Preparation and Properties of Waterborne-Polyurethane Coating Materials Containing Conductive Polyaniline

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Abstract: We have prepared an aqueous dispersion of poly(aniline-dodecyl benzene sulfonic acid complex) (PANI-DC) that has an intrinsic viscosity ($[\eta]$) near 1.3 dL/g using aniline as a monomer, dodecyl benzene sulfonic acid (DBSA) as a dopant/emulsifier, and ammonium peroxodisulfate (APS) as an oxidant. We found that the electrical conductivity of a PANI-DC pellet was 0.7 S/cm. A waterborne-polyurethane (WBPU) dispersion, obtained from isophorone diisocyanate/polytetramethylene oxide glycol/dimethylol propionic acid/ethylene diamine/triethylene amine, was used as a matrix polymer. We prepared blend films of WBPU/PANI-DC with variable weight ratios (from 99/1 to 66/34) by solution blending/casting and investigated the effects that the PANI-DC content has on the mechanical and dynamic mechanical properties, hardness, electrical conductivity, and antistaticity of these films. The tensile strength, percentage of elongation, and hardness of WBPU/PANI-DC blend films all decreased markedly upon increasing the PANI-DC content. The antistatic half-life time ($\tau_{1/2}$) of pure WBPU film was about 110 s, but we found that those of WBPU/ultrasound-treated PANI-DC blend films decreased exponentially from 1.2 s to 0.1 s to almost 0 s upon increasing the PANI-DC content from 1 wt% to 15 wt%, respectively.

Keywords: conducting polymers, polyaniline, polyurethanes, polymer blends, antistaticity.

Introduction

Ever since the successful synthesis of conducting polyacetylene in 1977 by Shirakawa *et al.*,¹ electrical conducting polymers have generated a tremendous interest due to their potential application in batteries,² electrochromic devices,³ sensors,⁴ electromagnetic interference (EMI) shielding screens^{5,6} and substitutes for metallic conductors or semiconductor in wide variety of electrical devices.⁶ Some applications of PANI having electrical conductivity between 10⁻¹⁰ ~10⁻² S/cm are hole injection layers for flexible light emitting diodes,⁷ antistatic materials,⁸ corrosion protection,⁹ and ion sensors.¹⁰

Among the conducting polymers, polyaniline (PANI) is under extensive study even today because of its high environmental stability, low cost, and relatively simple polymerization process. ¹¹⁻¹³ In spite of various advantages, PANI has received limit of application until several years ago, because PANI is neither soluble nor fusible in organic solvents as well as water. ¹³ Cao *et al.*, have first achieved the development of PANI with better solubility in common solvents. ¹⁵⁻¹⁷ Through a counter ion-induced processability method,

DC have been investigated with various matrix polymers such as polycarbonate, ¹⁹ polyurethane, ²⁰ styrene-butadiene-styrene (SBS), ²¹ polystyrene (PS), ¹³ and poly (vinyl alcohol) (PVA). ²² Jeevanandas groups ¹⁹ prepared PANI/PC blends with electrical conductivity $5.7 \times 10^{-5} \sim 4.7 \times 10^{-2}$ S/cm. On the other hand, Ho *et al.* ²⁰ prepared PANI/PU blends, which showed electrical conductivity from 0.57 to 23.5 S/cm and tensile strength of $2.11 \sim 5.55$ Mpa. The PANI/SBS blends with electrical conductivity of $10^{-2} \sim 10^{0}$ S/cm were prepared

where a specific functionalized protonic acid was used as protonation agent. It was reported that the protonic acids

such as dodecyl sulfuric acid (DSA),³ dodecylbenzene sulfonic acid (DBSA),⁴ sodium dodecyl sulfonate (SDS),¹² and

sulfosalicylic acid (SSA)¹⁸ rendered polyaniline "soluble" in

organic solvents in its doped state. An important example of

these protonic acids is DBSA, whose long alkyl chain increases the solubility of PANI-DBSA conducting salt in

toluene, xylene, etc., and acts as a surfactant, inducing some

compatibility with polymer matrix with similar structure.¹⁵

A PANI with improved processibility was synthesized via

emulsion polymerization in an aqueous solution of DBSA-

Polymer blend films containing conducting polymer PANI-

by Leyva *et al.*²¹ Roichman *et al.*¹³ reported that the electrical conductivity of PANI/PS blends were in the range of 10⁻¹⁵ to

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aniline salt.12

10° S/cm. Rupali groups²² prepared conducting composites PANI/PVA with electrical conductivity of 10⁻⁵~10° S/cm.

