

Morphological, structural and electrical properties of polypyrrole nanocoated bamboo cellulose fibre

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Bamboo cellulose fibres have been coated with polypyrrole and the coated fibres are then characterized for various properties. The changes in surface morphology and particle distribution are studied by scanning and transmission electron microscopy which indicate the formation of nano-coating of polypyrrole over the fibre surface, as the average diameter of the particles forming the surface layer is found 50 nm. Fourier transform infrared spectroscopy reveals that the chemical structure of the natural fibres remains unchanged even after the nano coating, though the individual characteristics of pyrrole appears therein. Electrical resistance of the coated fibres, measured by two probe method, shows decreasing trend with increasing pyrrole concentration. The value ranges from $1075 \text{ K}\Omega \text{ cm}^{-1}$ to $0.159 \text{ K}\Omega \text{ cm}^{-1}$ from 0.1% to 5% pyrrole. Further, it shows Ohmic nature for both the coated and uncoated fibres. Dielectric behavior of the current-voltage (I-V) plots of the coated fibres exhibits highly dispersive dielectric loss and similar behavior in its AC conductance, at low frequency range up to 7 kHz; beyond which its conductance is stabilized.

Keywords: Bamboo fibre, Dielectric properties, Electrical resistance, Nanocoating, Polypyrrole

1 Introduction

Cellulose, considered as the most abundant organic compound derived from biomass, is mostly found as a natural fibrous material, but use of synthetic cellulose is also increased because of its diverse applications. Natural cellulose with hierarchical self assembly of polymer chains exhibits physical and chemical properties which are not seen in synthetic fibres¹, but it was possible to control these properties in synthetic fibres by means of surface coating of polymers². Cellulose was reported to have a strong affinity for certain conducting polymers (CPs) like polypyrrole (PPy) and polyaniline (PAni)³. Recent advances in surface coating of individual cellulose fibres with metal oxide gel layers is a step towards fabricating smart materials for producing conductive textiles⁴, but surface layer of organic polymer makes the natural fibres more user friendly than a metal oxide layer. However, chemical and electrochemical coating of CPs over the cellulose fibre was a challenging task for a long time because of the difficulties in controlling the surface agglomeration as the CP particles are prone to deposit in irregular form over the polymer chain and hinder its uniform layer formation on the fibre surface. As a result, the fine structure of the fibrous cellulosic

material was disrupted due to the inhomogeneous deposits of CP material. The problem could be minimized by nanocoating of a surface layer on the cellulose surface. The first successful experiment on nano-coating of polypyrrole on natural cellulose was reported by Huang *et al*⁵. They reported a polymerization induced adsorption process for producing an ultrathin film of insoluble polymer over a substrate of cellulose fibres in commercial filter papers. In this study, a similar surface layer of PPy has been deposited over the bamboo fibres by means of polymerization induced adsorption, without disrupting its hierarchical cellulosic structure.

Deposition of the PPy on the bamboo fibre surface was confirmed from the microscopic as well as spectroscopic observations. The nature and size of the particles incorporated over the fibre surface were investigated by scanning electron microscope (SEM) and transmission electron microscope (TEM) which indicated modifications in the surface morphology of the fibres. Fourier transform infra red (FTIR) spectroscopy is used for determining any structural change in the bamboo fibre after incorporation of PPy. It was found that the PPy coating rendered certain drastic changes in the electrical properties of the fibres which were studied by current voltage characterization and impedance analysis in the low frequency range.

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It was found that the PPy coating on the fibrular structure of bamboo cellulose resulted in a PPy-cellulose bi-hybrid composite. The material produced as such can be used in conductive textiles⁶ due to its considerable DC conductivity and dielectric relaxation, resulting in increased AC conductivity over a useful range of operating frequency.

2 Materials and Methods

2.1 Materials

Bamboo fibres were received as gift sample from Hindustan Paper Corporation (HPC), Jagiroad, Assam. Pyrrole (C_4H_4NH) was bought from Aldrich, ferric chloride ($FeCl_3$) (anhydrous) from William's Lab. and hydrochloric acid (HCl) from Fisher Scientific. These chemicals were certified as analytical grade with very high purity and used without further purification, except pyrrole, which was double distilled under reduced pressure prior to use. Double distilled water was used for preparation of all aqueous solutions. Table 1 shows the supplier name, purity, molecular weight, structure and function of the experimented chemicals.

