

# Dodecylbenzene Sulfonic Acid/Hydrochloric Acid Co-doping System을 이용한 Polyaniline 합성 및 Polyaniline/Waterborne-Polyurethane 블렌드에 관한 연구

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## Preparation and Properties of Polyaniline Co-doped with Dodecyl benzenesulfonic Acid/Hydrochloric Acid and Its Blend with Waterborne-Polyurethane

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### 1. Introduction

Conducting polymers are finding increasing number of applications in various electronic devices such as chemical sensors, electrochromic display, light emitting diodes, etc. Polyaniline(PANI) ranks among highly prospective conduction polymers. PANI was first synthesis in 1862[1] and has been extensively studied as a conducting polymer since the 1980s[2]. The side range of electrical, electrochemical and optical properties coupled with good environmental stability makes PANI potentially attractive for application as an electronic material. It can be obtained in several forms with different structures of the repeat unit, depending on the synthesis conditions. The emeraldine base constitutes a form of PANI, which after protonation provides the highest electrical conductivity[3]. However, in spite of various advantages, PANI is neither soluble nor fusible in organic solvents as well as water. Consequently, finding a procedure to prepare a soluble PANI has remained an interesting goal.

Recently, several methods have been developed to improve the processibility of PANI by increasing its solubility in various solvents. (1) By postprocessing, which involves (a) neutralization of the emeraldine salt to form the emeraldine base and (b) the protonation of the latter base with a second protonic acid. Cao et al.[4,5] reported that the PANI doped with dodecylbenzenesulfonic acid(DBSA) or camphor sulfonic acid became soluble in various organic solvents such as chloroform and xylene. This procedure could be used to fabricate a flexible light-emitting diode(LED)[6]. (2) By grafting copolymerization of aniline onto a modified polymeric surfactant[7] or by using a polymeric acid such as polystyrene sulfonic acid as template for the oxidative polymerization[8]. These approaches significantly improved the processibility of PANI. (3) By introducing some substituents such as alkyl groups[9] and sulfonic acid groups[10] onto the backbone of PANI. These groups allowed the undoped and doped forms of PANI to become soluble in some common organic solvents and even water. In addition, a soluble doped PANI was prepared via emulsion polymerization method.

The typical polymerization of aniline in a HCl aqueous solution results in an un-processible PANI, whose conductivity is in the range from very small to 10 S/cm. A PANI with improved

processibility was synthesized via the polymerization in an aqueous solution of DBSA aniline salt[11].

In the present paper, the chemical oxidative polymerization of aniline dodecyl benzenesulfonic acid(PD) and aniline hydrochloride acid(PH) salts was investigated. This pathway was selected, because one expects the PD salt moieties of the polymer to enhance its solubility, hence the processibility, while the PH salt moieties to provide a good conductive structure for the resulting polymer. Blends of conducting polymer and waterborne-polyurethane(WPU) were produced from aqueous dispersion of both components. For this study, WPU was chosen because of its excellent processibility, non-toxic, adhesion to various substrates, and good mechanical property. Although solution blend is very popular to obtain conducting polyblend films, it has not been explored in WPU-based conducting blends. These are composed of electrically conducting particles of micrometer size dispersed in an insulating polymer matrix. Such materials still maintain most of the electrical conductivity inherent to PANI. Moreover their preparation provides an additional control over mechanical and useful properties of products based on PANI. The effect of blend ratio on the electrical conductivity, morphology, and mechanical property of PH-PD/WPU blend were investigated.

## 2. Experimental

### 2.1. Materials

Aniline(Aldrich, 99%) was distilled under reduced pressure prior to use. DBSA(Aldrich, 99%), hydrochloric acid(Aldrich, 35%), ammonium peroxodisulfate(APS, Aldrich, 99%), dibutyl tin dilaurate(DBTDL, Aldrich, 99%) and methanol(Aldrich, 99%) were used as received. Isophorone diisocyanate(IPDI, Aldrich, 98%), triethylamine(TEA, Sigma, 99%), ethylene diamine(EDA, Aldrich, 99%), methyl ethyl ketone(MEK, Sigma, 99%) and N-methyl-2-pyrrolidone(NMP) were used after dehydration with 4Å molecular sieves for one day. Poly(tetramethylene oxide)glycol(PTMG, Unin Carbide,  $M_n=2,000$ ) was dried over calcium hydride at room temperature for 24hours. Dimethylol propionic acid(DMPA, Aldrich) were dried in a vacuum oven(100°C) for at least 5 hours.

