

Chapter 6

Polypyrrole nanocoating on bamboo cellulose fibre

6.1 Introduction

The growing demand of eco-friendly materials sparks off the growth of green polymer composite and in many approaches green polymeric materials have been synthesized from cellulose using different coupling agents, for reinforcement of its mechanical properties [1]. Using a variety of organosilane materials, Xie et al. reported such reinforcements in which silane, used as coupling agent, increased the level of interfacial adhesion of cellulose with the target polymer matrices and also improved the mechanical properties of the resulting fiber/polymer composite. Addition of nanofillers and nanoparticles is another efficient way to enhance the fibre-matrix interface which generally leads to high performance multi-scaled material [2-4]. Jianguo Huang reported uniform polypyrrole nanocoating on morphologically complex cellulosic materials without disrupting the hierarchical network structures of individual cellulose fibers [5]. Inspired from this work, we propose a chemical method to regenerate bamboo cellulose fibre by surface coating of PPy nano. The regenerated cellulose fibre (RCF) thus synthesized is characterized for various properties, and also their electrical properties. Electrical conductivity shows low frequency dispersion like that of PPy. Surface nanolayer of PPy over bamboo fibre retains the properties of PPy and at the same time does not disrupt hierarchical cellulosic structure, thus producing modified cellulose fibre (MCF). It is expected that the process developed for MCF from original bamboo cellulose would be also suitable for other cellulosic fibers of natural origin.

6.2 Experimental

Oxidative polymerization of pyrrole is initiated by FeCl_3 in acidic medium. To prepare the PPy cellulose bi-hybrid composite, two mL of aqueous solution of FeCl_3 is added drop wise into 40.0 mL pyrrole solution with constant stirring. The reaction mixture turns greenish black within a minute and black precipitate of PPy is gradually formed. The clear filtrate, having nanosized PPy is used for coating of the bamboo cellulose fibres. 20 mL of this solution is poured over bamboo fibres and sonicated for 60 minutes. Gradual change of colour is observed changing its colouration into reddish brown. This is due to deposition of PPy on the fibre surface. Three different pyrrole concentrations, viz. 0.1%, 1% and 5% taken in wt/wt ratio are used. The filtered fibres are washed with 2-propanol and de-ionized water, followed by drying in air flow and conventionally characterized by SEM, TEM and FT-IR.

6.3 Result and discussion

6.3.1 Nature of PPy coating on fibre

The increasing pyrrole concentration results in thicker PPy coating over the fibre surfaces. This is also eminent from gradual change in color of the polymer mixture with the fibres from greenish black to black and then reddish brown. The change in color observed in the filtrate is shown in Fig. 6.1 and in each case black precipitate is found, subsequent to chemical polymerization and adsorption of the polymer.

