Preparation and Properties of Waterborne Polyurethane-urea/Sodium Alginate Blends for High Water Vapor Permeable Coating Materials

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ABSTRACT: To improve the water vapor permeability of coating materials, aqueous sodium alginate (SA) solution was blended with waterborne polyurethane-urea (WBPU) dispersions synthesized by prepolymer mixing process. The content of SA for stable WBPU/SA dispersions was found to be below 30 wt %. As the SA content increased, the number and density of total micropores (tunnel-like micropores/isolated micropores) formed after dissolution of SA in water increased, and the water vapor permeability of coated Nylon fabric also increased remarkably. These results clearly demonstrate that utilizing WBPU/water soluble polymer SA blends as coating materials and then dissolving SA in water surely facilitate obtaining prominent breathable fabrics. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1168–1176, 2007

Key words: waterborne polyurethane; SA; water vapor permeability; dissolution; micropore

INTRODUCTION

Because most polymers are thermodynamically incompatible, heterogeneous polymer blends also have various degrees of incompatibility. It is well known that nearly all polymer blends comprise one polymer domain dispersed in the matrices of the other polymer. One of the most direct ways of examining the morphology (i.e., how the phases are arranged in space) of blends is by microscopy.

Waterborne polyurethane-ureas (WBPUs) are nontoxic and nonflammable and do not pollute air. In addition, they exhibit excellent adhesion to many surfaces including glass, rubber, and polymeric fiber.[1–4] Most WBPUs contain ionic groups in their molecular structure, and show excellent mechanical properties because of the presence of interchain Coulombic forces and hydrogen bondings.[5] The ionic groups lead to self-emulsification of WBPU in aqueous media. WBPUs have been widely used in the textile industry for breathable coating, sueding, antistatic, and nonformaldehyde applications.[6–10] For resin-coated fabrics,[11–12] softness, handle, permeability, and mechanical properties are required. In the applications of breathable coating fabrics, the water vapor permeability (WVP) was the most important factor.

There are several methods by which breathable waterproof fabric such as microporous fabric, hydrophilic fabric, and the fabric based on microfilaments can be prepared.[13] Waterproof breathable fabrics that are used to construct sportswear and foul weather garments were grouped together according to their manufacturing methods irrespective of their brand names: cotton ventiles, microfibre fabrics, PTFE laminated fabrics, poromeric polyurethane laminated fabrics, and hydrophilic laminated fabrics.

There are a lot of researches about how to use polyurethanes in making breathable products, such as porous polyurethane film[14–16] and hydrophilic nonporous polyurethane products.[11,17–19] The advantage of hydrophilic polyurethane coatings over laminating method of microporous polyurethane film is that the former has good adhesion on textile substrate and it is less expensive. However, it is almost impossible to make the high water vapor permeable fabric by direct coating of hydrophobic polyurethane. Incorporation process of microporous structure into the coated layer on the fabric is subsequently needed after coating process to improve the higher WVP of fabrics. Systematic studies on this method are rarely available in the open literature.

The main objective of this investigation was markedly to improve the WVP of direct coated fabric by the formation of micropore structure in the coated Nylon fabrics. To this end, in this study, WBPU/SA were used as coating materials for fabrics, and then water soluble polymer SA were removed by dissolution of SA in water. WBPU was synthesized by prepolymer mixing process using isophorone diisocyanate (IPDI)/2,2-bis (hydroxymethyl) propionic acid

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(DMPA)/poly(tetramethylene ether) glycol (PTMG)/ ethylenediamine (EDA)/triethylamine (TEA) in an emulsion system. Coating materials were prepared by solution blending WBPU dispersion with aqueous SA solution. The effect of SA content on the viscosity of coating materials was investigated. The effects of SA content and dissolution conditions on the dissolution percentage and number/mean size of micropores of coating material films were examined using scanning electron microscopy (SEM). The thermal degradation/dynamic mechanical thermal properties of coating material film samples were also investigated. The changes of WVP of coated Nylon fabrics according to the changes of SA content and dissolution condition were studied.

EXPERIMENTAL

Materials

Poly(tetramethylene oxide) glycol [PTMG, number-average molecular weight (M_n) = 2000, Aldrich Chemical, Milwaukee, WI] was degassed at 70°C under vacuum overnight before use. IPDI (Aldrich Chemical), methyl ethyl ketone (MEK, Aldrich Chemical), ethylene diamine (EDA, Aldrich Chemical), TEA (Aldrich Chemical), and N-methyl-2-pyrrolidone (NMP, Aldrich Chemical) were used after dehydration with 4 Å molecular sieves for one day. DMPA (Aldrich Chemical) were dried at 100°C under vacuum (1–2 mmHg) for 5 h before being used. Dibutyl tin diaurate (Aldrich Chemical) and hardener (ARF-30, main component: polyisocyanate, solid content: >99, NCO percentage: 20, Dongsung, Busan, Korea) were used without further purification. Sodium alginate (SA, Aldrich Chemical) was dried at 100°C under vacuum for 3 h before use.

Synthesis of waterborne polyurethane

The WBPU was synthesized using the prepolymer mixing process.[5] The PTMG was placed in a four-neck round-bottom flask equipped with a thermometer, a stirrer, an inlet of dry nitrogen, a condenser, and a heat jacket, and degassed under vacuum at 90°C for 30 min. Then DMPA/NMP (1/1 wt ratio) was added to the flask, and the mixture was allowed to cool until 40°C under moderate stirring. IPDI/MEK (2.15/1 wt ratio) was added to the flask, and heated to 85°C under moderate stirring (175–200 rpm). The reaction mixture was allowed to react at 85°C until the theoretical NCO content was reached. The change of NCO content during reaction was determined by the standard dibuthylamine back-titration method (ASTM D1638). Then, MEK (about 20 wt %) was added to the NCO-terminated prepolymer mixture to adjust the viscosity of reaction mixture. TEA was added to the reaction mixture for neutralizing the carboxyl group of the NCO-terminated polyurethane prepolymer. After 30 min of neutralization reaction, distilled water (60 wt % per solid) was added to the reaction mixture under vigorous stirring (1300–1500 rpm). The neutralized prepolymer was chain-extended by dropping EDA at 40°C for 1 h and the reaction continued until NCO peak (2270 cm^{-1}) in the IR spectrum had completely disappeared. All the aqueous dispersions (40 wt % solid content) were obtained by evaporating MEK and the subsequent addition of an adequate amount of water.

