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Conductive polymer composites prepared in volcanic spring water

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ABSTRACT

Polyaniline (PANI)/vinylon composite was prepared with 2-step process.The composite structure was confirmed with the FT-IR. PANI/spider silk composite was synthesized in volcanicspring water. The preparation of the composite can be carried out with no addition of sulfuric acid because natural acid type volcanicspring water functions as acid reagent for the polymerization reaction. This polymerization is promising for industrial applications for production of polyaniline.

Keywords: Polyaniline, spring water, green chemistry, spider silk, vinylon.

Introduction

Volcanic spring water has been familiar with human health and contributed for relax from ancient time. Constituents of volcanicspring water have variety depends on regions in the world. For example, fountain water from near sea contains salt, while volcano contains sulfur. Technologies for volcanic spring water have been developed from research on engineering and materials science [1]. The volcanic spring water as natural resources has not been used for industrial applications. Use of volcanic spring water for industry may have great possibilities in view point from green chemistry.

Conductive polymers composites and textiles have been studied for preparation of electro-active organic materials [2–6].

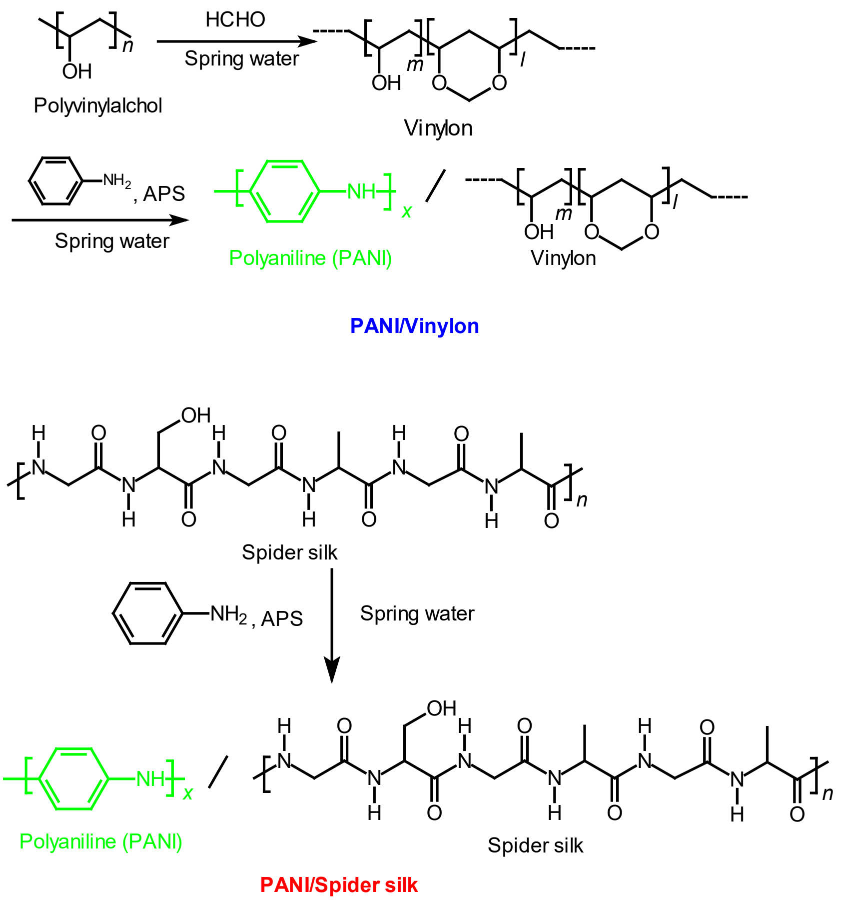
We have researched on synthesis of polyaniline (PANI) as a conductive polymer [7,8] PANI can be prepared in water under acid condition. Addition of ammonium persulfate (APS) affords to polymerization of aniline with radical reaction. Employment of volcanic spring water for polymerization of aniline can be convenient because volcanic spring water contains acid.