2.2 Methods

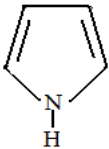
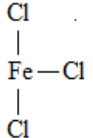
Oxidative polymerization of pyrrole (Py) was initiated by $FeCl_3$ in acidic medium. To prepare the PPy cellulose bi-hybrid composite, 2 mL $FeCl_3$ was added drop-wise into 40.0 mL pyrrole solution in 5% HCl, with constant stirring^{7,8}. The reaction mixture turned greenish black within a minute and black precipitate of PPy was formed. The filtrate was used for the bulk coating of the bamboo cellulose fibres. 20 mL of the solution was poured into a beaker containing bamboo fibres and sonicated for 60 min. Gradual colour change was observed when treated with the polymer solution with different Py concentrations. Remnants of the solution were rejected by filtration. Three different pyrrole concentrations, viz. 0.1%, 1% and 5% were taken in wt/wt ratio for the coating. The filtered fibres were washed with 2-propanol and de-ionized water, followed by drying in air flow.

The increasing pyrrole concentration resulted in an embedded PPy coating with differentiated particle structure. This was also eminent from gradual change in colour of the polymer mixture with the fibres from greenish black to black and then reddish brown (Fig. 1).

2.3 Analytical Characterizations

The surface morphology of polypyrrole and the treated fibre was analyzed by SEM (JEOL LA 6380, Japan) in the high vacuum mode with an accelerating

Table 1 — Supplier name, purity, molecular weight, structure and function of the chemicals

Chemical	Supplier	Purity, %	Mol. weight g/mol	Structure	Function
Pyrrole	Aldrich	99	67.09		Monomer
Ferric chloride	Williams Lab	99.9	162.21		Oxidizing agent
Hydrochloric acid	Fisher Scientific	99.95	36.46	$H - Cl$	Solvent

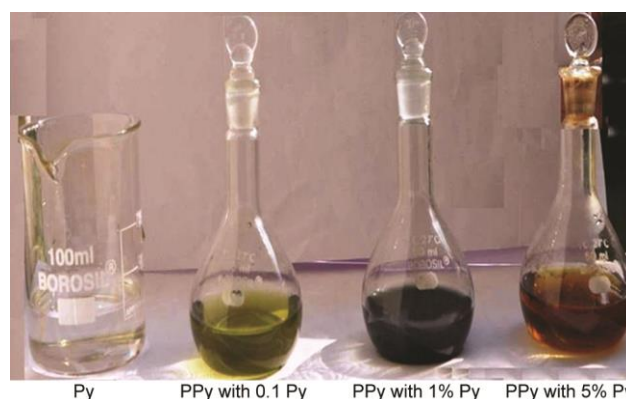


Fig. 1 — Colour change in polymerization solution (filtrate) when Py polymerized to form PPy with different concentrations

voltage of 30 kV. The samples were subjected to Au/Pt sputtering to minimize charging effects prior to imaging and then mounted on a aluminum stub using double sided adhesive tapes.

The modified fibres were probed by TEM (JEM-2100, JEOL, Japan) with an operating voltage of 300 kV (Cs 0.6 mm, resolution 1.7 Å). Images were recorded using a charge coupled device (CCD) camera (Model keen view, SIS analysis, size 1024, pixel size 23.5 - 23.5 μM) under low dose conditions on as-synthesized samples. The samples were sonicated for 10 min prior to their transfer to the TEM grid. The fibre diameters and the size of the particles appearing in the surface were measured by using image processing software (Image J).

FTIR was carried out on samples prepared in KBr using a Shimadzu FTIR Affinity 1 Spectrophotometer. Spectra were recorded in the range of 300 - 3000 cm^{-1} at

4 cm⁻¹ resolution, for PPy and its coated fibres to find out any functional change in the fibre due to PPy coating.

