Synthesis and Properties of Highly Hydrophilic Waterborne Polyurethane-Ureas Containing Various Hardener Content for Waterproof Breathable Fabrics

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ABSTRACT: As part of an ongoing search for highly hydrophilic waterborne polyurethanes for waterproof breathable fabrics, a waterborne polyurethane [waterborne polyurethane-ureas (WBPU): P70, the number indicates the poly(ethylene glycol) (PEG) content] dispersion was synthesized from PEG (70 wt %) and dimethylol propionic acid (14 mol %) as the hydrophilic/ionic components, 4,4'-diisocyanato dicyclohexylmethane as a diisocyanate, ethylenediamine as a chain extender, and aliphatic tri-isocyanate as a hardener. To determine the best highly hydrophilic WBPU coatings for waterproof breathable fabrics, this study focused on the effect of the hardener content(0–1.2 wt %) in the WBPU P70 sample on the dynamic thermal mechanical properties, contact angle/surface energy, water swelling, water insolubility, and water vapor transmission rate (WVTR). The contact angle, water swelling, glass transition temperature, modulus, and strength increased with increasing hardener content, whereas the surface energy, water insolubility, and WVTR decreased. Sample P70/0.5 (cured sample containing 0.5 wt % of hardener) showed relatively good dimensional stability in water (high water insolubility), strong hydrophilicity (low-water contact angle/high-surface energy/high water absorption), and a high WVTR, highlighting its promising applications in waterproof breathable fabrics. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1745–1751, 2013

INTRODUCTION

Several methods can be used to prepare breathable waterproof fabric, such as microporous, hydrophilic, and fabrics based on microfilaments.[1] Waterproof breathable fabrics, which are used to construct sportswear and inclement weather garments, were classified as cotton ventiles, microfiber fabrics, polytetrafluoroethylene (PTFE) laminated fabrics, poromeric polyurethane laminated fabrics, and hydrophilic laminated fabrics according to their manufacturing methods. Microporous membranes allow air to pass through the permanent, air-permeable pore structure, whereas hydrophilic membranes permit the transmission of water through a molecular mechanism (absorption–diffusion–desorption).[2] A large number of hydrophilic polymers, such as poly(vinyl alcohol), poly(acrylic acid, poly(ethylene oxide), etc., are too sensitive to water, resulting in complete dissolution, or are unable to withstand the rigors of normal use. The most preferred way of overcoming these deficiencies is to optimize the hydrophilic–hydrophobic balance of the nonporous membrane. Hence, the strength and durability requirements are fulfilled mainly by the hydrophobic component.

Many studies have examined ways of using polyurethanes in breathable products, such as porous polyurethane films[3–5] and hydrophilic nonporous polyurethane products.[6–9] To produce direct-coated fabrics with a micro-porous structure, other studies[10,11] used waterborne polyurethane/water soluble poly(vinyl alcohol) blend and waterborne polyurethane/water soluble sodium alginate blends as coating materials for fabrics. The poly(vinyl alcohol) and sodium alginate were then removed by dissolving these water soluble polymers in water. Hydrophilic films and coatings require swelling of the membrane to assist water vapor diffusion but this swelling should be restricted to prevent complete dissolution or breakdown of the polymer in water or other solvents that the product would likely come into contact with. The level of hydrogen bonding, hydrophobicity, and length of the covalent crosslinks/crosslink density are important variables that control polymer swelling and the water vapor permeability (WVP) of the coated fabric.

Table I. Sample Designation, Composition, Water Insolubility, Equilibrium Water Absorption, and Equilibrium Water Content of Highly Hydrophilic Polyurethane-Urea (WBPU) and WBPU Containing Various Contents of Hardener

Sample designation	Composition (mol)					DMPA (mol %)	PEG content (wt %)	Hardener (wt %)	Water insolubility (%)	Water absorption (%)	Equilibrium water content (%)
	H_{12}MDI	PEG	DMPA	TEA	EDA						
Pristine WBPU P70	1.1	0.43	0.31	0.31	0.36	14	70	0	Soluble	–	–
P70/0.25	1.1	0.43	0.31	0.31	0.36	14	70	0.25	58.0	100.5	91
P70/0.50	1.1	0.43	0.31	0.31	0.36	14	70	0.50	93.0	645	87
P70/0.75	1.1	0.43	0.31	0.31	0.36	14	70	0.75	94.5	482	83
P70/1.00	1.1	0.43	0.31	0.31	0.36	14	70	1.00	96.2	457	82
P70/1.25	1.1	0.43	0.31	0.31	0.36	14	70	1.25	97.5	399	80

