

## Surface Graft Polymerization of Conducting Polyaniline on Waterborne Polyurethane-Urea Film and Its Phenol Sensing

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**ABSTRACT:** Waterborne polyurethane-ureas (pristine WBPU: WBPU-19 and WBPU-24, fixed soft segment content: 60 wt %) containing dimethylol propionic acid (DMPA)/ethylene diamine (EDA) contents (19/16.8 and 24/11.4 mol %) were prepared. The polyaniline (PANI)-graft-WBPU (PANI-*graft*-WBPU) films were prepared by oxidative graft polymerization of aniline on the surface layer of WBPU films. This study focused on the effects of reaction conditions (concentrations/treating times/temperatures of aniline and APS) and DMPA content on the %grafting, conductivity, and mechanical properties of PANI-*graft*-WBPU films. To obtain the maximum %grafting (PANI-*graft*-WBPU-19: 6.2, and PANI-*graft*-WBPU-24: 7.4) and conductivity (PANI-*graft*-WBPU-19:  $3.6 \times 10^{-2}$  S/cm, and PANI-*graft*-WBPU-24:  $4.7 \times 10^{-2}$  S/cm), the optimum concentrations/treating times/temperatures of aniline and APS, were found to be 0.35M/10 min/25°C and 0.2M/10 min/0°C, respectively. The tensile strength of film samples was found to be increased in the order of PANI-*graft*-WBPU-19>pristine WBPU-19>PANI-*graft*-WBPU-24>pristine WBPU-24. The PANI-*graft*-WBPU-19 (%grafting: 6.2) films on exposure to 0–10,000 ppm phenol solutions showed a well-defined response behavior, demonstrating high promise for application in aqueous phenol sensors. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** polymer synthesis; waterborne polyurethane-urea; polyaniline; surface graft polymerization; chemical sensor

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### INTRODUCTION

Waterborne poly(urethane-urea)s (WBPU)s systems have extremely good film-forming properties because of their ionic character and the absence of dispersants. The ionic monomer DMPA of WBPU can improve mechanical properties, adhesive strength, and aqueous dispersion stability.<sup>1,2</sup>

Electrical conducting polymers have generated a tremendous interest because of their potential application in the fields of batteries, energy storage, electro-chromic devices, sensors, electromagnetic interference (EMI) shielding screens, and substitutes for metallic conductors or semiconductors in the various range of electrical devices. All conducting polymers exhibit highly reversible redox behavior with a distinguishable chemical memory and hence considered as a prominent new material for the fabrication of chemical and biological sensors. The adsorption and desorption of volatile species causes a measurable change in the resistance of conducting polymers. Conducting polymeric sensors have many advantages over other sensors. First, a wide variety of polymers are available. Second, they are readily grown by electrochemical polymerization of the monomer and thirdly, they operate at room temperature.

Among various conducting polymers, polyaniline is one of the most promising conducting materials due to its facile synthesis, low cost, remarkable environmental stability, relative high conductivity, and unique redox behavior. Unlike other conjugated polymers, polyaniline has a simple and reversible acid/base doping/dedoping chemistry enabling control over properties such as free-volume, solubility, electrical conductivity, and optical activity. It is also inexpensive and offers a high yield (>90%) of the polymerization reaction. These properties coupled with excellent room temperature stability make polyaniline a promising candidate for room temperature sensors. Therefore, conducting polyaniline has been used as a sensing material for different vapors like methanol, ethanol, acetone and benzene, and aqueous phenol. The field of molecular recognition continues to make great strides, with powerful implications for specific chemical sensor and also provides an alternative model approach for chemical identification.

Despite various advantages, pure polyaniline has received a limited application until several years ago, because the pure polyaniline is neither soluble nor fusible in organic solvents as well as water. Therefore, the solution/heat-processable polymer

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materials containing polyaniline have gradually become one of the prominent topics in the frontier of materials science. The development of PANI with better solubility in common solvents was first achieved by Cao et al.<sup>3,4</sup> They reported that the counter ion can induce processibility of the resulting polyaniline complex, by using a suitably functionalized protonate polyaniline.

The incorporation of polyaniline into an electrical insulating conventional polymer matrix has received attention due to the possibility of combining the good processability and mechanical performance of the conventional polymer with electrical and optical properties of polyaniline. These blends/composites<sup>5–11</sup> are normally obtained by in situ polymerization of aniline in the presence of the insulating flexible polymer or by mixing soluble or fusible polyaniline with other conventional or modified polymers in solution or melts. There are some other studies on the conductive polymer-coated fabrics,<sup>12</sup> polyaniline-nylon 6 composite fabric,<sup>13</sup> and polyaniline-containing filter paper.<sup>14</sup> However, polyaniline is usually immiscible when mixed with other matrix polymers, and a phase separation restricted the formation of integrated materials. If the compatibility of polyaniline/matrix polymer or substrate material is enhanced then mechanical and electrical properties would potentially increase.

