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DIELECTRIC PROPERTIES OF POLYPYRROLE MULTI-WALLED CARBON NANOTUBES NANOCOMPOSITES

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This work mainly concerns with the preparation and characterization of polypyrrole (PPy) and multi-walled carbon nanotubes (MWCNTs) reinforced polypyrrole (PPy) nanocomposites. We have synthesized the pure polypyrrole (PPy) and PPy/MWCNTs nanocomposites by in-situ polymerization method of pyrrole in aqueous dispersion of multi-walled carbon nanotubes (MWCNTs) using $FeCl_3.6H_2O$ as an oxidant. The amount of MWCNTs in nanocomposites varied in the range of 0-10% by weight in pure polypyrrole (PPy).The structure of the polypyrrole-MWCNTs as investigated by X-rays diffraction (XRD), and FTIR spectra indicate that MWNTs acted as the core in the formation of a coaxial nanostructure for the composites. Dielectric studies of the nanocomposites exhibited significant increase in dielectric constant and loss factor with the increase of MWCNTs in the composites which has been attributed to increase of charge carriers due to increased π-electrons in the nanocomposites.

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1. Introduction

Before thirty years ago all carbon based polymers were inflexibly regarded as insulators and hence were significantly used by the electronics industry for this important characteristic. The newly found Carbon nanotubes (CNTs) and conducting polymers (CPs), materials have exhibited the outstanding properties. From these points of views a new class of polymers has being discovered which intrinsically conductive (ICPs) [1] are. Conjugated polymers are types of conducting polymers consist of alternating single and double bonds along its linear chains. These double bonds are very sensitive to physical or chemical interactions as well as to the conductivity of the CPs [2-4].

The combination of CPs and CNTs furthermore exposes medical effects which propose a different mechanism to produce new multifunctional materials with larger potential in application [5, 6]. The CPs/CNTs have many applications whish consist of mechanical, thermal, electrical, electrochemical characteristics etc. Polypyrrole possess better electrical conductivity, good environmental Stability, low cost and simplicity of preparation [7, 8]. In polymeric materials electronic transport has become a waste area of research to know the general theory of polymer physics [9-19].

Sishen Xian et al [20] prepared the polypyrrole and carbon nanotubes composites using in situ-polymerization technique. TEM show that CNT-PPY has uniform tubular structure with diameter less than 100 nm. Other physical properties and molecular structure were discussed using FTIR.

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Maria Omastova et al [21] have been prepared Aniline and pyrrole with the same molar ratio of ammonium peroxydisulfate (oxidant) and of hydrochloric acid in aqueous solutions. The oxidation of pyrrole was faster; the induction period typical of aniline oxidation was absent in the case of pyrrole. It is mentioned that the conductivities of polyaniline and polypyrrole were reduced. Polyaniline was produced in phosphoric acid solutions of different contents exhibits conductivity ≈10 $S\ cm^{-1}$. Due to the increase in the phosphoric acid contents the conductivity of polypyrrole was decreased. The FTIR spectra revealed the type of protonation by investigating the ammonium salts resulted after deprotonation.

Yunze Long et al [22] synthesized a multi-walled carbon nanotube/polypyrrole (CNT/PPy) noncable through an in situ chemical oxidative polymerization method. This paper reported the dependence of temperature as well as the contents MWCNTs on conductivity follows a charge-energy-restricted tunneling model ($ln\sigma(T) \propto T^{-1/2}$). The results indicate that at the percolation threshold the total CNT conductive paths can vary and significantly increase the electrical properties of the CNT/PPy composites.

Shih-Hsiang Lin et al [23] prepared of polypyrrole (PPy) and PPy/MWNT composites. For the characterization of the structure and morphology of these composites “Raman spectroscopy”, “Fourier transform infrared (FTIR)”, “field emission scanning electron microscopy (FESEM)”, and “high-resolution transmission electron microscopy (HRTEM)” were used. FESEM and HRTEM analysis showing the composites of PPy/MWNT was the core (MWNT) shell (PPy) tubular shape. Moreover, 150% increase in the conductivities at room temperature was observed in case

$3wt$ % PPy/MWCNT composites as compared to pure PPy, also increasing Raman but IR spectra of the composites were identical to those of PPy.

