Synthesis of polyaniline grafted cellulose suitable for humidity sensing

S K Shukla*
Department of Polymer Science, Bhaskaracharya College of Applied Sciences,
University of Delhi, Delhi 110 075, India

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Polyaniline-grafted-cellulose (PANi-cellulose) copolymer is prepared by a chemical method using cupric sulphate as initiator. The representative PANi-cellulose samples are characterized by Fourier transform infrared spectroscopy (FTIR), thermal gravimetric differential thermal analysis (TG-DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The data reveal the formation of electrically conducting and hydrophilic copolymer. The film of PANi-cellulose is casted on a glass slide by spin coating technique and used for humidity sensing of a controlled humid environment by monitoring electrical resistance. The resistance continuously decreased from ~ 32 MΩ to 10.0 MΩ with increase in relative humidity in the range of 5-90%. The observed sensing parameters are sensitivity 0.22, response time 40 s, recover time 60 s and stability for more than 60 days.

Keywords: Copolymer, PANi-cellulose, Electrical resistance, Chemical characterization, Humidity sensing

Electrically conducting biopolymers are widely used in various optical and electrical devices including chemical and biochemical sensors. The methods used for optimization of electrical conductivity are copolymerization, metal oxides encapsulation and doping conducting fillers like graphite. Among these methods copolymerization is advantageous due to the formation of controlled molecular network. Tiwari et al. have prepared grafted conducting biopolymer (polyaniline grafted chitosan) for sensing breast cancer cells by monitoring electrical properties. Further, cellulose is a naturally occurring biopolymer, abundantly available in nature from plants to other living organism such as plankton, algae, fungi, and bacteria. The chemical engineering routes such as microbial, melt compounding, radiation induced compounding have been used to develop speciality features in cellulose. However, one most common feature of cellulose is hydrophillicity, which is an important property to develop humidity sensors due to better adsorption sites for H₂O molecules.

Nowadays, humidity sensors are in demand due to their applications for human comforts, industrial control, packaging of food and medicines. The available humidity sensors are based on the monitoring of electrical, optical and mass transport properties. However, electrical type sensors bear many advantages such as long life and robust nature but still not fully commercialized due to lack of better sensitive materials. Encouraged with our earlier finding, efforts have been made to optimize electrical resistance of cellulose. The present study reports the grafting of polyaniline onto cellulose chain to improve the electrical conductivity of cellulose. Further, the electrical resistance of PANi-cellulose film on glass substrate was monitored under controlled humid environment to explore its use for humidity sensor.

Experimental Procedure

Materials
Cellulose (microcrystalline), aniline (99.5%), glacial acetic acid, cupric sulphate pentahydrate (99.5% purity) from Merck were used without any further purification.

Methods

Synthesis of grafted copolymer
The co-polymerization of aniline and cellulose was carried out in an acidic solution. Aniline (10 mL) and 5 g cellulose were dissolved in 200 mL of aqueous 2% HCl solution with stirring on a magnetic stirrer. In resultant solution 5mL one molar aqueous copper sulphate solution was added drop by drop with continuous stirring, and stirring was further continued for one hour. The resultant solution was then left for 3-4 h and a dark black-green precipitate was obtained. The precipitate was filtered, washed with...
distilled water and methanol and dried at 50°C in vacuum oven for 24 h.

Characterization

FTIR spectra were recorded with Perkin Elmer (RK-1310) FTIR spectrometer in KBr phase. X-ray diffraction pattern was taken with Rigaku Rotaflex (RAD/Max-200B) X-ray diffractometer at a scanning rate of 2°/min. TG-DTA curves were recorded with DTG-60, Shimadzu, thermal analyser at a heating rate of 5°C/min in N₂ atmosphere. Scanning electron microscopic pictures were taken with the help of Hitachi-3700, scanning electron microscope. However, electrical properties were measured with RISH-MAX digital laboratory multimeter.

Estimation of humidity sensing behaviour

The adsorbed water content by the film at a given value of RH was measured by measuring mass change of PANi-cellulose film after exposing at different RH values. The percentage water adsorption was calculated from Eq. (1).