Preparations of WBPU/SA blends

The WBPU/SA blends were prepared by solution blending using WBPU and aqueous SA solution. The various WBPU/SA blends prepared in this way are identified in Table I.

Viscosity

The viscosity of WBPU/SA blends was measured with Brookfield viscometer (model LVTDV-II+) over the temperature range of 25–75°C and 10–100 rpm.

Preparation of WBPU/SA films

WBPU/SA films were prepared by pouring the WBPU/SA blends solutions into a Teflon disk at ambient conditions. The films (typically about 0.12 mm thickness) were dried in vacuum at 50°C for 2 days and stored in a desiccator at room temperature.

TABLE I
Composition, Particle Size, Solid Content, and Pure WBPU and WBPU/SA Blends Dispersions

Sample designation	Composition						Particle size (μm)	Solidcontent (wt %)
	H$_{12}$MDI	PTMG (M$_n$ = 2000)	DMPA	EDA	TEA	WBPU/PVA		
WBPU	2.5	1	0.7	1	0.7		0.25	40
WBPU/SA[a]-5	2.5	1	0.7	1	0.7	95/5	–	40
WBPU/SA-15	2.5	1	0.7	1	0.7	85/15	–	40
WBPU/SA-30	2.5	1	0.7	1	0.7	70/30	–	40

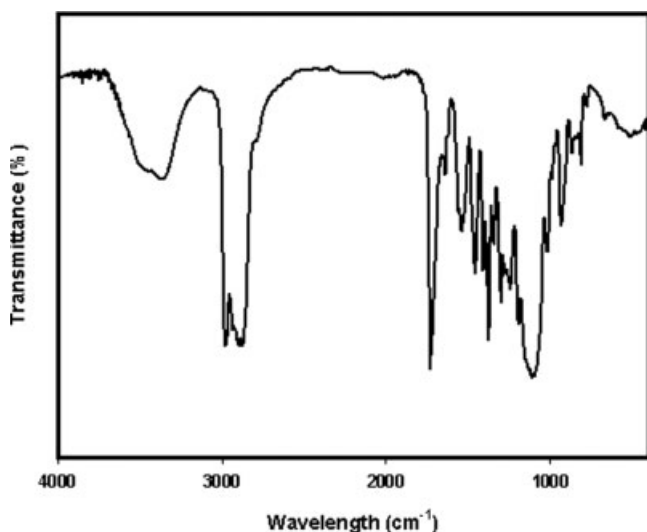[a] Concentration of SA in aqueous SA solution used: 7 wt %.

Figure 1 FTIR spectrum of pure WBPU film.

Coating to Nylon fabrics

The coating materials were formulated from WBPU/SA/hardener (Desmodur, DA). The WBPU/SA blend containing high SA content (30 wt %) had a high viscosity (>3000 cps). So, they were directly used as coating materials. The hardner contents were 0, 3, 5, and 7 wt %. The formulated coating materials were coated onto Nylon fabrics using steel bar and filler, and then dried at 100°C for 5 min. The thicknesses of coated layer on Nylon fabrics were about 0.127, 0.248, or 0.487 mm.

Dissolution condition of water-soluble polymer SA

Dissolution temperature and time were 25–90°C and 1–5 h, respectively. Higher dissolution temperature and time was more effective in dissolving SA. Therefore, the water soluble polymer SA in WBPU/SA blend films and coated Nylon fabrics were dissolved in water using shaking water bath at 90°C for 4 h. After dissolving SA, the remained films and coated Nylon fabrics were dried at 80°C for 1 day.

Characterization

The dissolution percentage was determined as follows: Dissolution percentage = [weight of dissolved SA (dried weight of undissolved sample − dried weight of dissolved sample)/SA weight determined from the blend ratio of WBPU/SA blend coating material] × 100.

Infrared spectra of pure WBPU was measured using a FTIR spectrometer (Impact 400D, Nicolet, Madison, WI) in the wave number of 400–4000 cm^{-1} at room temperature. For each IR spectrometer sam-

ple, 32 scans at a 4 cm^{-1} resolution were collected in the transmittance mode.

The viscosity of WBPU/SA blends was measured in the temperature of 25–75°C using a Brookfield viscometer (Model LVDV II+, spindle No. 6).