By using in-situ chemical-oxidative polymerization in water solution having different rations of MWCNTs Al. Darabont et al [24] prepared the polypyrrole (PPY) and multi-walled carbon nanotubes (MWCNTs) composites. A novel mixed nanostructure of multi-wall CNTs treated with PPy including its magnetic behavior is prepared when water based Fe_3O_4 nanofluid is added to polymerization solution. The diagnostics of PPy nanocomposites were carried out using different techniques (TEM, SEM, FTIR and XRD). TEM analyzed that MWCNTs are coated with a thin PPy layer in PPY/MCNTs composites. It was evident that infrared (IR) spectra are mainly used for identification of the key variations particularly in the ring oscillation bands of pyrrole and its composites. This difference could occur due to the polymer and CNTs interaction which can change the polymer confirmation. The change in the crystalline structure of multiwall CNTs does not vary significantly by the interaction with PPy as confirmed by “XRD” analysis.

HongfanGuo et al [25] prepared PPy/multi-walled carbon nanotube (MWCNT) nanocomposites through the in situ chemical oxidative polymerization method by introducing oil water microemulsion system which has been used efficiently for synthesizing polypyrrole (PPy) nanoparticles. They concluded on the basis of their study on structure and physical properties of the PPy/MWCNT nanocomposites that PPy can coat MWCNTs to form core shell structure. The bulk structure of PPy is not destroyed by the substitution of MWCNTs, and that PPy in the PPy/MWCNT nanocomposites has same structure as pure PPy. With the increase in the MWCNT monomer mass ratio the conductivities of PPy/MWCNT nanocomposites are greater as compared to pure PPy.

Tzong-Ming Wu et al [26] prepared polypyrrole PPy/multiwalled carbon nanotube (MWCNT) composites by using in situ chemical oxidation polymerization method, and also added different concentrations of cationic surfactant cetyltrimethyl ammonium bromide (CTAB). The structure and morphology characterization of these samples was carried out by using Raman spectra, FTIR, SEM, and TEM. The concentration of c/MWCNTs into PPy increases the thermal stability and electrical conductivity in the order of $1-2$ in PPy, because MWCNTs acts as a conducting bridge. By adding CTAB content in the composites reduced the thickness of PPy layer coated on the surface of MWCNT, which in turn enhances the conductivities of the composites.

Juying Zhou et al [27] showed an improvement in polypyrrole (PPy) films onto multiwall carbon nanotubes (MWCNTs) which make it ultrathin and thickness-tunable and ethanol is added during facile process for the controlling the structure and thickness of PPy film. Due to the addition of ethanol the coated PPy films can be simply tuned and also adjusting a mass ratio of pyrrole to MWCNTs. Furthermore, the thickness of PPy appreciably affects the electronic conductivity and capacitive performance of the PPy/MWCNT composites. The method may offer a facile approach for adapting the polymer coating on carbon nanotubes (CNTs) for carbon-based device applications.

C. Cassignol et al [28] found from both differential scanning calorimetry (DSC) and dynamical mechanical thermal analysis (DMTA) give the glass transition temperatures of conducting composites, obtained by blending carbon nanotubes (CNTs). The decrease in the glass transition temperature,T_g up to some degree due to the filler contents in the vicinity of the percolation threshold, and is connected with a plasticization phenomenon. In composites displaying an insulator-conductor transition at which the glass transition temperature and mechanical modulus of the composites pass through a minimum.

