Structural, AC conductivity, dielectric and impedance studies of polypyrrole/praseodymium calcium manganite nanocomposites

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In-situ polymerization of a series of nanocomposites viz. 10, 20, 30, 40 and 50 wt % of Praseodymium Calcium Manganite Oxide (Pr_{0.75}Ca_{0.25}MnO₃) (PCM) nano manganites in polypyrrole (PPy) were prepared by chemical polymerization technique. The crystalline nature of all the nanocomposites was confirmed by powder X-ray diffraction (XRD). The orthorhombic structure with space group Pnma was confirmed by the well-fitted Rietveld refined XRD data. The average particle size was observed to be in the range of 42 to 60 nm. Scanning Electron Microscope (SEM) confirmed the spherical nature of the particles. The TEM confirmed the crystallinity and Fourier Transform Infra-Red Spectroscopy (FTIR) showed that the stretching frequencies shifted towards higher frequencies for the nanocomposites suggesting better conjugation due to chemical interaction between the PPy and PCM particles. AC conductivity versus frequency showed that at higher frequencies the AC increases obeying Jonscher's power law. The correlated barrier hopping (CBH) model is therefore used to describe the conduction mechanism. For all composites, the dielectric constant and tangent loss revealed a frequency- and temperaturedependent character. The real and imaginary impedance were both frequency and temperature dependent. The impedance data were analyzed by fitting Nyquist plots using ZsimpWin software which confirmed non Debye type of behavior. This study highlights on the interactions between conduction processes, grain boundaries, and grains.

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1. Introduction

Dielectric materials have drawn attention in recent years. These materials have applications in various industrial devices such as voltage controlled oscillators, microwave filters, dynamic access memory, and telecommunication technologies [1]. In the past two decades, nanocomposites of organic-inorganic materials have become an extensively studied subject as these doped materials bring interesting properties [2] of not only organic but also inorganic materials [3]. Rigorous efforts were made in view to improvise the electrical and dielectric properties of $R_{1-x} A_x MnO_3$, mixed valence perovskite structured manganese oxides via partial substitution of either A-ions (A = alkaline earth cation like Ca^{2+} , Sr^{2+} , Ba^{2+} , etc) or R-ions (R=rare earth cation like Pr^{3+} , La^{3+} , Nd^{3+} etc). These manganites when doped exhibit a variety of electronic, magnetic and crystallographic phases.

Recently, many nano-sized conducting polymers synthesized, such as nanoparticles and their nanocomposites [4] of polyaniline (PANI) and polypyrrole (PPy), have attracted many researchers due to their application in gas/humidity sensors and super-capacitors as electrode materials. PPy $[-(C_4H_4-NH)-]_n$, which was synthesized for the first time in the year 1916, has become an attractive conducting polymer due to its simplistic synthesis, tunable conductivity,

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special transport properties and good stability [5]. It is unique due to its co-planar structure that is slanted in a solid state aided by conjugation interaction which is quite promising for several applications. Its nanocomposites have shown potential applications in supercapacitors [6], sensors [7], catalysts, electromagnetic interference shielding materials, fuel cells and so on. Other than carbon/conducting polymer nanocomposites [8], transition metal oxide / conducting polymer nanocomposites that contain transition metal oxides such as MnO_2 , Fe_2O_3 and TiO_2 are used for supercapacitors. Praseodymium oxide (Pr_6O_{11}) holds a special position in the rare-earth oxides series [9]. Pr_6O_{11} nanoparticles play a vital role in sensor and electronic materials due to the hopping of electrons between the valence states of the lattice. The two electrical characteristics of materials that can be analyzed are: (1) the capacitive (insulating) nature and (2) the resistive nature. This analysis helps us to determine the dielectric loss of a material. The dissipation of electrical energy due to dielectric relaxation or dielectric resonance under ac is accounted as dielectric loss or tangent loss of material.

Size reduction produces a direct effect on the electronic and magnetic properties of the system. Some class of manganites shows insulator to metal transition at a temperature T_{IM} along with paramagnetic to ferromagnetic transition at the Curie temperature (T_C). The literature says most of the nano manganites belong to this category. Some literature says T_C either increases or decreases with a decrease in particle size [10-13]. But it was also reported like T_C is unaffected by size reduction [10] for La_{2/3}Ca_{1/3}MnO₃.

The contribution to electrical properties from the grain, grain boundaries, and electrodeelectrolyte interface may be studied by Cole-Cole plots or Nyquist plots in a certain range of frequencies. The Nyquist plot resolves in terms of semicircle arcs. For three distinct semicircles, high frequency, intermediate, and lower-frequency arcs ascribe to grain effect, grain boundary effect, and electrode effect as these three regions have distinguished relaxation or conduction processes [14]. Debye relaxation with a single semicircle or single relaxation time is for perfect crystals only.