Hydrophilic polyurethanes are composed of soft segments, which are water soluble or highly water swellable, and hard segments made from conventional diisocyanates, which are normally insoluble in water.[9] Hydrophilic polyurethanes with high WVP can be used as biomaterials,[12–15] filter membranes,[16] biosensors,[17,18] and water permeable materials.[19,20] On the other hand, it is almost impossible to prepare a high-water vapor permeable fabrics by a direct coating with hydrophobic polyurethane. The advantage of hydrophilic polyurethane coatings over the laminating method of microporous polyurethane films is that the former has good adhesion to textile substrates and is less expensive.

Waterborne polyurethane-ureas (WBPUs) are nontoxic and nonflammable materials. They also exhibit excellent adhesion to many substrate surfaces including glass, rubber, and polymeric fibers.[21–24] Most WBPUs contain ionic groups in their molecular structure and show excellent mechanical properties due to the presence of inter-chain Columbic forces and hydrogen bonding.[25] The carboxylic ions of dimethylol propionic acid (DMPA) in the polymer are hydrophilic and act as anionic centers and internal emulsifiers. DMPA is commonly incorporated into the WBPU back-bones as it is effective for water dispersion in the neutralization reaction with triethylamine (TEA).[26–28] The hydrophilicity of poly(ethylene glycol) (PEG)-based polyurethanes can be varied, either by increasing the overall content (wt %) of the hydrophilic component, PEG, or by altering the length of the hydrophilic segments. Previous studies[29,30] examined the sorption of water vapor by hydrophilic segmented polyurethanes containing different molecular weight/compositions of poly(ethylene oxide) and/or poly(propylene oxide) oligomers. Polyurethane-urea-based liquid bandage materials were prepared using hydrophilic PEG.[31] The polyisocyanate hardener, which is used in many industrial coatings and adhesive applications, has attracted less attention. Most related studies were performed in industrial laboratories and have not been published. Moreover, reports of dimensionally stable, highly hydrophilic, direct-coating polyurethane using a polyisocyanate hardener are particularly rare. The main aim of this study was to improve the WVP of direct coating fabrics using highly hydrophilic polyurethane.

In this study, the PEG/DMPA-based highly hydrophilic waterborne polyurethanes were synthesized from a polyaddition reaction using PEG/DMPA as a hydrophilic/ionic component, 4,4′-diisocyanato dicyclohexylmethane (H_{12}MDI) as a diisocyanate, ethylenediamine (EDA) as a chain extender, and aliphatic triisocyanate as a hardener. Water soluble PEG and ionic compound DMPA were used to control the hydrophilicity of the waterborne polyurethane. The cross-linking agent (hardener) with tri-isocyanate groups was used to prevent the complete dissolution or breakdown of a highly hydrophilic polymer in water, or other solvents. The effects of the hardener content on the water contact angle/surface energy, dynamic mechanical properties, water insolubility (%), water absorption (%), equilibrium water content (%), and water vapor transmission rate (WVTR) (g/m^2/day) of the samples were examined.
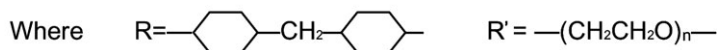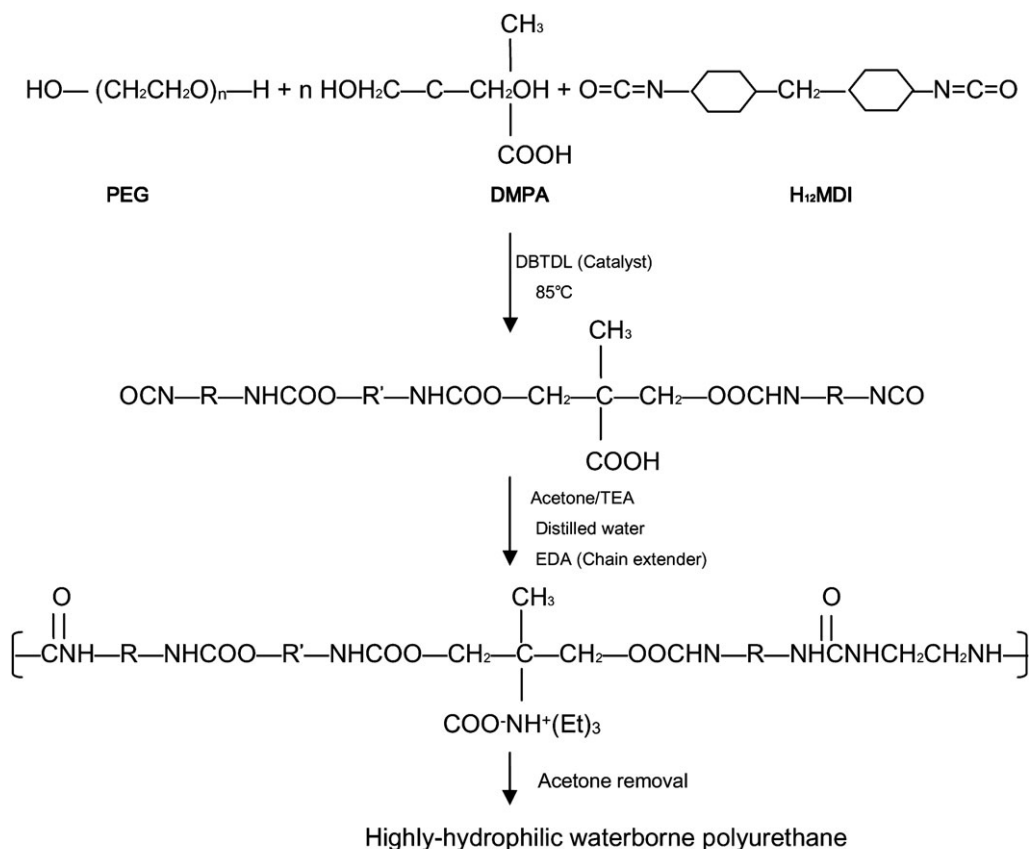
EXPERIMENTAL