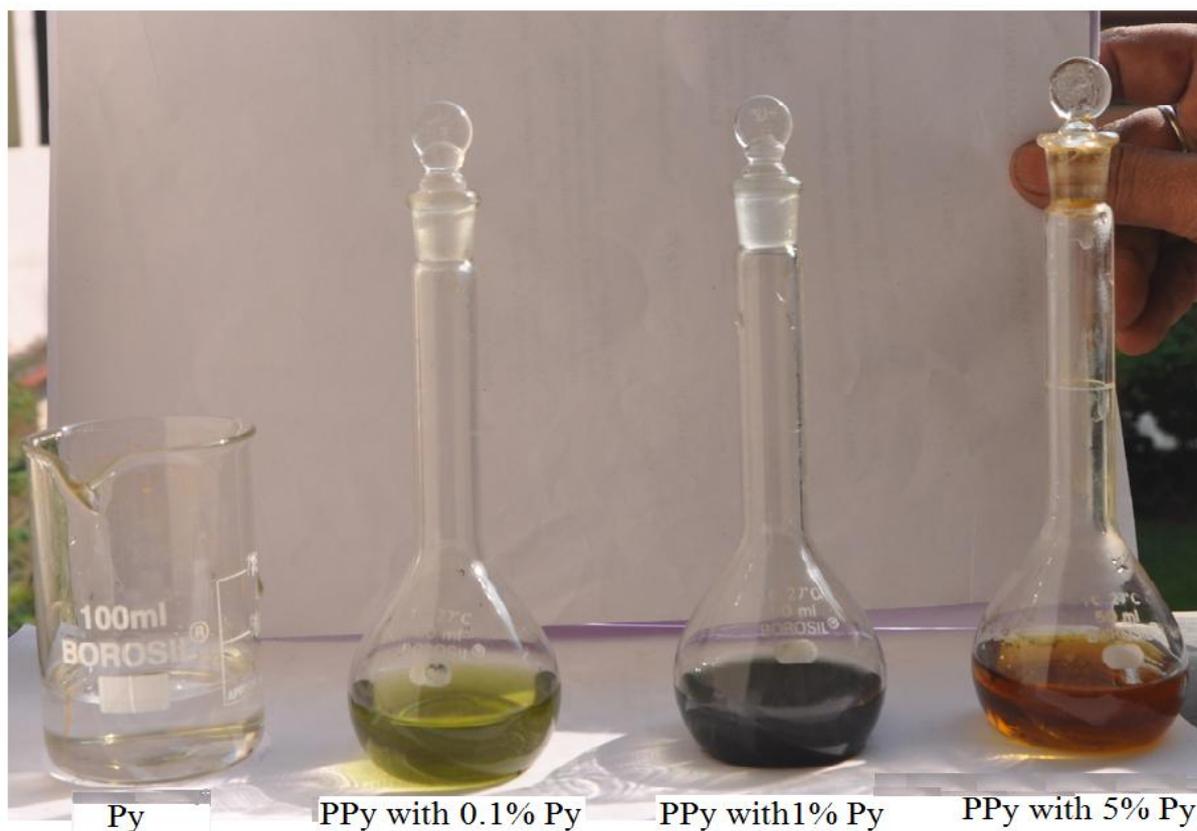


Fig 6.1 Change of colour of polymeric solution with monomer concentration

The resistance of the fibre is measured at room temperature. The applied voltage ranges from 0.1 to 1.0 V and the resulting dc current is measured. The conductivity is calculated from the slope of the $I - V$ graph, using different thickness of the sample. The dielectric properties of the fibre sample are measured with an impedance analyzer, having a four terminal Nickel plated Cobalt electrodes of 38 mm diameter and 1mm spacing. The capacitance C_p and C_0 without and with the sample respectively and parallel resistance R_p with the sample between the electrodes are measured for determination of the complex dielectric function. The dissipation loss due to dielectric test fixtures and the correction coefficient are considered to eliminate the effect of stray capacitance during evaluation of the complex dielectric function in the frequency range 10 Hz-7 KHz, at 30° C.

6.3.2 SEM micrographs

The influence of the PPy layer on the structure and morphology of the bamboo fibre is

