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Study of Temperature Dependent Electrical Conductivity and Dielectric Properties of PPY/SWCNT/PVA Composites

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Abstract

The effect of temperature on the DC and AC electrical conductivities of pure PPy and PPy/SWCNT as well as PPy/SWCNT/PVA composites has been discussed in this paper. The activation energies for these materials have been calculated using Arrhenius equation. The values of activation energies for pure PPy, PPy/SWCNT and PPy/SWCNT/PVA are found to be 1.83 eV, 3.166 eV and 6.6 eV, respectively. The increment of conductivity with temperature has been explained on the basis of reduction of energy band gap and hopping of charge carriers. PPy, PPy/SWCNT and PPy/SWCNT/PVA are found to exhibit larger dielectric constants than pure PVA. The enhanced dielectric constant of the composites has been correlated with the increase of molecular ordering due to addition of carbon nanotubes.

Key words. Polypyrrole; Single wall carbon nanotubes; Polyvinyl alcohol; conducting polymer; electrical conductivity; dielectric constant.

1 Introduction

Intrinsically conducting polymers (ICP) such as polyaniline (PANi), polypyrrole (PPy), polythiophene (PTh) and their derivatives have been studied intensively during the last two decades due to their high electrical conductivity, good environmental stability and other fascinating physical properties. PPy has been extensively studied among these conducting polymers, due to its excellent conductivity, high yield in redox process, gas sensing ability,

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optimum performance at room temperature and environmental stability[1-4]. The demand for electrically conducting polymers as needed in the electronics industry has in the past been met by using high loadings of conductive powders such as silver, gold and graphite (sometime as high as 80% by weight) with the polymer matrix[5]. There are a number of disadvantages to this approach, including high cost and deterioration in other properties of the polymer.

At present the research interest in conducting polymers is going on because of their versatile promising applications in the field of energy storage[6], sensors[7], electronic and optical devices[8] and so on. Synthesizing composite materials is an effective way to combine the features of different materials and tailor the properties to achieve the desired material performance. One of the highly applied methods of obtaining high electrical conductivity and desirable properties is through preparing composites of polypyrrole with other insulating polymers having desirable mechanical properties[9-10]. The polymer composites can be prepared either by electrochemical or chemical polymerization. In this technique, a number of insulating polymers, namely, poly (styrenesulphonate)[10], polycarbonate[11], poly (vinyl chloride)[12], rubber[13], poly(vinyl alcohol)[14], *etc.* have been combined with polypyrrole in aqueous or organic medium to produce polypyrrole polymer composites which will have the conducting properties of polypyrrole with some of the superior mechanical properties of the insulating polymer.

The infusibility and insolubility of conducting polymers generally make them poorly processable either by solution technique or by melt processing methods[15,16]. These drawbacks can be overcome either by forming copolymers of pyrrole, or by forming PPy composites or blends with commercially available polymers or inorganic materials which offer better mechanical and optical properties, stability and processability[17,18]. A general method for creating PPy composites is the in situ polymerization of pyrrole in presence of organic or inorganic substances. Other useful approach for the improvement of the processability and the mechanical properties of insoluble polymers is the blending with soluble matrix polymers. Considering some advantages of poly (vinyl alcohol) (PVA) such as its high strength, flexible molecular chains, good adhesion to electrodes and its ductile nature, some works on the preparation of PPy/PVA composites has already been reported in the literature[19,20].

Carbon nanotubes (CNTs) exhibit excellent mechanical and electronic properties. The amazing mechanical and electronic properties of CNTs make them ideal candidates as fillers in lightweight polymer composites designed for structure or functional applications. CNTs have also provoked enormous interest in their fundamental behaviour and a wide variety of potential applications. CNTs can be either metallic or semiconductive, depending on their helicity[21]. In the past few years much research on fabrication of various polymer/CNTs composites has been reported[22-24]. The variation of DC conductivity of PPy with respect to the varying SWCNT and PVA contents in the PPy/SWCNT/PVA ternary composites has also been reported[25]. The binary composites having 0.5 wt% SWCNT in PPy matrix and the ternary composite having 25 wt% of PPy/ 0.5wt%SWCNT in PVA matrix have been found optimum[25] for industrial applications. This paper reports the effect of temperature on DC and AC conductivities of PPy/SWCNT/PVA ternary blends in continuation of the results reported earlier[25]. The effect of frequency on the dielectric constant of the studied materials is also being reported in this paper.