Materials
PEG (number-average molecular weight, M_n = 2000 g/mol, Aldrich Chemical, Milwaukee, WI) was degassed at 70°C under vacuum overnight before use. H_{12}MDI (Aldrich Chemical, Milwaukee, WI), 2,2-bishydroxymethylpropionic acid (DMPA, Aldrich Chemical, Milwaukee, WI), EDA (Aldrich Chemical, Milwaukee, WI), TEA (Junsei Chemical), acetone (Aldrich Chemical, Milwaukee, WI), dibutyltindilaurate (Aldrich Chemical, Milwaukee, WI), and tri-isocyante hardner (hexamethylene diisocyanate cyclictrimer, CORONATE HX, Nippon Polyurethane Industry Co., Japan) were used without further purification.

Synthesis of Highly Hydrophilic Polyurethane-urea (WBPU)
Table I lists the composition of highly hydrophilic polyurethane-urea synthesized in this study. The highly hydrophilic polyurethane-urea was synthesized using a prepolymer mixing process (Scheme 1). PEG was placed in a four-necked separable flask equipped with a thermometer, stirrer, condenser with a drying tube, dry nitrogen inlet, and a heat jacket, and was degassed in a vacuum at 90°C for 30 min. DMPA/NMP (1/2, w/w) was then added to the flask and the mixture was allowed to cool to 45°C with stirring at 200 rpm. H_{12}MDI was then added to the flask and the mixture was heated to 85°C under ~200 rpm stirring. The reaction mixture was allowed to react at 85°C until the theoretical NCO content was reached. The change in NCO value during the reaction was determined using the standard dibutylamine back titration method (ASTM D 1638). Acetone was then added to the NCO-terminated

Scheme 1. Synthesis of highly hydrophilic polyurethane-urea dispersions.

prepolymer mixture to adjust the viscosity of the solution. TEA was added to the resulting reaction mixture to neutralize the carboxyl group of the NCO-terminated prepolymer. After 30 min neutralization, distilled water (70 wt %) as a dispersant was added to the reaction mixture with vigorous stirring at 1000 rpm. The neutralized prepolymer was chain-extended until the NCO peak (2270 cm^{-1}) in the IR spectra of WBPUs had disappeared. All the WBPUs were obtained by the evaporation of acetone at about 55°C and the subsequent addition of an adequate volume of distilled water. The solid content of WBPU prepared in this study was 30 wt %.