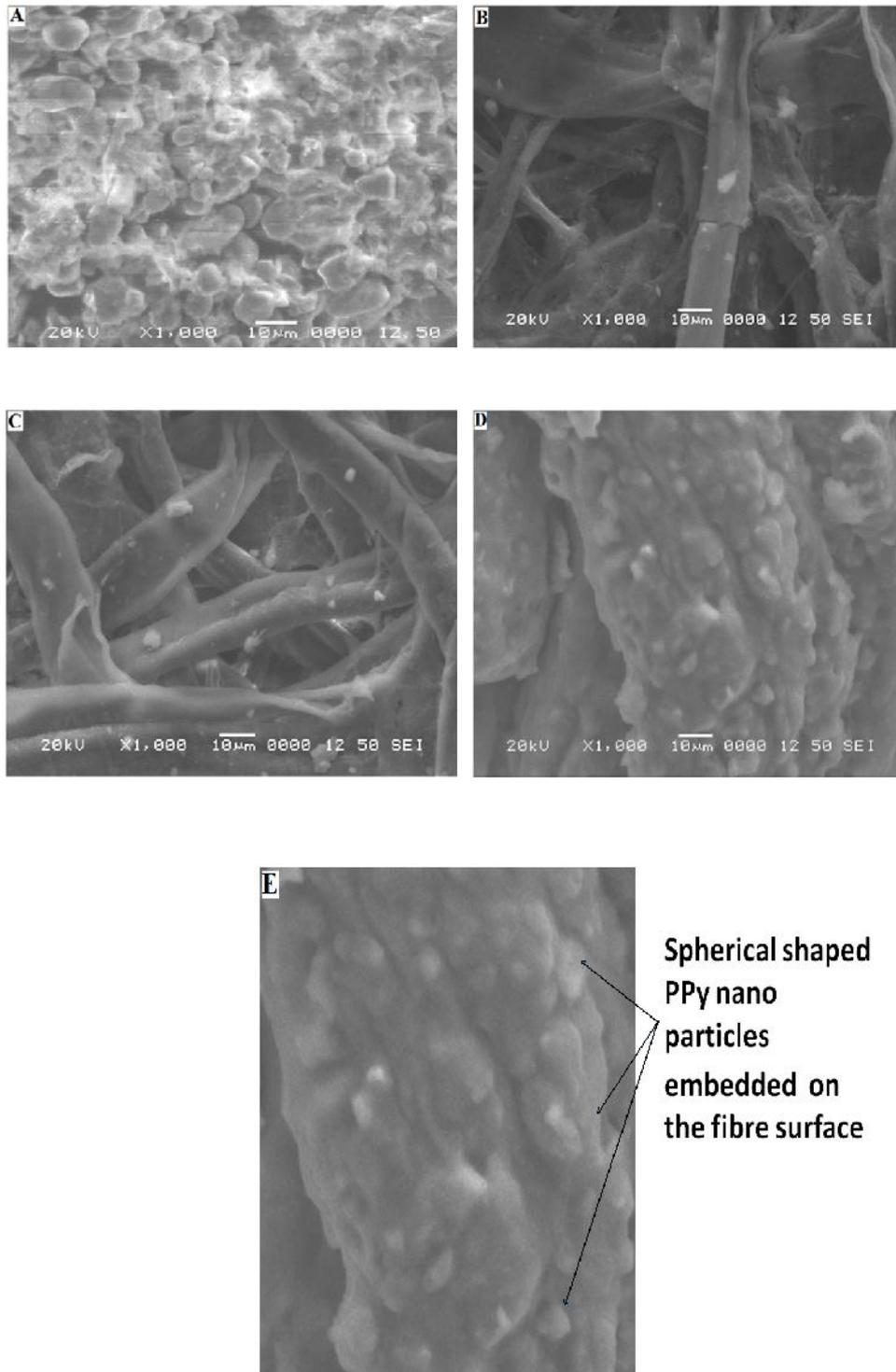
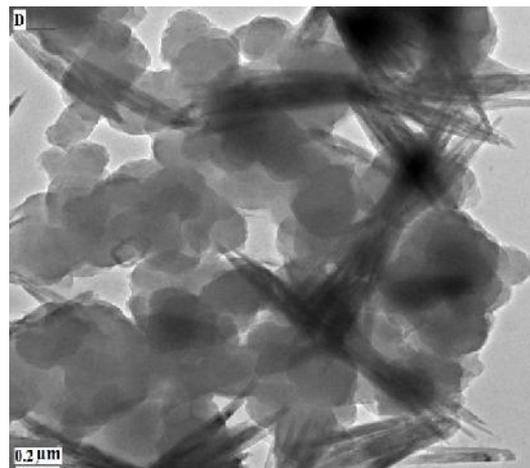
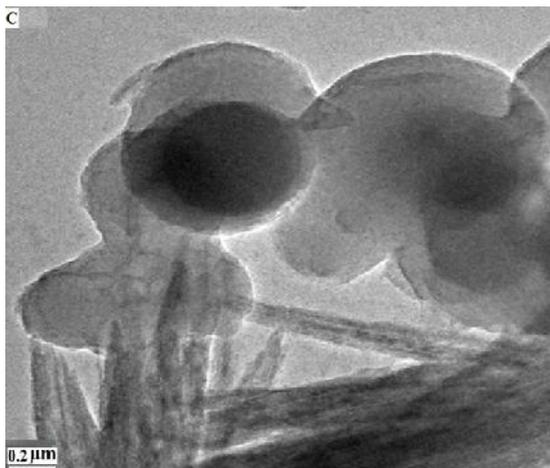
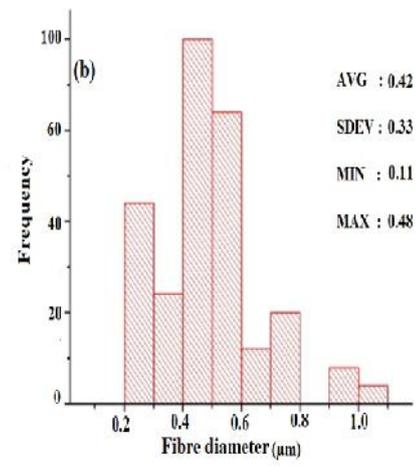
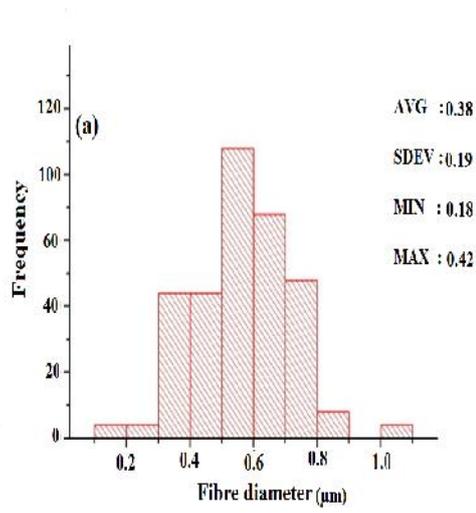
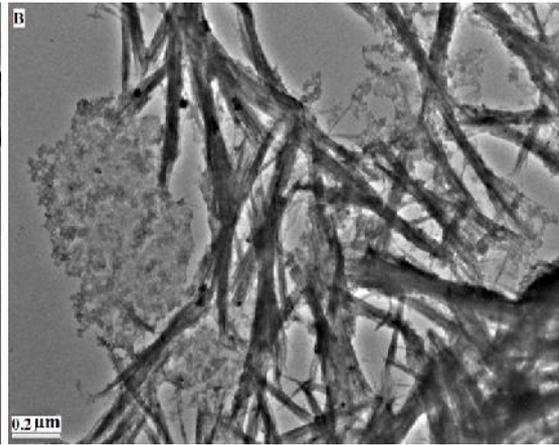
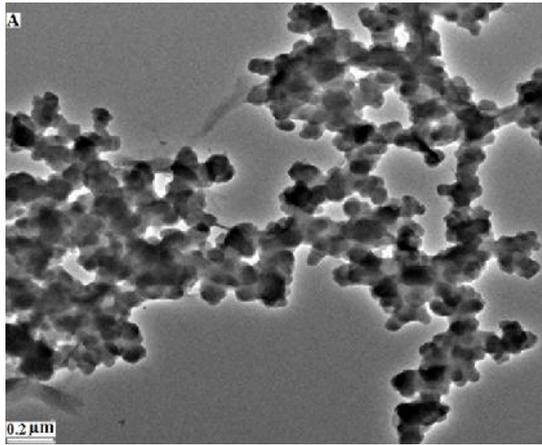