The coating of different materials with conducting electroactive polymers, i.e., polyaniline, polypyrrole, polythiophene, and their derivatives, provided by means of chemical polymerization, has been reviewed by Malinauskas.<sup>15</sup> The topics covered include the deposition of conducting polymers (1) by bulk oxidative chemical polymerization, (2) by surface-located polymerization, and (3) by coating of micro- and nanoparticles. The primary bond between conducting polymer and matrix/substrate material is very attractive because of their higher performances due to higher compatibility between two components. Therefore, there are some studies on the graft polymerization of aniline on the surfaces of polypropylene-*graft*-polyacrylic acid films,<sup>16</sup> aniline-primed substrates,<sup>17</sup> modified glass,<sup>18</sup> modified Si(100),<sup>19</sup> and aminopropyl silica nanoparticles.<sup>20</sup>

In this study, we report on a novel method for grafting of polyaniline onto WBPU film surface layer. The method involves initial conversion of carboxylic acid salt groups of WBPU film into carboxylic acid groups via aqueous HCl treatment, followed by treating the WBPU having carboxylic acid groups with aniline. The carboxylic acid groups of the WBPU film are reacted with aniline containing amino group to form new salt groups by acid-base reaction. The WBPU surface layer which now contains new salt groups and excess aniline monomer is then subjected to oxidative graft polymerization of aniline monomer to result in a grafted polyaniline layer on WBPU surface layer (PANI-*graft*-WBPU), i.e., the aniline monomers absorbed in WBPU surface layer were graft copolymerized by chemical oxidative polymerization via the treatment with aqueous ammonium persulfate (APS)/HCl as an oxidant/doping acid. The method used here has the advantages of electroless polymerization, such as simple reaction setup, choice of various substrates for different applications and the ability to easily obtain a large area film.

Conducting polymers have many advantages over other sensors in that a wide variety of polymers are available and readily obtained by both chemical and electrochemical polymerization of monomers. Conducting polymers have gained popularity as competent sensing materials for various organic vapours<sup>21</sup> and hazardous gases<sup>22</sup> due to their applicability at room temperature. Few reports are available that give an account of the use of polyaniline as a sensor for alcohol vapours.<sup>23,24</sup> Phenolic compounds are pollutants of industrial wastewaters and are released into the environment during many industrial processes. Numerous biosensors, primarily based on tyrosinase have been reported for the detection of phenol compounds.<sup>25–27</sup> However, no reports are available on the studies of PANI-*graft*-WBPU as a variable resistance sensor for aqueous phenol solutions. Therefore, the polyaniline-*graft*-WBPU (PANI-*graft*-WBPU) prepared in this study was used as a chemical sensor material for aqueous phenol solutions.

In this context, this study focused on the effects of reaction conditions of graft polymerization and the DMPA content of WBPU on the %grafting [(grafted PANI weight/pristine WBPU film weight) × 100] and conductivity of PANI-*graft*-WBPU films. The thermal and mechanical properties of pristine WBPU and PANI-*graft*-WBPU films were compared, and the sensor performance of PANI-*graft*-WBPU film for aqueous phenol was also studied. Sensor response studies were carried out to see the changes in the normalized electrical resistance of the PANI-*graft*-WBPU films on exposure to different concentrations of various aqueous phenol solutions (0 ppm–10,000 ppm). The repetitive response behavior (resistance vs. time) of PANI-*g*-WBPU-19 (%grafting: 6.2) film with resistance value of 220Ω on exposing to 100 ppm aqueous phenol solution was also investigated.

## EXPERIMENTAL

### Materials

Aniline monomer (Aldrich Chemical, Milwaukee, WI) was distilled under reduced pressure prior to use. Hydrochloric acid (OCI Company, Korea), and ammonium peroxodisulfate (APS, Aldrich Chemical, Milwaukee, WI) were used without further purification. Poly(tetramethylene ether) glycol [PTMG, number average molecular weight ( $M_n$ ) = 2000 g/mol, Aldrich Chemical, Milwaukee, WI) was dried at 90°C and 1–2 mmHg for 3 h before use. 4,4'-dicyclohexylmethane diisocyanate ( $H_{12}$ MDI, Aldrich Chemical, Milwaukee, WI), tri-ethylamine (TEA, Junsei Chemical), ethylene diamine (EDA, Aldrich Chemical, Milwaukee, WI), dibutyltin dilaurate (DBTDL, Aldrich Chemical, Milwaukee, WI) as catalyst, distilled water, methyl ethyl ketone (MEK, Aldrich Chemical, Milwaukee, WI), and *N*-methyl-2-pyrrolidone (NMP, Aldrich Chemical, Milwaukee, WI) were used after dehydration with 4-Å molecular sieves for 1 day. Dimethylol propionic acid (DMPA, Aldrich Chemical, Milwaukee, WI) was dried in a vacuum oven for 5 h at 100°C.

### Preparation of WBPU and WBPU Films

Two waterborne polyurethane-ureas (WBPU) containing different DMPA and EDA contents were synthesized by using the prepolymer mixing process method (Scheme 1). PTMG was placed in a four-necked, round-bottom flask equipped with a



the reaction mixture was cooled to 40°C and distilled water was added to the mixture under vigorous stirring (1300–2500 rpm). The neutralized prepolymer was chain-extended by dropping EDA/water (1/13 = w/w) at 40°C for 1 h, and the reaction continued until the NCO peak (2270 cm<sup>-1</sup>) in the IR spectra had completely disappeared. WBPU dispersion (40 wt % solid content) was obtained by evaporation of MEK and the subsequent addition of an adequate amount of distilled water. The composition of WBPU prepared in this study is given in Table I. WBPU films were prepared by pouring the dispersion into a Teflon disk and drying under ambient conditions for 24 h, and then peeling it off from the Teflon disk. The films were vacuum dried at 60°C for 24 h under 20 mmHg to remove moisture and solvent. The vacuum dried films (typically about 0.21–0.23 mm thick) were stored in a vacuum desiccator over concentrated sulfuric acid.

