therefore, it's not discussed in here. The strength increases with the increase in PEGME chain length. In particular, the N-PDEA550 PU was even close to the strain axis showing the lack of strength. This shows that the NAPU with the shorter pendant group could affect the molecular orientation. For the PEGME chain length at 750 g/mol, though the PEGME still influenced the orientation of the molecule chain, the enthalpy of soft segment was increased. Therefore, the N-PDEA2000 PU has the highest strength because of the PEGME chain length not producing enough self-crystallization.

Coated fabric

The hydrophilicity of NAPU-coated fabric was evaluated by measuring the contact angle between water drops and the surface of the coated fabric. The results are also listed in Table IV, where the contact angle decreases with the increase in PEGME chain length, but increases in PEGME2000. The reason for such behavior may be attributed to the fact that although the hydrophilicity increases with an increase in the PEGME chain length, the N-PDEA2000 PU produced a crystalline in its pendant group, thereby resulting in a hydrophobic nature of the coated fabric. The trend of WVP followed the order: N-PDEA750 PU > N-PDEA550 PU > N-PDEA350 PU > N-PDEA2000 PU, this result agreed with the contact angle test except the N-PDEA 2000 PU. Figure 6 showed the scanning electronic microscopic (SEM) photography. As we can see that N-PDEA 2000 PU has very few surface micro-pores, therefore, it has lower WVP. The waterproof

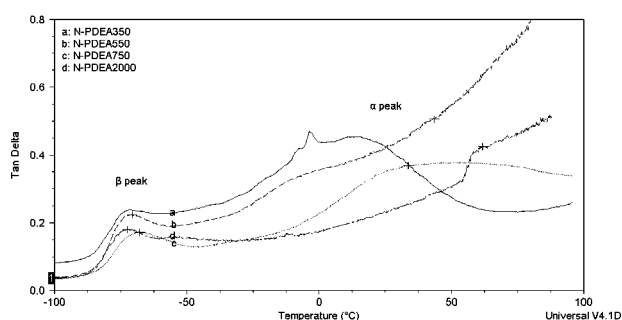


Figure 4 The DMA curves of NAPU casting films.

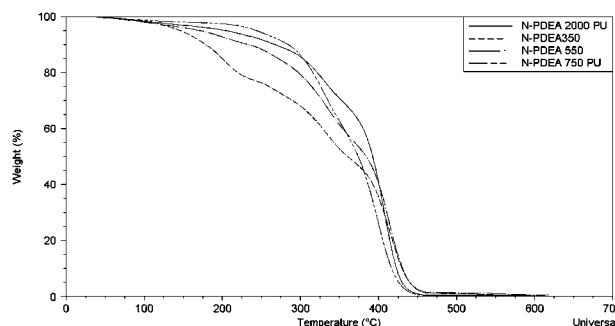


Figure 5 The TGA curves of NAPU casting films.

TABLE IV
Tensile Strength of NAPU Casting Films and the Physical Properties of NAPU-Coated Fabric

Symbol	Mechanical properties		Coated fabric properties			
	Strength (g/mm ²)	Elongation (%)	Thickness (mm)	Contact angle ^a	WVP (g/m ² /24 h)	WP (mmH ₂ O)
Untreated	–	–	0	114	7634	0
N-PDEA350 PU	NA	NA	0.030	98	3240	1300
N-PDEA550 PU	0.1	1572.5	0.027	87	4160	1650
N-PDEA750 PU	35.0	405.0	0.043	81	4547	3000
N-PDEA2000 PU	138.7	250.0	0.022	92	3014	3357

^a The contact angle was measured between pure water and coated fabric.

increases with increasing PEGME chain length. This is because the crystallization degree of NAPU increases with increasing PEGME chain length. Besides, the SEM photography (as Fig. 6) showed the micropore size of PU membrane increases with decreasing PEGME chain length, resulting in the water having difficulty passing the film. Therefore, the waterproofing increased as the PEGME chain length increased.

CONCLUSION

This study described the influence of PEGME chain length of NAPU on its physical properties and application to coated fabric. The nonionic aqueous poly-

urethane (NAPU) prepared H₁₂MDI, PTMG2000, and a series of synthesized dispersing center with a different side chain length. The results are summed up in the following:

1. The surface tension and average particle size increases with increasing PEGME chain length.
2. The PEGME chain length is less influential to the melting point of soft part, but is significant to its heat of fusion.
3. The tensile strength of NAPU film increases with increasing PEGME chain length and the trend of elongation was opposite.

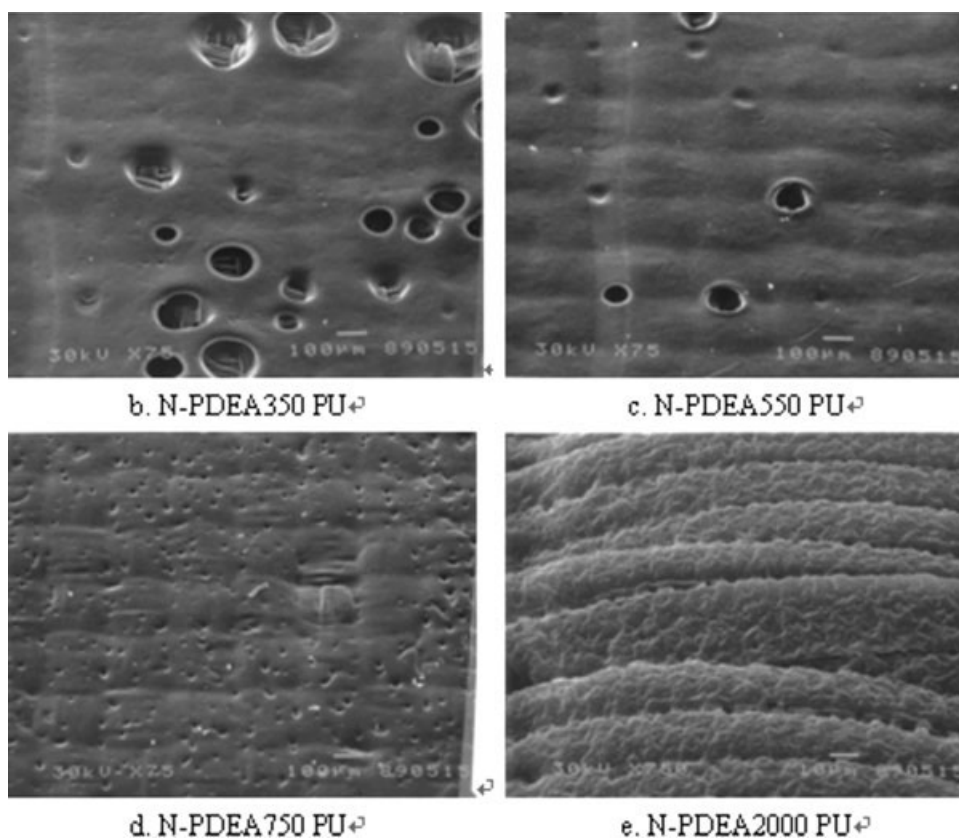


Figure 6 The SEM photographs of coated fabrics.

4. The WVP of coated fabric followed the order: N-PDEA750 PU > N-PDEA550 PU > N-PDEA350 PU > N-PDEA2000 PU, and the waterproofing of coated fabric increases with increasing PEGME chain length.

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