The resistance of the fibre was measured at room temperature using a Keithley Sourcemeter (Model 2400). To ensure good contact, silver paint was pasted on both the ends of the filament shaped fibre of length (L), width (w) and thickness (d). The voltage V , applied between 0.1 volt and 1 volt and resulting DC current I were measured. The conductivity (σ) was calculated from the slope of the $I - V$ graph, using the following equation⁹:

$$\sigma = \frac{\Delta I}{\Delta V} \frac{L}{wd} \quad \dots (1)$$

where $\frac{\Delta I}{\Delta V}$ is the conductance of the sample obtained; L , the length; w , the width; and d , the thickness of the sample.

The dielectric properties of the fibres were measured with an impedance analyzer (Model HIOKI 3532-50 LCR), having four terminals nickel plated cobalt electrodes of 38 mm diameter and 1mm spacing. Fibre pallets of surface area (A) and thickness (t) were tested, measuring their capacitance (C_p) and parallel resistance (R_p) with the sample between the electrodes. $C_0 = 0.008854 A/t$ in pF was the geometrical capacitance of vacuum of the same dimension as

that of the sample. The complex dielectric function $\epsilon^*(\omega) = \epsilon' - j\epsilon''$ and ac electrical conductivity were calculated by using the following equations¹⁰:

$$\epsilon' = \frac{C_p}{C_0} \quad \dots (2)$$

$$\epsilon'' = \frac{\epsilon'}{\omega C_p R_p} = \epsilon' D \quad \dots (3)$$

where ϵ' (f) (dielectric polarization), and ϵ'' (f) (DC conduction loss) are the two components of the dielectric function and calculated by using the following relationships¹¹:

$$\epsilon'' = \frac{\sigma_{dc}}{\epsilon_0 \omega} \quad \dots (4)$$

$$\sigma_{ac} = \epsilon_0 \epsilon' \tan \delta \quad \dots (5)$$

3 Results and Discussion

3.1 Morphological Study

3.1.1 SEM Study

The PPy and its influence on the structure and morphology of the bamboo fibres surface layer have been investigated by SEM [Figs 2 (A) – (D)]. Figure 2(E) depicts how the PPy particles are entangled in the