Thermal gravimetric analysis (TGA) of about 5 mg of blend WBPU/SA films were made with Perkin Elimer LTD (TGA7, USA) under nitrogen atmosphere at the heating rate of 5°C/min from room temperature to 600°C.
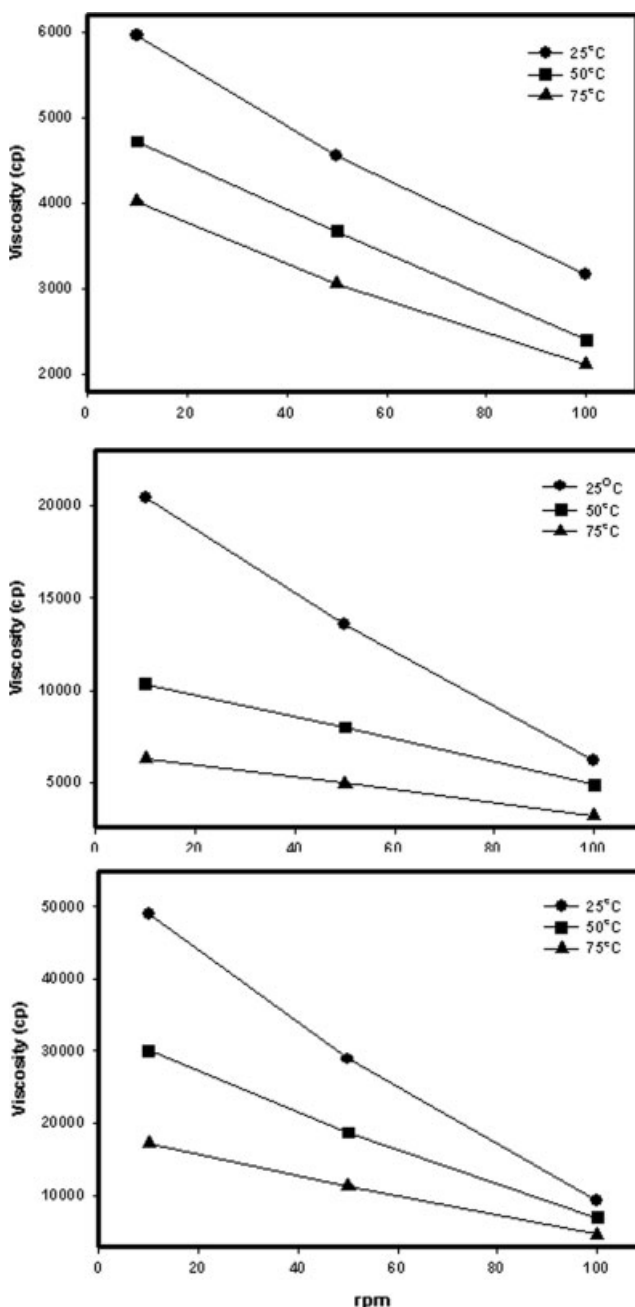

Figure 2 Viscosity versus rpm for (a) WBPU/SA-5, (b) WBPU/SA-15, and (c) WBPU/SA-30 at various temperatures (25°C, 50°C, 75°C).
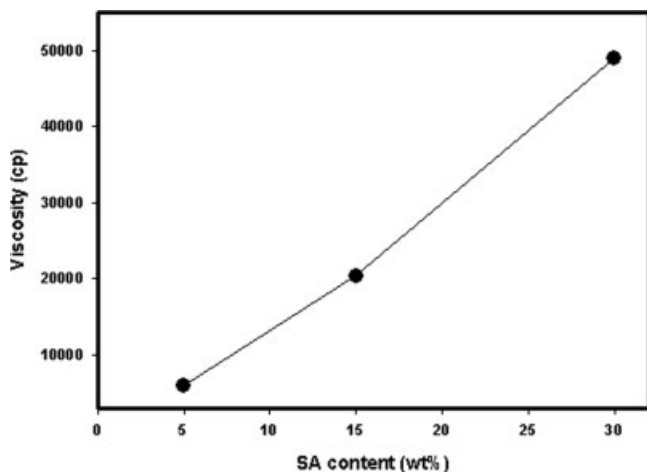
Figure 3 Relationship between viscosity and SA content at 25°C and 10 rpm.

The thermal dynamic mechanical behaviors of WBPU/SA were measured at 4 Hz using DMTA (DMA Q800 V7.1 Build 116) with the heating rate 3°C/min. The dimension of specimens was $5 \times 5 \times 0.2$ (mm^3) for DMTA measurement.

Stress–strain curves for dumbbell shaped WBPU/SA blends were obtained with mechanical tensile tester (Tinius Olsen 1000, USA) at the speed of 20 mm/min according to ASTM D-412.

Morphology of thin films of coating material was studied by SEM (Hitachi S-4200). The samples were coated in conventional manner with a thin layer of gold palladium to prevent changing.

The WVP was determined using an evaporation method described in ASTM E9663-T. The mouth of the test dish is covered with test specimen, and the edges are sealed with sealing material. The whole assembly is weighed and placed in an air-circulated, temperature-controlled, and humidity-controlled chamber. The condition of the chamber is temperature of (40 ± 2)°C, (50 ± 5)% of relative humidity, and 0.8 m/s of air movement. WVP percentage was determined as follows: WVP% = (WVP of coated Nylon fabric/WVP of Nylon fabric) × 100.

RESULTS AND DISCUSSION

Particle size and identification of WBPU

The composition, particle size, and solid content of pure WBPU dispersion prepared in this study are shown in Table I. Generally, it is known that the average particle size of WBPU is not directly related to the physical properties of the emulsion cast films.[20] However, control of particle size is important with regard to the particular application of WBPU. For example, relatively bigger particles are preferred in surface coating for rapid drying, and smaller ones are desira-