Fig. 6.2 SEM micrographs of PPy(A) and PPy coated fibres with Py concentration 0.1%(B), 1% (C) and 5%(D). The PPy surface layer in the fibre as curved out from (D) is shown in (E).

investigated by SEM and shown in Fig.2 (A-D), A is for PPy and B-D for PPy coated fibres with different Py concentrations 0.1%, 1% and 5% respectively. The size of the PPy particles agglomerated over the cellulosic surface is found to be decreasing from 80 to 50 nm with increased concentration of pyrrole. It is also found that the length of the cellulose surface remains unchanged while the polymerization induced adsorption of Py on the surface of bamboo fibres results in formation of the PPy nanolayer slightly increasing its original width from 9 μ m. Thus a high aspect ratio is obtained in the nanocrystalline structure which would be the possible reason of huge entanglement of suggested qubits between the fibre and the PPy nanolayer [7, 8].

6.3.2 TEM micrographs

The PPy deposited on the surface of the bamboo fibres is seen to be sparingly distributed in the lower monomer concentrations, while it appears more and more homogeneous and uniform with increased Py concentration at 5%, leading to a pattern resembling quantum entanglement of the PPy particles over the cellulosic substrate. This results in formation of a continuous pathway for the charge carriers associated with the PPy particles facilitating increased electrical conductivity of the fibres (to be seen in the sections to follow) due to polymer coating and is the cause of characteristic dielectric behavior exhibited by CP's at lower frequencies [9]. The microscopic observations from Figs 6.2 and 6.3 reveals that the PPy layer with 5% Py concentration is more potent than the two lower concentrations in terms of structural and functional changes in morphology.



