

Chemical Polymerisation of Aniline in the Presence of Sericin

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ABSTRACT

A series of polyaniline/sericin composites were prepared by oxidative polymerisation of aniline in the presence of sericin. The preparation of polyaniline composites containing sericin were confirmed by Fourier-transform infrared spectroscopy. From the result of electron spin resonance spectroscopy, the electron spin concentration of the composites decreases with sericin/aniline ratio in the polymerisation. Circular dichroism absorption spectroscopy measurements revealed that sericin influences aggregation state of polyaniline. Scanning electron microscopy suggested that the polyaniline composites show granular morphology. The composites display macroporous structure after carbonization.

Keywords: polyaniline; sericin; composite; conductive polymer

1. INTRODUCTION

Among many type of fibres, silk is the most widely used fibre because of pleasant texture and unique sheen. Silk consists of fibrous protein, fibroin. It is well known that silk is obtained by reeling cocoon filament of silk worm. Cocoon filament is distinctive structure which is high strength fibroin covered with scleroprotein, sericin. Sericin plays a role of a protein glue to fix fibroin fibers together in a cocoon. However, a large amount of sericin has been discarded during silk processing. Recently, sericin's high hydrophilicity, biocompatibility, antioxidative effect and high cell proliferation promoting action have attracted much attention. Now, it has been studied on applications for cosmetics and medical materials. Polyaniline is one of the conductive polymers having been widely investigated in the past decade. Due to the stabilities environmentally, low cost, high electroconductivity, and simple synthetic method in water solvent, many electronic devices using polyaniline have been developed such as chemical sensors, secondary cell electrodes, and element of transistors. In this research, a novel conductive polymer composite of polyaniline and sericin was synthesised by chemical oxidative polymerisation and investigated its optical properties and morphology. This is a basic study for exploring possibility of application of sericin in organic electronics.

2. RESULTS AND DISCUSSION

2. 1. Synthesis

Distilled aniline (20 mg), (+)-10-camphorsulfonic acid (28.5 mg), sericin (the quantities were listed in Table 1) and water (2 mL) were stirred in vial. The mixture was cooled to 0 °C and stirred for 1 h. Ammonium peroxodisulfate (APS) (60 mg in 2 mL water) was dropped into the mixture. After 24 h, the dark green precipitate was washed into a large volume of methanol, water, and filtered. The crude product was dried under vacuum to afford a black powder.

Table1. Preparation of PANI/sericin and PANI/(+)-CSA.

Entry	aniline (g)	sericin (g)	sericin/aniline	Product (g)
P1	2.0	–	–	–
C1	0.5	0.3	0.6	0.68
C2	0.02	0.02	1	0.02
C3	0.02	0.04	2	0.03
C4	0.02	0.1	5	0.1

2. 2. IR

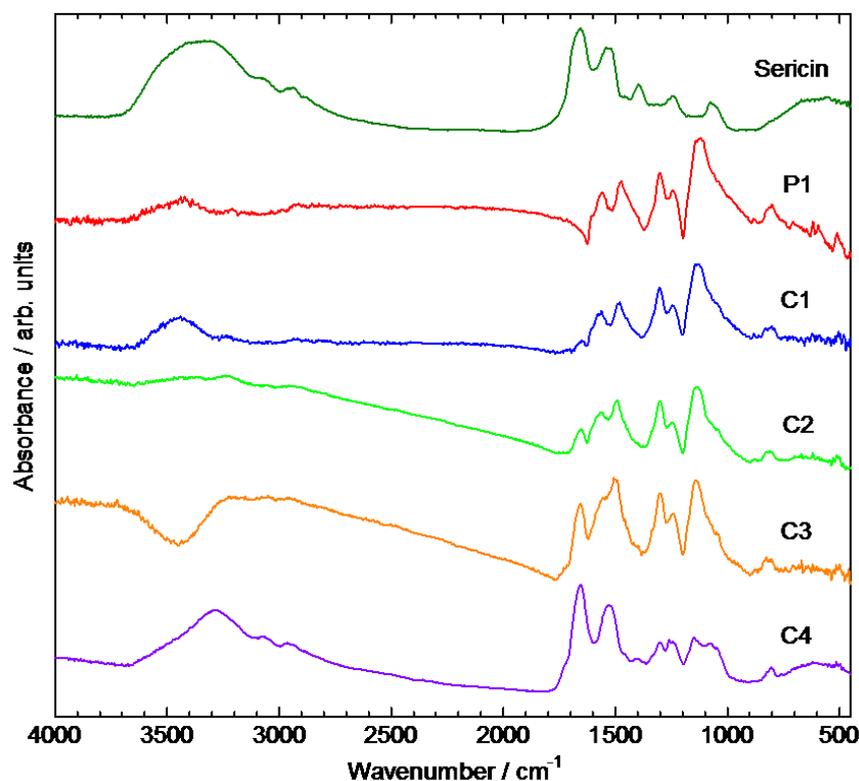


Figure 1. Fourier-transform infrared (FTIR) spectra of sericin, P1, C1, C2, C3, and C4.