Preparation of Pristine Highly Hydrophilic WBPUs and WBPUs Films Containing Hardener

Highly hydrophilic polyurethane-urea containing hardener was prepared by mixing a highly hydrophilic polyurethane-urea dispersion and hardener. Table I lists the hardener content in the highly hydrophilic polyurethane-urea. The pristine highly hydrophilic WBPUs films were prepared by pouring the pristine WBPU dispersion into a Teflon disk followed by drying at room temperature for 2 days. Highly hydrophilic polyurethane-urea containing hardener films were prepared by pouring the aqueous dispersion on a Teflon disk, followed by drying at room

temperature for 1 day and curing at 100°C for 10 min. The films (typically ∼0.2 mm thick) were dried in a vacuum at 60°C for 1 day and stored in a desiccator at room temperature.

Coating to Nylon Fabrics

The highly hydrophilic polyurethane-urea containing hardener materials were coated on nylon fabrics using a steel bar and dried at 100°C for 10 min. The thicknesses of the coating layer on the nylon fabrics were ∼0.2 mm.

Characterization

A Fourier transform infrared spectrometer (Impact 400D, Nicolet, Madison, WI) was used to identify the polyurethane-urea structure. For each sample, 32 scans at a 2 cm^{-1} resolution were collected in transmittance mode.

Dynamic mechanical analysis (Q800 V7.5 Build 127) was carried out in thin film extension mode at 3 Hz of frequency and 20 μm of amplitude. The samples were a 0.2-mm thick solution cast film, which were heated from −80 to 80°C at a heating rate of 5°C/min. The measurements were done in the linear viscoelastic range.

The contact angles of water and benzene were measured at 25°C using a contact angle goniometer (Erma Contact Angle

Meter, Japan). The reported results are the mean of five measurements. The contact angle, which is a measure of the surface wettability, was used to determine the hydrophobicity and hydrophilicity. The surface energy of the solid film can be calculated using the following equation:

$$\gamma_s = \gamma_s^{\mathrm{d}} + \gamma_s^{\mathrm{p}}$$

where γ_s represents the surface energy of the solid film, γ_s^{d} represents the dispersion force, and γ_s^{p} represents the polarity force. γ_s^{d} and γ_s^{p} can be calculated from the following equations:

$$\gamma_{11} = (1 + \cos\theta_1) = 2(\gamma_{11}^{\mathrm{d}}\gamma_s^{\mathrm{d}})^{1/2} + 2(\gamma_{11}^{\mathrm{p}}\gamma_s^{\mathrm{p}})^{1/2}$$

$$\gamma_{12} = (1 + \cos\theta_2) = 2(\gamma_{12}^{\mathrm{d}}\gamma_s^{\mathrm{d}})^{1/2} + 2(\gamma_{12}^{\mathrm{p}}\gamma_s^{\mathrm{p}})^{1/2}$$

where γ_{11} and γ_{12} represent the surface tension of the two testing liquids, including the dispersion item and polar item. The following relationships between them were $\gamma_{11} = \gamma_{11}^{\mathrm{d}} + \gamma_{11}^{\mathrm{P}}$ and $\gamma_{12} = \gamma_{12}^{\mathrm{d}} + \gamma_{12}^{\mathrm{P}}$. Under the conditions that the values of γ_{11}^{d}, γ_{11}^{P}, γ_{12}^{d}, and γ_{12}^{P} are given, γ_s^{d} and γ_s^{p} can be obtained by determining θ_1 and θ_2. Hence, the surface energy of γ_s can be obtained. The testing liquids used were water ($L1$) and benzene ($L2$), and their γ_{11}^{d}, γ_{11}^{P}, γ_{12}^{d}, and γ_{12}^{P} were 21.8 mN/m, 51.0 mN/m, 28.9 mN/m, and 0 mN/m, respectively.[32]

The water absorption (%) was calculated using the following equation:

$$\text{Water absorption (\%)} = [(W_S - W_d)/W_d] \times 100$$

where W_s and W_d are the weight of the swollen and dried film sample, respectively. The polyurethane-urea films were immersed in distilled water at regular time intervals at 37°C. After removing the excess surface water with filter paper, the weight of the swollen sample was measured until there was no further increase in weight. The equilibrium water content was calculated using the following equation:

$$\text{Equilibrium water content (\%)} = [(W_S - W_d)/W_d] \times 100$$

where W_s is the weight of polyurethane-urea film sample at equilibrium swelling and W_d is the weight of the dried sample.

The insolubility of the polyurethane-urea films in water (wt %) was estimated by measuring its insoluble part after extraction in distilled water at 40°C for 1–5 days. The insoluble part was dried to a constant weight at 100°C. The water insolubility (wt %) was calculated using the following equation:

$$\text{Water insolubility (wt\%)} = (W_t - W_i)] \times 100$$

where W_i and W_t are the dried weight of film sample before and after extraction, respectively.

