

Preparation and Properties of Waterborne Polyurethane/Polyaniline Codoped with Dodecyl Benzene Sulfonic Acid and Hydrochloric Acid Blends

Ji-Yun Kwon,¹ Young-Seok Koo,² Han-Do Kim¹

¹Department of Textile Engineering, Pusan National University, Busan, 609-735 Korea

²Department of Clothing and Textiles, Pusan National University, Busan, 609-735 Korea

Received 29 September 2003; accepted 18 December 2003

DOI 10.1002/app.20437

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A conductive poly(aniline codoped with dodecyl benzene sulfonic acid and hydrochloric acid) [PANI-D/H, yield: 32.2%, intrinsic viscosity ($[\eta]$): 1.39 dL/g, electrical conductivity: 7.3 S/cm] was synthesized by chemical oxidative polymerization from aniline-dodecylbenzene sulfonic acid salt (A-DS)/aniline-hydrochloric acid salt (A-HS) (6/4M ratio) in an aqueous system. Waterborne polyurethane (WBPU) dispersion obtained from isophorone diisocyanate/poly(tetramethylene oxide)glycol/dimethylol propionic acid/ethylene diamine/triethylene amine/water was used as a matrix polymer. The blend films of WBPU/PANI-D/H with various weight ratios (99.9/0.1–25/75) were prepared by solution blending/casting. Effect of PANI-D/H content on the mechanical property, dynamic mechanical property, hardness, electrical conductivity, and antistaticity of WBPU/PANI-D/H blend films was investigated. The dynamic storage modulus and initial tensile modulus increased with increasing PANI-D/H content up to 1 wt %, and then it was significantly decreased about the content. With increasing PANI-D/H content, the glass transition temperature of soft segment (T_{gs}) and hard segment (T_{gh}) of

WBPU/PANI-D/H blend films were shifted a bit to lower the temperature. The tensile strength and hardness of WBPU/PANI-D/H blend films increased a little with increasing PANI-D/H content up to 0.5 wt %, and then it was dramatically decreased over the content. The elongation at break of WBPU/PANI-D/H decreased with an increase in PANI-D/H content. From these results, it was concluded that 0.5–1 wt % of PANI-D/H was the critical concentration to reinforce those various properties of WBPU/PANI-D/H blend films prepared in this study. The electrical conductivity of WBPU/ultrasonic treated PANI-D/H (particle size: 0.7 μm) blend films prepared here increased from 4.0×10^{-7} to 0.33 S/cm with increasing PANI-D/H content from 0.1 to 75 wt %. The antistatic half-life time ($\tau_{1/2}$) of pure WBPU film was about 110 s. However, those of WBPU/ultrasonic treated PANI-D/H blend films ($\tau_{1/2}$: 8.2–0.1 s, and almost 0 s) were found to decrease exponentially with increasing PANI-D/H content (0.1–9 wt %, and above 9 wt %). © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 700–710, 2004

Key words: conducting polymers; polyurethanes; blends

INTRODUCTION

Electrical conductive polymers have generated a tremendous interest because of their potential application in batteries,¹ electrochromic devices,² sensors,³ electromagnetic interference (EMI) shielding screens,^{4,5} and substitutes for metallic conductors or semiconductor in the various range of electrical devices.⁵ Some applications of PANI having electrical conductivity between 10^{-10} and 10^{-2} S/cm are hole-injection layers for flexible light-emitting diodes,⁶ antistatic materials,⁷ corrosion protection,⁸ and ion sensors.⁹

Polyaniline (PANI) is under extensive study even today because of its high environmental stability, low cost, and relatively simple polymerization process.^{10–12} Despite various advantages, PANI has received a limited application until several years ago,

because PANI is not soluble or fusible in organic solvents and water.¹³ The development of PANI with better solubility in common solvents was first achieved by Cao et al.^{14–16} through a counterion-induced processibility method, where a specific functionalized protonic acid was used as a protonation agent. It was reported that the protonic acids such as dodecyl sulfuric acid (DSA),² dodecyl benzene sulfonic acid (DBSA),³ sodium dodecyl sulfonate (SDS),¹¹ and sulfosalicylic acid (SSA)¹⁷ rendered polyaniline soluble in organic solvents in its doped state. Among those systems that have been reviewed, an important example of these protonic acids is DBSA, whose long alkyl chain increases the solubility of PANI-DBSA conducting salt in various solvents such as chloroform, *N*-methyl-2-pyrrolidone, toluene, xylene, etc. and acts as a surfactant, inducing some compatibility with polymer matrix with similar structure.¹⁴ A PANI with improved processibility was synthesized via emulsion polymerization in an aqueous solution of DBSA–aniline salt.^{1,3,11,18,19}

Correspondence to: H.-D. Kim (kimhd@pusan.ac.kr).

A chemical oxidative polymerization of aniline–DBSA/aniline–hydrochloric acid was performed in an aqueous solution because the former monomer stimulates the solubility and the latter contributes to the conductive structure of the synthesized polymer. This approach significantly improved the conductivity and processibility of PANI.¹¹

Various polymers such as polycarbonate,²⁰ polyurethane,²¹ styrene–butadiene–styrene (SBS),²² polystyrene (PS),¹² and poly(vinyl alcohol) (PVA)²³ were used as matrix polymers for polymer blends containing conductive polymer PANI. Jeevananda's group²⁰ prepared PANI/PC blends with electrical conductivity 5.7×10^{-5} – 4.7×10^{-2} S/cm. On the other hand, Ho et al.²¹ prepared PANI/PU blends, which showed electrical conductivity from 0.57 to 23.5 S/cm and tensile strength of 2.11–5.55 mPa. The PANI/SBS blends with electrical conductivity of 10^{-2} – 10^0 S/cm were prepared by Leyva et al.²² Roichman et al.¹² reported that the electrical conductivity of PANI/PS blends were in the range of 10^{-15} – 10^0 S/cm. Rupali's group²³ prepared PANI/PVA composite with electrical conductivity of 10^{-5} – 10^0 S/cm.

Waterborne polyurethanes (WBPU) are nontoxic and nonflammable and do not pollute air. In addition, water dispersions (emulsions) of WBPU permit the application of polyurethane from an aqueous medium. WBPU have been used for a wide range of commercial applications such as adhesives and coatings for various substrates.^{24–26} However, research on WBPU containing conducting polymer can hardly be found.

Based on the earlier investigation of the preparation and properties of WBPU/conductive polyaniline–DBSA complex composites,²⁷ we prepared poly(aniline–dodecyl benzene sulfonic acid complex) (PANI-DC) with electrical conductivity near 0.7 S/cm and WBPU/PANI-DC composite films.

The WBPU was synthesized by the polyaddition reaction by using isophorone diisocyanate, poly(tetramethylene oxide)glycol, dimethylol propionic acid, ethylene diamine, and triethylamine. A series of blend films of WBPU/PANI-D/H (99.9/0.1–25/75 wt %) were prepared by solution blending/casting from aqueous WBPU and PANI-D/H blends. The effects of magnetic stirring or ultrasonic vibration treatments on the mean particle size of pure PANI-D/H and the electrical conductivity of WBPU/PANI-D/H blend films were investigated. The influence of PANI-D/H content on the mechanical property, dynamic mechanical property, hardness, conductivity, and antistaticity was investigated.