2 Experimental

The detailed procedure of preparation of PPy and its composites with SWCNT and PVA has been reported earlier[25]. Hioki Impedance Analyzer IM 3570 was used for measuring the AC and DC conductivities as well as the dielectric constant of samples.

The dielectric constant, ε', was calculated from capacitance which was measured using the impedance analyzer. It was calculated using the following relations:

$$\varepsilon' = (C_s d) / (\varepsilon_0 A),$$

where d is thickness, A is the effective cross-sectional area of the sample and ε_0 is permittivity of free space.

3 Results and Discussion

3.1 Temperature Dependence of DC Conductivity :

The dc electrical conductivity is evaluated from conductivity data at lower frequencies. The temperature dependence can be expressed by the following Arrhenius equation[12,16]:

$$\sigma_{dc} = \sigma_0 \exp(E_a/kT)$$

where σ_0 can be considered as the limiting value of conductivity at an infinite temperature, E_a is the activation energy for conduction, k is Boltzmann constant, and T is the absolute temperature. The semilogarithmic relation of this equation for different materials is shown in Figure 1, where the solid lines represent the best-fitted value to obtain slope. The activation energy is calculated from the slope of parallel straight lines. The values of activation energies for pure PPy, PPy/SWCNT and PPy/SWCNT/ PVA are found to be 1.83 eV, 3.166 eV and 6.6 eV, respectively.

It is interesting to note that the activation energy of the PPy/SWCNT composite is smaller whereas the conductivity is higher than the PPy/SWCNT/PVA composite. This can be due to the creation of larger number of polarons and bipolarons and the presence of these charge careers contributes to the enhancement in the conductivity of binary PPy/SWCNT composite. The formation of continuous bipolaron bands takes place with the increase in doping of SWCNT. The separation between these bipolaron bands increases at the expense of the band edges. It can be concluded that the upper and lower polaron bands merge with conduction and valence bands[26], respectively for a very heavily doped polymer leading to a wider separation between these bands which eventually leads to a higher value of activation energy.

The dc conductivity of tested materials is found to increase with increasing temperature. The rising temperature provides increments in free volume and segmental mobility[27]. These two entities then permit free charges to hop from one site to another which gives rise in conductivity. Electrical conductivity of PPy

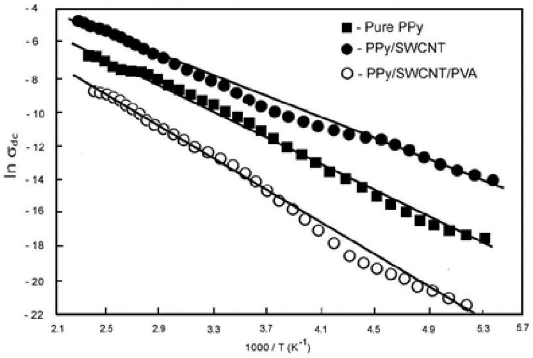

Figure 1. Temperature dependence of DC conductivity of pure PPy and PPy/SWCNT, PPy/SWCNT/PVA composites

involves movement of positively charged carriers or electrons along polymer chain and hopping of these carriers between polymeric chains. The term hopping refers to the sudden displacement of charge carriers from one site to another neighboring site and in general includes jumps over a potential barrier and quantum mechanical tunneling[28]. In case of the studied materials this could be due to the significant reduction of energy gap between valence and conduction bands which makes it easy for the electrons to hop from valence band to conduction band[29] and hence gives higher dc conductivity values as compared to other temperatures[30].

3.2 Temperature Dependence of AC Conductivity :

Figure 2 exhibits the temperature and frequency dependence of the ternary PPy/SWCNT/PVA composite. It is evident that the AC-conductivity is both frequency and temperature dependent and enhances with increase of both frequency and temperature.

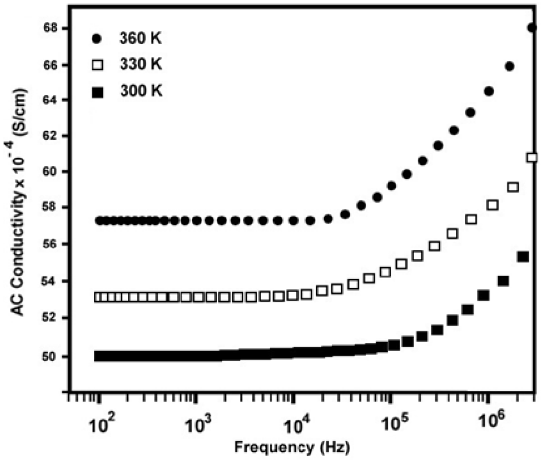

Figure 2. Temperature and frequency dependence of PPy/SWCNT/PVA ternary composite

