

Water soluble polyaniline/polysaccharide composite: Polymerization, carbonization to yield carbon micro-bubbles



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ABSTRACT

We report synthesis of water soluble polyaniline composite using polysaccharide, alginic acid, by oxidative chemical polymerization. Spectroscopy measurements for the composites with infrared (IR), UV–vis spectroscopy, electron spin resonance (ESR), and scanning electron microscopy (SEM) were carried out. We confirmed water solubility of the composite and carbonization allowed the composite to form carbon micro-bubble structures.

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1. Introduction

Conducting polymers [1] have raised great interest because of their many possible applications [2]. Among them, polyaniline (PANI) has been also carried out on many studies such as polymerization mechanism, reversibility in the doping/dedoping process, and chemical stability [3–7]. Many kinds of polyaniline composites with organic/inorganic acid [2,8–11], minerals [12–14], or metals [15,16] have been reported about their properties (i.e. dichroism, solubility in various solvents, formation of fiber/tube/sphere nano structures [17,18]). Besides, carbonized polyaniline has been studied [19]. Polyaniline maintains the fine structure after carbonization. Recently, conjugated polymer composite using shizophyllan (β -1,3-glucan) for wrapping onto the polymer chain has been reported [20]. The composite material shows unique properties. Here, we report synthesis and carbonization of polyaniline composites using alginic acid.

2. Experimental

2.1. Materials

Aniline (Wako Chemical, Japan) was purified by distillation. Alginic acid, N-methylpyrrolidone (NMP) (Tokyo Chemical Industry, Japan), ammonium persulfate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$) (Kanto chemical, Japan) were used as received.

2.2. Instruments

Infrared (IR) absorption spectra for the polymers were obtained using a JASCO IR 550 Fourier transform spectrometer (Japan) with the KBr method. Ultra visible (UV–vis) spectra were recorded on a JASCO V-630 spectrophotometer. Electron spin resonance (ESR) measurements were carried out using a JEOL JES TE-200 (Japan) spectrometer with 100 kHz modulation. Scanning electron microscopy (SEM) observations and energy dispersive X-ray spectrometry (EDS) were performed with a JEOL JSM-521 (Japan).

2.3. Preparation of polyaniline composites

Aniline (1 g, 11 mmol) and alginic acid (0.5, 1, 1.5 g) were added to distilled water (100 mL) in an Erlenmeyer flask. The solution was stirred for 3 h and cooled to 0 °C. Then, APS (1.2 g, 5.3 mmol) was

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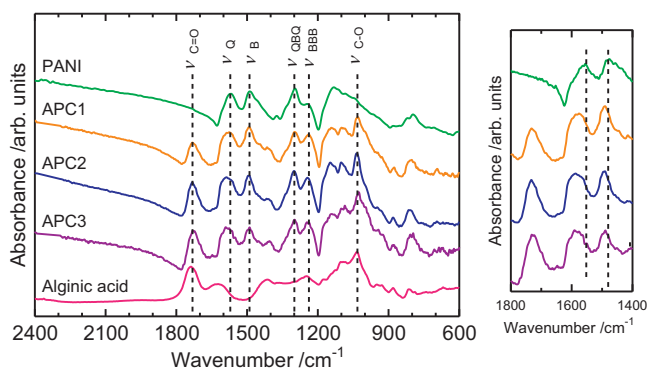


Fig. 1. Infrared (IR) spectra of polyaniline (PANI) and three types of compounds.

added into the flask, and stirred further 48 h at 0 °C. The mixture was filtered, and washed with a large volume of water/methanol in several times. After filtration, the cake like compounds was collected and dried in a vacuum for 6 h. We obtained three samples with different of PANI/alginate acid ratio. The composites are abbreviated as APC.

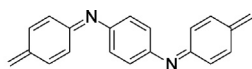
2.4. Carbonization of polyaniline composite

Carbonization of the composites was carried out under argon flow for 1 h at 900 °C. Yield of carbonized PANI was 44% and carbonized APC 1, APC 2, and APC 3 were 32, 22, and 31%, respectively.

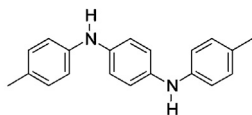
3. Results and discussion

3.1. IR absorption spectra

Fig. 1 shows IR spectra of as prepared PANI (H_2SO_4 doped) and the APC 1–APC 3. The polyaniline shows some characteristic bands at 1552 cm^{-1} (ν_Q) and 1473 cm^{-1} (ν_B), which are ascribed to C=C stretching vibration of quinonoid (Q) and benzenoid (B) structures. The absorption bands at 1300 cm^{-1} (ν_{QBQ}) and 1240 cm^{-1} (ν_{BBB}) are due to C–N stretching absorption of QBQ and BBB structures, respectively [21]. Moreover, the absorption bands at 1730 cm^{-1} ($\nu_{C=O}$) and 1033 cm^{-1} ($\nu_{C=O}$) are assigned to carboxyl group and glycoside bond of alginate acid, respectively. Absorption bands at long wavelength are well known as characteristic bands of PANI.