EXPERIMENTAL

Materials

Aniline monomer (Aldrich, Milwaukee, WI) was distilled under reduced pressure prior to use. DBSA

(Sigma, Milwaukee, WI), hydrochloric acid (HCl; Aldrich), ammonium peroxodisulfate (APS, Aldrich), dibutyl tin dilaurate (DBTDL, Aldrich), and methanol (Sigma) were used as produced. Isophorone diisocyanate (IPDI; Aldrich), triethylamine (TEA; Sigma), ethylene diamine (EDA, Aldrich), methyl ethyl ketone (MEK, Sigma), and *N*-methyl-2-pyrrolidone (NMP; Aldrich) were used after dehydration with 4 Å molecular sieves for 1 day. Poly(tetramethylene oxide) glycol (PTMG; $M_n = 2000$ g/mol, Aldrich) was dried over calcium hydride at room temperature for 24 h. Dimethylol propionic acid (DMPA, Aldrich) was dried in a vacuum oven for 5 h at 100°C.

Preparation of aqueous PANI-D/H dispersion and its pellet

The preparation procedure of aqueous poly(aniline codoped with dodecyl benzene sulfonic acid and hydrochloric acid) (PANI-D/H) dispersion is as follows: viscose emulsion of aniline/DBSA/HCl/water was prepared by mixing monomer aniline (1.86 g, 0.2 mol) with DBSA (5.22 g, 0.12 mol)/HCl (0.15 g, 0.08 mol) dissolved in deionized water (80 mL) under stirring at room temperature. To prepare the aqueous dispersion of PANI-D/H, oxidizing initiator APS (1.2 g, 0.1 mol) dissolved in the deionized water (20 mL) was slowly added to aniline/DBSA/HCl/water emulsion under stirring at 0°C for 30 min and subsequently stirred for 1.5 h at room temperature. The molar ratio of APS to aniline was 1/2. As APS was dropped into aniline/DBSA/HCl/water emulsion, the white color of the initial emulsion was changed to a bright green color after about 1 h and then changed to a dark green color at room temperature. The dark green color reaction mixture was poured into methanol to precipitate the dark green color PANI-D/H product. The dark green color PANI-D/H was filtered by using a glass filter and washed six times with methanol and water alternately, followed by dispersing in water to prepare aqueous dispersion of PANI-D/H. The aqueous dispersions of PANI-D/H were prepared by the purified PANI-D/H (0.5 g) being dispersed in water (10 mL) under magnetic stirring (600 rpm/30 min/room temperature) or ultrasonic vibration (30 min/room temperature). From our preliminary experiments, the optimum conditions of magnetic stirring and ultrasonic vibration were found to be 600 rpm for 30 min at room temperature and 30 min at room temperature, respectively. The composition of feed reactants for PANI-D/H is shown in Table I. Intrinsic viscosity of PANI-D/H prepared in this study was measured by using a Ubbelohde viscometer at 25°C in *N*-methyl-2-pyrrolidone as solvent. The purified PANI-D/H was dried in a vacuum at about 60°C for 3 days and then weighed for the determination of the yield. The pellet of PANI-D/H (diameter: 10 mm; thickness: 0.1 mm) for testing

TABLE I
Sample Designation, Composition, and Characteristics of Polyaniline Codoped with Dodecyl Benzene Sulfonic Acid and Hydrochloric Acid (PANI-D/H) and Sample Designation and Composition of Waterborne-Polyurethane (WBPU)

Sample designation	Composition (mol)				Yield (%)	Intrinsic viscosity $[\eta]^a$	Elemental analysis data (wt %)					Mean particle size (μm)		Conductivity (S/cm)	
	Aniline monomer	DBSA	HCl	APS			C	H	N	S	Cl	(S + Cl)/N ^b	Mechanical stirring ^c		Ultrasonic treatment ^d
PANI-D/H	0.20	0.12	0.08	0.1	32.2	1.39	65.79	6.54	7.33	5.42	4.67	0.58	1.6	0.7	7.3
Sample designation	Composition (mol)														
	PTMG ($M_n = 2000$)					DMPA					TEA		Solid content (wt %)		
WBPU	2.5					1.0					0.5		30		

^a Intrinsic viscosity ($[\eta]$) of PANI-D/H prepared in this study was determined using Ubbelohde viscometer at 25°C in *N*-methyl-2-pyrrolidone as solvent.

^b (S + Cl)/N ratio was given on molar base.

^c Wet PANI-D/H was treated with magnetic stirring (600 rpm/30 min/room temperature).

^d Wet PANI-D/H was treated with ultrasonic vibration (30 min/room temperature).

was prepared by compressing under the pressure of 0.1 ton at room temperature.

Synthesis of WBPU

WBPU was synthesized by the polyaddition reaction by using isophorone diisocyanate, poly(tetramethylene oxide) glycol, dimethylol propionic acid, ethylene diamine, and triethylamine. Composition and solid content of the WBPU used in this study is given in Table I. The preparation method of the WBPU is described in our previous articles.^{24–26}

Preparation of WBPU/PANI-D/H blends and their films

WBPU/PANI-D/H blends were prepared by mixing the WBPU and aqueous PANI-D/H dispersion with stirring (600 rpm) for 2 h at room temperature. The weight ratios of WBPU/PANI-D/H blends were 99.9/0.1–25/75 (see Table II). Films for testing were prepared by the dispersions being cast onto a Teflon disk under ambient conditions. The blend films were allowed to dry at 50°C for about 1 day, and then the remaining moisture was removed at 60°C under 20 mmHg for 2 days.

Characterization

FT infrared spectrum of PANI-D/H powder was recorded in the range of 500–4000 cm^{-1} by using FTIR spectrometer (Impact 400D, Nicolet, Madison, WI) by the KBr disk method at a resolution of 4 cm^{-1} for 32 scans. Elemental analysis was carried out to determine the elements (C, H, N, S, Cl) of the PANI-D/H powder by using an elemental analyzer (Vario EL III, Germany). The particle size of PANI-D/H was determined by using a particle size analyzer (Galai Production Ltd., Israel) and laser-scattering equipment (Autosizer, Melvern IIC, USA). Shimadzu UV-1601 spectrometer (Japan) was used to obtain UV-Visible absorption spectrum of PANI-D/H. The thermal behavior of conductive polymer PANI-D/H was examined by using a DSC 220C (Seiko, Japan) at a heating rate of 10°C/min under a nitrogen atmosphere. The dynamomechanical behavior of WBPU and WBPU/PANI-D/H composite films was measured at 4 Hz by using DMTA (DMTA MK III, Rheometrics Scientific Inc., USA) with a heating rate of 3°C/min. The dimension of film sample was 5 × 5 × 0.2 mm for DMTA measurement. The mechanical measurements were made in simple extension on dumbbell specimens by using a tensile tester (Tinius Olsen 1000, USA) at a crosshead speed of 20 mm/min according to ASTM D-412. Electrical conductivity of PANI-D/H pellet and WBPU/PANI-D/H blend films were measured by using a surface resistance detector (CMT-SR1000N, CM