FTIR measurements were carried out for sericin, P1, C1, C2, C3 and C4 to confirm chemical structure (Figure 1). Absorption bands derived from polyaniline are observed at 1562 cm^{-1} (quinoid (Q) C=C stretching), 1475 cm^{-1} (benzenoid C=C stretching), 1303 cm^{-1} (C-N stretching), and 1116 cm^{-1} (N=Q=N). On the other hand, absorption bands corresponding to protein, amide I, II, and III are observed at 1660 , 1537 , and 1244 cm^{-1} , respectively.

Amide I absorption represents C=O stretching of the amide group. Amide II absorption arises from N-H bending coupled to C-N stretching. Amide III contains contributions from C-N stretching and N-H in-plane bending vibration. All composites, C1, C2, C3, and C4 contains absorption bands of 1660 cm^{-1} (amide I), 1303 cm^{-1} (C-N stretching) and 1121 cm^{-1} (N=Q=N).

This result confirms formation of polyaniline/sericin composites. Here, absorption bands at 1660 and 1537 cm^{-1} (amide I and II) are intense compared to that at 1537 , 1475 and 1116 cm^{-1} (quinoid (Q) C=C stretching, benzenoid C=C stretching and N=Q=N stretching), as increasing with sericin/aniline ratio. This result implies that recovered amount of polyaniline is lesser than that of sericin. Compared with P1, the absorption band of N=Q=N stretching of all composites are shifted to high wavenumbers due to interaction between sericin and polyaniline.

2. 3. Electrochemical property

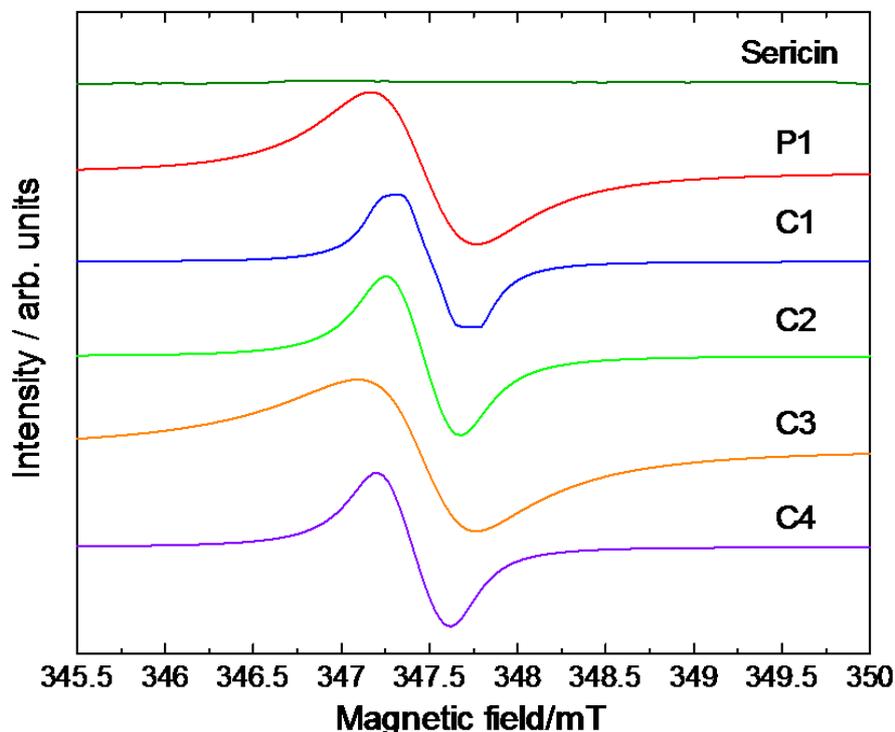


Figure 2. Electron spin resonance (ESR) spectra of sericin, P1, C1, C2, C3, and C4.