We attempt polymerization reaction with volcanic spring water for obtaining PANI with no use of sulfuric acid, which is usually used for the polymerization of aniline for production of PANI. In this research, preparation of vinylon [9], conductive composite of PANI/vinylon, and PANI spider silk were carried out.

Volcanic spring water

Volcanic spring water for a reaction solvent in this study was kindly gifted by Zao volcanic spring water Co, Japan. The spider silk used in this study was obtained in U.Tsukuba (Figure 1).

Figure 1. An image of spider.



Scheme 1. Synthesis of PANI/vinylon and PANIspider silk. APS = ammonium persulfate.

Polyaniline/vinylon composite

A solution of polyvinylalcohol (PVA, 2.0 g), a small amount of formaldehyde in the spring water (60 mL) was stirred for one night to obtain vinylon. Circular polarized interference optical microscopy (C-DIM) images confirmed the formation of vinylon fiber prepared in this study show in Figure 2. This can be the first example of synthesis of vinylon in natural spring water.

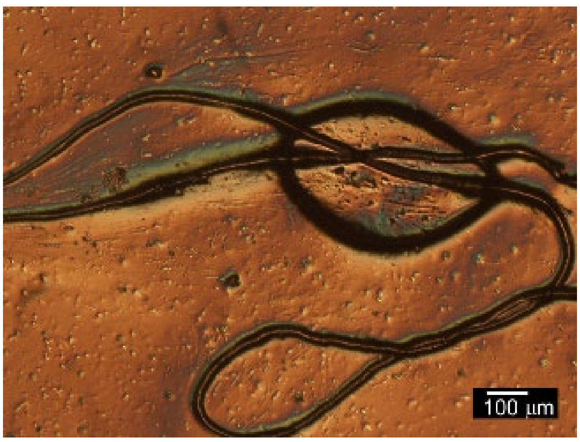


Figure 2. A circular polarized interference optical microscopy (C-DIM) image of vinylon.

Subsequently aniline (1.0 g) was added to the solution. At this time pH of the solution was to be 3.21. Then, APS (1.5g) was added to the solution. pH of the solution was decreasing. Color of the solution turned from purple suspension to greenish yellow. After 24 h, APS (2.08 g) was further added to the solution.The solution was poured into a large volume of methanol and washed thoroughly and filtered to obtain PANI/vinylon composite.

Polyaniline/spider silk composite

First, a solution of aniline (0.5 g) and spider silk (0.6 mg) in the spring water (4.0 g) was stirred. Then, APS (1.0 g) was added at 0 °C to initiate polymerization. After 13.5 h, APS (0.5 g) was further added to the solution and stirred for 12 h. The solution was filtered, washed with a large volume of methanol, and filtered again. The sample was dried under reduced pressure to obtain PANI/spider silk composite (Figure 3).

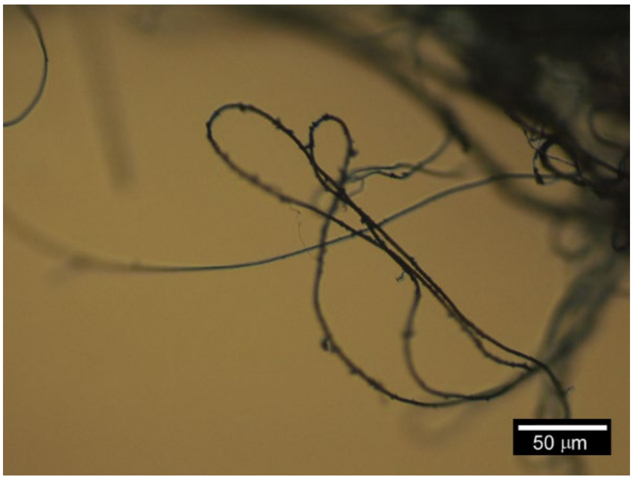


Figure 3. Optical microscopy image of polyaniline/spider silk composite.