### Preparation of Polyaniline-graft-WBPU (PANI-g-WBPU) Films

To convert the salt group (triethylammonium carboxylate salt groups) of DMPA into carboxylic acid group, the WBPU film was treated with aqueous HCl solution (1.5M) at room temperature for 2 h. After pad-drying with tissues, the WBPU film was dipped into aqueous aniline solutions with various concentrations (0.25–0.45M) at various temperatures (0–75°C), to add aniline monomer into the WBPU surface layer. After draining off the liquid using a paper towel, the film was dipped in a 1.5M HCl aqueous solution containing APS (various concentrations: 0.1–0.4M) at various temperatures (0–50°C) for various reaction times (0–5 h), for graft copolymerization of aniline monomer onto WBPU surface. To remove the formed hom-PANI, the PANI-g-WBPU films were washed and sonicated with distilled water and methanol thoroughly, and then dried under vacuum at 40°C for 2 days. The preparation process of PANI-g-WBPU film is presented in Scheme 1.

### Characterization

Grafting degree (%grafting) of PANI-graft-WBPU was determined by the following equation:

$$\text{Grating degree (\%)} = (W_t - W_0) / W_0 \times 100$$

where  $W_t$  is the dry weight of PANI-graft-WBPU at grafting time  $t$  and  $W_0$  is the dry weight of pristine WBPU. The weight of grafted PANI is  $W_t - W_0$ .

The chemical components of pristine WBPU and typical PANI-g-WBPU film samples were confirmed by the Fourier transform spectroscopy (FTIR 6700, Thermo scientific, USA). The FTIR spectra of the samples were recorded in the range of 4000–650 cm<sup>-1</sup> using ATR (ZnSe crystal) apparatus at a resolution of 4 cm<sup>-1</sup> and 32 scans. A constant compression load was applied to the samples.

The tensile properties were measured at room temperature using a United Data System tension meter (SSTM-1 United Data Systems, Instron, Japan) according to the ASTM D 638 specifications. A crosshead speed of 20 mm/min was used. The values quoted are the average of five measurements.

**Table I.** Sample Designation, Composition, Mechanical Properties of Samples

Sample designation	Composition (mole)						Mechanical properties				
	H <sub>12</sub> MDI	PTMG (M <sub>n</sub> = 2000)	DMPA	EDA	TEA	EDA contents (mol %/wt %)	DMPA contents (mol %/wt %)	Soft segment contents (wt %)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
WBPU-19	1.1	0.31	0.42	0.37	0.42	16.8/2.2	19/5.7	60	29	464	92.7
WBPU-24	1.1	0.32	0.53	0.25	0.53	11.4/1.4	24/7.0	60	23	507	90.3
PANI-g-WBPU-19 (%grafting: 6.2)						Reaction conditions:					
						• Aniline concentration, treating time and temperature: 0.35M, 10min and 25°C					
						• APS concentration, treating time and temperature: 0.2M, 10min and 0°C					
PANI-g-WBPU-24 (%grafting: 7.4)						Reaction conditions:					
						• Aniline concentration, treating time and temperature: 0.35M, 10min and 25°C					
						• APS concentration, treating time and temperature: 0.2M, 10min and 0°C					

Electrical conductivity of PANI/WBPU films were measured with a surface resistance detector (CMT-SR1000N, CM, Kyonggi, Korea) and the usual four-probe method. The electrical conductivity of PANI/WBPU films can be calculated by the following equation:

$$\sigma = l \cdot I / (d \cdot t) (V)$$

Where  $l$ (cm) is the distance of between the electrodes,  $I$  is the current,  $d$ (cm) is the length of film contacted with probes,  $t$ (cm) is the film thickness, and  $V$  is the voltage.

Phenol sensing experiments were performed by immersing in aqueous phenol solutions at room temperature/drying in air (40°C, 10 min) cycles along with continuous monitoring of the changing electrical resistance. Some data is presented as normalized resistance as the following equation:

$$\text{Normalized resistance}(R_n) = R_t/R_0$$

Where,  $R_0$  is the initial electrical resistance of the PANI-graft-WBPU sensor and  $R_t$  is its electrical resistance measured at  $t$  time exposing on aqueous phenol solutions.

Resistance was measured using LCR Meter (NF Corporation, Japan). The concentrations of aqueous phenol solutions tested in this study are 0, 50, 100, 500, 1000, and 10,000 ppm.

The response and recovery experiments of the aqueous phenol solution (100 ppm) were performed by immersing/drying cycles.

## RESULTS AND DISCUSSION

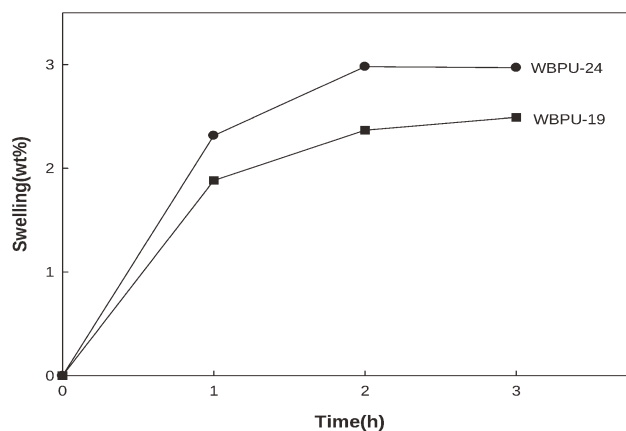
### Preparation and Composition of Pristine WBPU

The two pristine WBPU (WBPU-19 and WBPU-24) were prepared by using prepolymer mixing process method (Scheme 1), and their sample designation and composition are shown in Table I.

The soft segment content (60 wt %) and length (2000 g/mol) for WBPU-19 and WBPU-24 samples were kept constant, whereas the composition of DMPA/chain extender EDA was significantly varied: The mol % of DMPA/EDA of WBPU-19 was 19.0/16.8, and those of WBPU-24 was 24.0/11.4. The effect of DMPA/EDA content on the %grafting and properties was investigated in this study.