TABLE II
Designation, Composition, Conductivity, Mechanical, and Dynamic Mechanical Properties
of WBPU/PANI-D/H Samples

Sample designation	Composition (wt %) WBPU/PANI-D/H ^a	Conductivity (S/cm) ^b		Tensile strength (Mpa)	Initial tensile modulus (Mpa)	Storage modulus (Mpa)	Elongation at break (%)
		A-surface	G-surface				
WBPU/PANI-D/H	100/0	2.5×10^{-12}	2.5×10^{-12}	6.6	102.0	7.09	1280
WBPU/PANI-D/H0.1	99.9/0.1	4.0×10^{-7}	3.8×10^{-7}	6.6	201.0	7.12	1257
WBPU/PANI-D/H0.3	99.7/0.3	5.0×10^{-7}	5.0×10^{-7}	6.6	218.0	—	1250
WBPU/PANI-D/H0.5	99.5/0.5	1.1×10^{-6}	1.0×10^{-6}	6.8	222.0	7.14	1240
WBPU/PANI-D/H0.7	99.3/0.7	2.0×10^{-6}	1.9×10^{-6}	6.5	222.0	—	1235
WBPU/PANI-D/H1	99/1	3.0×10^{-6}	3.0×10^{-6}	6.4	215.0	7.28	1230
WBPU/PANI-D/H5	95/5	2.2×10^{-3}	2.1×10^{-3}	4.8	174.0	—	1154
WBPU/PANI-D/H9	91/9	0.01	0.01	4.4	138.0	7.15	1100
WBPU/PANI-D/H23	77/23	0.11	0.10	3.0	80.2	6.80	950
WBPU/PANI-D/H38	62/38	0.25	0.24	2.1	65.2	—	820
WBPU/PANI-D/H50	50/50	0.30	0.30	1.4	60.0	6.74	708
WBPU/PANI-D/H60	40/60	0.32	0.30	0.9	56.4	—	590
WBPU/PANI-D/H75	25/75	0.33	0.31	0.7	49.0	—	400
WBPU/PANI-D/H	0/100	7.30	7.30	—	—	—	—

^a The mixture of PANI-D/H/water (0.5 g/10 ml) was treated with ultrasonic vibration for 30 min.

^b Electrical conductivity of glass-contacted surface (G-surface) and air-exposed surface (A-surface) of blend films.

Co. Ltd., Korea) and the usual four-probe method. The antistaticity of blend samples was measured by using Static Honestometer (Shishido Co. Ltd., Japan). In the case of pure PANI-D/H, the electrical conductivity was measured on pressed pellet. The morphology of WBPU/PANI-D/H blend films was observed by SEM (Hitachi S-4200 Field Emission SEM, KBSI).

RESULTS AND DISCUSSION

The intrinsic viscosity of conductive polymer PANI-D/H prepared in this study was found to be about 1.39 dL/g. The yield and conductivity of PANI-D/H synthesized in this study are 32.2% and 7.3 S/cm, respectively (see Table I).

The components (C, H, N, S, Cl) of the PANI-D/H determined by elemental analysis were given in Table I. It contained 7.33 wt % nitrogen, 5.42 wt % sulfur, and 4.67 wt % chlorine. From these elemental results, it was found that the doping level of conduction polymer PANI-D/H prepared in this study was about 58 mol %.

Generally, the emeraldine salt of PANI doped with DBSA/HCl has three absorption peaks in UV-Visible absorption spectrum: an absorption peak at 360 nm corresponding to the π - π^* transition of the benzenoid ring, and two absorption peaks at about 430 and 800 nm assigned to the polaron/bipolaron band transitions.^{12,18,28-30} It was also found that the PANI-D/H prepared in this study had these three absorption peaks.

FTIR spectrum of conducting polymer PANI-D/H was shown in Figure 1. The characteristic bands are observed at near 1567–1579 and 1303–1308 cm^{-1} , which were assigned to C=C stretching of the quinoid

rings^{18,31} and C—N stretching of secondary amine of PANI backbone,²¹ respectively. It was found that these absorption bands of PANI-D/H are in complete agreement with those of the PANI doped with a protonic acid.³²

Figure 2 shows the DSC thermogram of dried PANI-D/H prepared powder. The strong endothermic peak around 90–190°C was due to the release of moisture and the T_g of undoped (or dedoped) PANI.³³⁻³⁵ The endotherm peak over a temperature zone of 220–290°C was assigned to morphological change in the PANI system.^{33,34} The PANI-D/H prepared here was also found to have these endotherm peaks. From these results, it was found that the PANI-D/H prepared in this study had the same structure as the PANI-D/H described in previous studies.³³⁻³⁵

Generally, smaller particle size material is needed to make homogeneous mixture of WBPU/PANI-D/H. From the results of the preliminary experiment of drying, the particle size of PANI-D/H dispersion prepared in this study increased with increasing drying time, indicating that the PANI-D/H particles are significantly associated with each other during the drying process. Therefore, to prepare fine dispersion of PANI-D/H, the as-washed PANI-D/H was directly dispersed in water by treatment of magnetic stirring or ultrasonic vibration. In this study, the effect of these treatments on the mean particle size of aqueous PANI-D/H dispersion was compared. The mean particle size of magnetic stirring (with 600 rpm for 30 min at room temperature) and ultrasonic vibration (for 30 min at room temperature) treated PANI-D/H was about 1.6 and 0.7 μm , respectively. From this result, the ultrasonic vibration treatment was found to be more effective than the magnetic stirring. The smaller particle