Experimental method for Preparation of polypyrrole

$FeCl_3.6H_2O$ was dissolved in 50ml distilled water and then stirrer for one hour.Then appropriate amount of pyrrole (PPy) was added slowly drop wise in the suspension at room temperature in the absence of light. The monomer to oxidant was kept in the ratio of 1:2.For complete polymerization the suspension was left for 24 hours. Finally to remove$FeCl_3.6H_2O$and other adherent material suspension was washed and filtered with distilled water again and again. Then the resultant greenish black powder was dried at 90C^o in vacuum oven for 24 hours [29].

Synthesis of polypyrrole and MWCNTs composites

$FeCl_3.6H_2O$ and 10% MWCNTs of pyrrole were dissolved in 50ml distilled water and stirrer constantly for 60 minutes. Then pyrrole was poured in to solution drop wise slowly during stirring. Then the suspension was left for 24 hours for polymerization. In this step $FeCl_3.6H_2O$ and other raw materials are removed by washing and filtering with distilled water again and again. The past obtained was dried at 90C^o in vacuum oven for 24 hours.

Similarly 5% and 3% MWCNTs of pyrrole and polypyrrole composites were prepared in the same method as above.

2. Results and Discussions

XRD pattern of PPy, MWCNTs and their composites are given in the figure 1 (a-e). In PPy (Fig. 1 (b)) there is no intense (crystalline) peak except a wide and relatively weak diffraction peak in the range $2\theta = 25.2^0$ from the intermolecular spacing have been observed for PPy, indicates that the PPy are amorphous in nature [30, 31, 32]. The X-rays pattern of the MWCNTs show strong peaks at $2\theta = 25.6^0$ and $2\theta = 42.005^0$corresponds to the (002) and (100) reflection of the graphite like structure respectively [30, 33, 34, 35]. It was also noticed that the XRD patterns of 5% as well as 10% MWCNT/PPy nanocomposites showed typical peaks at $2\theta = 25.775^0$ and at$2\theta = 26.525^0$.

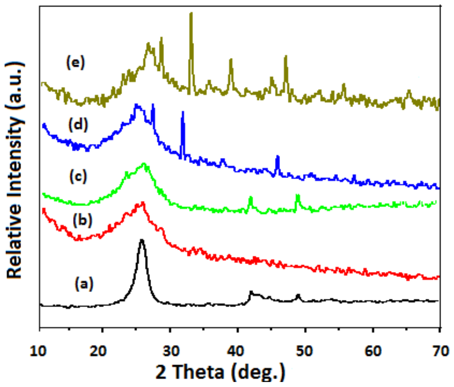

Fig.1 XRD pattern of (a) pure MWCNTs, (b) pure PPy, (c) 3%, (d) 5% and (e) 10% MWCNT/PPycomposites.

FTIR transmittance spectra of PPy, MWCNTs and their composites in powders are shown in Fig. 2.$[(a)-(e)]$. All major peaks of PPy [36, 37-41] could be found in the PPy spectra. The peaks near 900 cm^{-1}, 1170 cm^{-1}indicates the doping state of PPy.

The characteristic transmittance bands at 1007.6 cm^{-1} and at 1035 cm^{-1} of pure PPy are attributed to $C-H$ deformation vibration and $C-N$ stretching vibration respectively. The peaks of the $C-N$ symmetric ring stretching mode are situated at 1442 cm^{-1} and that of $C-C$ asymmetric ring stretching mode are observed at 1536 cm^{-1}. The broad band appeared at 1300 cm^{-1} as well as 3000 cm^{-1} to 3500 cm^{-1} explains the $C-H$ and $C-N$in plane deformation vibration. The above characteristics peaks of PPy are observed in the spectra of PPy/MWCNTs nanocomposites, but few shifts have been observed in all these peaks. So it could be demonstrated that the original structure of PPy is not changed due to doping with MWCNTs, and there are possibly π-π non covalent bonds interactions b/w PPy and MWCNTs. From spectra it is clear that there are shifts in C–O peaks from 1007.6 cm^{-1}, 1129.5 $cm^{-1}$and 1500 cm^{-1} in pure PPy to higher wave number values in the nanonocomposites. The peak at 1007.6 cm^{-1} in pure PPy shifts to 1025.8 cm^{-1}, 1036.5 $cm^{-1}$and 1039.2 cm^{-1} in the nanocomposites samples with 3%, 5% and 10% MWCNTs. Similarly the peak at 1129.5 cm^{-1} in pure PPy shifts at 1139.1 cm^{-1}, 1151.6 cm^{-1} and 1162.4 cm^{-1} in the nanocomposites samples with 3%, 5% and 10% MWCNTs and the peak at 1500 cm^{-1} in pure PPy shifts to 1502 cm^{-1}, 1505.2 cm^{-1} and 1505.3 cm^{-1} in case of PPy/MWCNTs nanocomposites with 3%, 5% and 10% MWCNTs. which is caused by the presence of the MWCNTs as the composite materials.