### Effect of Reaction Conditions on the %grafting and Conductivity of PANI-graft-WBPU

The grafting process is also shown in Scheme 1. The %grafting and conductivity of PANI-g-WBPU films can be tuned by the reaction conditions, such as the aqueous HCl treating time, concentrations of aniline and APS, reaction temperatures and reaction times. To convert the triethylammonium carboxylate salt groups of WBPU surface layer into carboxylic acid groups, aqueous HCl was treated to pristine WBPU-19 and WBPU-24 samples. Figure 1 shows the effect of treating time of aqueous HCl solution (2M) on the swelling (wt %) of pristine WBPU. The swelling% of WBPU increased with increasing aqueous HCl treating time up to about 2 h, and then leveled off. The swelling% (about 3 wt %) of WBPU-24 was higher than that (about

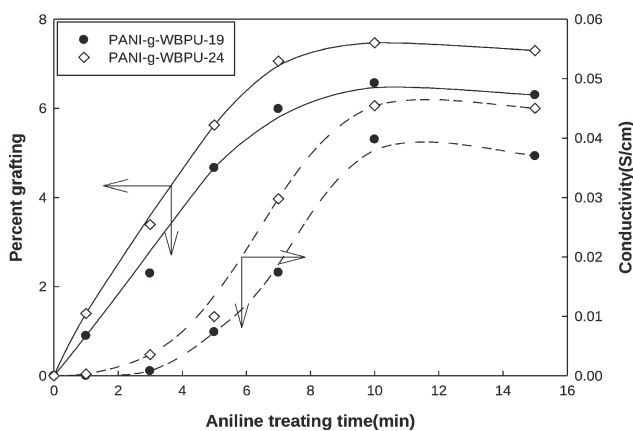


**Figure 1.** Effect of treating time of aqueous HCl solution (2M) on the swelling (wt %) of pristine WBPU.

2.4 wt %) of WBPU-19 at 2 h of aqueous HCl treating time, indicating that groups with higher salt content could absorb more aqueous HCl. It was also found that the graft polymerization of aniline occurred on the HCl-treated WBPU sample while it hardly occurred on pristine WBPU. This indicated that the absorbed aniline monomer could graft polymerize in the HCl-treated WBPU surface layer via the formation of salt groups through the reaction of carboxylic acid groups of WBPU with amino groups of aniline. However, the aniline monomer could not anchor on the unmodified surface of pristine WBPU and therefore, the polymerization of aniline almost did not appear on it. Therefore, the treating time of aqueous HCl solution (2M) was fixed at 2 h. By preliminary experiment and analysis, the optimum concentration/temperature of aniline and APS to obtain the highest %grafting and conductivity was found to be around 0.35M/25°C and 0.2M/0°C, respectively. Therefore, these conditions were also fixed when the effect of treating time of aniline and APS on the %grafting and conductivity was investigated.

The effect of the treating time of aniline on the %grafting and conductivity of WBPU-19 and WBPU-24 samples are shown in Figure 2. The %grafting and conductivity increased markedly with increasing treating time of aniline up to near 10 min, and then leveled off or decreased a little. Figure 3 shows the effect of treating time of APS on the %grafting and conductivity of WBPU-19 and WBPU-24 samples. The %grafting and conductivity also increased significantly with increasing treating time of APS up to about 10 min, and then leveled off or decreased a little. From these results, it was found that the optimum concentration/treating time/treating temperature of aniline and APS for the best %grafting and conductivity were 0.35M/10 min/25°C and 0.2M/10 min/0°C, respectively. It was also found that the best film samples [PANI-graft-WBPU-19 (%grafting: 6.2, conductivity:  $3.6 \times 10^{-2}$  S/cm) and PANI-graft-WBPU-24 (%grafting: 7.4, conductivity:  $4.7 \times 10^{-2}$ ) obtained from the optimum conditions seemed to have an almost smooth surface of greenish color, but SEM observation showed multiple layers of cloud-shaped grafted-PANI on the WBPU-19 surface layer (see Figure 4).



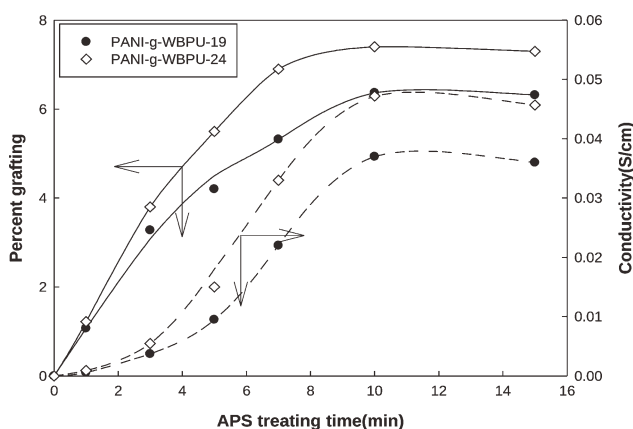


**Figure 2.** Effect of aniline reacting time on the percent grafting and conductivity of PANI-g-WBPU (The fixed concentration and temperature of aniline: 0.35M and at 25°C. The fixed concentration, treating time, and temperature of APS: 0.2M, 10 min, and 0°C.).