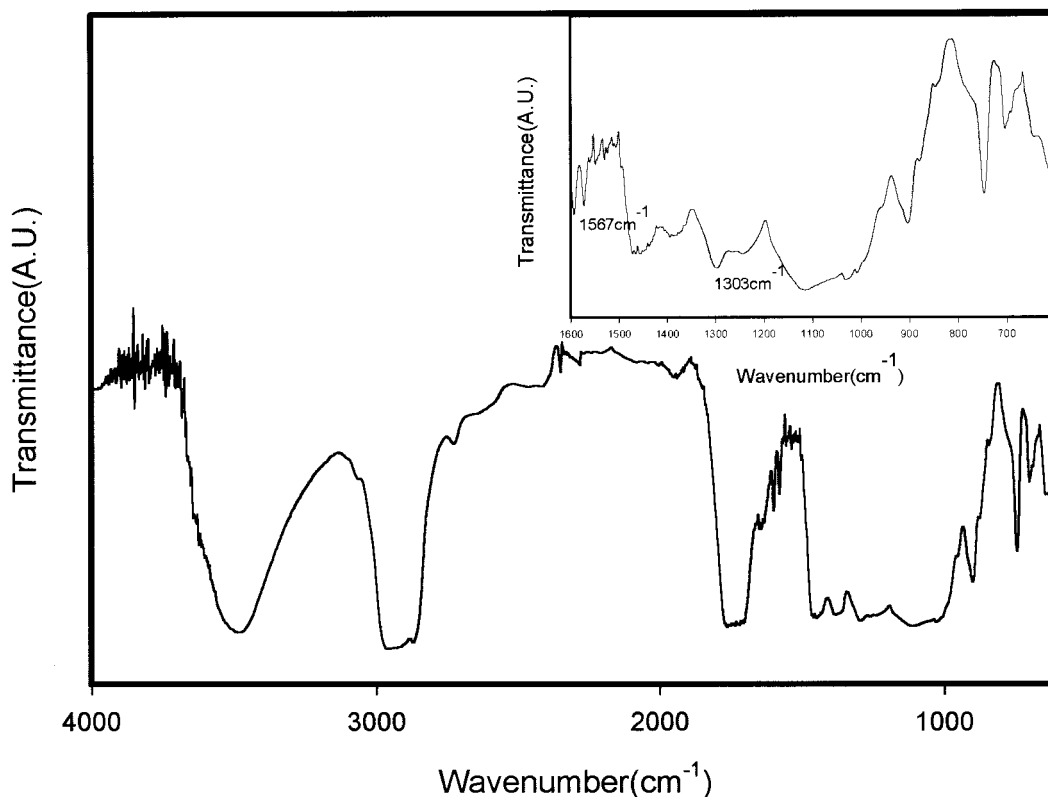


Figure 1 FTIR spectrum of PANI-D/H.

size of PANI-D/H will be effective to make the finer network texture of PANI-D/H in WBPU/PANI-D/H blends.

The temperature dependence of the dynamic storage modulus and loss $\tan \delta$ of the WBPU and WBPU/PANI-D/H blend films are shown in Figure 3 and storage modulus values of selected blend film samples

at 25°C are given in Table II. The storage modulus increased with increasing PANI-D/H content up to 1 wt %, and then it was decreased. The loss $\tan \delta$ peaks at lower temperature are assigned to the glass transition of soft segments (T_{gs}) of WBPU, and the loss $\tan \delta$ peaks at higher temperature assigned to the glass transition temperature of hard segments (T_{gh}) of

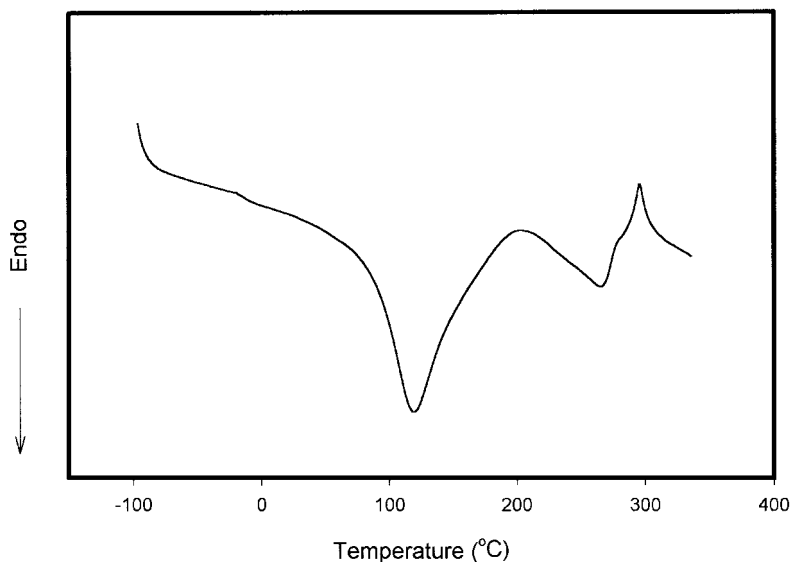


Figure 2 DSC thermogram of PANI-D/H.

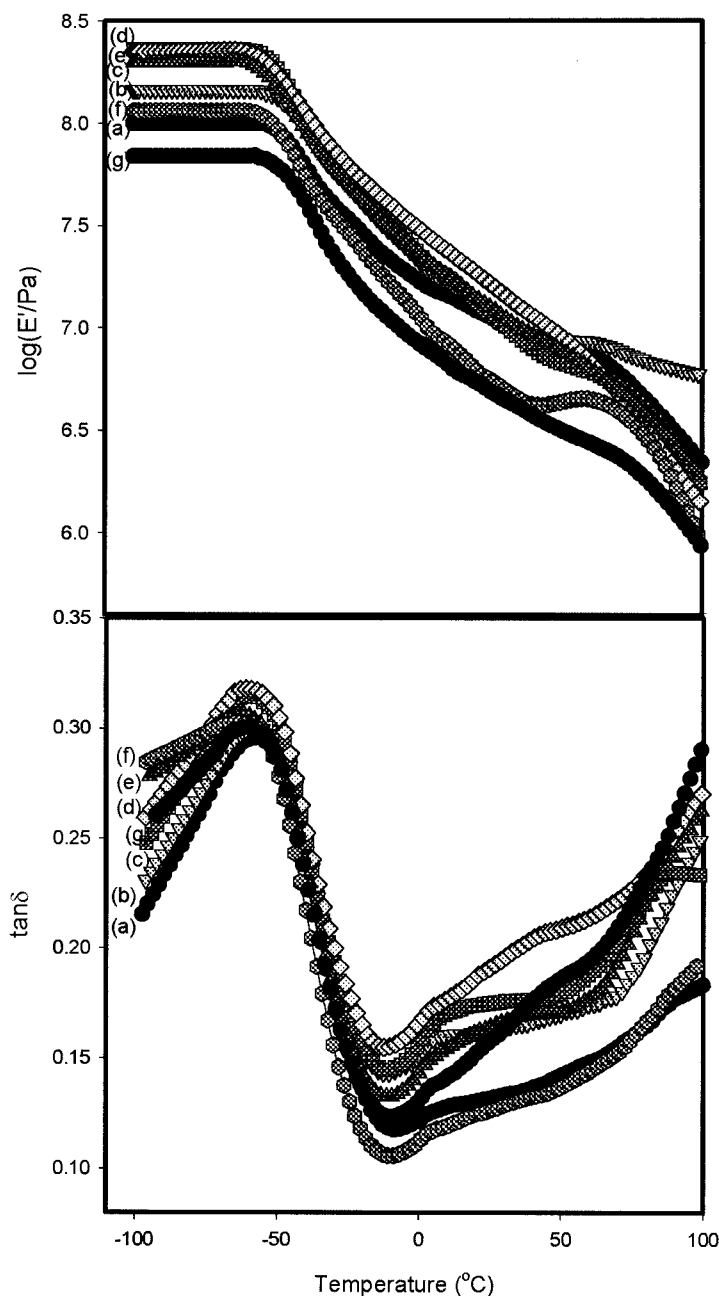


Figure 3 Storage modulus (E') and $\tan \delta$ as a function of temperature for (a) WBPU, (b) WBPU/PANI-D/H0.1, (c) WBPU/PANI-D/H0.5, (d) WBPU/PANI-D/H1, (e) WBPU/PANI-D/H9, (f) WBPU/PANI-D/H23, and (g) WBPU/PANI-D/H50 blend films.