These composites show similar behavior up to 10^4 Hz, viz. that there is no significant variation in the conductivity with frequency during this range. This behavior could be due to the fact that the distance between the conductive grains is short enough for the conduction to be dominated by the thermal fluctuation of the carriers' concentration across the insulating barriers. It is observed that the conductivity goes on increasing as frequency is increased further. This indicates that there may be charge carriers, which can be transported by hopping through the defect sites along the polymer chain. The increase in AC conductivity with respect to temperature confirms the semiconducting behaviour of the ternary PPy/SWCNT/PVA composite.

3.3 Dielectric Behaviour :

The frequency-dependent dielectric constants for pure PPy, PPy/SWCNT and PPy/SWCNT/PVA composites are shown in figure 3. High values of dielectric constants have been found for these materials at room temperature. These large values may be due to the presence of highly conducting bridges caused by carbon nanotubes and easy charge transfer through well ordered polymer chains in disordered regions as suggested by Joo *et al*[31]. Dielectric constant decreases as the frequency is increasing and this remains nearly constant after the frequency 10^4 Hz. The dielectric constant is found to change rapidly at low frequencies, whereas it becomes almost constant at higher frequencies. This behaviour has been observed in unblended PPy, PPy/SWCNT and PPy/SWCNT/PVA composites. The inset of figure shows the frequency dependent dielectric constant of pure PVA.

It can be observed from figure 3 that the value of dielectric constant is greater for binary PPy/SWCNT composite, whereas it decreases considerably in case of PPy/SWCNT/PVA ternary composite. The large dielectric constant of the PPy/SWCNT composite can be attributed to the interface effect between the SWCNTs and the polymer[32]. A higher dielectric constant for PPy/SWCNT composite can be interpreted by an increase in crystallinity due to clustering of nanotubes in the polymer matrix. The resulting orderness in this composite increases the interfacial interactions between the polymer and the carbon nanotubes, leading to maximum space charge polarization[33]. All these three materials (pure PPy, PPy/SWCNT and PPy/SWCNT/PVA) exhibit much higher dielectric constant than pure PVA as indicated in Table 1.

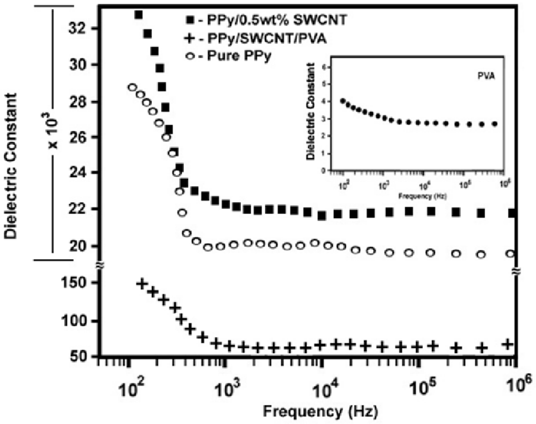

Figure 3. Dielectric constants of pure PVA, pure PPy and PPy/SWCNT, PPy/SWCNT/PVA composites

Table 1. Values of maximum dielectric constant of studied materials

Material	Maximum Dielectric Constant
Pure PVA	4
Pure PPy	28,960
PPy/SWCNT composite	33,874
PPy/SWCNT/PVA composite	152

4 Conclusions

The DC and AC conductivities of the PPy/SWCNT and PPy/SWCNT/PVA composites increase with increasing temperature. This observation suggests their semiconducting behaviour. The hopping of free charges from one site to other due to increment in free volume and segmental mobility is the reason for increase in conductivity of these materials due to rising temperature. This hopping of charge careers can also be due to reduction in energy gap between valence and conduction bands. The rising AC conductivity beyond 10^4 Hz can also be explained on the basis of hopping of charge careers at defect sites. Pure PPy and the two composites, namely PPy/SWCNT and PPy/SWCNT/PVA exhibit higher dielectric constants at room temperature than pure PVA. The addition of SWCNT with PPy enhances the dielectric constant of the composite. This increment in dielectric constant can be due to increased molecular ordering of PPy/SWCNT composite due to addition of carbon nanotubes. This behaviour makes PPy/SWCNT as well as PPy/SWCNT/PVA composites good candidates for making super-capacitors.

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