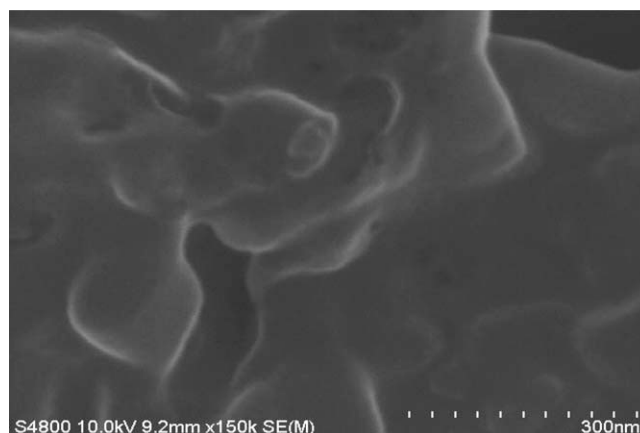
### Characterization Using FTIR Spectrometer with ATR Apparatus

The FTIR spectra of pristine samples (WBPU-19 and WBPU-24) films and grafted samples [PANI-*graft*-WBPU-19 (%grafting: 6.2) and PANI-*graft*-WBPU-24 (%grafting: 7.4)] films are shown in Figure 5. The characteristic IR peaks, such as the N–H stretching vibration peak near 3321  $\text{cm}^{-1}$  and the C=O peak near 1707  $\text{cm}^{-1}$  were attributable to the urethane-urea groups in pristine WBPUs. The characteristic peaks are 1303  $\text{cm}^{-1}$ , 1481  $\text{cm}^{-1}$ , and 1577  $\text{cm}^{-1}$  which were assigned to C–N stretching of secondary amine of PANI backbone, C=C stretching vibration of benzenoid ring, and C=C stretching vibration of quinoid ring, respectively. The PANI-*graft*-WBPU film samples had both two characteristic peaks of WBPU/PANI, indicating the presence of PANI in WBPU surface layer.

Infrared spectrometer was used to evaluate the different kinds of hydrogen-bonded carbonyl groups. The spectra were analyzed with a curve-resolving technique based on linear-

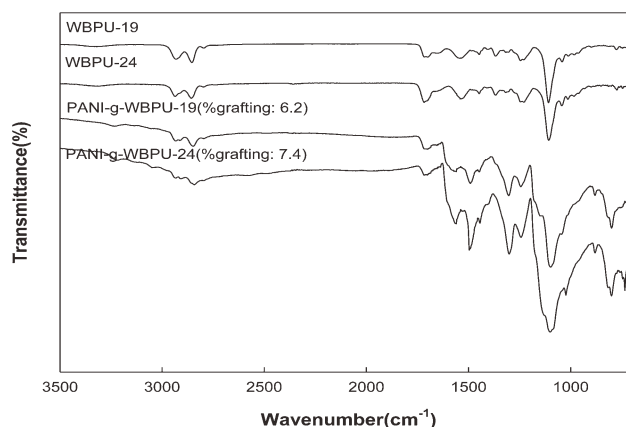


**Figure 3.** Effect of APS treating time on the percent grafting and conductivity of PANI-g-WBPU (the fixed concentration, treating time, and temperature of aniline: 0.35M, 10 min, and 25°C. The fixed concentration and treating temperature of APS: 0.2M and 0°C).