WBPUs are nontoxic, nonflammable, and do not pollute air. In addition, water dispersions (emulsions) of WBPUs permit the application of polyurethane from an aqueous medium. WBPUs have been used for a wide range of commercial application such as adhesives and coatings for various substrates. ¹⁶⁻¹⁹ However, research on WBPUs containing conducting polymer can hardly be found.

In this study, the conducting polymer PANI-DC was prepared by chemical oxidative polymerization from anilinedodecylbenzene sulfonic acid salt in an aqueous system. Waterborne-polyurethane (WBPU) as a coating material was synthesized by polyaddition reaction using isophorone diisocyanate, poly (tetramethylene oxide) glycol, dimethylol propionic acid, ethylene diamine, and triethylamine. To obtain coating materials having antistatic property, we prepared a series of waterborne polyurethane (WBPU)/PANI-DBSA complex (PANI-DC) (100~66/0~34 wt%) using solution blending from aqueous WBPU and PANI-DC dispersions. The effects of magnetic stirring or ultrasonic vibration treatments on the mean particle size of pure PANI-DC and the electrical conductivity of WBPU/PANI-DC blend films were investigated. Studies have been made on the influence of PANI-DC contents on the dynamic mechanical property, mechanical property, hardness, conductivity, and antistaticity.

Experimental

Materials. Aniline monomer (Aldrich Chemical, Milwaukee, WI, USA) was distilled under reduced pressure prior to use. Dodecyl benzene sulfonic acid (DBSA, Sigma, Milwaukee, WI), ammonium peroxodisulfate (APS, Aldrich Chemical, Milwaukee, WI), dibutyl tin dilaurate (DBTDL, Aldrich Chemical, Milwaukee, WI) and methanol (Sigma, Milwaukee, WI) were used as received. Isophorone diisocyanate (IPDI, Aldrich Chemical, Milwaukee, WI), triethylamine (TEA, Sigma, Milwaukee, WI), ethylene diamine (EDA, Aldrich Chemical, Milwaukee, WI), methyl ethyl ketone (MEK, Sigma, Milwaukee, WI) and N-methyl-2pyrrolidone (NMP, Aldrich Chemical, Milwaukee, WI) were used after dehydration with 4 Å molecular sieves for one day. Poly (tetramethylene oxide) glycol (PTMG, $M_n = 2,000 \text{ g/}$ mol, Aldrich, Milwaukee, WI) was dried over calcium hydride at room temperature for 24 h. Dimethylol propionic acid (DMPA, Aldrich Chemical, Milwaukee, WI) were dried in a vacuum oven (100 °C) for at least 5 h.

Preparation of Aqueous PANI-DC Dispersion and Its Pellet. The preparation procedure of aqueous poly (aniline-dodecyl benzene sulfonic acid complex) (PANI-DC) dispersion is as follows; viscose emulsion of aniline/DBSA/water was prepared by mixing monomer aniline (17.3 mL, 0.15 mol) with DBSA (73.3 g, 0.225 mol) dissolved in de-ionized water (350 mL) under stirring at room temperature. To prepare the

aqueous dispersion of PANI-DC, oxidant APS (17.1 g, 0.075 mol) dissolved in de-ionized water (50 mL) was slowly added to aniline/DBSA/water emulsion under stirring at 0°C for 24 hrs. The molar ratio of APS to aniline was 1/2. As APS was dropping into aniline/DBSA/water emulsion, the white color of starting emulsion was changed to bright green color after about 5 hrs and then to dark green color at near 24 hrs. Therefore, the reaction was carried out for 24 hrs to ensure the complete polymerization of aniline for dark green color PANI-DC product. The dark green color reaction mixture was poured into methanol to precipitate the dark green color PANI-DC product. The dark green color PANI-DC was filtered using a glass filter, and washed 6 times with methanol and water alternately, followed by dispersing in water to prepare aqueous dispersion of PANI-DC.