WBPU. The T_{gs} and T_{gh} of pure WBPU film were -58 and 8.7°C , respectively. With increasing PANI-D/H contents from 0.1 to 50 wt %, the T_{gs} and T_{gh} of WBPU/PANI-D/H blend films decreased from -58 to -63.9°C and from 7.1 to 4.5°C , respectively. With increasing PANI-D/H content, the T_{gs} and T_{gh} of WBPU/PANI-D/H blends are slightly shifted to lower temperature, indicating that WBPU is slightly compatible with PANI-D/H.

Strain–stress curves of WBPU and WBPU/PANI-D/H blend films are shown in Figure 4. Figure 5 and

Table II represent the initial modulus, tensile strength, and elongation at break against the PANI-D/H content of the polymer blends. The mechanical properties of pure PANI-D/H pellet could not be determined because pure PANI-D/H pellet was very weak. Initial tensile modulus of blend films increased up to 1 wt %, and then it was decreased above the content. The tensile strength of blend films slightly increased with increasing PANI-D/H content up to 0.5 wt %, and then it was remarkably decreased (see Table II). In the case of lower content of PANI-D/H below 1 wt %, the

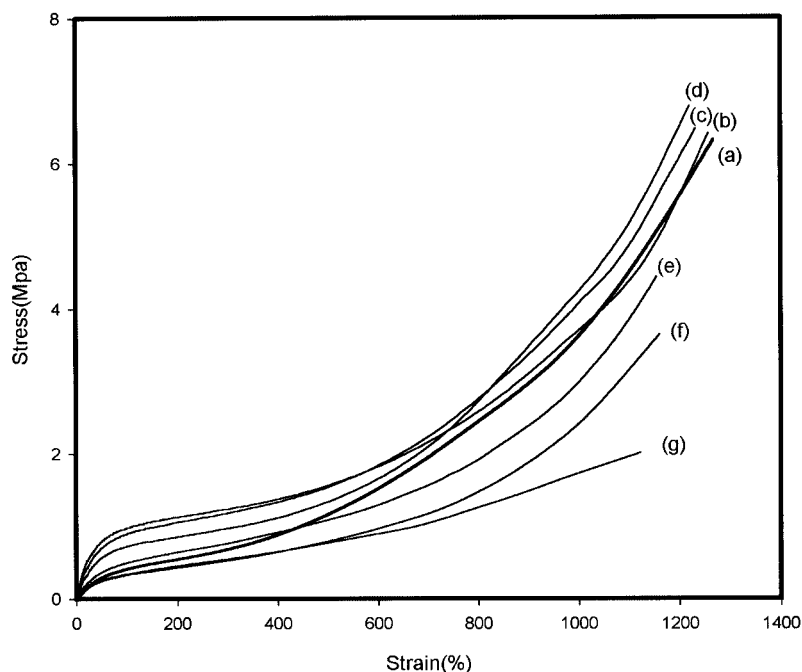


Figure 4 Strain–stress curves of (a) WBPU, (b) WBPU/PANI-D/H0.1, (c) WBPU/PANI-D/H0.3, (d) WBPU/PANI-D/H0.5, (e) WBPU/PANI-D/H9, (f) WBPU/PANI-D/H23, and (g) WBPU/PANI-D/H38 blend films.

increases of initial tensile modulus and tensile strength values might be due to the reinforcing effect of PANI-D/H component in the WBPU matrix. This also means that the WBPU/PANI-D/H blend was a compatible system in the PANI-D/H content of 0.5–1 wt %. However, in the case of higher content of PANI-D/H, the decreases of these tensile properties might be attributed to the defective structure of WBPU/PANI-D/H blend. The PANI-D/H component might be functioning as a defect in the WBPU matrix when the PANI-D/H was higher in content. The elongation at break of WBPU/PANI-D/H decreased with increasing of PANI-D/H content significantly (see Table II).

Generally, hardness reflects the resistance to local deformation, which is a complex property, related to crosslink density, plasticity/elasticity, strength/modulus, and porosity of the matrix.^{25,26} Figure 6 gives the variation of hardness with the PANI-D/H content of the WBPU/PANI-D/H blend films. The hardness of WBPU/PANI-D/H blend films was slightly increased with increasing PANI-D/H content up to 0.5 wt %, and then it was dramatically reduced. The decrease of hardness is presumably due to the defective structure of WBPU/PANI-D/H as mentioned above.

From these results, it was concluded that 0.5–1 wt % of PANI-D/H was the critical concentration to reinforce those various properties of WBPU/PANI-D/H films prepared in this study.

The electrical conductivity of WBPU/PANI-D/H blend films was examined by using a four-probe tech-

nique. The electrical conductivities of WBPU/PANI-D/H blend films and PANI-D/H pellet are shown in Table II. The electrical conductivity of PANI-D/H pellet and WBPU film was 7.3 and 2.5×10^{-12} S/cm, respectively, indicating that WBPU was a typical insulating polymer and PANI-D/H was a polymer with fairly high conductivity. Figure 7 shows the relationship between conductivity and PANI-D/H content for magnetic stirring and ultrasonic vibration treated film samples. The conductivity of ultrasonic vibration treated samples was higher than those of magnetic stirring treated samples at the same PANI-D/H contents. The higher conductivity of ultrasonic treating based sample is primarily due to the finer particle size of PANI-D/H. This finer particle of PANI-D/H might make the formation of the finer network texture of conductive polymer PANI-D/H in the WBPU matrix.

The electrical conductivity of WBPU/PANI-D/H blend films increased with increasing PANI-D/H contents. This indicates that the conducting path (i.e., conducting network in WBPU/PANI-D/H blend) increased with increasing PANI-D/H content. The conductivity of blend film samples was measured on both sides of glass-contacted surface (G-surface) and air-exposed surface (A-surface) of blend films (see Table II). The sample WBPU/PANI-D/H75 containing maximum PANI-D/H contents (75 wt %) had the highest conductivity (A-surface: 0.33 S/cm and G-surface: 0.31 S/cm). When the content of PANI-D/H was at a lower level (below 50 wt %) in the WBPU/PANI-D/H blends, there is no significant conductivity difference