### 2.2. Synthesis of PH-PD

To prepare a polymer based on PD and PH, aniline(1.86g) was added with stirring to a flask(located in an ice bath) containing distilled water(80g), DBSA and HCl in a selected molar ratio with a molar ratio of aniline/(DBSA+HCl)=1. APS(1.2g) was dissolved into 20g distilled water and then added slowly to the aniline solution with stirring for 1 h at 0°C. This was followed by stirring for 1.5 h at room temperature. The polymer was precipitated with methanol, washed with distilled water several times and then dried in vacuum at about 50°C for 24 h. The product was weighed for the determination of the yield.

### 2.3. Synthesis of WPU

DMPA was dissolved in NMP(50/50 w/w) in a 4 necks round-bottom flask equipped with a thermometer, a stirrer, an inlet of dry nitrogen, a condenser, and a heat jacket. Then PTMG was placed in the flask and degassed under vacuum at 80°C until the theoretical NCO- terminated prepolymer mixture to adjust the suitable viscosity of solution. And then TEA was added to the reaction mixture for neutralizing the carboxyl groups of the NCO-terminated PU prepolymer. After 30min of neutralization reaction, distilled water was added to the reaction mixture. The neutralized prepolymer was chain-extended by dropping EDA at 40°C and the reaction continued until NCO absorption peak in IR spectra had completely disappeared. All the aqueous dispersions(40wt% solids) were obtained by evaporating MEK and then by adding the adequate amount of water.

### 2.4. Blend preparation

The PH-PD complex(0.5g) was added to water(10g) and treated with ultrasonic vibration for

30min. The PH-PD aqueous dispersion was added to the PU aqueous dispersion at various amounts in order to obtain the desired composition. The mixed solutions were magnetic stirred for 1 h. Blend films were prepared by casting these blend solutions on teflon plates at 50°C for 24 h.

### 2.5. Characterization

Particle size of PH-PD complex was done using Particle size Analyzer(Galai Production Ltd.) and light-scattering equipment (Autosizer, Melvern IIC). The transmittance of the PH-PD complex was recorded in a Shimadzu UV-1601 spectrophotometer. Electrical conductivity of the PH-PD pellet and blends were measured by using a Surface Resistance Detector and the usual four-probe method. In the case of pure PH-PD complex, the electrical conductivity was measured on dried pressed pellets.

## 3. Results and discussion

The UV absorption spectra of the synthesized polymer for different PH-PD ratio in the feed are presented in Figure 1. They exhibit three absorption peaks: an absorption at 350 nm corresponding to the  $\pi$ - $\pi^*$  transition of the benzenoid ring[11], and two absorption peaks at about 430 and 800 nm, which can be assigned to the polaron band transitions. These three peaks constitute a typical emeraldine salt spectrum.

The particle size of the synthesized polymer for PH-PD molar ratio in 6:4 are presented in Figure 2(untreated) and 3(treated with ultrasonic vibration). The particle size of PH-PD increased with drying time. Figure 4 and 5 shows the mean particle size of PH-PD molar ratio in the feed before and after ultrasonic treatment as a function of drying time. PH-PD particle size of both systems was increased proportionally with increasing drying time. The particle size of PH-PD treated with ultrasonic vibration was significantly smaller than that of PH-PD.

The maxima in the conductivity and yield can be explained by taking into account the aggregation of PD complex induced by its hydrophobic hydrocarbon chains. A high local concentration of aniline is thus generated, which tends to increase the polymerization rate. However, at large PH-PD molar ratio, the PD aggregates generate a "gel-like" structure. The polymerization rate of PH-PD complex and molecular weight of the polymer are affected by the slow diffusion of the oxidant in the gel. For low PH-PD molar ratio, the extent of aggregation is smaller, but the diffusion of the oxidant is gradually intensified. The effect of PH-PD molar ratio in the feed on the conductivity and yield of the resulting polymer are shown in Figure 6. With increasing PH-PD molar ratio, both the conductivity and yield first increase and then decrease, passing through a maximum conductivity of 7.25 S/cm and a maximum yield of 32.5 % at a molar ratio of about 6:4. The conductivity of the polymer is comparable to that of the insoluble HCl doped PANI compressed pellet, but much larger than that of PD alone[11].