The moisture permeability was determined by measuring the WVTR across the material according to ASTM E96/E96M-05. The coated fabrics were mounted on the mouth of cylindrical aluminum cups (diameter: 60 mm) containing 10 mL of water. The coated fabrics were fastened using Teflon tape across the
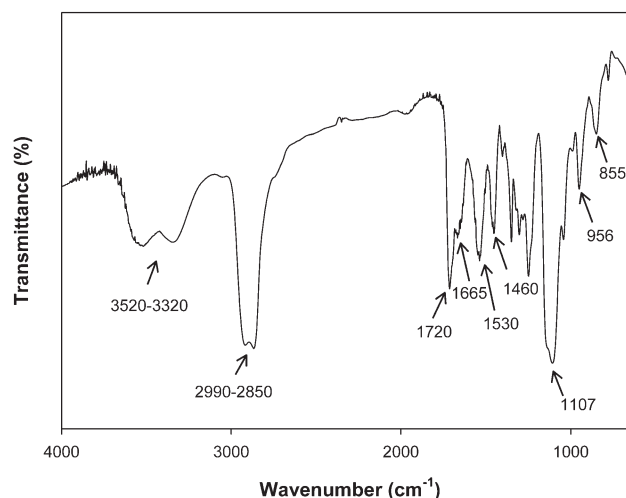

Figure 1. FTIR spectrum of PEG/DMPA-based WBPU (P70) prepared in this study.

edges to prevent water vapor loss through the boundary, and kept in an incubator at 35°C and 35% relative humidity. The WVTR and WVP percentage were calculated using the following formulae:

$$\text{WVTR} = [(W_i - W_t)/A \times 24] \times 10^6 \text{g/m}^2/\text{day WVP\%}$$
$$= (\text{WVTR of coated nylon fabric/WVTR of nylon fabric}) \times 100$$

where WVTR is expressed in g/m^2/day, A is the area of the cup mouth (mm^2), and W_i and W_t are the weights of cup containing water before and after the permeation of water in an incubator, respectively.

RESULTS AND DISCUSSION

Synthesis and Identification of WBPU (P70)

Table I lists the compositions of pristine WBPU P70 and cross-linkable WBPU samples. It is well known that the use of a larger amount of DMPA results in a smaller mean particle size and higher stability of the WBPU dispersion.[33,34] Generally, water soluble PEG is used most widely to achieve good hydrophilicity as well as good strength, good processability, low fouling potential, high stability in temperature and pH, minimum cell adhesion, and protein absorption. Preliminary experiments revealed the WBPU dispersion containing 20 mol %/60 wt % of DMPA/PEG at a fixed EDA content to be stable with a water contact angle of 21°, whereas the DMPA/PEG 4 mol %/80 wt % based WBPU dispersion was unstable. In this study, the optimum DMPA and PEG contents to obtain a stable WBPU dispersion and higher hydrophilic film (lower water contact angle: 11°) were 14 mol % and 70 wt %, respectively.