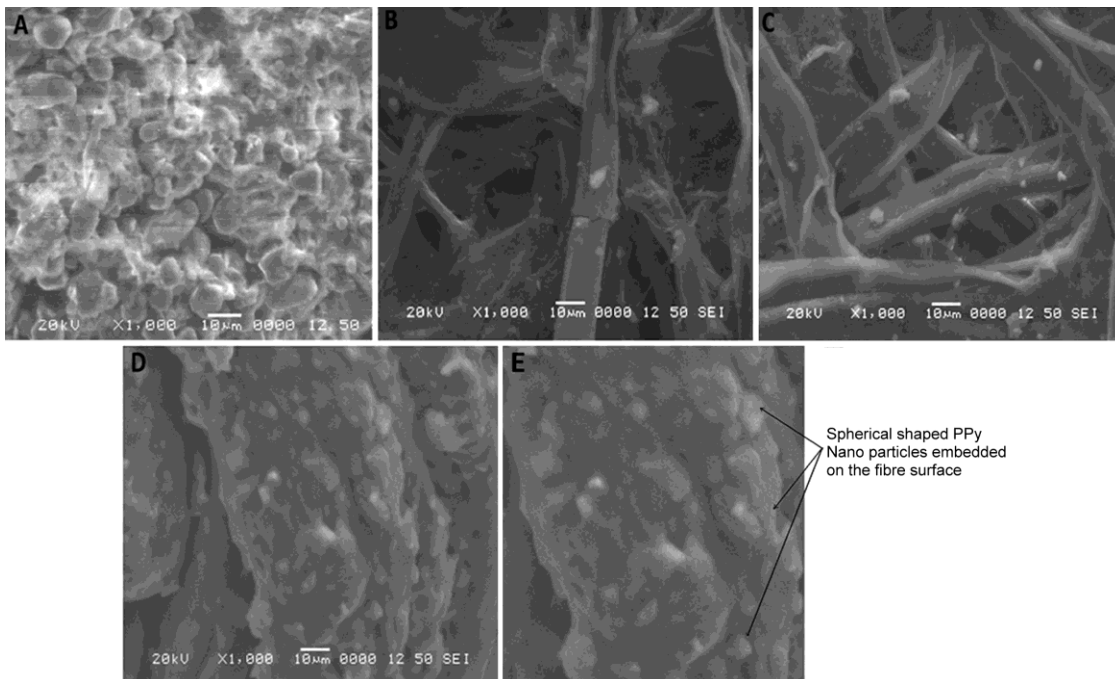


Fig. 2 — SEM micrographs of PPy(A) and PPy coated fibres with concentration 0.1%(B), 1% (C) and 5%(D); (E) –PPy surface layer in the fibre as curved out from (D)

fibre surface which is an interface dissected from Fig. 2(D). Nayak *et al.*¹² found that the polymer type incorporated over fibre surface affects its morphology as well as its diameter. The changes in morphology of the fibres are observed after the polymer coating, while its diameter changes from 0.42 μm to 0.63 μm , which is also shown in the histograms (Fig. 3). It is also observed from the distribution pattern of the particles that with increased Py concentration, smaller sized particles are more agglomerated over the surface than the inside core. Thus, a high aspect ratio is obtained in the fibrous nano-structure, thus creating the possibility of huge entanglement of the quibits between the fibre and the PPy monolayer¹³.

3.1.2 TEM Study

Figures 3(A)-(D) show the TEM micrographs for PPy and PPy coated cellulose fibres for different monomer concentrations of 0.1, 1 and 5%. PPy deposited on the fibre surface are sparingly distributed at the lower monomer concentrations, but becomes more and more homogeneous and uniform with increased Py concentration, leading to a pattern resembling quantum entanglement of the PPy particles over the cellulosic substrate at 5% Py. The PPy particles of the average size (290 nm) are embedded on the fibre surface increasing their average diameter from 0.42 μm at 0.1% monomer concentration to 0.63 μm at 5% [Figs. 3(E)-(H)] which shows the distribution and dimension of the particles on fibres, corresponding to Figs 3(A)-(D). Electrical conductivity of CP largely depends on its surface morphology as well as the particle dimension and their distribution inside the core¹⁴. It is inferred from Fig. 3 that a continuous pathway for the charge carriers is formed in the fibres after PPy coating is incorporated, which facilitates the increased electrical conductivity in the coated fibres and gives characteristic dielectric behavior exhibited by CPs at lower frequencies.

3.2 FTIR Study

Figure 4 shows the FTIR spectra for PPy and its coated fibres for three different monomer concentrations (0.1%, 1% and 5%). The characteristic PPy peaks are found in its spectrum, while PPy coated bamboo fibres show the spectra similar to that of untreated bamboo cellulose¹⁵. Fibres fabricated with polymer coating of 0.1% and 1% monomer concentration show similar spectra, while certain changes are observed in 5% coating. It happens probably due to cross-linking of the cellulosic bonds

corresponding to C—H₂, C—H and C—O—H stretching, which becomes significant at higher monomer concentration during the adsorption. Most of the cellulose peaks characteristics of untreated bamboo cellulose¹⁶ are found to be blue shifted in the spectrum of PPy coated fibres. The spectrum of PPy coated (5%) fibres shows the absorption bands at 1912 cm^{-1} due to C—H stretching, while the band generally found in bamboo cellulose at 1431 cm^{-1} and 1316 cm^{-1} representing C—H₂ bending and wagging are found to be shifted towards 1377 cm^{-1} and 1012 cm^{-1} respectively. The absorption bands at 1201 cm^{-1} for C—O—H in plane bending at C-6 are shifted towards 905 cm^{-1} , while the bands normally found in bamboo cellulose at 1158 cm^{-1} and 901 cm^{-1} for C—O—H stretching at the β -(1 \rightarrow 4) glucosidic linkage are shifted towards 745 cm^{-1} and 710 cm^{-1} in the 5% coated fibres. The main absorption peaks and its associated functionality^{15,16} for PPy and its coated fibres are shown in Table 2.