## 4. References

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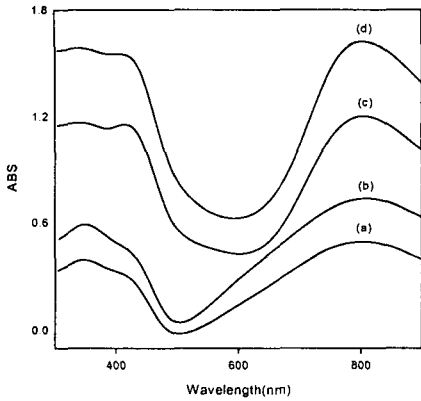


Figure 1. UV-spectra of AH-AD dispersion : AD-AH molar ratio (a) 2:8 (b) 3:7 (c) 4:6 (d) 5:5

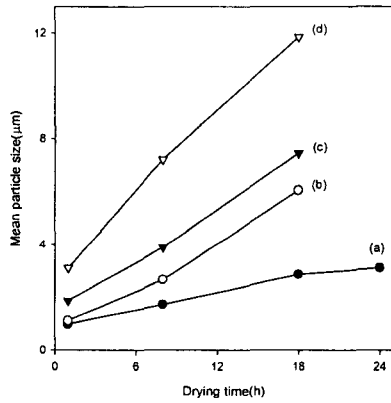


Figure 2. The mean particle size of PH-PD : PH-PD molar ratio (a) 2:8 (b) 3:7 (c) 4:6 (d) 5:5

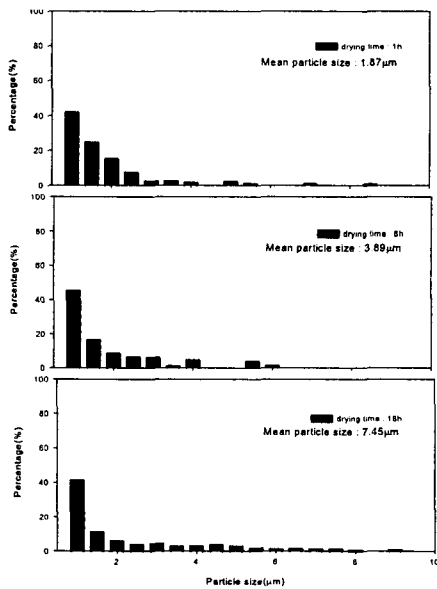


Figure 4. Probability number density graphs for PH-PD (molar ratio 4:6) dried at various time

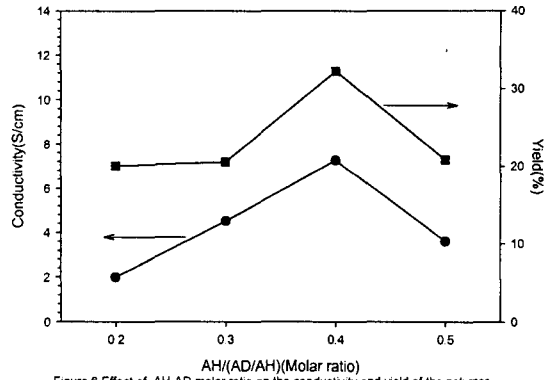


Figure 6 Effect of AH-AD molar ratio on the conductivity and yield of the polymer

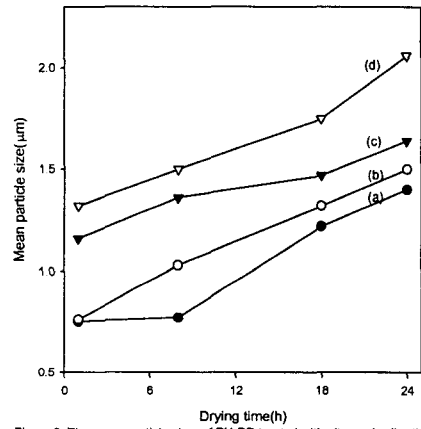


Figure 3. The mean particle size of PH-PD treated with ultrasonic vibration : PH-PD molar ratio (a) 2:8 (b) 3:7 (c) 4:6 (d) 5:5

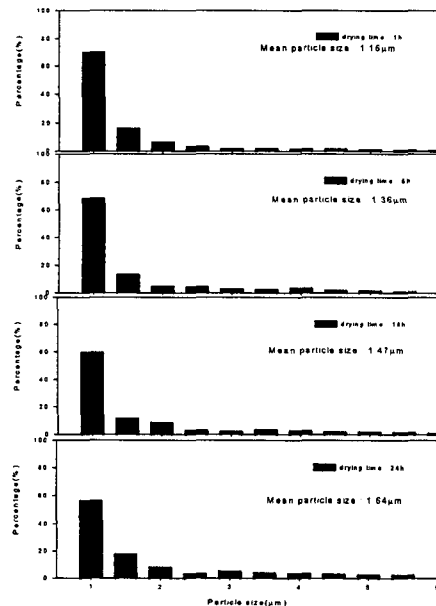


Figure 5. Probability number density graphs for PH-PD (molar ratio 4:6) dried at various time and treated with ultrasonic vibration