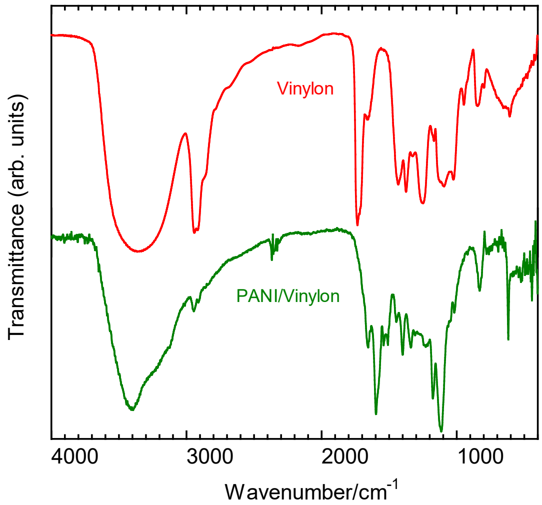


Figure 4. Fourier transform infrared (FT-IR) spectroscopy result of vinylon and PANI/vinylon composite

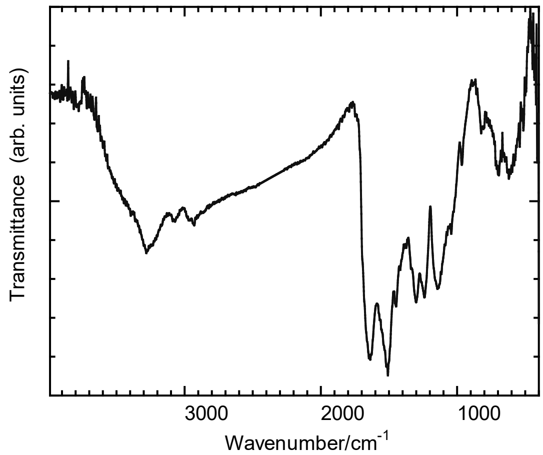


Figure 5. Fourier transform infrared (FT-IR) spectroscopy result of polyaniline/spider silk composite.

Infrared absorption spectroscopy

Fourier transform infrared (FT-IR) spectroscopy measurements confirmed chemical structures of the vinylon and PANI/vinylon composite and polyaniline/spider silk composite, as shown in Figs 4,5.

Intense absorption band at around 3403 cm^{-1} is assignable to OH stretching of vinylon. Absorption at 2943 cm^{-1} is due to $\nu_{CH3,CH2}$, (alkyl C-C stretching). An absorption band observed at 1730 cm^{-1} may be due to C=O stretching of aldehyde because small amount of unreacted acetaldehyde is contained in the vinylon. Ether absorption (C-O-C) is observed at 1247 cm^{-1}.

As for PANI/vinylon composite, an absorption band at 827 cm^{-1} is due to C-H out-of-plane vibration of phenylene group. An absorption at 2940 cm^{-1} is due to C=C stretching of alkyl group. An absorption band at 1195 cm^{-1} is C-O-C stretching of ether oxygen. Absorption bands due to aniline units as monomer repeat unit of PANI are observed at 1653-1510 cm^{-1}. This assignment confirmed formation of PANI and vinylon composites.

Further, chemical structure of polyaniline/spider silk composite shows OH stretching vibrations at 3282 cm^{-1}. An absorption band at 2938 cm^{-1} is due to alkyl C-C stretching of spider silk. Benzenoid structure of monomer repeat unit of polyaniline is observed at 1515 cm^{-1}. The absorption at 1644 cm^{-1} is attributed to quinonoid structure. C-N stretching vibration of the aniline unit is shown at 1239 cm^{-1}.

Conclusions

Vinylon was synthesized in the volcanic water medium. PANI/vinylon composite and PANI/spider composite were successfully prepared in the acid type spring water. This synthesis can be valid for application of production of conductive polymer because volcanic natural water can be used without addition of sulfuric acid for the polymer synthesis.

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