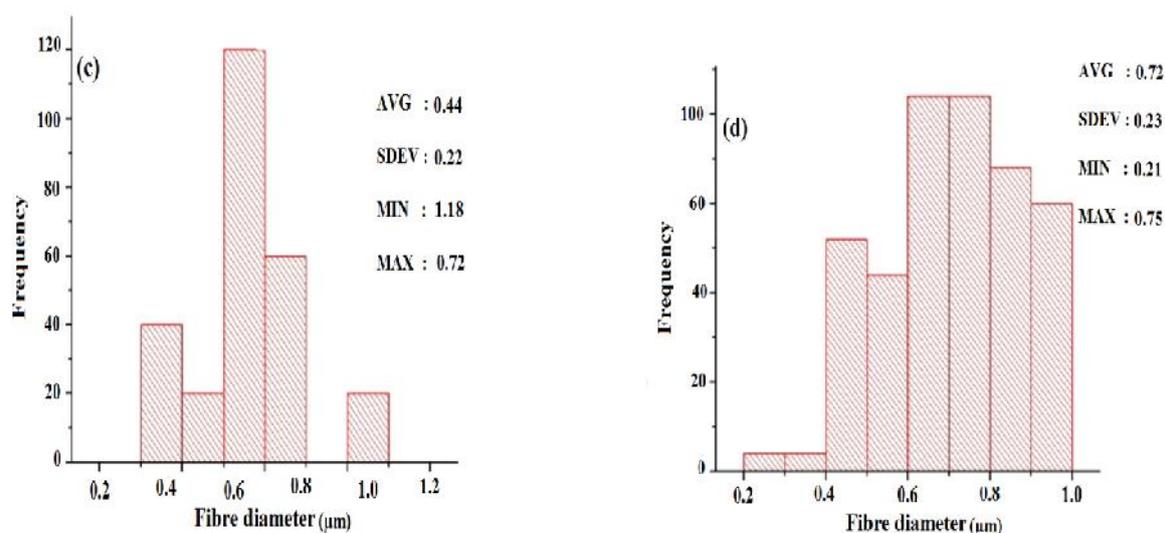


Fig. 6.3 (A-D) shows the TEM micrographs for PPy and PPy coated cellulose fibres for different monomer concentrations of 0.1, 1 and 5%. The histogram shows the distribution pattern of particle size for respective TEM images.

6.3.3 FTIR studies

Fig 6.4 shows the FTIR spectra for uncoated cellulose and the coated fibre for three different monomer concentrations viz. 0.1%, 1% and 5% respectively. While the characteristic cellulose peaks are found in its spectrum, the PPy coated bamboo fibre gives the spectra similar to that of untreated bamboo cellulose [10] but with mostly blue shifted peak positions. The FTIR spectra of the fibres fabricated with polymer coating of 0.1% and 5% monomer concentrations are similar, 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 becoming significant at higher concentration of Py. Most of the cellulose peaks characteristic of untreated bamboo cellulose is found to be blue shifted in the spectrum of PPy coated fibres. 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 shifted to 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 is shifted to 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 (1-4) glucosidic linkage is shifted to 745 cm^{-1} and 710 cm^{-1} in the PPy coated (5%) fibres [11-13]. The main absorption peaks and its associated functionality for cellulose, coated as well as uncoated, are enlisted in table 6.1.

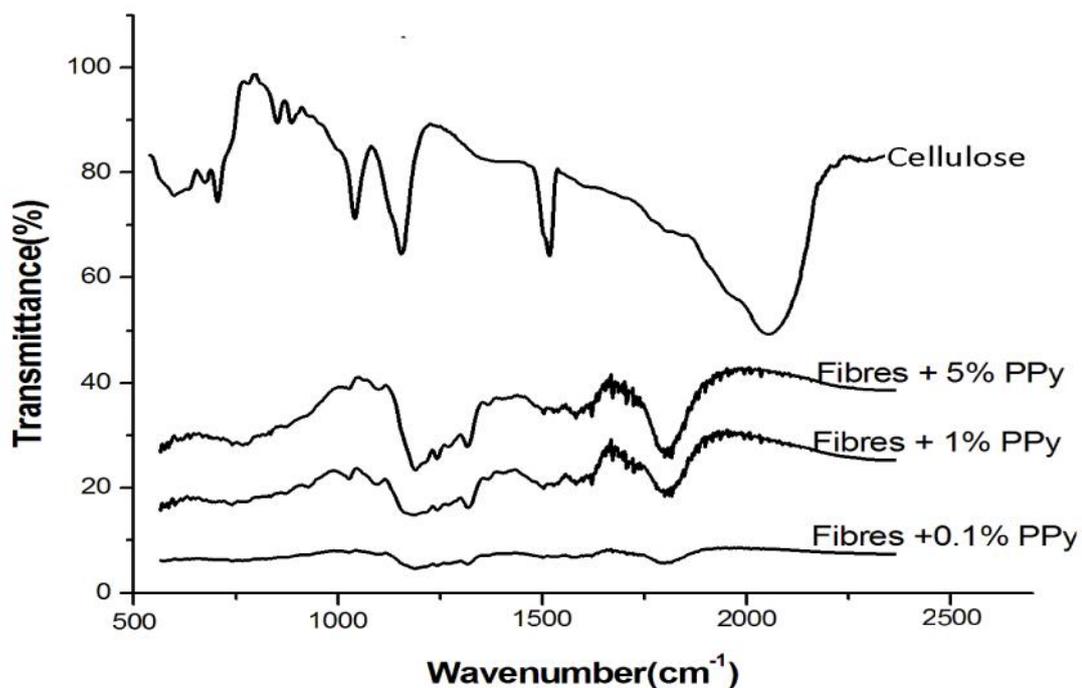


Fig. 6.4 FT-IR spectra of Cellulose and PPy with cellulose fibre: pure and coated with PPy

Table 6.1 Main absorption peaks in the FTIR spectrum

Material	Wave number (cm ⁻¹)	Functionality
PPy	1535	C = C stretching of pyrrole ring
	1407	C - N stretching vibration in the 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 ring deformation or C - H rocking
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 the (1 - 4) glucosidic linkage.
	640, 672	Out of plane bending at C - O - H

6.3.4 Electrical 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 solution. The Current-Voltage (I-V) plot in the voltage range of 0.1 to 1 Volt for PPy and its coated fibres are shown in Fig 6.5, while the changing trend of its resistivity with monomer concentration is shown in Fig 6.6.