The aqueous dispersion of PANI-DC was prepared by the purified PANI-DC (0.5 g) being disperse 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-DC is shown in Table I. Intrinsic viscosity of PANI-DC prepared in this study was measured using Ubbelohde viscometer at 25 $^{\circ}$ C in chloroform as solvent. The purified PANI-DC was dried in vacuum at about 60 $^{\circ}$ C for 3 days and then weighed for the determination of the yield.

The pellet of PANI-DC (diameter: 10 mm, thickness: 0.1 mm) for testing was prepared by compressing under a pressure of 0.1 ton at room temperature.

Synthesis of WBPU. Waterborne polyurethane (WBPU) was synthesized by the polyaddition reaction 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.²³⁻²⁵

Preparation of WBPU/PANI-DC blends and Their Films. WBPU/PANI-DC blends were prepared by mixing WBPU and aqueous PANI-DC dispersion with stirring for 2 hrs at room temperature. The weight ratios of WBPU/PANI-DC were 99/1~66/34 (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 one day, and then the remaining moisture was removed at 60 °C under 20 mmHg for 2 days.

Characterization. FT infrared spectrum of PANI-DC powder was recorded in the range of 500~4000 cm⁻¹ 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) of the PANI-DC powder using Ele-

Table I. Sample Designation, Composition and Characteristics of Poly(aniline-dodecyl benzene sulfonic acid complex) (PANI-DC), and Sample Designation and Composition of Waterborne-polyurethane (WBPU)

Sample designation	Composition (mole)			- Yield	Intrinsic I	Elen	Elemental analysis data (wt%)				Mean particle size (μm)		Conductivity
	Aniline monomer	DBSA	APS	(%)	Viscosity $[\eta]^a$	С	Н	N	S	S/N"	Mechanical stirring ^c	Ultrasonic treatment ^d	· Conductivity (S/cm)
PANI-DC	0.150	0.225	0.100	41	1.3	68.20	6.30	6.72	7.80	0.50	1.14	0.12	0.7
Sample designation	Composition (mole)									- Solid content			
	IPDI		($ \begin{array}{c} \text{PTMG} \\ (M_n = 2,000) \end{array} $		DMPA			EDA		TEA		(wt%)
WBPU	2.5			1.0		0.5		1.0		0.5		30	

aIntrinsic viscosity ([η]) of PANI-DC prepared in this study was determined using Ubbelohde viscometer at 25 °C in chloroform as solvent.

mental analyzer (Vario EL III, Germany). The particle size of PANI-DC was determined using Particle Size Analyzer (Galai Production Ltd., Israel) and lazer-scattering equipment (Autosizer, Melvern IIC, USA). UV-VIS absorption spectrum of an aqueous PANI-DC dispersion measured in the range between 200 and 900 nm by Shimadzu UV-1601 spectrometer (Japan). The sample was diluted 50 times with distilled water in order to get proper absorption spectrum. The thermal behavior of conductive polymer PANI-DC was examined using a DSC 220C (Seiko, Japan) at the heating rate of 10°C/minute under a nitrogen atmosphere. The dynamo-mechanical behavior of WBPU and WBPU/PANI-DC blend films was measured at 4 Hz using DMTA (DMTA MK III, Rheometrics Scientific Inc., USA) with the heating rate of 3 °C/minute. The dimension of film sample was $5 \times$ 5×0.2 (mm³) for DMTA measurement. The mechanical measurements were made in simple extension on dumbbell specimens using a tensile tester (Tinius Olsen 1000, USA) at a cross-head speed of 20 mm/minute according to ASTM D-412. Electrical conductivity of PANI-DC pellet and WBPU/PANI-DC blend films were measured using a Surface Resistance Detector (CMT-SR1000N, CM Co. Ltd., Korea) and the usual four-probe method. The antistaticity of blend samples was measured using Static Honestometer (Shishido co. Ltd., Japan). In the case of pure PANI-DC, the electrical conductivity was measured on pressed pellet.

Results and Discussion

Identification of PANI-DC. The intrinsic viscosity of conducting polymer PANI-DC prepared in this study was found to be about 1.3 dL/g. The yield and conductivity of PANI-DC synthesized in this study are 41% and 0.7 S/cm, respectively (see Table I).

The components (C, H, N, S) of the PANI-DC determined by elemental analysis were given in Table I. It contained 7.8 wt% of sulfur and 6.7 wt% of nitrogen. From these elemental results, it was found that the doping level of conducting polymer PANI-DC prepared in this study was about 50 mole%.