In-situ ESR spectra of sericin, P1, C1, C2, C3 and C4 were examined (Figure 2). All spectra except for sericin indicate existence of the radicals as charge carriers in these polymers. The g -value, line width (ΔH_{pp}), spin concentration and electrical conductivity of the samples are summarised in Table 2. The g -value of the all composites shift slightly to lower magnetic field and the peak width of C1, C2 and C4 are sharpened compared with P1. Spin concentration and electrical conductivity of these composites decrease with sericin/aniline ratio in the polymerisation, suggesting that the polarons of composites are delocalised, however electrical conductivities of composites are lower than that of P1 due to steric hindrance by sericin.

Table 2. ESR results and electrical conductivity.

Polymer	Sericin/Aniline	g -value	ΔH_{pp} [mT]	N_s [spins/g]	σ [S/cm]
Sericin	–	–	–	–	–
P1	0	2.00386	0.586	2.73×10^{20}	0.81
C1	0.5	2.00426	0.425	2.37×10^{20}	11.6×10^{-2}
C2	1	2.00446	0.410	5.93×10^{19}	4.99×10^{-4}
C3	2	2.00457	0.586	1.41×10^{20}	8.73×10^{-5}
C4	5	2.00441	0.410	1.72×10^{19}	–

2. 4. Optical property

CD spectra of P1, C1, C2, C3 and C4 were measured (Figure 3). From these spectra except for C3 and C4, negative signals are obtained. The signal at around 600 nm of C1 is more intense than that of P1. Furthermore, signals of C2 are shifted to high wavelengths compared with that of P1. Interestingly, C3 and C4 have no CD signal. This can be due to the fact that aggregation of polymer depends on amount of sericin in the polymerisation.

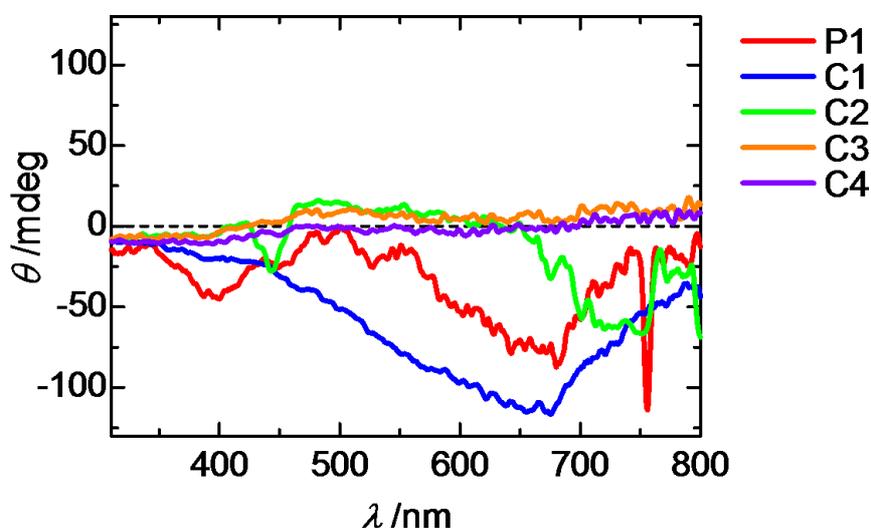


Figure 3. Circular dichroism (CD) spectra of P1, C1, C2, C3, and C4.