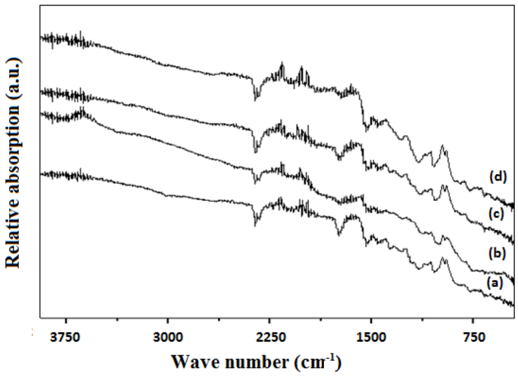

Fig. 2 (a) FTIR of pure MWCNTs (b) pure PPy (c) 3% MWCNT/PPy)(d) of 5% MWCNT/PPy nanocomposites

Capacitance and dissipation factor were determined by using LCR meter Model 4275 (Wayne Kerr) in the frequency range $100Hz$ to $1MHz$. The dielectric constant was calculated at each frequency by using the above Wayne Kerr LCR meter Model and is given by the formula (1)

$$\acute{\varepsilon} = cd/A \tag{1}$$

Where
$\acute{\varepsilon}$= relative permittivity,
C = capacitance,
d = thickness of the sample,
A = area of cross section and
ε_0= permittivity of free space.
Using the relation (2) the dielectric loss was calculated as

$$\varepsilon\text{“} = \acute{\varepsilon}D \tag{2}$$

Where “D” is the dissipation factor is measured by LCR meter at different frequencies. Frequency dependence of Dielectric constant at room temperature for PPy and PPy/MWCNTs nanocomposites is shown in the figures 3 $(a - d)$. The dielectric constant and dielectric loss of the samples is shown in combined form in figures (4 &5).

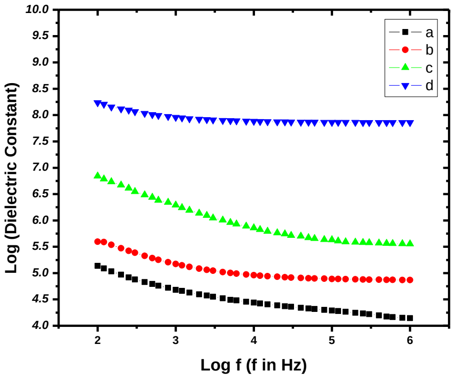

Fig.3 Log (Dielectric constant) Vs Log (Frequency) of (a) PPy, (b) 3%, (c) 5% and (d) 10% MWCNT/PPycomposites.

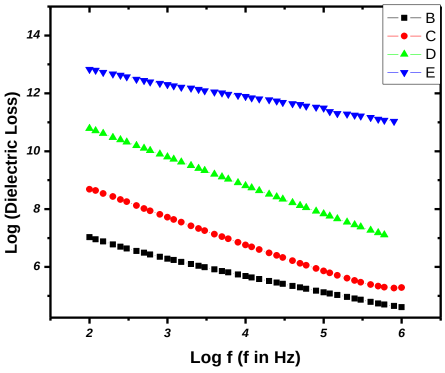

Fig.4 Log (Loss factor) Vs Log (frequency) of (a) PPy, (b) 3%, (c) 5% and (d) 10% MWCNT/PPycomposites.