3.3 Electrical Properties

3.3.1 DC Resistance

Electrical resistance of PPy coated bamboo cellulose fibre of length 1cm shows a marked decrease with increasing percentage of monomer concentration in the polymerization solution¹⁷. The increasing concentration of Py in the polymerization mixture gradually increases the surface density of CP particles in the polymer coating of the fibres, resulting in gradual decrease of its resistivity, found as 1075, 124 and 0.159 K Ω /cm with Py concentration of 0.1%, 1% and 5% respectively. The large change in resistivity is probably because of the doping effect of the CP particles which gradually decrease with increasing concentration of PPy and attains an optimum level at 5% concentration.

This fact is in consistency with the SEM and TEM results also. The current-voltage (I-V) characterizations in the voltage range 0.2 - 1 volt for PPy and its coated fibres are shown in Fig. 5, while the changing trend of its resistivity with the changing monomer concentration in the coating solution are shown in Fig. 6.

3.3.2 Dielectric Properties

Figure 7 shows AC conductance vs frequency for PPy and its coated fibres with different Py concentrations. The inset shows the dielectric loss with frequency for PPy. As explained in section 2.3, AC conductivity has a functional relationship with the

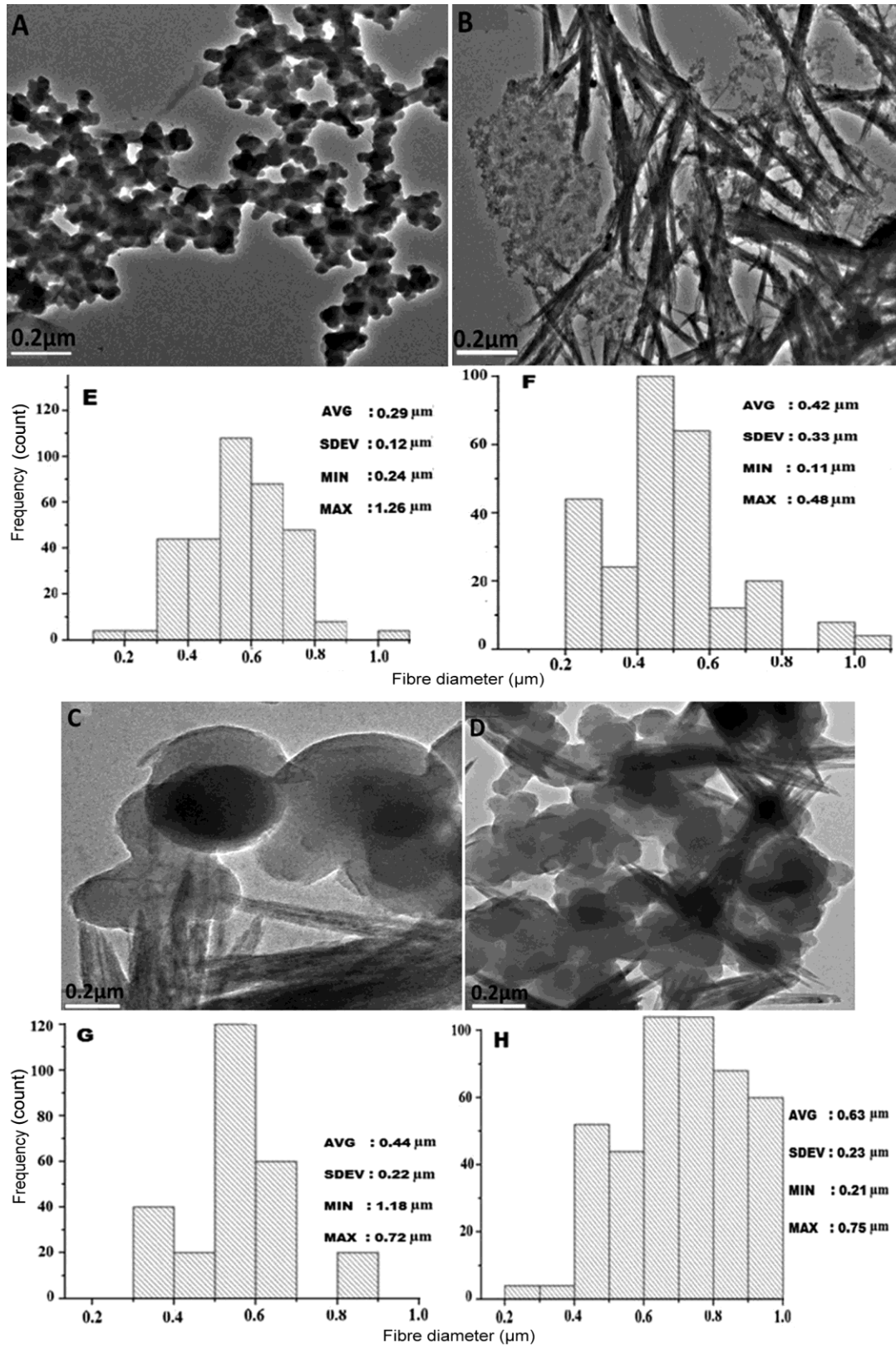


Fig. 3 — TEM images of PPy(A) and PPy coated fibres with concentration 0.1%(B), 1%(C), and 5%(D). The histograms in (E), (F), (G) and (H) represent the particle distribution for A, B, C and D

Table 2— main absorption peaks in FTIR spectrum

Material	Wave number cm ⁻¹	Functionality
PPy	1535	C = C stretching of Py ring
	1407	C–N stretching vibration in ring
	1153	C–H in plane deformation
	1075	N–H in plane deformation
	925	C–H out of plane deformation
	658	C–C out of plane deformation
Fibres with PPy	1912	C–H stretching
	1377,1012	C–H ₂ bending and wagging
	905	C–O–H in plane bending at C-6
	745,710	C–O–H stretching at β–(1→4) glucosidic linkage
	640,672	Out of plane bending at C–O–H

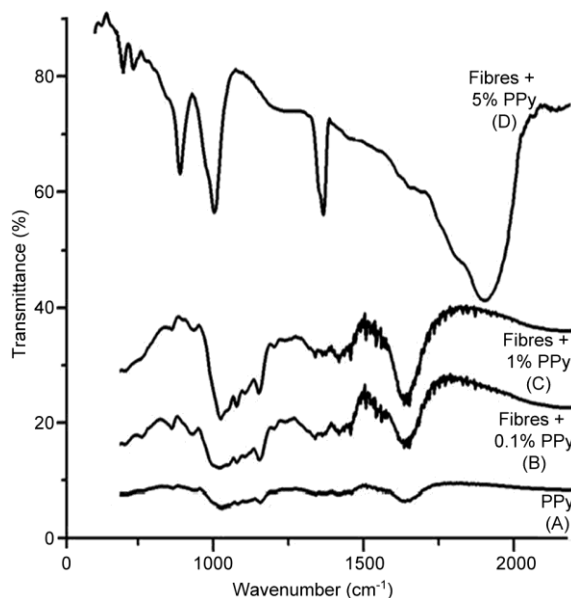


Fig. 4 — FTIR profile of PPy(A) and PPy coated fibres with PPy concentration 0.1%(B), 1% (C) and 5%(D)

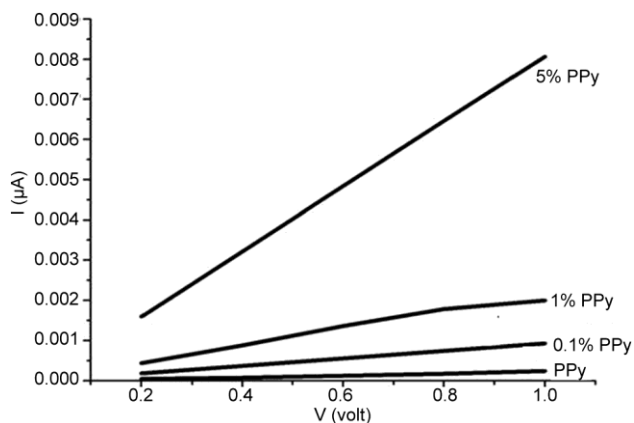


Fig. 5 — I-V characteristics of PPy and PPy coated fibres with concentration (A) 0.1%(B), 1%(C) and 5%(D)