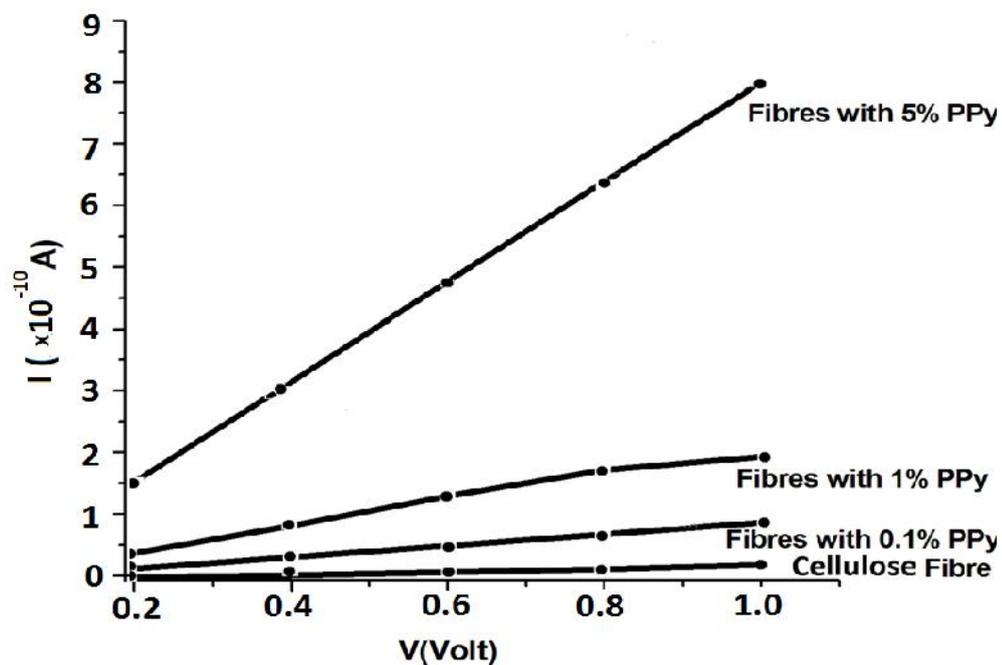


Fig.6.5 I-V characteristics of fibres, uncoated and coated

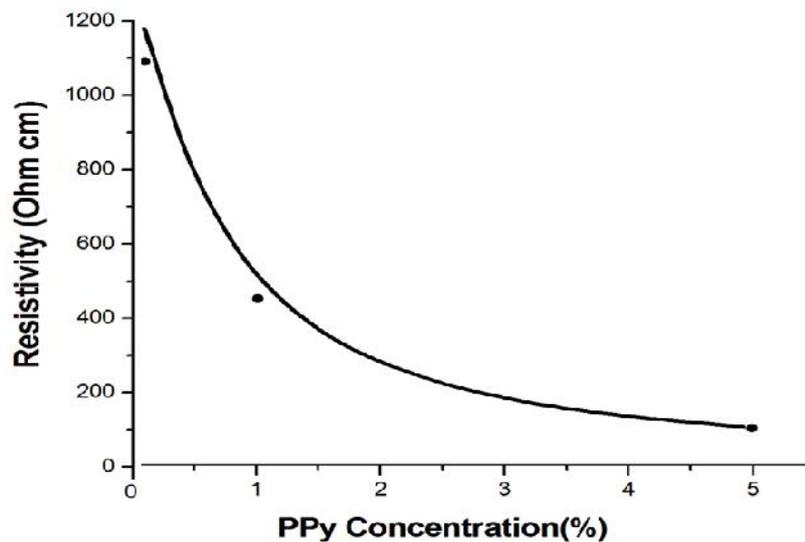


Fig.6.6 Resistivity of coated fibres with monomer concentration

The increasing concentration of Py in the polymerization mixture increases the surface density of CP particles in the polymer coating of the fibres which in turn results in gradual decrease of its resistivity and is found to be 1075, 124 and 0.159 K /cm with Py concentration of 0.1%, 1% and 5% respectively. This fact is in consistency with the SEM and TEM results also.

6.3.5 Dielectric properties

Fig 6.7 shows AC conductance vs. frequency for PPy and its coated fibres with different Py concentrations. Inset shows dielectric loss vs. frequency for PPy. As explained in sec 2.3 above, ac conductivity (σ_{ac}) has a functional relationship with dielectric loss (ϵ'') which accounts for the formation of polarons and bipolarons in the case of doped CP [14].