Figure 1 shows the FTIR spectrum of PEG/DMPA-based WBPU (P70) prepared in this study. Urethane/urea groups with H$_{12}$MDI showed the characteristic peaks of the N—H stretching band at 3520–3320 cm^{-1}, C=O stretching band at 1740–1700 cm^{-1}, amide II (N—H bending/C—N stretching) band at 1530 cm^{-1}, CH$_2$ scissor vibration band at 1475–1450 cm^{-1}, and CH$_2$
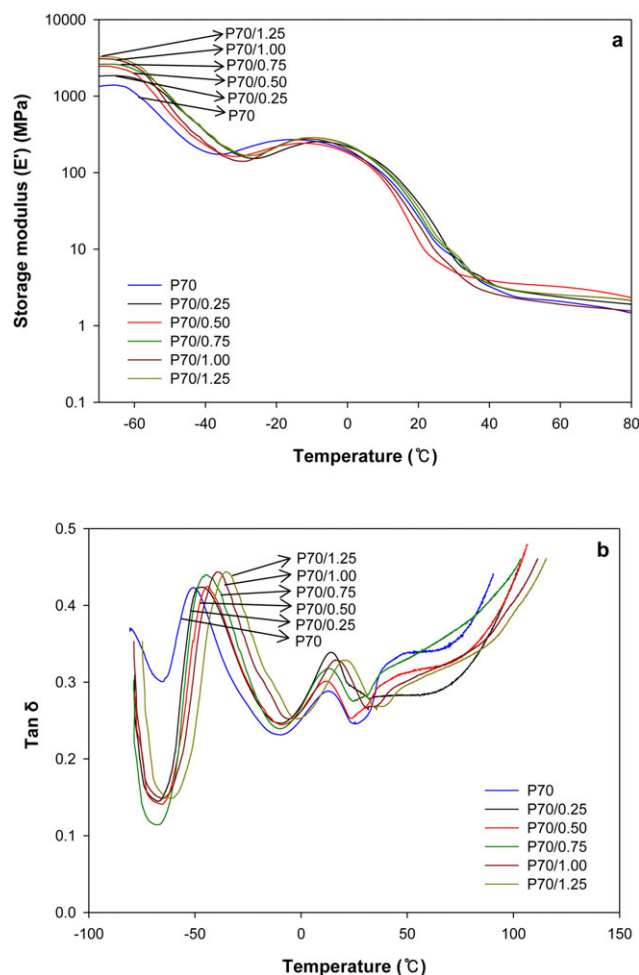
Figure 2. (a) Storage modulus (E') and (b) loss tangent δ of p70 samples containing various contents of hardener. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

rocking in methylene chains band at 740–720 cm^{-1}. The band at 3520–3320 cm^{-1} was attributed to the N—H stretching band of urethane-urea. The hydroxyl group of DMPA/PEG has an IR band at 3500 cm^{-1}. However, the number of terminal hydroxyl group in WBPU is very small fraction. Therefore, the band at 3520–3320 cm^{-1} is mostly attributed to the N—H stretching band of urethane urea. The characteristic peaks for PEG, such as —CH$_2$— symmetric stretching at 2990–2850 cm^{-1}, C—O stretching at 1200–1015 cm^{-1}, C—C stretching at 965–920 cm^{-1}, and CH out-of-plane deformation at 850–790 cm^{-1}, were observed. The band centered near 1665 cm^{-1} was assigned to the stretching of hydrogen-bonded carboxylic carbonyl groups, which originate from the DMPA salt group. From these results, the chemical structure of PEG/DMPA-based WBPU (P70) synthesized in this study was identified.

In addition, a previous study[35] found that the cured (cross-linked) WBPU material using polyisocyanate hardener contained newly formed small allophanate and biuret peaks (^{1}H NMR spectra peaks) at 6.88 and 6.91 ppm, respectively. This suggests that the hardener NCO group reacts with a urethane/urea group to form a crosslinked structure in WBPU.

Dynamic Mechanical Properties

Dynamic mechanical thermal analysis was used to determine the compositional dependence of the local scale motion, as well as the cooperative segmental motion that might exist in the WBPU containing hardener. However, the DMA measurement was not conducted on the WBPU-coated nylon fabrics. The WBPU-coated nylon fabrics were too thick for such measurement. Figure 2 presents the storage modulus (E') and loss tangent (tan δ) for the WBPU film samples. The storage modulus increased with increasing hardener content. Two loss peaks in WBPU were observed because of the glass transition temperature of the amorphous soft segment (T_{gs}) at the lower temperature and the glass transition temperature of the amorphous hard segments (T_{gh}) at the higher temperature The distinct main peak at the lower temperature (T_{gs}, near −40°C) was assigned to the glass transition of soft segment in pristine WBPU P70. On the other hand, the smaller peak at the higher temperature (T_{gh}, near 20°C) in pristine WBPU P70 was attributed to the smaller content of amorphous hard segment components. The glass transition peaks of the pristine WBPU P70 sample near −40°C and 20°C were shifted to a higher temperature with increasing hardener content. This is probably due to the restricted segment motions with increasing hardener content in WBPU.