The conductivity of polymer nanocomposites depends on different factors such as size, the morphology of the fillers, dopant concentration and interface interaction. In the present work synthesis, characterization, AC conductivity, dielectric and impedance studies of PPy and PPy/PCM nanocomposites are reported.

2. Experimental analysis

2.1. Materials

Pyrrole monomer, ammonium persulfate (APS), praseodymium oxide (Pr6O11), absolute ethanol, calcium carbonate, manganese carbonate, ethanol, and HNO3 were procured from spectrochem Pvt. Ltd., Mumbai, India. All chemicals were of analytical grade and were used as received. The double-distilled water was used throughout.

2.2. Synthesis

2.2.1. Synthesis of Pr_{0.75} Ca_{0.25} MnO₃ (PCM) nanoparticles

The sol-gel process was used to synthesize $Pr_{0.75}Ca_{0.25}$ MnO₃ (PCM) nanoparticles. Pure Pr_6O_{11} , CaCO₃, and MnCO₃ taken in stoichiometric ratios are dissolved in suitable amounts of nitric acid, ethylene glycol and distilled water. The mixture was heated to 180°C till it changes to a thick brown sol. This was heated further for 6 hours at 250°C in a muffle furnace to get polymeric precursor which was later sintered for 6 hours at 700°C to synthesize PCM nanoparticles (15).

2.2.2. Synthesis of Polypyrrole (PPy)

The in-situ chemical polymerization approach was employed to create polypyrrole using monomer pyrrole. Ammonium persulphate (APS) was used as an oxidizing agent. APS of 0.6 M was dissolved in 100 ml of distilled water and filled in a burette. To 100 ml of distilled water, 0.3 M pyrrole was added to a flask with a magnetic bead and fixed in an ice filled tray to allow the reaction to take place in the temperature range of 0 °C to 5 °C. Then the tray was placed on a magnetic stirrer with a spinning speed of 400 revolutions per minute (rpm). APS was added

dropwise to the pyrrole solution. The reaction was let go on for 5 hours. The precipitate was then filtered and then dried in a muffle furnace at 100 °C to obtain Pure PPy powder.

2.2.3. Synthesis of PPy/PCM nanocomposites

The in situ chemical oxidation process was used to synthesize PPy/PCM nanocomposites. The same procedure was repeated by adding 0.3g of PCM for PPy/PCM-10, 0.6g of PCM for PPy/PCM-20, 0.9g of PCM for PPy/PCM-30, 1.2g of PCM for PPy/PCM-40 and 1.5g of PCM for PPy/PCM-50 with pyrrole.

2.3. Characterization

XRD analysis of PCM nanoparticles, pure PPy and PPy/PCM nanocomposites was carried out using Rigaku Ultima-IV model diffractometer (Cu K α radiation of wavelength λ being 1.5406 Å) in the range of 100 – 800 to analyze the crystal structure, phase formation, lattice parameters and crystallite size. TESCAN Vega 3 Scanning Electron Microscope was used for morphological study and EDAX was used to study the elemental analysis. TEM model JEM2100 EX instrument with 80 kV of accelerating voltage and high resolution transmission electron microscopy (HRTEM) model Technai G2 F-30 operated at 300 kV has been employed to analyze the shape and size of the particles. FTIR spectra were recorded on Perkin Elmer Spectrum 2 spectrometer in the wavenumber range of 400–4000 cm⁻¹ for all the synthesized samples. AC conductivity (σ_{ac}), dielectric and impedance studies were carried out using Wayne Kerr 6500B high-precision impedance analyzer in the frequency range 100 Hz – 1 MHz.

3. Results and discussions

3.1. XRD Analysis

Fig. 1(a) shows Rietveld fitting of XRD of PCM nanoparticles. The reflection from planes (204), (002), (022), (040), (202) and (004) are seen. This confirms the orthorhombic crystal structure with space group Pnma (no. 62). The observed peak positions at 23⁰, 33⁰, 41⁰, 47⁰, 59⁰ and 68⁰ match with the JCPDS card no. 89-795. XRD pattern of pure PCM nanoparticles, pure PPy and all PPy/PCM nanocomposites is shown in fig.1b. The XRD pattern of PPy/PCM nanocomposites showed that the peaks of PCM are retained in the composites, which confirms the semi-crystalline nature of composites. The XRD pattern of pure PPy showed a broad peak at $2\theta = 25^{0}$ that characterizes the amorphous nature of PPy [16, 17]. The average crystallite size (D) of PCM nanoparticles calculated using Scherrer's formula $D = k\lambda / \omega \cos\theta$ was found to be 42 nm, where λ , k, θ and ω are the wavelength of X-rays (1.54 Å), the phase factor (0.9), Bragg angle and Full width at half maximum (FWHM) respectively.