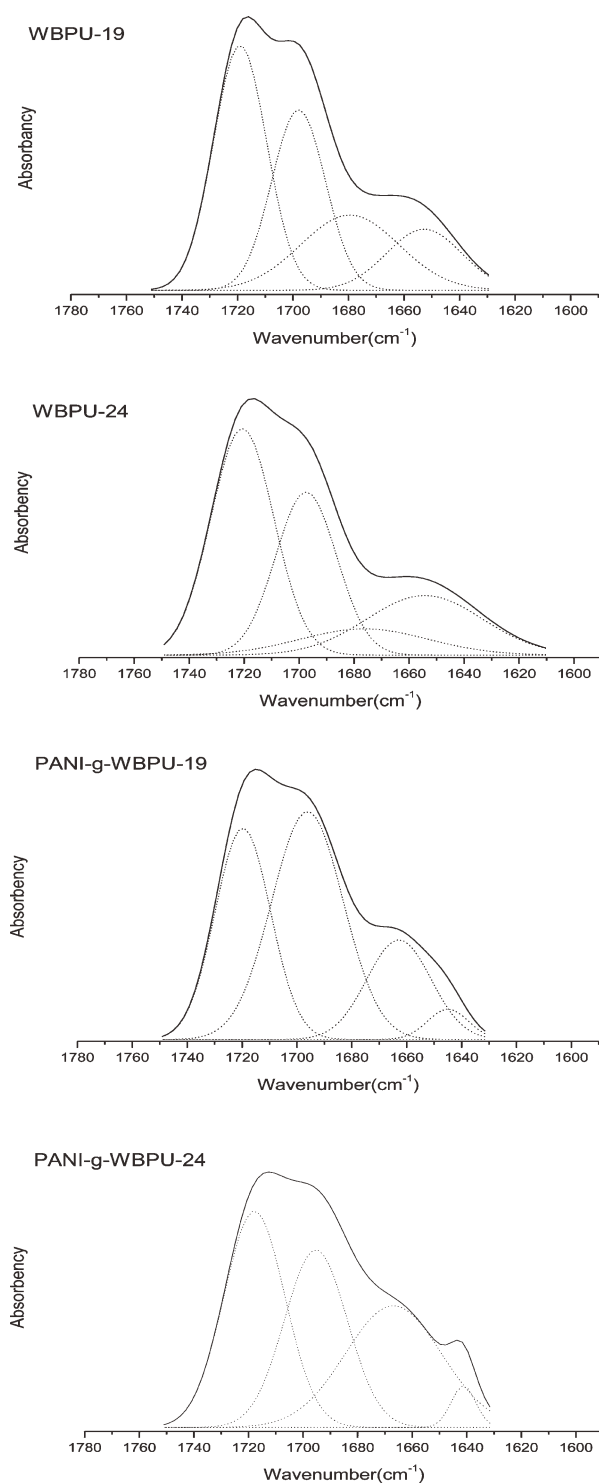


**Figure 4.** SEM image of PANI-g-WBPU-19 (%grafting: 6.2).

squares analysis to fit the combination of Lorentzian and Gaussian curve shapes. Curve fitting of the C=O stretching region was performed for pristine WBPUs (WBPU-19 and WBPU-24) and grafted samples [PANI-*graft*-WBPU-19 (%grafting: 6.2) and PANI-*graft*-WBPU-24 (%grafting: 7.4)]. Figure 6 shows the decomposition of C=O stretching for WBPU-19, WBPU-24, PANI-*graft*-WBPU-19 (%grafting: 6.2) and PANI-*graft*-WBPU-24 (%grafting: 7.4) samples. The peak frequency and fraction of the free, disordered and ordered hydrogen-bonded carbonyl groups, and DMPA carboxylic acid group for the samples are presented in Table II. The total fraction of the carbonyl groups participating in hydrogen bonding is expressed as  $X_B = C_B/C_T$  where  $C_T$  is the total peak area of carbonyl groups and  $C_B$  is the peak area of hydrogen-bonded carbonyl groups. From these results, it was found that the  $X_B$  of WBPU-19 was higher than that of WBPU-24. The higher hydrogen bonding fraction of WBPU-19 might be due to the higher urea groups via higher EDA/lower DMPA contents of WBPU-19 than WBPU-24. By comparing WBPU-19 and PANI-*graft*-WBPU-19 (%grafting: 6.2), WBPU-24 and PANI-*graft*-WBPU-24 (%grafting: 7.4), the grafted samples [PANI-*graft*-WBPU-19 (%grafting: 6.2) and PANI-*graft*-WBPU-24 (%grafting: 7.4)] were found to have



**Figure 5.** FTIR spectra of WBPU-19, WBPU-24, PANI-WBPU-19 (%grafting: 6.2), and PANI-g-WBPU-24 (%grafting: 7.4) film samples obtained by FTIR spectrometer using ATR apparatus.



**Figure 6.** Decomposition of C=O stretching for WBPU-19, WBPU-24, PANI-g-WBPU 19 (%grafting: 6.2), and PANI-g-WBPU-24(%grafting: 7.4) film samples.

lower free carbonyl group fraction and higher hydrogen-bonded carbonyl group fraction ( $X_B$ ) than those of pristine WBPU (WBPU-19 and WBPU-24). This might be due to the contribution of NH group of grafted PANI to the hydrogen bonding. The fraction of DMPA carboxylate groups showed a distinct

decrease when the grafting occurred. This should be attributed to the blocking of DMPA carbonyl group by enveloping them with grafted PANI. It was also found that the hydrogen-bonded C=O peak position and DMPA carboxylate peak position were shifted toward lower frequencies when the grafting happened. The grafting of PANI onto WBPU was found to be affected the hydrogen-bonding state and content. The higher  $X_B$  of grafted WBPU samples compared to pristine WBPU may induce the higher tensile strength of grafted WBPU samples described later.

#### Dynamic Mechanical Analysis

The chain extender EDA in WBPU made symmetrical urea groups, meanwhile DMPA having two different side chains formed bulky and unsymmetrical urethane groups. It is generally accepted that the urea group of EDA component has higher polarity and symmetry than the urethane group of DMPA component. The mechanical properties of WBPU are dependent on the polarity and symmetry of their structures. The temperature dependence of the dynamic storage modulus and loss  $\tan \delta$  of the pristine WBPU films and PANI-g-WBPU films are shown in Figure 7. The storage modulus of WBPU-19 was higher than that of WBPU-24. This might be due to the higher EDA content of WBPU-19 sample than WBPU-24. The soft segment  $T_g$  (the peak temperature of loss  $\tan \delta$ ) increased in the order of PANI-g-WBPU-24 > WBPU-24 > PANI-g-WBPU-19 > WBPU-19. From this result, it was found that the soft segment  $T_g$  of WBPU increased with increasing %grafting and DMPA content. This is considered to be due to the incorporation of higher bulky DMPA unit into soft segment PTMG region when larger amount of DMPA component was used.

#### Mechanical Properties and Hardness of Pristine WBPU and PANI-g-WBPU Films

Strain-stress curves of pristine WBPU-19/WBPU-24 and PANI-g-WBPU-19 (%grafting: 6.2)/PANI-g-WBPU-24 (%grafting: 7.4) films are shown in Figure 8. The mechanical properties and hardness are shown in Table I. The tensile strength of the pristine WBPU-19 having lower DMPA/higher EDA content was higher than that of the pristine WBPU-24 containing higher DMPA/lower EDA. The higher tensile strength of pristine WBPU-19 than pristine WBPU-24 might also be due to the higher polar and symmetrical urea groups attributable to higher content of EDA. Generally, the tensile strength of samples (fiber and film samples) falls when the samples are chemically treated. However, in this research, the chemically treated sample (PANI-graft-WBPU) films had higher tensile strength than their pristine WBPU films. The higher tensile strength of grafted samples should be attributable to the inter-knotting action of grafted PANI chains and the increase of hydrogen bonding fraction ( $X_B$ ). The tensile strength of samples increased in the order of PANI-g-WBPU-19 > pristine WBPU-19 > PANI-g-WBPU 24 > pristine WBPU-24. However, the elongation at break increased in the order of PANI-g-WBPU 24 > pristine WBPU-24 > PANI-g-WBPU-19 > pristine WBPU-19. The elongation at break of WBPU-24 was higher than that of WBPU-19. The higher elongation at break of WBPU-24 might be due to not only the lower urea group content but also the higher bulky texture obtained by using higher bulky DMPA content instead of EDA. It was also found that the elongation at break rose