Fig. 4 and 5 are presented earlier which shows the frequency dependence of dielectric constants and loss factors of pure PPy and PPy/MWCNTs nanocomposites in the form of log-log plots. From these figures we observed that the dielectric constant and dielectric loss possess high dielectric values at low frequencies due to the transportable charges within the polymer structure, the dielectric loss factor (imaginary part of permittivity) of greater value with the higher concentration of dopant can be explained in term of higher DC electrical conductivity and associated higher conductivity loss. Higher concentration of MWCNTs as well as increase in frequency will affect the dielectric loss and dielectric constant. It is observed from the figure (4 & 5) that the value of dielectric constant for 10% MWCNT/PPy nanocomposites is $1.72 * 10^8$, which is about 1000 times greater than pure polypyrrole ($\acute{\varepsilon} = 1.37 * 10^5$) at 100 Hz. The dielectric loss for 10%MWCNT/PPy nanocomposites reaches $1.093 * 10^{11}$which is about 10^7times higher than that of pure PPy ($4.48 * 10^4$) at 1 MHz. It is obvious from these plots that the increase in dielectric constant is very prominent at low frequencies. The frequency dependence of dielectric constant results from the fact that the relaxation time is necessary for the response to an applied electric field.

In case of charge carriers (group of electrons, small molecules or long polymer chain) controlled system, the dielectric relaxation is given to hopping of charge carriers between two localized sites. The dielectric loss in the samples due to DC conductivity is given by $\varepsilon''_{DC} = \sigma_{DC}/\varepsilon_0\omega$which is also described by frequency dependence $\omega^{-n}$with $n = 1$, without any typical peak [42, 43].

If the polymer possesses polar groups whose dipole moments do not cancel out, the real value of the dielectric constant will strongly depends on molecular confirmation, which in turn depends on dipoles. The change in confirmation is produced due to strong repulsion between parallel dipoles. This result depends on the correlation factor g, which for an amorphous polymer depends on the angle between the dipoles within those parts of the molecule that can rotate independently when the electric field is applied in a time of the order of 10^{-4} s[44].

The frequency dependence of dielectric constant can also be explained on Debye's effect [45] stated as "A material having dipoles will polarize in an electric field because dipoles molecule is an electric doublet". There will be polarization due to orientation polarization $P_r$and deformation polarization P_d".

Polarization due to orientation will decrease due to the increase in the frequency of the field and vanish at sufficiently high frequency [46].

Joo et al. [47] suggested that large positive dielectric constant shows large effective sizes of metallic islands and easy transport of the charge through well organized polymer chains between disordered regions.

When a small frequency electric field is applied to a movable charge carrier system, which can transfer over a distance in a material, resulting interfacial charge polarization when these charge carrier are not allowing to move is known as the Maxwell-Wagner effect [48, 49]. On the other hand when these charge carriers could not freely discharge or changed at the electrodes, these charges can be trapped within the vacancies of a material and resistance may also offer to its motion this is electrode polarization effect [50].

In nanocomposites, the PPy is conducting polymer, up to great extent like PANI, while the increase in the dielectric constant as well as dielectric loss both will result from the concentration of MWCNTs in nanocomposites because the core of MWCNTs is comparatively more conductive as well as lossy [51].

The composites of MWCNTs/PPy act as a capacitor, exhibit small leakage current density, which has prominent applications for the energy storage or peak load leveling [52].

It has been observed that the dielectric permittivity increases by dispersing conducting particles CNT/nanoparticles in the polymer material [53]. The increased dielectric permittivity in such composites arises from the conducting particles isolated by very thin dielectric layers to form micro capacitor. However, Dielectric loss is very high and difficult to control, because the particles can easily form a conducting path in the composites as the filler concentration nears the percolation threshold.