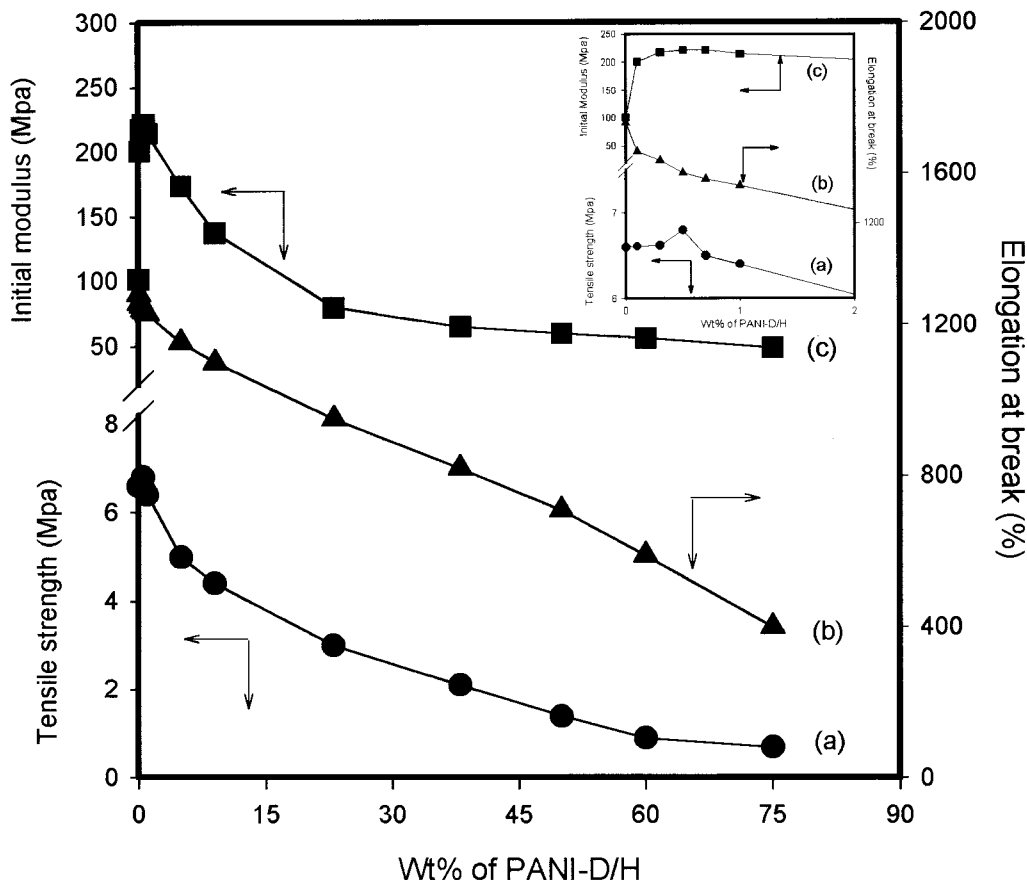


Figure 5 Effect of PANI-D/H contents on the tensile strength and elongation at break of WBPU/PANI-D/H blend films.

between G-surface and A-surface, indicating the homogeneous structure of WBPU/PANI-D/H blends. However, there is little difference in conductivity between G-surface and A-surface at the higher level of PANI-D/H content (above 50 wt %), which indicates the presence of heterogeneous mixture structure of WBPU/PANI-D/H blend films.

To enhance the antistaticity of WBPU coating material, aqueous dispersion of PANI-D/H treated with ultrasonic vibration was used as a conductive component in WBPU/PANI-D/H blends. The antistaticity of WBPU/PANI-D/H blend films was measured by using a static honsetometer. The half-life time of electrostatic charge ($\tau_{1/2}$) and maximum surface electrostatic potential (V_{max}) versus PANI-D/H content are shown in Figure 8. The maximum surface electrostatic potential (V_{max}) and the half-life time ($\tau_{1/2}$) of electrostatic charge for pure WBPU film were 57 kV and 110 s, respectively, indicating that the WBPU is a typical electrostatic material. By increasing the PANI-D/H content from 0.1 to 75 wt %, the maximum surface electrostatic potential (V_{max}) and the half-life time ($\tau_{1/2}$) of electrostatic charge was exponentially decreased and then approached to almost 0 s. The antistatic half-life times of blend film samples containing PANI-D/H 0.1–9 and 9–75 wt % were 8.2–0.1 s and

almost 0 s, respectively. Generally, it is known that polymers with $\tau_{1/2}$ lower than 10 s are considered as materials with good antistatic properties.³⁶ The sample WBPU/PANI-D/H0.1 containing 0.1 wt % of PANI-D/H, which have 8.2 s of $\tau_{1/2}$, was found to be a good antistatic material.

Figure 9 shows SEM photographs of typical WBPU/PANI-D/H blend film samples (WBPU/PANI-D/H23 and WBPU/PANI-D/H38). The WBPU/PANI-D/H film sample has a smooth surface when PANI-D/H content is below 30 wt % [see Fig. 9(a)]. However, with increasing PANI-D/H content over about 30 wt %, the aggregation of PANI-D/H appeared inside the film, resulting in the formation of PANI-D/H cluster on the surface [see Fig. 9(b)].

CONCLUSION

The dispersion of PANI-D/H with intrinsic viscosity ($[\eta]$) near 1.39 dL/g was prepared by chemical oxidative polymerization from A-DS/A-HS (6/4M ratio) in an aqueous system. The yield and conductivity of PANI-D/H pellet was 32.2% and 7.3 S/cm, respectively. Aqueous dispersion of PANI-D/H was prepared by washing as-polymerized PANI-D/H with

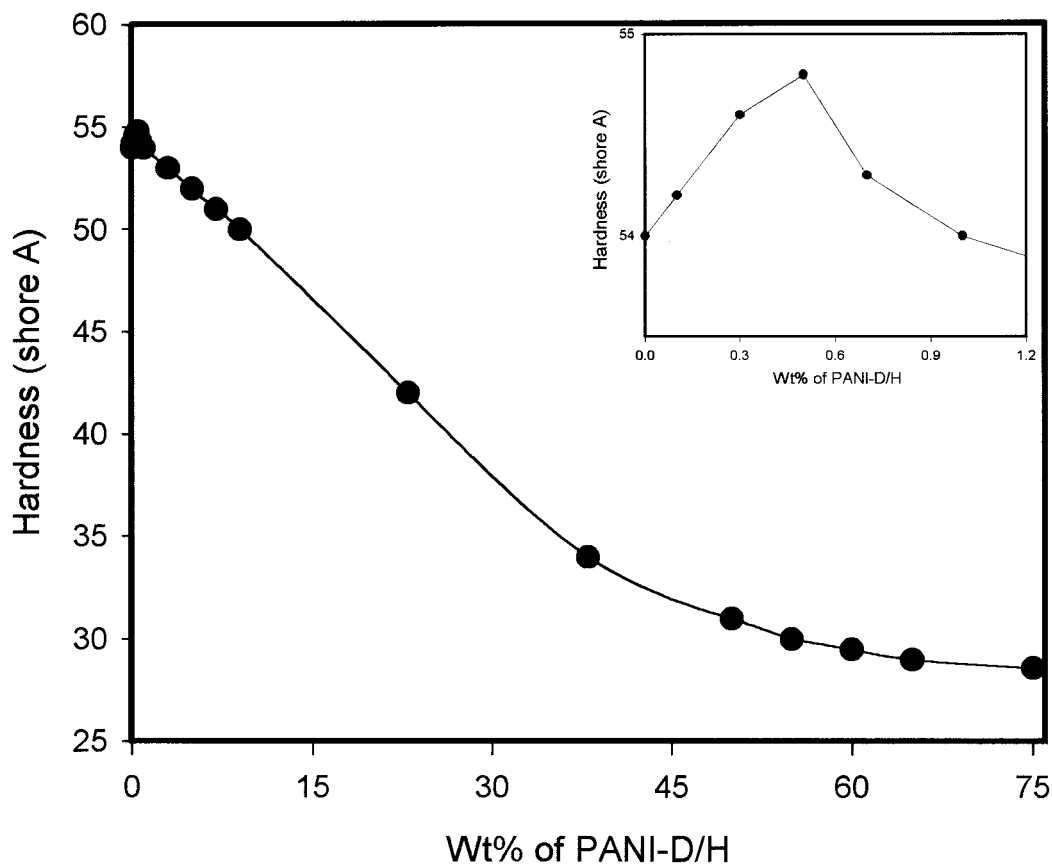


Figure 6 Effect of PANI-D/H contents on hardness of WBPU/PANI-D/H blend films.