Water/Benzene Contact Angles and Surface Energies of the Film Samples

Super-hydrophilic surfaces are surfaces that become completely and instantaneously wet by water (water droplet contact angle < 5° within 0.5 s or less). Generally, solid surfaces with a water contact angle below 30° are said to be highly hydrophilic. The water/benzene contact angles and surface energies of the film samples are shown in Figure 3. The water contact angle/surface energy (mN/m) of P70, P70/0.25, P70/0.50, P70/0.75, P70/1.00, and P70/1.25 were 11.0°/72.1 mN/m, 12.5°/71.7 mN/m, 15.0°/71.0 mN/m, 18.0°/70.0 mN/m, 21.5°/68.6 mN/m, and 25.0°/67.0 mN/m, respectively. The pristine P70 film sample had the lowest water contact angle (11°). This suggests that all the cured film samples (P70/0.25, P70/0.50, P70/0.75, P70/1.00, and P70/1.25) prepared in this study also had highly hydrophilic
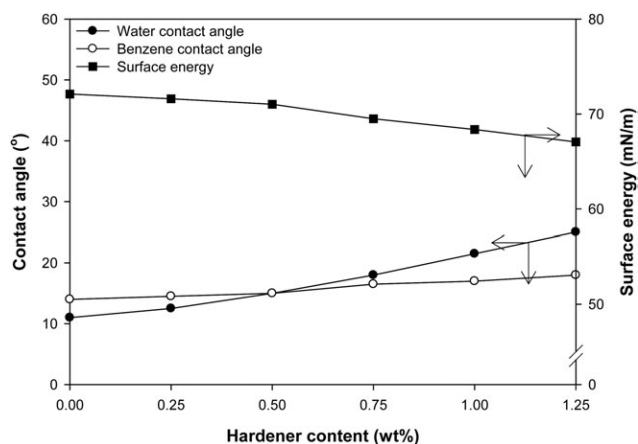

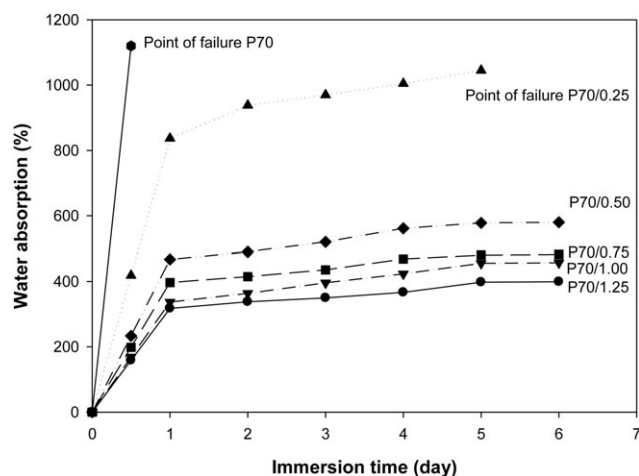**Figure 3.** Effect of hardener content on the water/benzene contact angles and surface energy.

Figure 4. Water absorption percent versus the immersion time of P70 samples containing various content of hardener.

Figure 5. Water insolubility versus extraction time of P70 samples containing various contents of hardener.

surfaces. The water/benzene contact angle of the film samples increased with increasing hardener content, whereas the surface energy decreased. This was attributed to the crosslinking and hydrophobicity of the hardener component. Additionally, because the hardener had a much lower molecular weight (MW: 504) than WBPU, the hardener in WBPU dispersion/hardener mixture might migrate slightly to the surface layer during curing (heating at 100°C) process, which resulted in more crosslinked structure in surface layer. It was likely that such crosslinked structure in surface layer led to the lower surface energy and higher water contact angle.

Water Absorption %, Water Insolubility %, and Water Vapor Transmission Rate

Figure 4 presents the water absorption as a function of the immersion time. The pristine P70 film sample without a hardener was dissolved in water after ~12 h immersion. The water absorption % increased with increasing immersion time and then leveled off. On the other hand, the water absorption % of the P70/0.25 film sample containing the lowest hardener content was difficult to determine after 5 days, meaning that the P70/0.25 sample is unsuitable for durable coatings. On the other hand, the P70/0.50, P70/0.75, and P70/1.00 film samples showed a lower level of water absorption % and maintained their dimensional stability after 6 days. The maximum water absorption and equilibrium water content of the film samples decreased with increasing hardener content (see Table I). The P70/0.5 sample was found to be the best hydrophilic polyurethane material with dimensional stability.