The decrease in the dielectric constant with the increase in frequency is due to the fact that the interfacial dipoles do not have sufficient time to orient themselves in the electric field dierection; therefore, with the increase in frequency, the tendency for the interfacial polarization is expected to decrease resulting in the decrease in the dielectric constant [53].

As discussed earlier that the increase of MWCNTs contents in nanocomposites will enhance the dielectric properties enormously. An increase in dielectric constant has been observed in conducting polymer (PPS) nanocomposites by R K Goyal et al [54].

AC conductivity was measured for pure PPy and the MWCNTs/PPy nanocomposites samples (A, B, C & D) using the LCR meter model 4275 in the frequency ranging from $100Hz - 1MHz$. Fig 6 shows the frequency dependence of AC conductivity for all the four samples at room temperature. AC conductivity in PPy/MWCNTS nanocomposites was increased more by two orders of magnitude comparatively larger than PPy in the range of frequencies $100\,kHz$ and was left to be constant. The threshold frequency increases with the increase in MWCNTs contents, AC conductivity increases rapidly by increasing the frequency in PPy and PPy/MWCNTs composites. According to hopping model of charge transport mechanism for a uniform dispersion of CNTs in polymers which contribute an ordinary frequency dependent of conductivity $\sigma(w)$, it can be described in a region of low frequency at which particular conductivity is examined, which is directed by a transition having gradual shrinking at greater frequencies to a AC conductivity depending on frequency can be approximated by the power law and is given by; [55, 56].

$$\sigma\,(f) = \,(Constant)\,f^{s} where\ 0 < s < 1 \qquad (1).$$

Where s is the slope for the nanocomposites determined from the best fit line for logarithmic plot of Eq.1 Fig.6 is given in the table 1

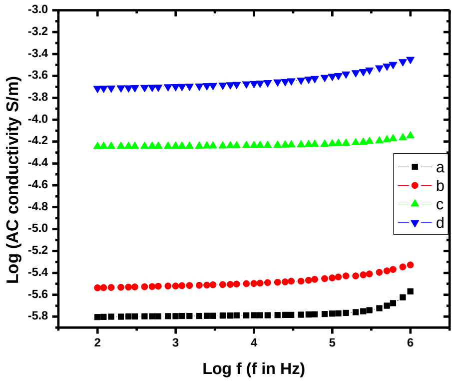

Fig.6 Variation of AC conductivity with frequency of (a) PPy,
(b) 3%, (c) 5% and (d) 10% MWCNT/PPy composites

Table 1Slope of frequency dependent of AC conductivity for PPy/MWCNTs nanocomposites

sample	Pure PPy	3% MWCNT/PPy	5% MWCNT/PPy	10% MWCNT/PPy
Slope ‘s’	0.25	0.18	0.17	0.14

Since the core of MWCNTs is conductive which increases the conductivity, therefore with the increase in the concentration of MWCNTs, AC conductivity of PPy/MWCNTs nanocomposites increases [57].

The nanotubes enhance the electrical conductivity due to larger surface area that acts as a conducting bridge, connect with the PPy conducting area and improving the effective percolation [58].

3. Conclusions

Polypyrrole /Multi-walled carbon nanotubes (MWCNTs) nanocomposites were successfully synthesized in the presence of $FeCl_3.6H_2O$ in aqueous solution using in situ polymerization of pyrrole. Formation of both polypyrrole (PPy) and PPy/MWCNTs nanocomposites and the interaction between MWCNTs and the polymer in the nanocomposites were confirmed by using fourier transform infrared spectroscopy (FTIR). Complete dispersion of MWCNTs in polypyrrole matrix and their well interacted structure was confirmed by X-rays diffraction.

AC conductivity of the MWCNTs/PPy nanocomposites is appreciably high as compared to the pure PPy and enhanced with the increase of MWCNTS contents as well as with the increase of frequency. Nanocomposites exhibited a very interesting dielectric behavior. With the increase in MWCNTs a significant increase in the dielectric constant and decrease in dielectric loss was observed.

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