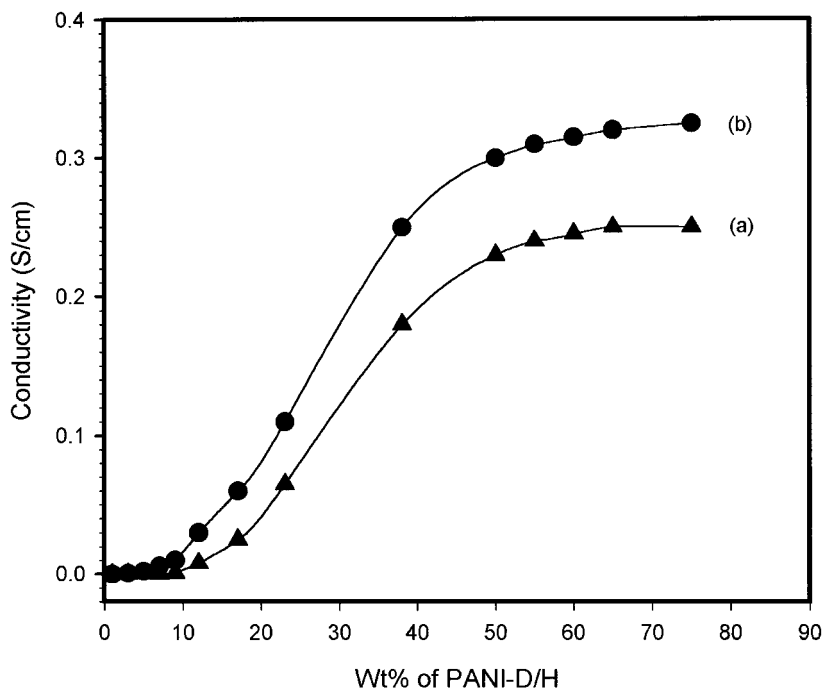


Figure 7 Effect of PANI-D/H contents on the electrical conductivity of WBPU/PANI-D/H blend films treated with (a) magnetic stirring (600 rpm/30 min/room temperature) and (b) ultrasonic vibration (30 min/room temperature).

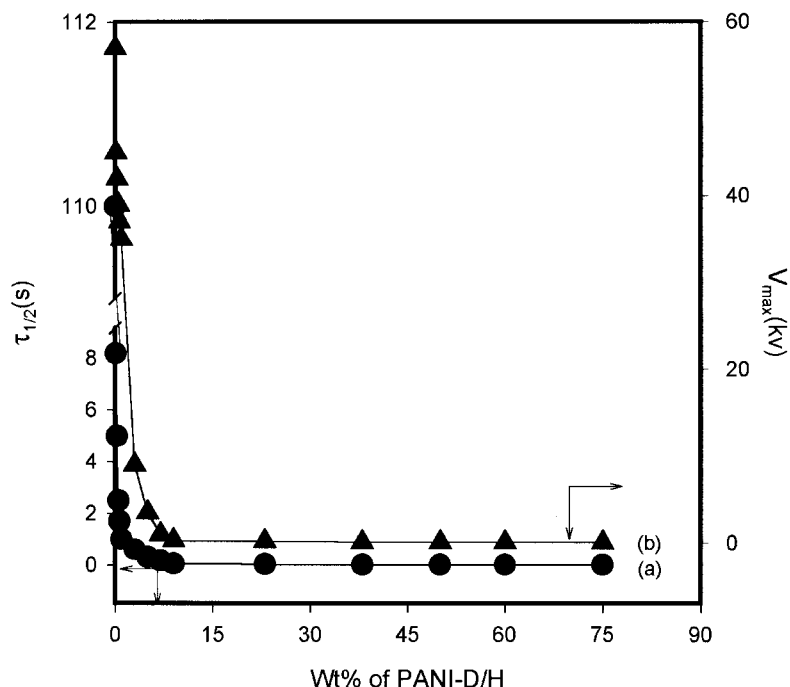


Figure 8 Effect of PANI-D/H contents on the antistatic properties of WBPU/PANI-D/H blend films: (a) antistatic half-life time ($\tau_{1/2}$, s) and (b) maximum surface electrostatic potential (V_{max} , kV).

methanol and water, followed by dispersing in water under magnetic stirring or ultrasonic vibration treatments. The mean particle size of ultrasonic vibration treated as-polymerized PANI-D/H (0.7 μm) was smaller than that of the magnetic stirring treated one (1.6 μm). The aqueous dispersion of WBPU was prepared by the polyaddition reaction using IPDI/PTMG/DMPA/EDA/TEA/water. The blend films of WBPU/PANI-D/H with variable weight ratios (99.9/0.1–25/75) were prepared by solution blending/casting.

The effect of PANI-D/H content on the mechanical property, dynamic mechanical property, hardness, electrical conductivity, and antistaticity of WBPU/PANI-D/H blend films was investigated. The dynamic storage modulus of WBPU/PANI-D/H blend films increased with increasing PANI-D/H content up to 1 wt %. However, the storage modulus of blend films decreased with increasing PANI-D/H content above 1 wt %. The T_{gs} and T_{gh} of pure WBPU film were -58 and 8.7°C , respectively. With increasing PANI-D/H content, T_{gs} and T_{gh} were a bit shifted to lower temperature. The initial tensile modulus of WBPU/PANI-D/H blend films was slightly increased with increasing PANI-D/H content up to 1 wt %, and then it was sharply decreased. The tensile strength of WBPU/PANI-D/H blend films increased a little with increasing PANI-D/H content up to 0.5 wt %, and then it sharply decreased. The elongation at break of WBPU/PANI-D/H blend films decreased with increasing of PANI-D/H content. The hardness of