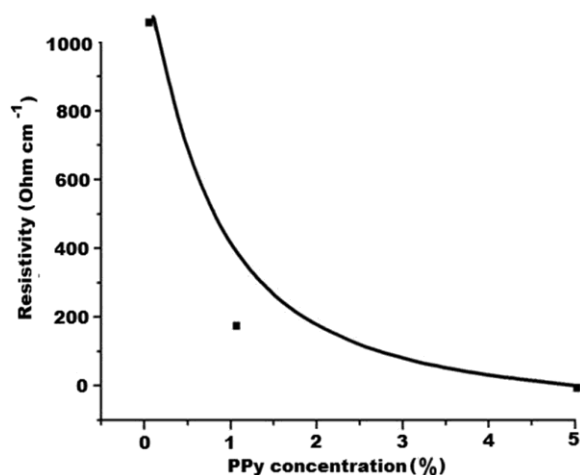


Fig. 6 — Resistivity vs. monomer concentration of PPy coated fibres

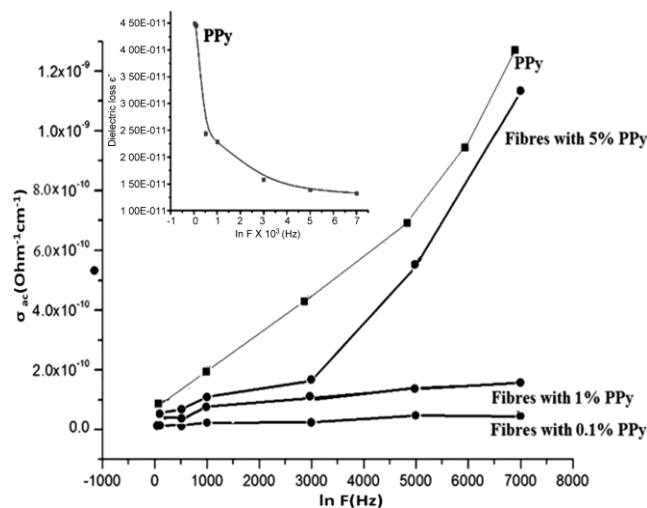


Fig. 7 — AC conductance vs. frequency in low frequency range for PPy and PPy coated fibres for 0.1%, 1% and 5%. Inset — Dielectric loss of PPy, responsible for AC conductance in the fibres when applied as surface coating

dielectric loss (ϵ''), which accounts for polaron and bipolaron formation in the case of doped CP¹⁸. Since AC conductance (σ_{ac}) is directly proportional to dielectric loss (ϵ''), increased value of dielectric loss of the bi-hybrid composite formed in the fibre surface accounts for its increased conductivity under the approximation that the polarization current density remains constant¹⁹, and it is also observed in our experiment. The prominent AC conductivity is the result of PPy coating on the fibres which is responsible for formation of secondary charge carriers, polarons and bipolarons²⁰. Such remarkable AC conductance in the low frequency range has not been reported earlier for virgin bamboo fibres, and we might conclude that

the dielectric behavior of PPy has been implanted in the fibres after the coating. The conductivity plot of PPy and its coated fibres possessed the following characteristics:

- (i) PPy exhibits low frequency dispersion due to which it shows feeble AC conductance in its un-doped state.
- (ii) The conductivity of coated fibre is found different from the virgin bamboo fibres with prominent effect of coating. Though virgin bamboo fibre is reported to exhibit Ohmic nature in case of DC conduction, its prominent AC conductivity is not observed. The effect of PPy coating results in considerable AC conduction in the low frequency range upto 7 kHz.
- (iii) A plateau region is observed in case of the coated fibres at very low frequency, while its conductivity shows a steep rise from 3 kHz to 7 kHz.
- (iv) The inset showing the plot of dielectric loss with frequency in the same frequency range could be used for explaining the change in AC conductivity of the coated fibres.
- (v) The functional relationship of dielectric relaxation and conductivity could be accessed from the figures by means of a suitable theory²¹, as explained hereunder.