ble when the deep penetration of dispersion into a substrate is an essential step. In general, it is desirable to have a particle size at least smaller than 10 μm for textile coatings. The average particle size and solid content of WBPU dispersion prepared in this study were found to be about 0.25 μm and 40 wt %, respectively. Figure 1 shows the FTIR spectrum of pure
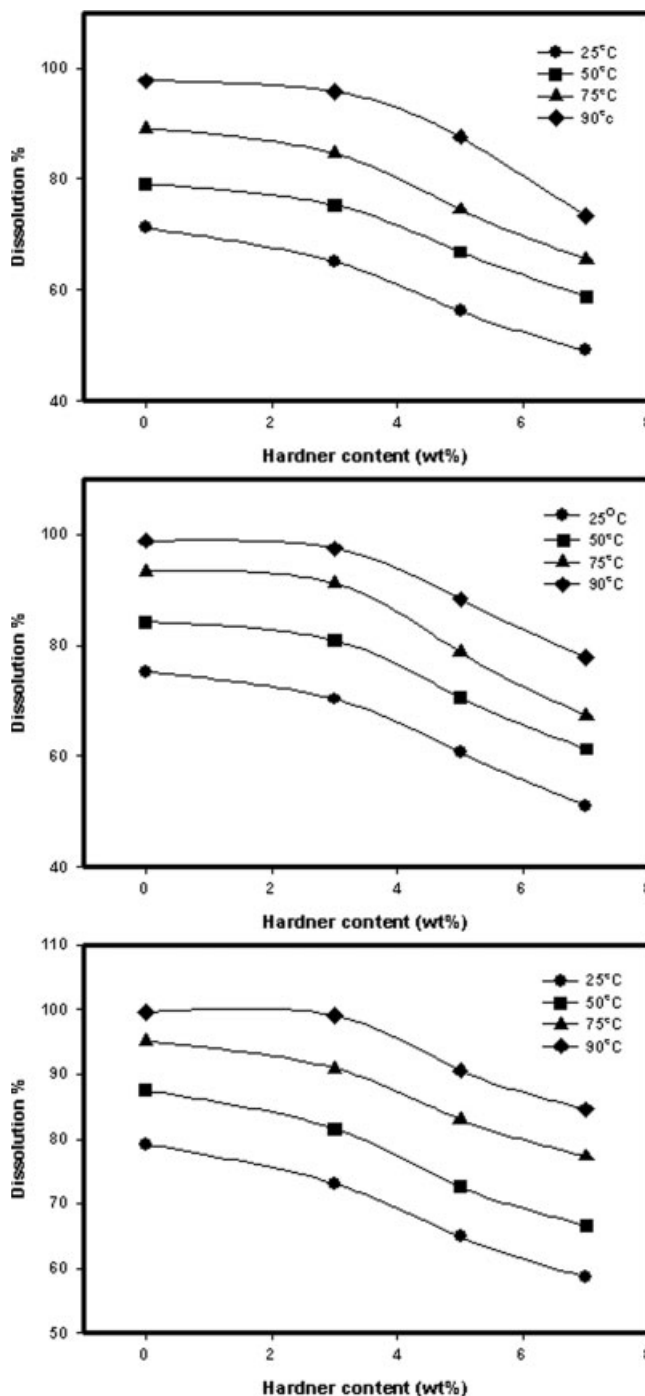

Figure 4 Dissolution percentage versus hardner content for (a) WBPU/SA-5, (b) WBPU/SA-15, and (c) WBPU/SA-30 with various dissolution temperatures (at a fixed dissolution time : 4 h).
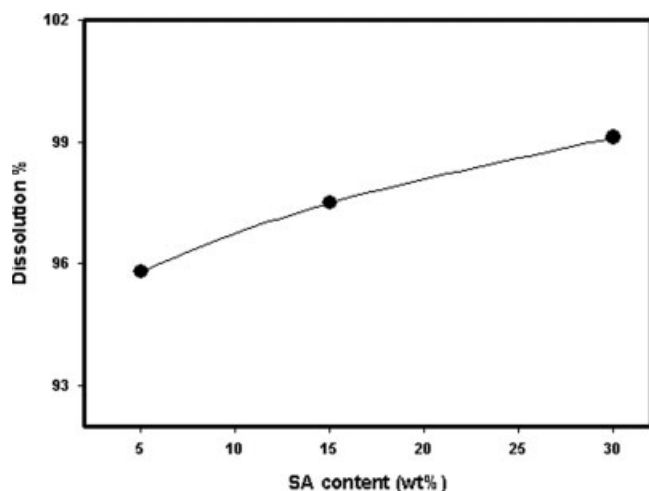
Figure 5 The effect of SA content on the dissolution percentage of WBPU/SA blend films.

WBPU film prepared here. The WBPU was identified by the characteristic IR peaks, such as N—H stretching vibration peak near 3340 cm^{-1}, —CH_2— stretching band at 1460 and 770 cm^{-1}, C—N—H stretching band at 1540 cm^{-1}, and the C=O group near 1730 cm^{-1}.