Figure 5 shows the water insolubility (%) of the film samples as a function of the extraction time, and Table I lists their water insolubility % at equilibrium. The water insolubility (%) of the P70/0.25 film sample decreased with increasing extraction time. On the other hand, the water insolubility (%) of all the samples except for the P70/0.25 sample decreased slightly with increasing extraction time up to 4 days, and then reached almost constant values (water insolubility % at equilibrium) in the range of 93–98%. The water insolubility (%) increased significantly with
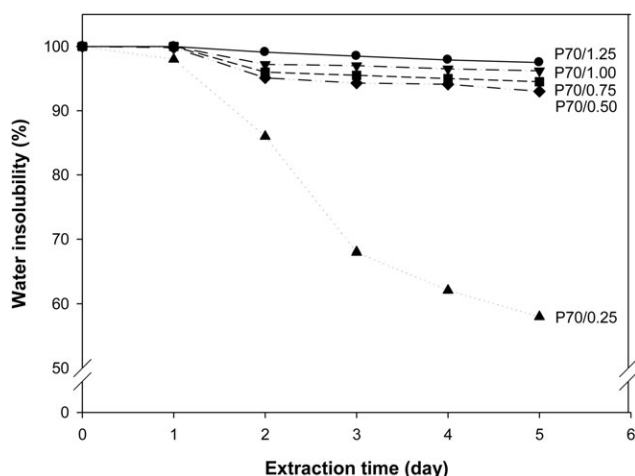
increasing hardener content. The increase in water insolubility % was attributed to the increased crosslinking in WBPU. Overall, the P70 samples containing 0.5–1.2 wt % of hardener showed reasonably good water-resistance.

A previous study[11] reported that the WVTR decreased significantly with increasing coating layer thickness. Figure 6 shows the WVTRs of the pristine nylon fabric and nylon fabric coated with P70 containing various hardener contents at a fixed thickness (~0.2 mm). The WVTR of the pristine nylon fabric was 3234 g/m^2/day. The WVTRs of the nylon coated with P70/0.25, P70/0.50, P70/0.75, P70/1.00, and P70/1.25 were 2843, 2350, 1980, 1570, and 1456 g/m^2/day, respectively. The WVTR decreased significantly with increasing hardener content. The decrease in WVTR must also be due to the increased crosslinking caused by the reaction of the hardener NCO group with urethane/urea. In addition, the hydrostatic pressure test method (AATCC 127) measures the resistance of a fabric to the penetration of water under hydrostatic pressure. The water resistance of the nylon fabric-coated P70 samples were ~7000 mm H_2O, indicating these coating materials to exhibit good waterproof
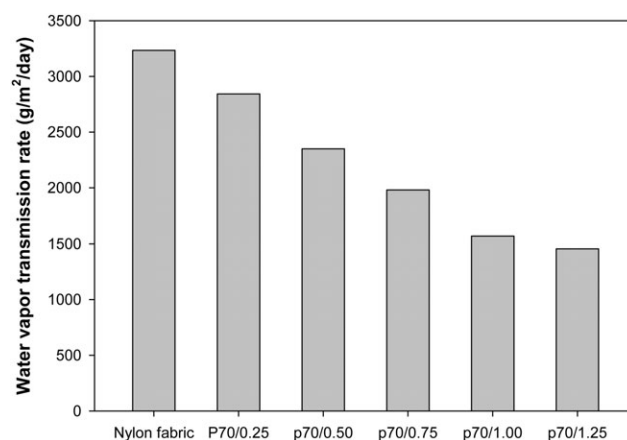

Figure 6. Effect of hardener content on the water vapor transmission rate of coated nylon fabrics.

behavior. Overall, the P70/0.50 coating sample was found to be the best material for waterproof breathable fabrics.

CONCLUSIONS

This preliminary study examined the stability of WBPU dispersions and the hydrophilicity (water contact angle) of WBPU film samples. The optimum DMPA/PEG contents to obtain a stable WBPU dispersion and most-hydrophilic film (lower water contact angle: 11°) were 14 mol %/70 wt %. To identify the most hydrophilic WBPU coatings for waterproof breathable fabrics, this study examined the effect of the hardener content in the WBPU P70 sample on the dynamic thermal mechanical properties, contact angle/surface energy, water swelling, water insolubility, and WVTR. The contact angle, water swelling, glass transition temperature, and storage modulus increased with increasing hardener content, whereas the surface energy, water insolubility, and WVTR decreased. The P70-0.25 sample was not a durable coating material. In contrast, the P70-0.5 (hardener content: 0.50 wt %) sample exhibited relatively good dimensional stability in water (good water insolubility, 93%), higher hydrophilicity (low-water contact angle/high surface energy, 15°/71.0 mN/m, and high water absorption, 645%), and a higher WVTR (2350 g/m^2/day). These results highlight the potential of the highly hydrophilic WBPU P70-0.50 sample as a direct coating material for waterproof breathable fabrics.

ACKNOWLEDGMENTS

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