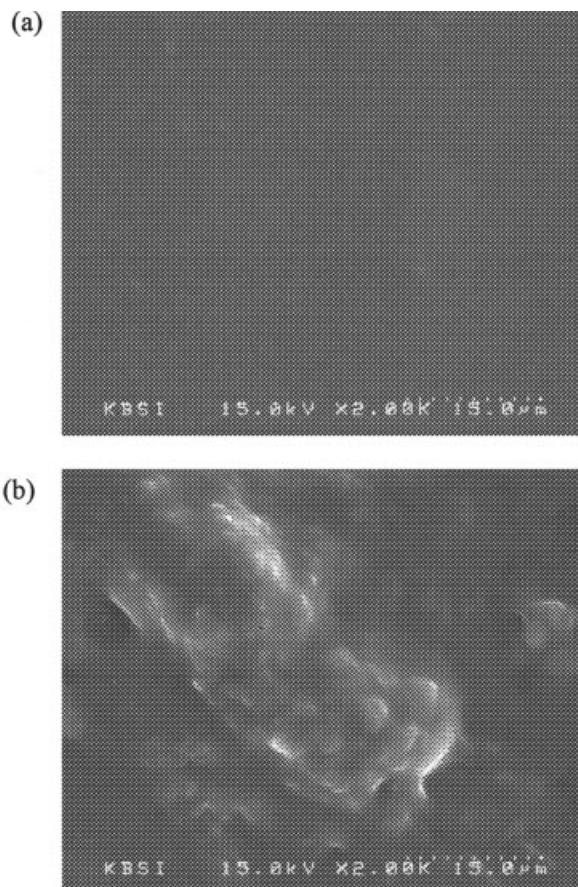


Figure 9 SEM photographs of (a) WBPU/PANI-D/H23 and (b) WBPU/PANI-D/H38 blend films.

WBPU/PANI-D/H blend films increased insignificantly with increasing PANI-D/H content up to 0.5 wt %, and then it decreased. From these results, we concluded that 0.5–1 wt % of PANI-D/H was the critical concentration to reinforce those various properties of WBPU/PANI-D/H blend films prepared in this study. The electrical conductivities of the pure PANI-D/H pellet and WBPU were 7.3 and 2.5×10^{-12} S/cm, respectively, indicating that the PANI-D/H was a typical conductive polymer, and WBPU was a typical insulating polymer. As the PANI-D/H content increased from 0.1 to 75 wt %, the conductivity of WBPU/ultrasonic treated PANI-D/H (particle size: $0.7 \mu\text{m}$) blend films increased from 4.0×10^{-7} to 0.33 S/cm. It was found that the WBPU/ultrasonic treated PANI-D/H blend film samples have higher conductivity compared with WBPU/magnetic stirring treated PANI-D/H (particle size: $1.6 \mu\text{m}$) blend film samples at the same PANI-D/H contents. The antistatic half-life time of pure WBPU film was about 110 s, indicating that WBPU is a typical electrostatic material. However, with increasing PANI-D/H content, the antistatic half-life time of WBPU/ultrasonic treated PANI-D/H blend films is exponentially decreased from 110 s to almost 0 s.

References

- Haba, Y.; Segal, E.; Nakris, M.; Titelman, G. I.; Siegmann, A. *Synth Met* 1999, 106, 59.
- Kim, B. J.; Oh, S. G.; Han, M. G.; Im, S. S. *Synth Met* 2001, 122, 297.
- Somani, P. R. *Mater Chem Phys* 2002, 9295, 1.
- Makela, T.; Sten, J.; Hujanen, A.; Isotalo, H. *Synth Met* 1999, 101, 707.
- Koul, S.; Chandra, R.; Dhawan, S. K. *Polymer* 2000, 41, 9305.
- Heeger, A. J.; Long, J. *Optics Photon News* August 1996, 24.
- Yam, P. *Sci Am* 1997, 8, 90 (special issue).
- Kinlwn, P. J.; Silverman, D. C.; Jeffreys, C. R. *Synth Met* 1997, 85, 1327.
- Haba, Y.; Segal, E.; Nakris, M.; Titelman, G. I.; Siemann, A. *Synth Met* 2000, 110, 189.
- Tom, L.; Ari, I. *J Electroanal Chem* 2002, 531, 43.
- Yin, W.; Ruckenstein, E. *Synth Met* 2000, 108, 39.
- Roichman, Y.; Titelman, G. I.; Silverstein, M. S.; Siegmann, A.; Nakris, M. *Synth Met* 1999, 98, 201.
- Nakajima, T.; Kawagoe, T. *Synth Met* 1986, 28, C6294.
- Cao, Y.; Smith, P.; Hegger, A. J. *Synth Met* 1992, 48, 91.
- Cao, Y.; Smith, P. *Polymer* 1993, 34, 3139.
- Cao, Y.; Smith, P.; Hegger, A. J. *Synth Met* 1993, 55–57, 3514.
- Kuramoto, N.; Tomita, A. *Polymer* 1997, 12, 3055.
- Han, M. G.; Cho, S. K.; Oh, S. G.; Im, S. S. *Synth Met* 2002, 126, 53.
- Lu, X.; Ng, H. Y.; Xu, J.; He, C. *Synth Met* 2002, 128, 167.
- Jeevananda, T.; Siddaramaiah; Annadurai, V.; Somashekar, R. *J Appl Polym Sci* 2001, 2, 383.
- Ho, K. S.; Hsieh, K. H.; Hagan, S. K.; Hsieh, T. H. *Synth Met* 1999, 107, 65.
- Leyva, M. E.; Barra, G. M. O.; Soares, B. G. *Synth Met* 2001, 123, 443.
- Rupali, G.; Amitabha, D.; Gountam, G. *Synth Met* 2001, 123, 21.
- Yang, J. E.; Kong, J. S.; Park, S. W.; Lee, D. J.; Kim, H. D. *J Appl Polym Sci* 2002, 86, 2375.
- Kwak, Y. S.; Kim, H. D. *Fibers Polym* 2002, 3, 153.
- Kwak, Y. S.; Park, S. W.; Lee, Y. H.; Kim, H. D. *J Appl Polym Sci* 2003, 89, 123.
- Kwon, J. Y.; Kim, E. Y.; Kim, H. D. *Polym Bull* to appear.
- Sun, Y.; Diarmid, M. A. G.; Epstein, A. J. *J Chem Soc Chem Commun* 1990, 529.
- Stejskal, J.; Kratochvil, P. *Synth Met* 1993, 61, 225.
- Roy, B. C.; Gupta, M. D.; Bhoumik, L.; Ray, J. K. *Synth Met* 2002, 130, 27.
- Chen, S. A.; Hwang, G. W. *Polymer* 1997, 38, 3333.
- Wang, Y.; Rubner, M. F. *Synth Met* 1992, 47, 255.
- Chan, H. S. O.; Ng, S. C.; Sim, W. S.; Seow, S. H.; Tan, K. L.; Tan, B. T. G. *Macromolecules* 1993, 26, 144.
- Ghosh, P.; Siddhanta, S. K.; Chakrabarti, A. *Eur Polym J* 1999, 35, 699.
- Ding, L.; Wang, X.; Gregory, R. V. *Synth Met* 1999, 104, 73.
- Omastova, M.; Chodak, I.; Pionteck, J. *Synth Met* 1999, 102, 1251.