2. 5. Morphology

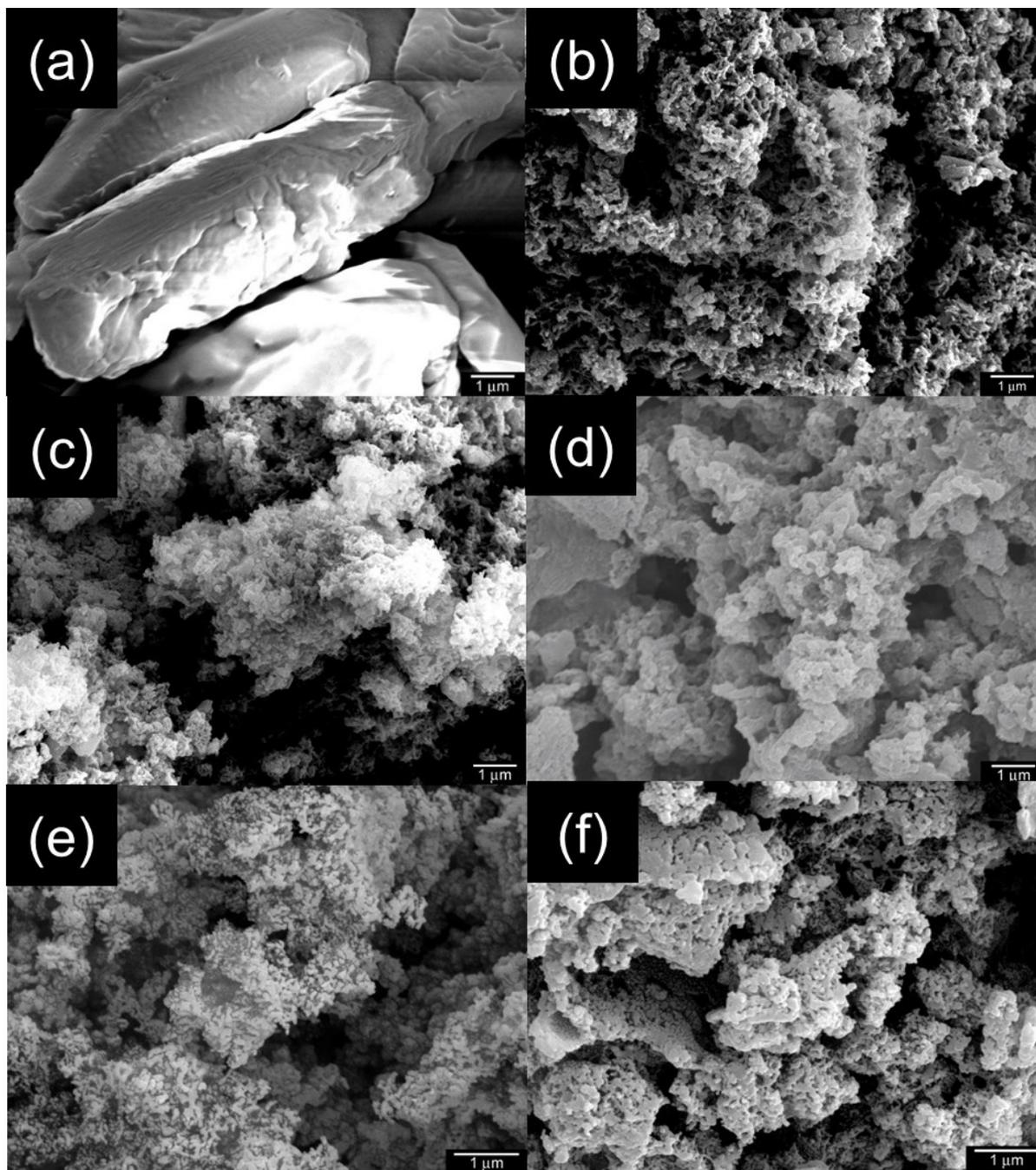


Figure 4. Scanning electron microscope (SEM) images of sericin (a), P1 (b), C1(c), C3(d), carbonised P1 (e), and carbonised C2 (f).

Figure 4 (a-d) shows SEM images of sericin, P1, C1 and C3. Figure 4 (e-f) shows SEM images of carbonised P1 and C2. Sericin and P1 show bulk and fibre structure, respectively. On the other hand, C1 and C3 show granular structure and polyaniline including sericin particle. Fibrous structure components of C3 were smaller than that of C1. From the images

of P1 and C2 (Figure. 4 (e-f)), P1 shows granular structure, while P2 shows macroporous structure after carbonisation. This discrepancy suggests that protein and water included in sericin were evaporated during carbonisation process and then macroporous structure appeared. This porous structure can be applied for gas absorption materials.

3. CONCLUSION

Optically active and electrical conductive polyaniline/sericin composites were synthesised by chemical oxidative polymerisation in aqueous solution. FTIR measurement indicated that interaction between sericin and polyaniline exists. The results of ESR and electrical conductivity measurements imply that the polarons of composites are well delocalised better than polyaniline alone, while electrical conductivities of composites are lower than that of polyaniline because of steric hindrance (insulation) by sericin. The composites form granular structure. Furthermore, macroporous structure was observed after carbonisation. A certain sericin/aniline ratio allows occasion of synergism of sericin and polyaniline in optical activity and formation of a bulk structure. The attempt in this research may open a new avenue for bio/polymer conjugated material.

Acknowledgement

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