**Table II.** Decomposition Results of the C=O Stretching

Sample designation	Peak position (cm <sup>-1</sup> )					Fraction of peak area				X <sub>B</sub> <sup>a</sup> (fraction)
	Peak (max)	Free carbonyl group	Disordered H-bonded C=O	Ordered H-bonded C=O	Carbonyl group of DMPA	Free carbonyl group	Disordered H-bonded C=O	Ordered H-bonded C=O	Carbonyl group of DMPA	
WBPU-19	1713	1720	1701	1679	1652	0.37	0.28	0.22	0.13	0.50
WBPU-24	1718	1721	1697	1676	1653	0.41	0.27	0.15	0.17	0.42
PANI-g-WBPU-19	1713	1719	1696	1662	1645	0.29	0.44	0.22	0.05	0.66
PANI-g-WBPU-24	1712	1717	1695	1666	1641	0.35	0.30	0.28	0.07	0.58

<sup>a</sup>X<sub>B</sub> = C<sub>B</sub>/C<sub>T</sub>, where C<sub>T</sub> is the total peak area of carbonyl groups and C<sub>B</sub> is the peak area of hydrogen-bonded carbonyl groups.

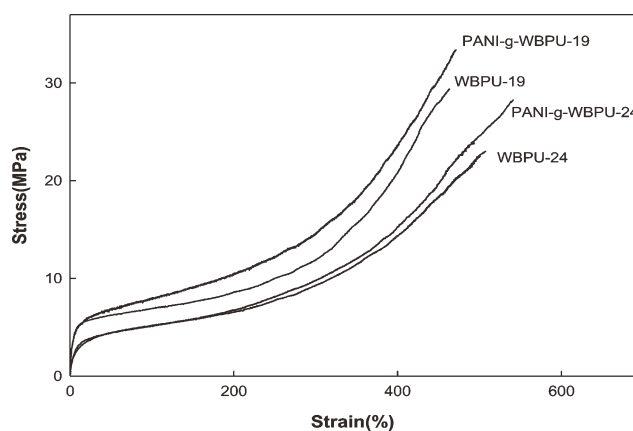
when grafting took place. This should be attributed to the easier movement of segments by incorporating grafted PANI into the segments. The hardness of WBPU-19 was a little higher than that of WBPU-24. The increase of hardness of grafted materials was found to be very small. This means that the chemical structural change of WBPU and PANI-graft-WBPU was not large enough to significantly affect the hardness result.

### Sensor Property of PANI/WBPU Films

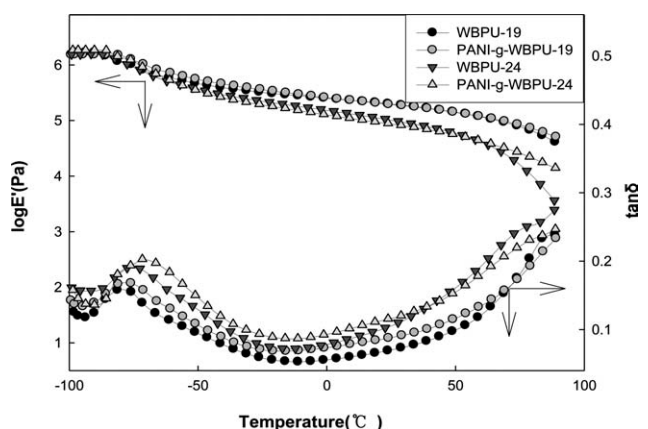
Sensor response studies were carried out to see the changes in the normalized electrical resistance of the PANI-graft-WBPU films on exposure to different concentrations of aqueous phenol solutions (0, 50, 100, 1000, 10000ppm). As the exposing (dipping) time increased, the normalized resistance of PANI-g-WBPU films in various aqueous phenol solutions decreased markedly and then leveled off after around 120 seconds of exposing time. The normalized resistance of PANI-graft-WBPU film decreased significantly and then leveled off with increasing aqueous phenol concentration from 0ppm to 10000ppm (see Figure 9). The well-defined response behavior of the PANI-graft-WBPU films on exposure to various phenol solutions demonstrates a remarkable potential for phenol sensor applications.

The oscillatory dipping in aqueous phenol solution was also conducted to investigate whether the responses to the aqueous phenol solution (100 ppm) were reversible and to examine how

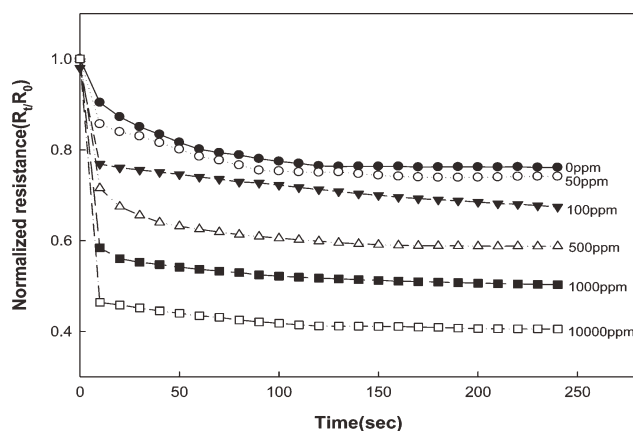
fast the PANI-graft-WBPU film could respond to the stimuli. The changes in resistance were monitored as a function of time as the films were dipped into the aqueous phenol solution and then dried. Figure 10 shows repetitive response behavior (resistance vs. time) of PANI-g-WBPU-19 (%grafting: 6.2) film with resistance value of 220 Ω on exposing to 100 ppm aqueous phenol solution. The resistance value continues to decrease with further exposure of PANI-g-WBPU film to the aqueous phenol



**Figure 8.** Stress–strain curves of WBPU-19, WBPU-24, PANI-g-WBPU-19 (%grafting: 6.2), and PANI-g-WBPU-24 (%grafting: 7.4) film samples.