The UV-VIS absorption spectrum of an aqueous PANI-DC dispersion is presented in Figure 1. Generally, the emeraldine salt of PANI doped with DBSA 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. ^{12,18,26-28} It was also found that the PANI-DC prepared in this study had these three absorption peaks.

FTIR spectrum of conducting polymer PANI-DC was shown in Figure 1. The characteristic bands are observed at near 1581 and 1310 cm⁻¹ which assigned to C=C stretching of the quinoid rings^{1,29} and C-N stretching of secondary

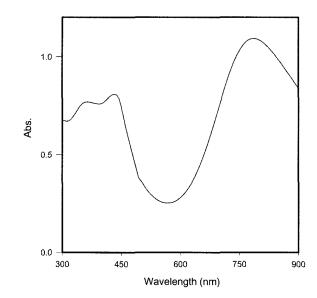


Figure 1. UV-spectrum of an aqueous PANI-DC dispersion.

^bS/N ratio was given on molar base.

^cWet PANI-DC was treated with magnetic stirring (600 rpm/30 minutes /room temperature).

^dWet PANI-DC was treated with ultrasonic vibration (30 minutes/room temperature).

amine of PANI backbone,³⁰ respectively. It was found that these absorption bands of PANI-DC are in complete agreement with those of the PANI doped with a protonic acid.³¹

Figure 3 shows the DSC thermogram of the PANI-DC powder under N_2 atmosphere. PANI-DC shows a broad endothermic peak over the temperature region of $80 \sim 190\,^{\circ}\text{C}$ that corresponds to successive or concomitant expulsion of moisture and dopant on heating and due to the T_g of undoped (or dedoped)-PANI.³¹⁻³⁷ An broad endothermic peak over a temperature region of $220 \sim 270\,^{\circ}\text{C}$ in the DSC curve which may denote dissociation of PANI-DC.³¹⁻³⁷ These results agree with other studies and it was found that the PANI-DC prepared in this study had the same structure as the PANI-DC described in previous studies.³¹⁻³⁷

Particle Size of PANI-DC. Generally, smaller particle size material is needed to make homogeneous mixture of

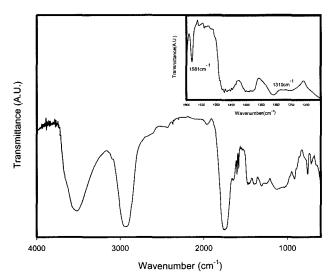


Figure 2. FT-IR spectrum of PANI-DC.

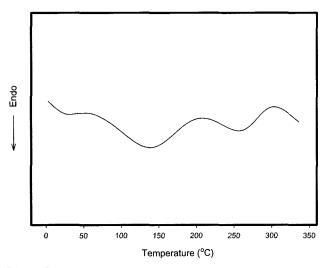


Figure 3. DSC thermogram of PANI-DC.

WBPU/PANI-DC. From the results of the preliminary experiment of drying we found that the particle size of a PANI-DC dispersion prepared in this study increased with increasing drying time, indicating that the PANI-DC particles are significantly associated with each other during drying process. Therefore, in order to prepare fine dispersion of PANI-DC, the as-washed PANI-DC 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-DC dispersion was compared. The mean particle size of magnetic stirring (with 600 rpm for 30 minutes at room temperature) and ultrasonic vibration (for 30 minutes at room temperature) treated PANI-DC was about $1.14 \,\mu m$ and $0.12 \,\mu m$, respectively. From this result, the ultrasonic vibration treatment was found to be more effective than the magnetic stirring. The smaller particle size of PANI-DC will be effective to make the finer network texture of PANI-DC in WBPU/PANI-DC

Dynamic Mechanical Analysis. The dynamic storage modulus (E') and loss $\tan \delta$ of the WBPU film and typical WBPU/PANI-DC blend films are shown in Figure 4. The E of WBPU film was maintained in the glassy plateau region from -100 to -60 °C, and then it was rapidly decreased due to the glass transition of soft segment in WBPU. The E of blend samples in glassy plateau region was increased as a function of the amount of PANI-DC.