QBQ structure 1 (Q = quinonoid, B = benzenoid)



BBB structure 2

The series of APCs show the characteristic bands. The composites show absorption bands at 1577 cm^{-1} (Q) and 1489 cm^{-1} (B), in place of 1552 cm^{-1} (Q) and 1473 cm^{-1} (B) of the pure PANI. The absorption bands shift can be due to transformation of quinonoid rings to a more benzenoid rings [22]. Because carboxyl group of alginate acid can play a role of dopant additionally [23]. In general, nitrogen atom of polyaniline is doped with sulfate ion, this can be referred to as primary doping. However, in this research, the PANI is doped by both sulfuric acid and alginate acid. In other words, double doping for polyaniline is occurred in this case. The

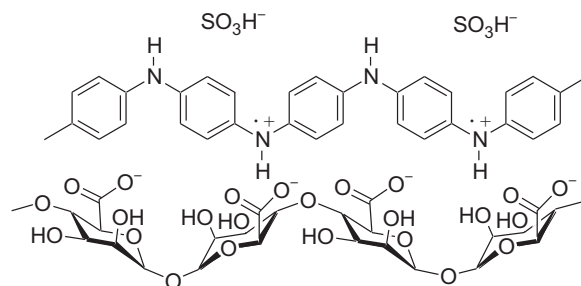


Fig. 2. Composite structure. Cations of polyaniline interacts with anions of alginate acid.

double doping allows the PANI to form the emeraldine salt in the composite (Fig. 2). On the other hand, intensity ratio of the two bands ($1577\text{ cm}^{-1}/1489\text{ cm}^{-1}$) is slightly increased with the amount of alginate acid in the APCs. These results indicate that the material thus synthesized is a form of composite of PANI and alginate acid, and have electronic interaction between PANI and alginate acid in the composites.

3.2. UV–vis spectra

Fig. 3 displays UV–vis spectra of the PANI and the composites in NMP solution. The absorption band at 325 nm is due to π – π^* transition of benzene ring, and the absorption band at 627 nm is ascribed to doping band derived from quinonoid structure. A series of the absorption spectra of the APCs in NMP solution showed doping band at around 620 nm (Fig. 3). On the other hand, the APCs in water solution (Fig. 4) show different absorption bands from the absorption bands in the NMP. The solubility of the composite in water is better than that in organic solvent (Supporting information, Tables S4 and S5). In addition, previous researches reported optical absorption of dependency on pH values [24,25]. Wan proposed that the absorption of doping band from quinonoid structure gradually decreases with increasing acidity (pH 4 to 1) [24], by contrast, a new absorption band appears at low energy region (long wavelength). Stejskal et al. [25] reported that a protonated form of PANI displays three absorption bands at around 350 , 430 , and 810 nm under a low pH condition. These results can be related with acid doping to the PANIs. In the present research, the doping can be enhanced by the alginate acid in the water (Fig. 4). Intrusion of water between the polyaniline and alginate acid promotes ionization and extension of the distance between the two polymers, resulting good solubility of the composite and good static interaction between polyaniline and alginate acid (Fig. 5). The extension

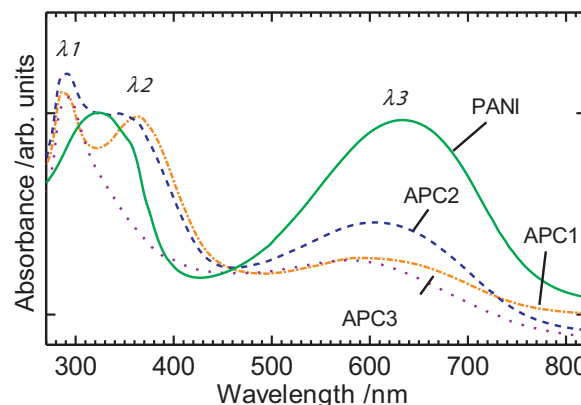


Fig. 3. UV–vis absorption spectra of pure PANI and the series of APCs in NMP solution (0.05 g/L). NMP = N-methylpyrrolidone.

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