Viscosity

The aqueous dispersion of WBPU/SA blends prepared in this study is a colloidal system in which larger amount of PU particles are dispersed in a continuous water soluble polymer (SA) matrix. Figure 2 shows the viscosity changes with revolutions per minute (rpm) of aqueous WBPU/SA blends dispersions having various SA contents at various temperatures. It was found that the viscosity was very sensitive to rpm and temperature. The viscosity decreased with increasing rpm of spindle, indicating that the rheological property of aqueous WBPU/SA dispersion showed non-Newtonian behavior. Figure 3 shows the effect of SA content on the viscosity at 25°C and 10 rpm. The viscosity of pure WBPU without SA is given 9.4 cps at 25°C. The viscosity of WBPU/SA increased from 5900 to 49,000 cps with increasing SA content from 5 to 30 wt %. It was found that high viscosity (above 3000 cps) is required for use in fabric coating, since the low viscosity coating material penetrated into the fabrics and leaked out to the backside of coated fabrics. From these results, it was found that all WBPU/SA samples could be used as a coating material without thickener.
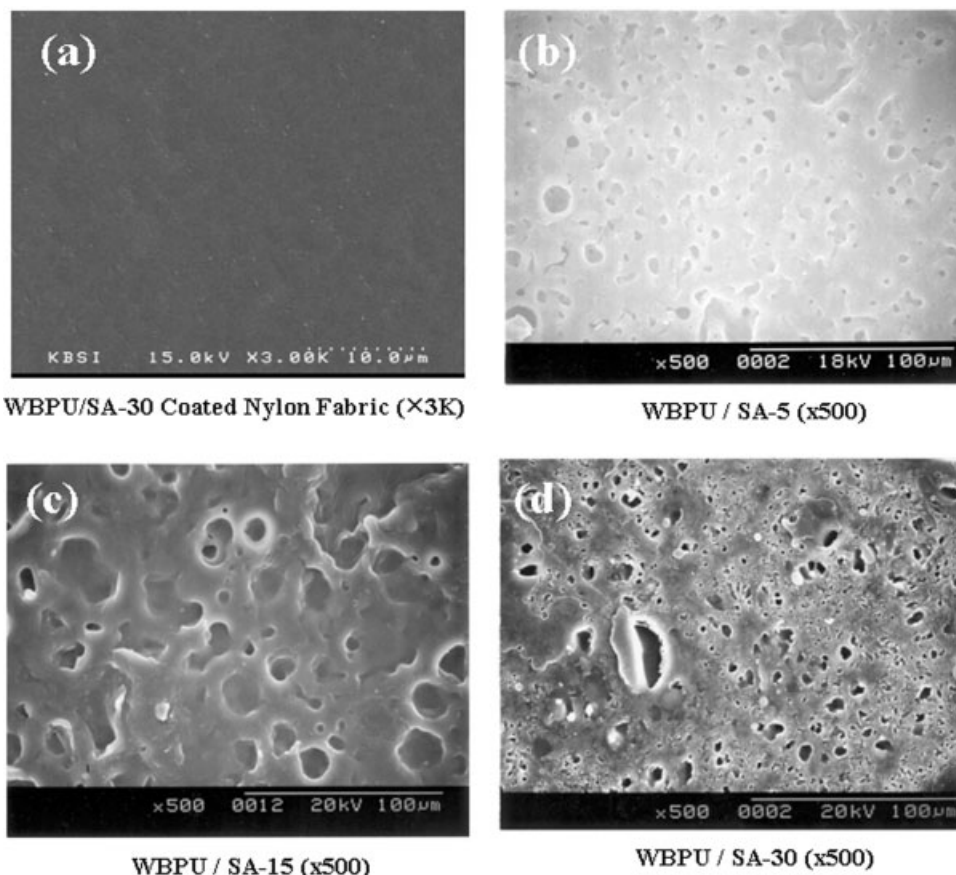

Figure 6 SEM micrographs of (a) WBPU/PVA-30 coated Nylon fabric surface before dissolution of SA, (b) WBPU/SA-5, (c) WBPU/SA-15, and (d) WBPU/SA-30 blends coated Nylon fabric surface after dissolution of SA in water.
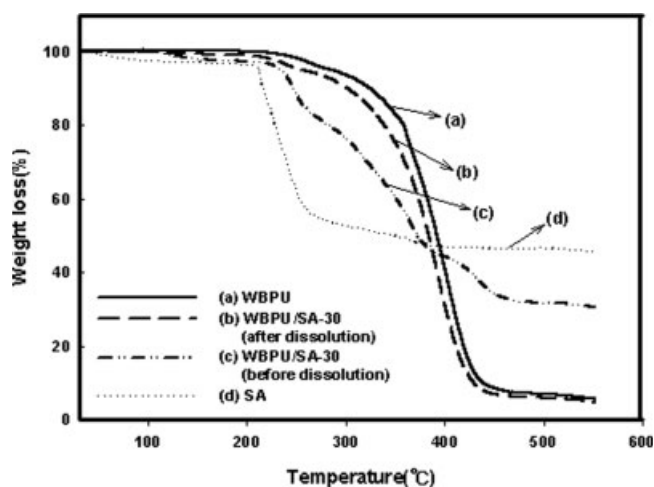
Figure 7 TGA curves of pure WBPU film, WBPU/SA-30 film before dissolution, WBPU/SA-30 film after dissolution, and SA film.

Dissolution percentage

WBPUs are deficient in chemical resistance, thermal resistance, and mechanical property because the WBPUs are linear thermoplastic polymers containing little gel that allows resolubility in solvents. Therefore, crosslinking is used in many industrial coatings and adhesive applications to improve solvent and chemical resistance, hardness, and mechanical properties of WBPUs. Hardner ARF-30 (polyisocyanate crosslinking agent) was used to improve properties. Figure 4 shows the relation between dissolution percentage and hardner content for WBPU/SA blends films with various dissolution temperatures at 4 h of dissolution time. The dissolution percentage increased with increasing dissolution temperature. The dissolution percentage decreased a little with increasing hardner content up to 3 wt %, and then decreased sharply. The hardner content that optimizes the dissolution of SA was found to be about 3 wt %. Figure 5 shows the effect of SA content on the dissolution percentage of WBPU/SA blend films. The dissolution percentage in the range of 96–99% increased with increasing SA content. This indicates that the higher portion of SA domain in WBPU matrix makes dissolution easier.

Morphology

Generally, it is possible to give new functions to polymer blends by controlling the morphology of blend. Polymer blends vary greatly in morphological complexity. The morphology of polymer blend films can be controlled by many factors, such as the blending sequence, chemical characteristics, viscosity, blending conditions, and interfacial tension of each component. Two type of morphology can be achieved; the first is an encapsulation type, in which the domain polymer