The loss $\tan\delta$ peaks at lower temperature are assigned to the glass transition of soft segments (T_g s) of WBPU, and the loss $\tan\delta$ peaks at higher temperature assigned to the glass transition temperature of amorphous hard segments (T_g h) of WBPU. The T_g s and T_g h of pure WBPU film were appeared at about -58 and 8.7 °C, respectively. These glass transition temperatures of WBPU were almost not changed with increasing PANI-DC content, indicating that it was interpreted in terms of possible incompatibility of WBPU and PANI-DC.

Mechanical Property of WBPU/PANI-DC blend films. Strain-stress curves of WBPU and WBPU/PANI-DC blend films are shown in Figure 5. Figure 6 and Table II represents the initial modulus, tensile strength, and elongation at break against the PANI-DC content of the blend samples. The mechanical properties of pure PANI-DC pellet could not be determined because pure PANI-DC pellet was very weak. The pure WBPU film has high tensile strength (6.6 Mpa) and elongation at break (1,280%). The tensile strength of WBPU/PANI-DC blend films progressively decreases with the increasing PANI-DC ratio in WBPU (see Table II). The decreases of these tensile properties might be attributed to the defective structure of WBPU/PANI-DC blend. The PANI-DC component might be functioning as a defect in the WBPU matrix. In blend system, the percent elongation decreased with increasing PANI-DC content. This might be due to the incompatibility and defective structure of WBPU/

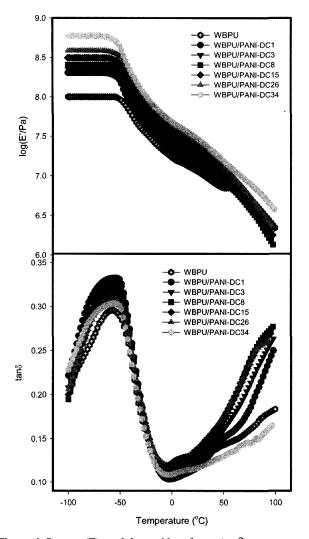


Figure 4. Storage (E) modulus and loss factor $(\tan\delta)$ temperature dependence of WBPU and WBPU/PANI-DC blend films.

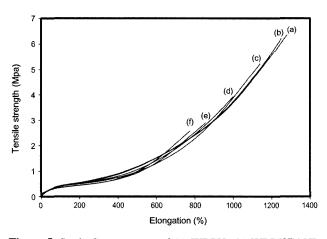


Figure 5. Strain-Stress curves of (a) WBPU, (b) WBPU/PANI-DC1, (c) WBPU/PANI-DC3, (d) WBPU/PANI-DC8, (e) WBPU/PANI-DC26, and (f) WBPU/PANI-DC34 blend films.

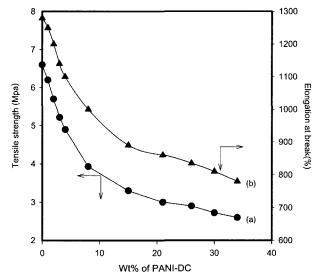


Figure 6. Effect of PANI-DC contents on (a) tensile strength and (b) elongation at break of WBPU/PANI-DC blend films.

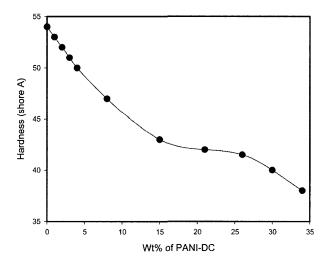


Figure 7. Effect of PANI-DC contents on hardness of WBPU/PANI-DC blend films.

PANI-DC blend system.

Hardness of WBPU/PANI-DC blend films. Generally, hardness reflects the resistance to local deformation, which is complex property, related to cross-link density, plasticity/ elasticity, strength/modulus and porosity of the matrix. ^{24,25} Figure 7 gives the variation of hardness with the PANI-DC content of the WBPU/PANI-DC blend films. The hardness of WBPU/PANI-DC blend films was significantly decreased with increasing PANI-DC contents. The decrease of hardness is presumably due to the defective structure of WBPU/PANI-DC as mentioned above.