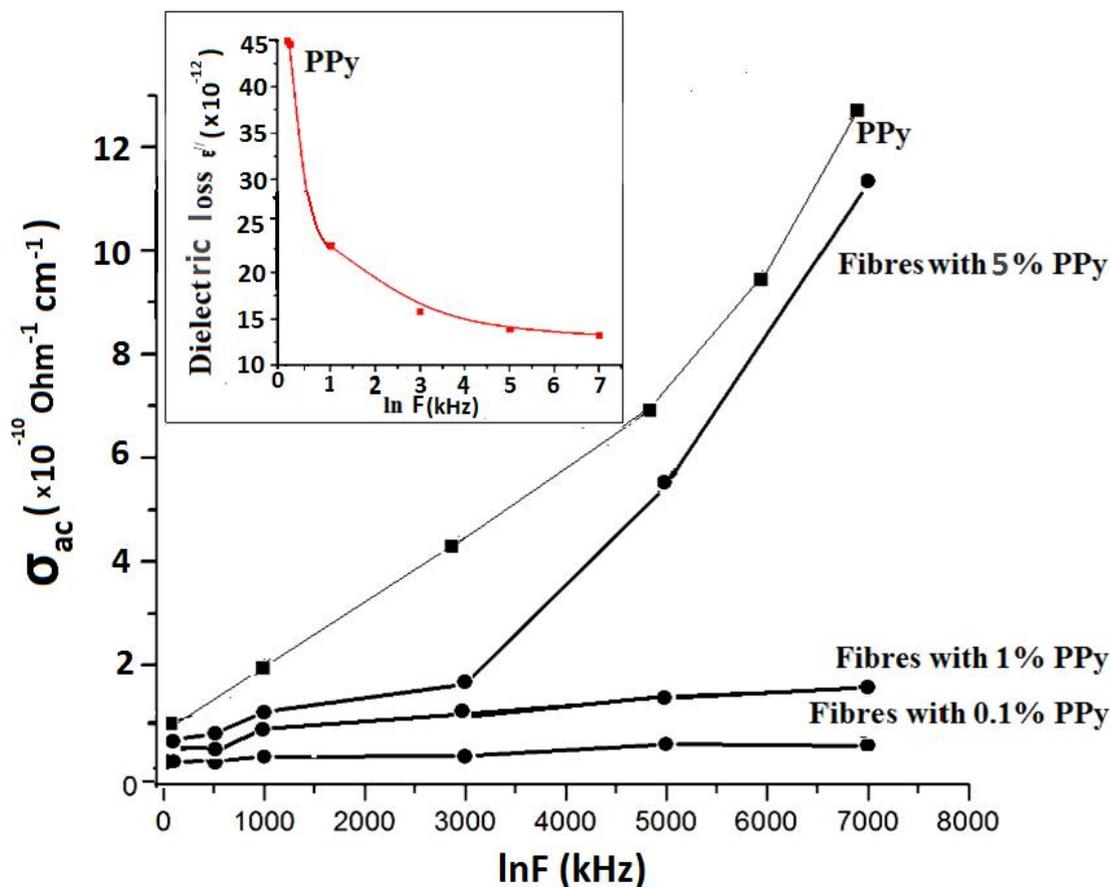


Fig. 6.7 ac conductivity of PPy and PPy coated fibres (differing concentration).

Inset shows dielectric loss of PPy which determines its ac conductivity.

Since σ_{ac} is directly proportional to ϵ'' , it is expected that in a certain polarization state, increasing dielectric loss of the bi-hybrid composite formed in the fibre surface would result in increasing conductivity under the approximation that the polarization current density remains constant [15]. Thus the prominent ac conductivity of the bamboo fibres is the result of its CP coating responsible for formation of secondary charge carriers in the form of polarons and bipolarons in the fibrous substrate. As shown in Fig. 6.7, the PPy coated fibres exhibit remarkable ac conductivity in the low frequency range 10 Hz to 7 KHz showing an increasing trend with increased Py concentration. AC conductivity (σ_{ac}) is calculated from the dielectric data using the relation [16]

$$\sigma_{ac} = \sigma_0 \tan \delta \dots (6.1)$$

The conductivity plot of PPy and its coated fibres possess the following characteristics:

- (1) The bamboo cellulose has shown almost constant conductivity in the frequency range of 1Hz to 7 KHz showing its Ohmic nature.
- (2) The conductivity plot of PPy coated fibre is different from the pure fibre and the effect of PPy coating is highly prominent and can be accessed from the curve.
- (3) A plateau region is observed in case of the coated fibres in the low frequency region while the conductivity is found with steep increase from 3 KHz to 7 KHz.
- (4) The inset shows the plot of dielectric loss with frequency in the same frequency range.
- (5) The functional relationship of dielectric relaxation and conductivity can be accessed from the two curves by means of a suitable theory, as explained in the next section.