3.4 Conductivity Growth vis-à-vis CP Coating

The conductivity spectra of PPy coated bamboo cellulose could be explained on the basis of Jump Relaxation Model (JRM)²². The frequency independent plateau in the low frequency region (<3 kHz) is attributed to the long range translational motion of ions which is responsible for DC conductivity. As the frequency increases (>3 kHz), the conductivity becomes non-linear. According to JRM, the conductivity at the low frequency region is associated with the successful hops of the ions to their neighborhood vacant sites due to longer time period, and the successive jumps result in long range translational motion of ions contributing to the DC conductivity²³, which is predominating in the lower frequency, making it steady up to 3 kHz. At high frequency, two competing relaxation processes occur, as shown below:

- (i) The ions jumping back to their initial positions in vain — unsuccessful hopping
- (ii) The neighborhood ions becoming relaxed with respect to the position of the excited ions retaining their new position — successful hopping.

The observed conductivity plot (Fig.7) is the result of such successful and unsuccessful hopping events. The increase in the ratio of successful and unsuccessful hopping results in a dispersive conductivity at higher frequency, while the predominance of only one leads to a stable pattern²⁴. A convenient formalism was proposed by Jonscher who investigated the functional relationship of electrical conductivity with frequency in a variety of materials, at constant temperature, as²⁵

$$\sigma(\omega) = \sigma_{dc} + A\omega^n \quad \dots (6)$$

where $\sigma(\omega)$ is the total conductivity; the sum of frequency independent part σ_{dc} and frequency dependent part $A\omega^n$ characterize all electrical dispersions; and n ($0 \leq n \leq 1$) is a temperature dependent constant, intrinsic to the material.

Different hopping mechanisms have been reported predicting different temperature/frequency relationship with the exponent n . For small polaron hopping n increases with temperature, while for large polaron hopping it decreases²⁶. Applying Jump Relaxation Model (JRM) to the frequency response of conductivity in the present study, it is possible to fit the data obtained in this study with a polynomial fit curve giving it a quadratic form ($n = 2$).

According to dielectric theory, dielectric loss represents the change in molecular activation energy, leading to distortion and polarization²⁷ of the molecules. When the molecules, induced by an electric field collides with each other, relaxation occurs due to their mutual impact, which causes dielectric loss ($\tan \delta$), expressed as the sum of polarization loss ($\tan \delta_p$) responsible for ionic conduction and conduction loss due to leak conductance ($\tan \delta_c$), the measure of electronic conduction of the material. Thus,

$$\tan \delta = \tan \delta_p + \tan \delta_c \quad \dots (7)$$

Decrease in activation energies in the conduction process, agrees with the decrease in relaxation activation energies when the hopping mechanism is modified. At a certain temperature, if the activation energy in the relaxation process is higher than that in the conduction process, the relaxation does not govern the conduction mechanism at that temperature. All types of carriers contribute to the conduction though may not contribute to the relaxation process²⁸. This might result in isotropic dielectric behavior, and is considered as taking place in the PPy coated fibre beyond the frequency of 7 kHz.

4 Conclusion

Oxidative polymerization of pyrrole leading to formation of a thin uniform coating of PPy over the cellulose fibre extracted from bamboo has been achieved by a process of polymerization induced adsorption. On incorporation of the coating layer, composition of bamboo cellulose remains preserved but its surface morphology and electrical conductivity are found to change drastically. Some interesting changes in these properties are observed while keeping it chemically intact. The electrical resistance decreases with increasing layer concentration while the dielectric properties exhibit strong low frequency dispersion as shown by standard conducting polymers like PPy, PANi, etc. Thus the bamboo fibre which has characteristic Ohmic resistance like other cellulose has exhibited a changeover to CP like dielectric behavior and a remarkable AC conductance in the low frequency range, enlarging the prospect of its use as a semiconductor material in electronic industries. The main feature of this study lies in the simplicity of the technique which is successfully used for making the PPy monolayer without using any dopant and without disturbing the chemical structure of cellulose in the fibre substrate. Hence, the properties of PPy can be blended in the bamboo fibre for its potential use as conducting textile, as well as a semiconductor material in the low frequency range of AC operating voltage.

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