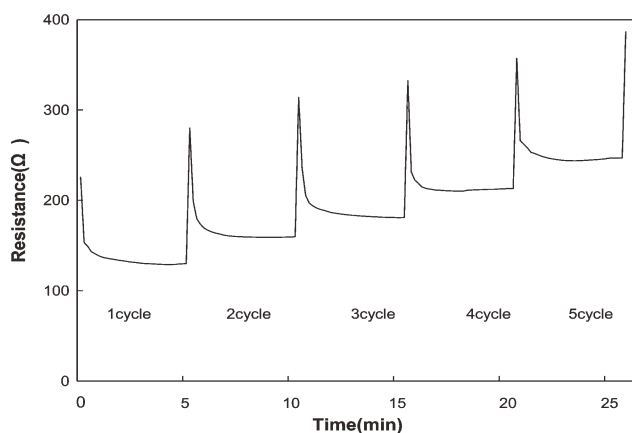


**Figure 7.** Storage modulus ( $E'$ ) and  $\tan \delta$  of WBPU-19, WBPU-24, PANI-g-WBPU-19 (%grafting: 6.2), and PANI-g-WBPU-24 (%grafting: 7.4) film samples.



**Figure 9.** Normalized resistance of PANI-g-WBPU-19 (%grafting: 6.2) on various phenol concentrations.





**Figure 10.** Repetitive response curves of PANI-g-WBPU-19 (%grafting: 6.2) on exposing to 100 ppm phenol solution.

solution (exposing of PANI-g-WBPU film to aqueous phenol concentration 100 ppm, followed by keeping it in 40°C for 10 min and then noting its original resistance value constitute a single cycle for response study). The same process was done repeatedly and the change in resistance for second, third, fourth, and fifth cycles were observed as shown by response cycle curves in Figure 10. It was observed that after each cycle, the resistance value never came back to its original value and stayed higher than the original level. However, sensor resistance showed little variation across all cycles. This means that the PANI-*graft*-WBPU materials prepared in this study could be used multiple times as a chemical sensor material. We found that PANI-g-WBPU-19 (%grafting: 6.2, conductivity:  $3.6 \times 10^{-2}$  S/cm) and PANI-g-WBPU-14 (%grafting: 7.4, conductivity:  $4.7 \times 10^{-2}$  S/cm) displayed the same trend of phenol sensing. 1.2% of difference in %grafting induced differences in conductivity ( $1.1 \times 10^{-2}$  S/cm) and resistance but did not cause any fundamental difference in phenol sensing.

## CONCLUSIONS

In this study, waterborne polyurethane-urea (WBPU: soft segment content: 60 wt %) were prepared from H<sub>12</sub>MDI as an aliphatic diisocyanate, PTMG (2000 g/mol) as a soft segment, EDA (16.8 and 11.4 mol %) as a chain extender, and DMPA (19 and 24 mol %) as an ionic diol. Preparation of polyaniline (PANI)-*graft*-WBPU films was successfully conducted by oxidative polymerization of aniline on the surface layer of WBPU films using oxidant ammonium persulfate (APS) as an initiator. The relationships between graft percentage and experimental conditions, such as the concentrations/treating time/temperature of aniline and APS, were extensively investigated. The effect of DMPA/EDA composition on the percent grafting, conductivity and properties was also studied. The %grafting and conductivity rose with longer reaction times of aniline and APS and then leveled off. The maximum %grafting (PANI-*graft*-WBPU-19: 6.2), and (PANI-*graft*-WBPU-24: 7.4) and conductivity (PANI-*graft*-WBPU-19:  $3.6 \times 10^{-2}$  S/cm, and (PANI-*graft*-WBPU-24:  $4.7 \times 10^{-2}$  S/cm) were obtained when concentrations/treating times/temperatures of aniline and APS were 0.35M/10 min/25°C and 0.2M/10 min/0°C, respectively. The pristine WBPU-19 with

lower DMPA/higher EDA recorded higher tensile strength than the pristine WBPU-24 carrying higher DMPA/lower EDA. Tensile strength of the PANI-*graft*-WBPU films exceeded that of the pristine WBPU films. Sensor response study was carried out to see the changes in the normalized electrical resistance of the PANI-*graft*-WBPU-19 films on exposure to various aqueous phenol solutions (0 ppm ~ 10,000 ppm). The normalized resistance of PANI-*graft*-WBPU films decreased markedly and then leveled off after around 120 s of exposing time. To investigate whether the responses to the aqueous phenol solution were reversible and to examine how fast the PANI-*graft*-WBPU film could respond to the stimuli, the oscillatory dipping in aqueous phenol solution (100 ppm, ~ fifth cycles) was also conducted. It was found that after each cycle, the resistance value never came back to its original value and stayed higher than the original level, however, sensor resistance showed little variation across all cycles. The PANI-g-WBPU-19 films exhibit a distinct response behavior, which testifies to their high potential for application as phenol sensors.

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