6.3.6 Conductivity growth vis-à-vis the CP coating: An analysis on change in hopping behavior with surface coating of PPy in the fibres

The conductivity spectra of PPy coated bamboo cellulose can be explained on the basis of Jump Relaxation Model (JRM) [16]. The frequency independent plateau in the low frequency region (below 3 KHz) is attributed to the long range translational motion of ions which is responsible for DC conductivity. As the frequency increases (above 3 KHz) the conductivity shows non-linearity. According to JRM, the conductivity at the low frequency region is associated with the successful hops of the ions to the vacant sites in their neighborhood. Due to longer time period, successive jumps results in long range translational motion of ions contributing to DC conductivity which is predominating in the lower frequency and takes a

steady value up to 3 KHz. At a high frequency two competing relaxation processes, viz. (i) unsuccessful hopping i.e., the jumping ions to transit back to their initial position, and (ii) successful hopping i.e. the neighborhood ions becoming relaxed with respect to the position of the excited ions and the excited ions retaining their new position [17]. The observed conductivity plot is the result of such unsuccessful and successful hopping events. Increased ratio of successful and unsuccessful hopping at higher frequencies result in dispersive conductivity while predominance of only one leads to a stable pattern. A convenient formalism is proposed by Jonscher, who investigates the functional relation of conductivity and frequency at constant temperature for a host of different materials [18] as,

$$\sigma(\omega) = \sigma_{dc} + A \omega^{-n} \dots\dots\dots(6.2)$$

Where $\sigma(\omega)$ is the total conductivity σ_{dc} is the frequency independent conductivity, A is the temperature dependent pre-exponential factor; n is the frequency exponent ($0 \leq n \leq 1$) which is a temperature dependent constant and an intrinsic property of the material. The term $A \omega^{-n}$ caters to the frequency dependence and characterizes all dispersion phenomena. Different hopping mechanisms have been reported by many researchers predicting different temperature/frequency relationship with the exponent n [19]. In the case of small polaron hopping n increases with temperature while for a large polaron hopping n decreases with temperature [20]. Applying the JRM to the frequency response of conductivity in the present study, it is possible to fit the data to the power law stated above and the polynomial fit curve of the data gives us a quadratic form ($n = 2$), at a moderate temperature of 30°.

According to dielectric theory, dielectric loss represents the change of energy that leads to molecular distortion and polarization. When the molecules, induced by an electric field are getting rubbed with each other, relaxation occurs due to their mutual impact, which

subsequently causes dielectric loss ($\tan \delta$). Dielectric loss is the sum of polarization loss ($\tan \delta_p$) and conduction loss due to leak conductance ($\tan \delta_c$) of the material, expressed as

$$\tan \delta = \tan \delta_p + \tan \delta_c \dots \dots \dots (6.3)$$

The first term is responsible for ionic conduction and the second is a measure of electronic conduction [21].

Decrease in activation energies in conductivity agrees with the decrement of relaxation activation energies when the hopping mechanism is modified. Decrease in activation energy makes the segmental motion easier, which increases the diffusion of charges [22-24]. If the activation energy of the relaxation process is higher than the conduction process at a certain temperature, the relaxation process does not govern the conduction mechanism at that temperature, and all types of carriers contribute to the conduction but may not contribute to the relaxation process [25]. It may lead to isotropic dielectric behavior, and is possibly taking place in the PPy coated fibre beyond the frequency of 7 kHz.

6.4 Conclusions

Oxidative polymerization of pyrrole leading to formation of a thin uniform coating of PPy over the cellulose fibre extracted from bamboo shows that coating has not affected the composition but surface morphology and electrical conductivity of the cellulose drastically change. The PPy coating over the cellulose fibre substrate is based on polymerization induced adsorption of the growing polymer chains from its solution, forming a thin film of PPy which results in interesting changes in the bamboo fibre keeping its chemical properties intact. The electrical resistance decreases with increasing layer concentration while the dielectric

properties exhibit strong low frequency dispersion characteristic of standard conducting polymers. Thus the bamboo fibre having characteristic Ohmic resistance exhibits a changeover to CP like dielectric behavior for its prospective use as a semiconductor material in electronic industry. The main feature of this study is the simplicity of the technique for incorporation of the PPy nanolayer without using any dopant and without disturbing the chemical structure of cellulose.

6.5 References

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