Electrical Conductivity and Antistaticity. The electrical conductivity of WBPU/PANI-DC blend films was examined using 4-probe techniques. The electrical conductivities of

WBPU/PANI-DC blend films and PANI-DC pellet are shown in Table II. The electrical conductivity of PANI-DC pellet and WBPU film was 0.7 S/cm and 2.5×10^{-12} S/cm, respectively, indicating that WBPU was a typical insulating polymer and PANI-DC was a fairly high conductive polymer. Figure 8 shows the relationship between conductivity and PANI-DC content for magnetic stirring and ultrasonic vibration treated film samples. The conductivity of ultrasonic

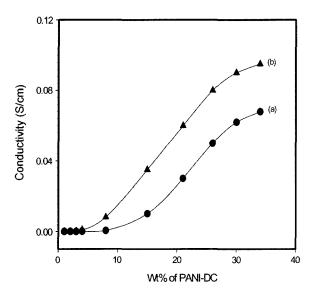


Figure 8. Effect of PANI-DC content on the electrical conductivity of WBPU/PANI-DC blend films treated with (a) magnetic stirring (600 rpm/30 min/room temperature) and (b) treated with ultrasonic vibration (30 min/room temperature).

vibration treated samples was higher than those of magnetic stirring treated samples at the same PANI-DC content. The higher conductivity of ultrasonic treating based sample is primarily due to the finer particle size of PANI-DC. This finer particle of PANI-DC might make the formation of the finer network texture of conductive polymer PANI-DC in the WBPU matrix. Consequently, a finer domain size exerts effects on the blend properties via texture control. The conductivity of WBPU/PANI-DC blend films increased with increasing PANI-DC contents. However, the stable blend film was not formed when the PANI-DC content was above 34 wt%. It is indicated that the conducting path, i.e. conducting network in WBPU/PANI-DC blend, increased with increasing PANI-DC contents. The conductivities of blend film samples were measured on both sides of glasscontacted surface (G-surface) and air-exposed surface (Asurface) of blend films (see Table II). The sample WBPU/ PANI-DC34 containing maximum PANI-DC contents (34 wt%) had the highest conductivity (A-surface: 8.3×10^{-2} S/cm and G-surface: 8.0×10^{-2} S/cm). G-surface conductivity was almost same as A-surface ones. This is generally due to the homogeneous dispersion of PANI-DC domain particles in the WBPU matrix.

In order to enhance the antistaticity of WBPU coating material, aqueous dispersion of PANI-DC treated with ultrasonic vibration was used as a conductive component. The antistaticity of WBPU/PANI-DC blend films was measured using static honsetometer. The half-life time of electrostatic charge ($\tau_{1/2}$) and maximum surface electrostatic potential (V_{max}) vs. PANI-DC content are shown in Figure 9. The maximum surface electrostatic potential (V_{max}) and the half-

Table II. Designation, Composition, Conductivity, Mechanical and Dynamic Mechanical Properties of WBPU/PANI-DC Samples

Complete in the continue	Composition (wt%)	Conductiv	ity (S/cm) ^b	Tensile strength	Elongation at break (%)	
Sample designation	WBPU/PANI-DC ^a	A-surface	G-surface	(Mpa)		
WBPU/PANI-DC	100/0	2.5×10^{-12}	2.5×10^{-12}	6.60	1280	
WBPU/ PANI- DC1	99/1	3.6×10^{-7}	2.2×10^{-7}	6.20	1250	
WBPU/ PANI- DC2	98/2	4.1×10^{-6}	2.8×10^{-6}	5.70	1200	
WBPU/ PANI- DC3	97/3	7.0×10^{-5}	6.1×10^{-5}	5.22	1140	
WBPU/ PANI- DC4	96/4	1.1×10^{-4}	9.8×10^{-5}	4.90	1100	
WBPU/ PANI- DC8	92/8	9.0×10^{-4}	4.0×10^{-4}	3.93	1000	
WBPU/ PANI- DC15	85/15	3.5×10^{-3}	2.0×10^{-3}	3.30	890	
WBPU/ PANI- DC21	79/21	1.1×10^{-2}	9.0×10^{-3}	3.00	862	
WBPU/ PANI- DC26	74/26	2.4×10^{-2}	2.0×10^{-2}	2.90	840	
WBPU/ PANI- DC30	70/30	5.0×10^{-2}	4.8×10^{-2}	2.72	810	
WBPU/ PANI- DC34	66/34	8.3×10^{-2}	8.0×10^{-2}	2.60	780	
WBPU/PANI-D/H	0/100	0.7	0.7	-	_	

[&]quot;The mixture of PANI-DC/water (0.5 g/10 mL) was treated with ultrasonic vibration for 30 minutes.