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\text{Water Content(\%)} = \frac{W_x - W_o}{W_o} \times 100 \quad \ldots (1)
\]

Where \( W_x \) and \( W_o \) are the mass of the film at given RH and in dry atmosphere, respectively. \( W_o \) was obtained by placing the film in a vacuum desiccator at room temperature (25°C) for 24 h. In order to evaluate the humidity-sensing behaviour of PANi-cellulose, a film was casted on a glass slide by spin coating technique at 2000 rpm after making 2% solution of PANi-g-Cellu in DMF. At both ends of the film electrical contacts were made by applying a layer of silver paste and electrical resistance were measured. The details of experimental set-up used for humidity sensing purpose is shown in Fig. 1

Results and Discussion

Spectral studies

FTIR spectra of cellulose, PANi and PANi-cellulose are shown in Fig. 2. On comparing it appears that spectra PANi-cellulose contains vibrational bands due to both PANi and cellulose. Further, the peaks appeared in PANi spectra at 1495, 1465 shifted at 1492, 1462 cm⁻¹ in composite, similarly the other two peaks in PANi spectra present at 1166 and 1113 merged and evolved as single peak at 1120 with a small peak at 1109 cm⁻¹. Further, IR peak of cellulose appearing in spectra at 1636 cm⁻¹ is shifted at 1630 cm⁻¹ in PANi-cellulose. These may indicate the formation of PANi-cellulose composite

UV-vis spectra of PANi, cellulose and PANi-cellulose are shown in Fig. 3. The spectra showed that bands at 380 and 520 nm in the case of PANi shifted towards lower wave length at 360 and 450 nm, respectively. This indicates some sorts of interaction between PANi and cellulose.

The X-ray diffraction pattern of cellulose and PANi-g-cellulose are shown in Fig. 4, it indicates the crystalline character of PANi-cellulose composite.
Thermal gravimetric differential thermal analysis

TG-DTA curves of PANi and PANi-Cellulose are shown in Fig. 5. The TG curve of PANi shows a weight loss up to 70°C and then becomes constant up to 210°C. The early weight loss may be due to removal of moisture. A sharp weight loss starts at 210°C with one step decomposition process. This has been further supported by an endothermic peak at 260°C. However, in the case of PANi-Cellulose there is continuous weight loss up to 225°C with an endothermic peak at 260°C and then a sudden weight loss with one step decomposition occurs. This has been further supported by an endothermic peak at 330°C. This result clearly indicates that PANi-cellulose is thermally more stable than PANi alone. This may be due to the formation of a composite.

Scanning electron microscopy

The SEM micrograph of PANi-cellulose is shown in Fig. 6, the picture shows two thread are twisted together. This may supports the graft copolymerization.

Electrical properties

The electrical conductivity of PANi-cellulose was measured by making a pellet with diameter 13 mm and thickness 0.42 mm. The observed electrical conductivity of cellulose, PANi and PANi-g-cellulose at room temperature were $2.0184 \times 10^{-10}$, 1.0542 and $1.25 \times 10^{-2}$ S cm$^{-1}$, respectively. The result shows that electrical conductivity of PANi-cellulose is quite high and can be used for devices.

Humidity sensing behavior

The variation in resistance of PANi-cellulose with increase in humidity is shown in Fig. 7. The resistance decreases with humidity. The curve is almost linear and hence shows its suitability for wide range humidity sensing applications. The linearity is better than PANi as reported earlier$^{18}$, due to high

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Fig. 3—UV spectra of cellulose, PANi-g-cellulose and PANi

Fig. 4—XRD spectra of cellulose and PANi-cellulose

Fig. 5—TG-DTA spectra of PANi (green, red); PANi-cellulose (black)

Fig. 6—SEM micrograph of PANi-cellulose
hydrophilic and chemically stable behavior in PANi-cellulose. The cellulose is not sensitive due to its non-conducting, porous and non-ionizing nature. Further, decrease in resistance reveals that the dissociative adsorption of water molecule takes place on PANi-cellulose surface. The first layer makes surface polar and subsequent layer generates hydronium and hydroxide ions. This increases the electrical conductivity and decreases resistance\(^{26}\). The change in resistance with time at 70% RH is shown in Fig. 8. This figure shows a decrease in resistance about 80% in 45 s. Thus, the response time for PANi-cellulose sensor will be about 45 s. Further after keeping the same film in dry atmosphere (desiccator) the resistance return back to its original resistance in 60 s, which is recovery time for sensing purpose.

Conclusions

PANi-cellulose was prepared at room temperature by chemical route. The grafted polymer was found crystalline in nature with improved electrical conductivity. PANi-cellulose was found suitable for humidity sensing properties.

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References