particles are surrounded by matrix polymer, and the second is an interpenetrating type. The WBPU/SA blend dispersion prepared in this study showed possibly two-phase system consisting of major component WBPU polymer particles dispersed in a continuous aqueous phase containing smaller amount component SA. The SEM micrographs of surfaces of WPBU/SA blends films before and after dissolution of SA in water at 90°C for 4 h are shown in Figure 6. The undissolved WBPU/SA-30 coated layer had a fairly smooth surface, as shown in Figure 6(a). However, it appeared that water attacked the entire sur-
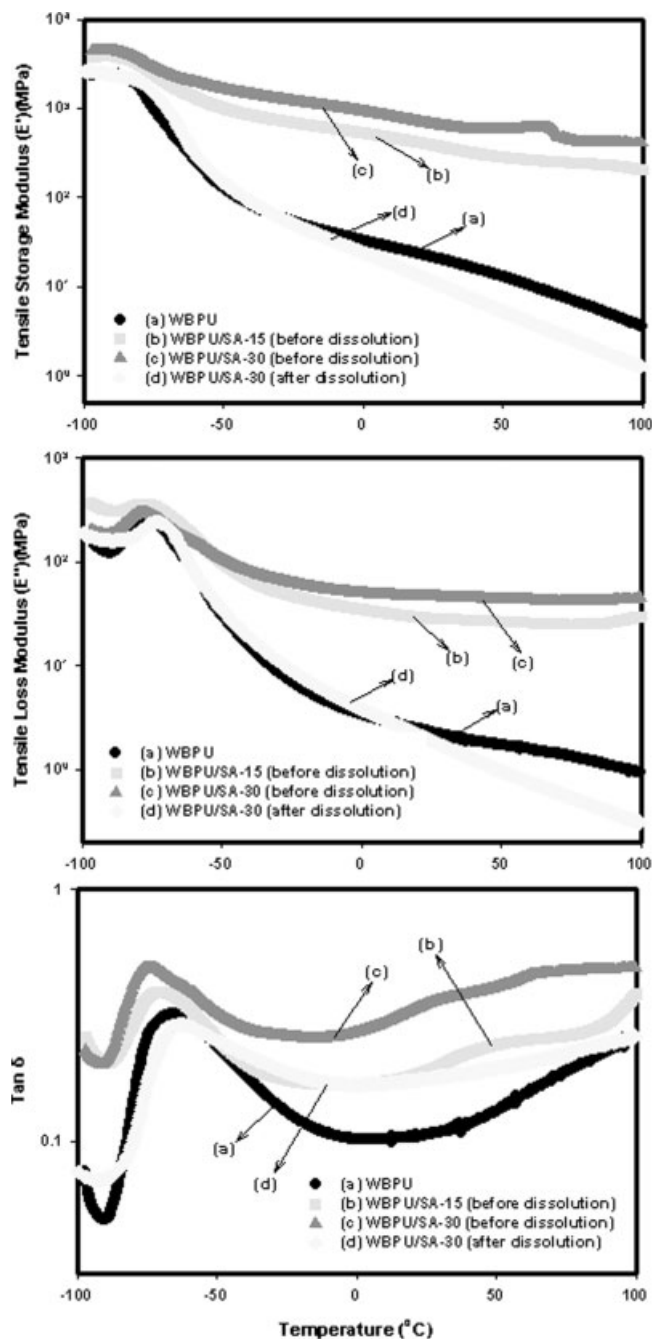

Figure 8 Dynamic storage modulus (E′), loss modulus (E″), and tan δ for WBPU/SA blend films.

| Sample designation | T_g (°C) by DMTA | | Sample designation | Before dissolution | | After dissolution | |
	T_{gs}	T_{gh}		Tensile strength (Mpa)	Elongation at break (%)	Tensile strength (Mpa)	Elongation at break (%)
WBPU	−65	57	WBPU	8.3	1468	8.0	1460
WBPU/SA-15	−70	58	WBPU/SA-5	6.1	1278	6.1	1145
WBPU/SA-30	−71	62	WBPU/SA-15	4.4	847	5.4	852
WBPU/SA-30[a]	−63	56	WBPU/SA-30	4.3	650	4.1	640

[a] After dissolution.

face of dissolved samples and resulted in its porous/tunnel-like structure on the coated fabrics samples surfaces [see Fig. 6(b–d)]. As SA content increased, the density (number/m^2) of micropores formed after removal of SA in WBPU/SA films increased; however, the size of the pore decreased. The decrease of pore size was possibly attributed to the collapse of matrix WBPU polymer. The size and density of micropores were in the range of 0.64–6.45 μm and 3.10×10^8–6.00×10^8 number/m^2, respectively. The morphology of surface was almost the same as those

of cross-sectional structures. Therefore, the cross-sectional SEM pictures were not here. These porous/tunnel-like structures should promote the WVP. The ratio of tunnel-like micropores to isolated micropores increased with increasing SA content. The WBPU/SA-30 blend sample showed larger amount of tunnel-like structure (open cell structure) resulted from higher amount of dissolved SA (30 wt %).