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

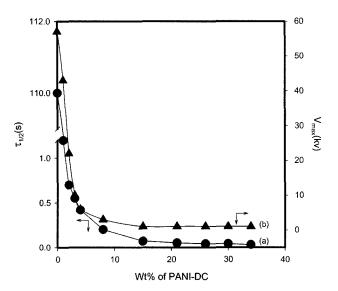


Figure 9. Effect of PANI-DC contents on the antistatic properties of WBPU/PANI-DC blend films: (a) antistatic half-life time $(\tau_{1/2}, \sec)$ and (b) surface electrostatic potential (V_{max}, kv) .

life time ($\tau_{1/2}$) of electrostatic charge for pure WBPU film were 57 kv and 110 seconds, respectively, indicating that the WBPU is a typical electrostatic material. With increasing the PANI-DC contents from 1% to 34 wt%, the maximum surface electrostatic potential (V_{max}) and the half-life time ($\tau_{1/2}$) of electrostatic charge decreased exponentially, and then approached to almost 0 second. The antistatic half-life times of blend film samples containing PANI-DC 1~8 wt% and 15~34 wt% were 1.2~0.1 seconds and almost 0 second, respectively. Generally, it is known that polymers with $\tau_{1/2}$ lower than 10 seconds are considered as materials with good antistatic properties.³⁸ The sample WBPU/PANI-DC1 containing 1 wt% of PANI-DC, which has 1.2 seconds of $\tau_{1/2}$, was found to be a good antistatic material.

Conclusions

Poly(aniline-dodecyl benzene sulfonic acid complex) (PANI-DC) with intrinsic viscosity ($[\eta]$) near 1.3 dL/g was synthesized by emulsion polymerization using aniline/DBSA/APS/water. Aqueous dispersion of PANI-DC was prepared by washing as-polymerized PANI-DC with methanol and water, followed by dispersing in water under magnetic stirring or ultrasonic vibration treatments.

The yield and conductivity of PANI-DC pellet was 41% and 0.7 S/cm, respectively. Aqueous dispersion of PANI-DC was prepared by washing as-polymerized PANI-DC with 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-DC (0.12 μ m) was smaller than that of magnetic stirring treated one (1.14 μ m). The aqueous dispersion of WBPU

was prepared by the polyaddition reaction using IPDI/PTMG/DMPA/EDA/TEA/water. The blend films of WBPU/PANI-DC with variable weight ratios (99/1~66/34) were prepared by solution blending/casting.

The effect of PANI-DC content on the mechanical property, dynamic mechanical property, hardness, electrical conductivity, and antistaticity of WBPU/PANI-DC blend films was investigated. The T_os and T_oh of pure WBPU film were -58 and 8.7 °C, respectively. These glass transition temperatures of WBPU were almost not changed with increasing PANI-DC content. The tensile strength and elongation at break of WBPU/PANI-DC blend films were decreased with increasing PANI-DC content. The hardness of WBPU/ PANI-DC blend films was decreased with increasing PANI-DC content. The electrical conductivities of the pure PANI-DC pellet and WBPU were 0.7 S/cm and 2.5×10^{-12} S/cm, respectively, indicating that the PANI-DC was a typical conductive polymer, and WBPU was a typical insulating polymer. As the PANI-DC content increased from 1 to 34 wt%, the conductivity of WBPU/ultrasonic treated-PANI-DC (particle size: $0.12 \mu m$) blend films increased from 3.6×10^{-7} S/cm to 8.3×10^{-2} S/cm. It was found that the WBPU/ultrasonic treated-PANI-DC blend film samples have higher conductivity compared with WBPU/magnetic stirring treated-PANI-DC (particle size: 1.14 µm) blend film samples at the same PANI-DC contents. The antistatic half-life time of pure WBPU film was about 110 seconds, indicating that WBPU is a typical electrostatic material. However, with increasing PANI-DC content, the antistatic half-life time of WBPU/ultrasonic treated-PANI-DC blend films is exponentially decreased from 110 seconds to almost 0 second. When the conducting polymer PANI-DC is introduced in the matrix polymer WBPU their electrical conductivity and antistaticity have exceedingly improved which may be suitable for many practical applications.

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