TGA behavior

TGA curves of pure WBPU, pure SA, and WBPU/SA-30 blend films samples before and after dissolution of SA are shown in Figure 7. The temperatures at 10 wt % weight loss of pure WBPU, WBPU/SA-30 blend samples before and after dissolution of SA, and pure SA are 303, 246, 295, and 215°C, respectively. The temperature at 10 wt % weight loss decreased with increasing SA content. This should be due to the higher thermal degradable behavior of SA. The degradation onset temperature of pure WBPU and dissolved WBPU/SA-30 (dissolution percentage: 99) was almost same, and the temperatures at 10 wt % weight loss of these samples did not present a marked con-
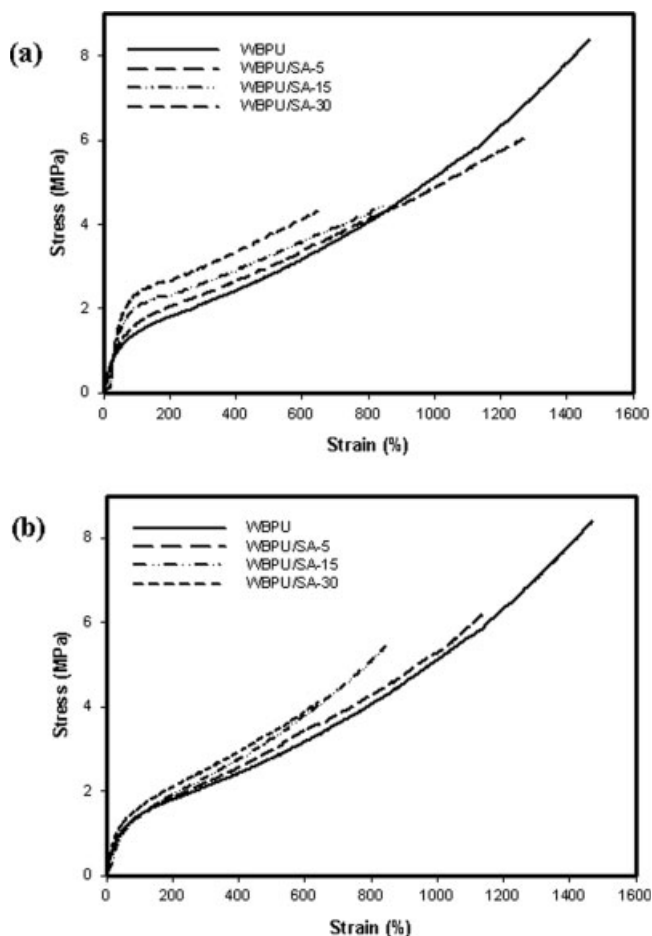

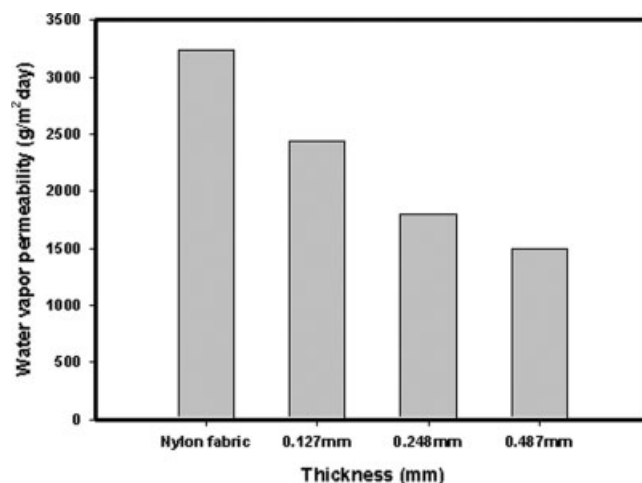**Figure 9** Stress–strain curves for WBPU/SA blends films (a) before dissolution and (b) after dissolution.

Figure 10 Effects of coating layer thickness on the water vapor permeability of WBPU/SA-15 blend coated Nylon fabrics.
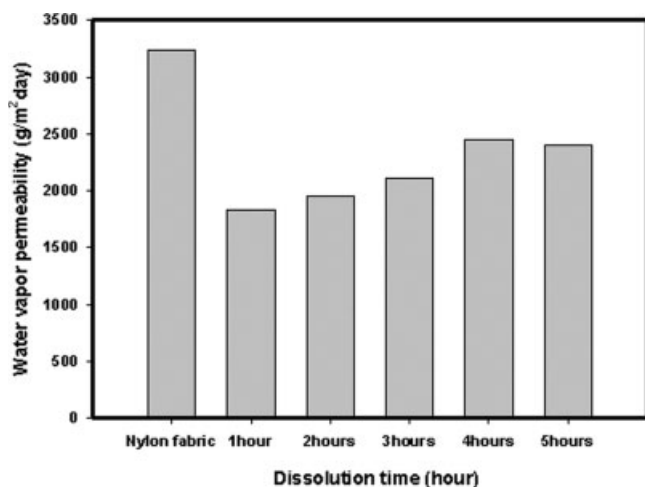
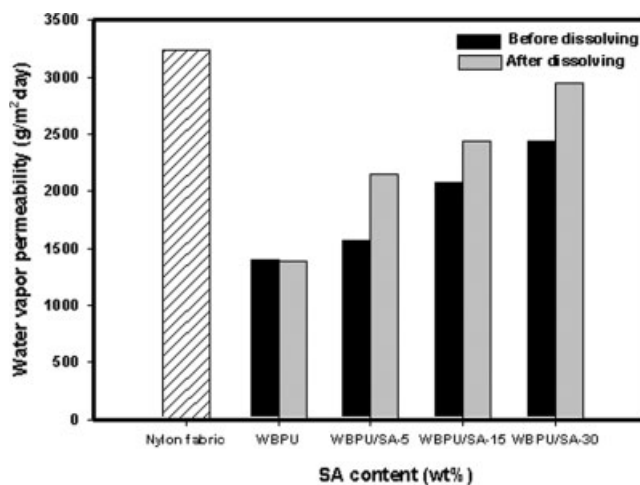**Figure 11** Effects of dissolution time on the water vapor permeability of WBPU/SA-15 blend coated Nylon fabric.

Figure 12 Water vapor permeability before and after dissolution for pure Nylon fabric, WBPU/SA blends coated Nylon fabrics.

TABLE III
Water Vapor Permeability (WVP), WVP %, and Water Resistance of WBPU/SA Blends Coated Nylon Fabrics

Sample designation	Water vapor permeability (g/m²/day)		WVP %		Water Resistance (mmH$_2$O)	
	Before dissolution	After dissolution	Before dissolution	After dissolution	Before dissolution	After dissolution
WBPU	1395	1395	44	44	10000	10000
WBPU/SA-5	1674	2146	52	66	160000	12000
WBPU/SA-15	2082	2445	64	76	80000	15000
WBPU/SA-30	2444	2942	76	91	56000	5000<

$$\text{WVP \%} = \frac{\text{WVP of coated Nylon fabric}}{\text{WVP of Nylon fabric}} \times 100$$

WVP of original Nylon fabric : 3234 g/m²/day

trast. This indicated that the qualitative analysis of dissolution was possible by TGA characterization.

DMTA behavior

Figure 8 shows the temperature dependence of the tensile storage modulus (E′), loss modulus (E″) and tan δ of pure WBPU, WBPU/SA-15, and WBPU/SA-30 and dissolved WBPU/SA-30 films, respectively. The DMTA results were summarized in Table II. The E′ of WBPU/SA blends films increased with increasing SA content significantly. This was probably due to the higher stiffening effect of the rigid polymer SA. Two loss modulus peaks were observed because of two glass-transition temperatures of the amorphous soft segments (T_{gs}) at a lower temperature and the amorphous hard segments (T_{gh}) at a higher temperature. However, the T_{gh} peak (near 57°C) of pure WBPU in E″ and tan δ curves was very weak. The distinct T_{gs} peak was attributed to the higher content of soft segments (70 wt %) of WBPU prepared in this study. With increasing SA content from 0 to 30 wt %,

the T_{gs} shifted a little from −63 to −71°C, but the T_{gh} increased slightly from 56 to 62°C. The increase of T_{gh} peak intensity was significant indicating that SA molecule interacted with amorphous hard segment. However, the peak intensity of T_{gs} was apparently not changed. The slight changes of peak intensity and T_g should be attributed to the lower compatibility of WBPU and SA. The peaks of tensile storage modulus (E′), loss modulus (E″) and tan δ of pure WBPU film were almost the same as those of dissolved WBPU/SA-30 (dissolution percentage: 99) film. This also indicated that the qualitative analysis of dissolution was possible by DMTA characterization.

Tensile properties

The stress–strain curves of the WBPU/SA films samples and their extracted films samples are shown in Figure 9 and their tensile properties are summarized in Table II. The tensile strength and elongation at break of pure WBPU film were 8.3 MPa and 1468%, respectively. As the SA content increased, the tensile

strength and the elongation at break decreased but the initial modulus increased. The tensile strength of dissolved film samples decreased a little compared with undissolved samples. However, the elongation at break of dissolved samples increased significantly. The initial modulus of dissolved samples came close to the modulus of pure WBPU. The changes of tensile properties might be attributed to the incorporation of SA and the structure change of after dissolution.

Water vapor permeability

Figure 10 showed that the relationship between WVP and coating layer thickness for the typical WBPU/SA-15 sample. The WVP of pure Nylon fabric were 3234 $g/m^2/day$. The WVP of WBPU/SA-15 coated Nylon sample decreased from 2942 to 1980 $g/m^2/day$ with increasing the thickness of coated layer from 0.127 to 0.487 mm. The effect of dissolution time on the WVP is shown in Figure 11. The WVP increased significantly with increasing dissolution time up to 4 h, and then decreased a little. From these results, the thickness layer, dissolution time, and dissolution temperature were fixed at 0.127, 4 h, and 90°C, respectively, which were regarded optimum for obtaining higher water permeability in Nylon fabrics coated with various WBPU/SA coating materials.

The WVP of pure Nylon fabric, pure WBPU coated Nylon fabric, and WBPU/SA (5–30 wt %) coated Nylon fabrics before and after dissolution of SA in water are shown in Figure 12 and Table III. The WVP of coated Nylon fabric was found to increase with increasing SA content. This might be due to the increase of hydrophilic component SA. The WVP of coated Nylon fabrics before and after dissolution were in the range of 1674–2444 and 2146–2942 $g/m^2/$ day, respectively. The WVP of coated Nylon fabrics after removal of SA was higher values than those of undissolved samples. WVP percentage [(WVP of coated Nylon fabrics/WVP of pure Nylon fabrics) × 100] also increased significantly with increasing SA content. WVP percentage for the WBPU/SA-coated Nylon fabrics before and after dissolution of SA in water were in the range of 52–76 and 66–91%, respectively. The higher WVP and WVP percentage of dissolved samples compared with undissolved samples should be attributed to the formed micropores in coated layer after dissolution of SA in water. The water resistances of dissolved and undissolved fabric samples are shown in Table III. Water resistance of WBPU coated Nylon fabric was about 10,000 mmH_2O. Water resistance of WBPU/SA coated Nylon fabrics before removal of SA were in the range of 56,000–160,000 mmH_2O; however, those of coated Nylon fabrics after removal of SA were in the range of above 5000–12,000 mmH_2O, indicating that these coating fabrics had good waterproof behavior. These results suggest that using WBPU/water soluble polymer SA blends as coating materials and then dissolving SA in water is an effective method to obtain prominent breathable fabrics.

CONCLUSIONS

High water vapor permeable coating materials were prepared by blending aqueous SA solution with WBPU synthesized by prepolymer mixing process using IPDI/DMPA/PTMG/EDA/TEA in an emulsion system. The coating materials were coated to Nylon fabrics. It was found that the content of SA for stable emulsions was about 30 wt %. The viscosity of WBPU/water soluble polymer aqueous dispersions (emulsion) was remarkably increased with increasing SA content. Therefore, WBPU/SA could be used as coating materials without thickner. The tensile strength of film sample after removal of SA decreased slightly with increasing SA content. The number and size of micropore formed on film sample increased with increasing SA content. The WVP of coated Nylon fabrics was found to increase notably with increasing SA content. WVP percentage also increased significantly with increasing SA content. The WVP percentage of WBPU/SA-coated Nylon fabrics before and after dissolution of SA in water were in the range of 52–76 and 66–91%, respectively. It was found that utilizing WBPU/water soluble polymer SA blends as coating materials and then dissolving SA in water surely facilitate obtaining prominent breathable fabrics.

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