Fig. 1. (a) Rietveld fitting of XRD of PCM nanoparticles and (b): XRD pattern of pure PPy and all PPy/PCM nanocomposites and pure PCM nanoparticles.

Compound	The average crystallite size (nm)		Microstrain 10 ⁻³	crystallinity (%)	δ (10 ¹⁶ lines per m ²)	Stacking fault (SF)	Interchain separation
	Scherrer's formula	W-H plot					distance R (Å)
PCM	14.36	16.02	8.45	64.17	0.92	0.076	
PPy/PCM-10	16.46	15.70	6.76	47.24	0.44	0.054	4.09
PPy/PCM-20	18.65	15.74	5.89	48.96	0.47	0.052	4.34
PPy/PCM-30	17.12	14.79	5.71	55.30	0.49	0.045	4.24
PPy/PCM-40	19.09	15.83	4.65	67.88	0.42	0.031	4.18
PPy/PCM-50	14.36	18.09	4.93	71.19	0.38	0.042	4.21

Table 1. Average Crystallite Size and Crystallinity of PPy/PCM nanocomposites and Pure PCM.

Table 1. Displays the average crystallite size and crystallinity of pure PCM and PPy/PCM nanocomposites. It was discovered that when the weight percent of PCM in PPy increased, so did the crystallinity of the composites.

3.2. FESEM, EDAX and TEM analysis

Figure 2(a) shows SEM micrographs with inset histogram and (b) EDAX for pure PCM nanoparticle. The PCM nanoparticles showed an orthorhombic crystal structure. The average particle size was observed to be in the range of 42 to 60 nm. Fig 3 shows FESEM images for PPy and PPy/ PCM nanocomposites with inset histograms. SEM images of pure PPy revealed that it had a cauliflower-like shape made up of groups of tiny grains and patterns resembling chains. The SEM micrographs of the nanocomposites depict the clusters of spherically shaped polymer in the composites. The PPy chains are found to be embedded with PCM nanoparticles.



Fig. 4. (a) SEM micrographs with inset histogram and (b) EDAX for pure PCM nanoparticle



Fig. 5. FESEM images for PPy and PPy/PCM nanocomposites with inset histogram.

Table 2. The	particle size of Pl	Pv. PCM/PPv	nanocom	posites and F	PCM nano	narticles i	from hist	ograms.
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Material	Particle size (nm)
РРу	532
PPy/PCM-10	226
PPy/PCM-20	186
PPy/PCM-30	205
PPy/PCM-40	166
PPy/PCM-50	223
PCM	42

Table 2 displays the particle sizes of PPy , PCM nanoparticles, and PCM/PPy nanocomposites. The particle size evolution was done by using ImageJ software. Due to an increase in nucleation sites during PPy polymerization, the particle size of the nanocomposites is smaller than that of PPy particles. Figure 4 shows the EDAX spectrum and the elemental compositions of pure PPy and PPy/PCM composites. The peaks in the spectra correspond to elements that constitutes the sample. No other impurities are found in the nanocomposites. From

the given data the atomic % of C, N, O, S, Ca, Mn and Pr elements are found to be maximum at PPy/PCM 50 wt% and minimum at 10 wt% respectively. It gives the additional validation for the stoichiometric composition of nanocomposites .



Fig 4.(a) - (f) EDAX spectrum and elemental composition of pure PPy and PPy/PCM nanocomposites



Fig. 6. TEM, HRTEM images and SAED pattern for PCM nanoparticles

TEM, HRTEM, and SAED patterns for PCM nanoparticles are shown in Fig. 5. They exhibit brilliant lattice fringes spaced 0.26 nm apart, which is equal to the d-spacing of the (111) lattice plane. The SAED pattern shows the bright spots with a diffused ring pattern, revealing the

polycrystalline nature. The XRD patterns and the diffraction patterns indexed to the (002), (040), and (202) planes are in good agreement.



Fig. 6. TEM images for PPy and PCM/PPy nanocomposites.

Fig. 6 shows TEM images for PPy and PPy/PCM composites. The PPy particles are spherical in size ranging from 500-600nm. For all the nanocomposites the PPy covers the agglomerated PCM particles. Fig. 7 shows SAED patterns for PPy and PPy/PCM composites. Pure PPy shows a spherical shape with a continuous ring network due to the benzene ring in Polypyrrole. Because of the in-situ polymerization technique of synthesis, the PCM nanoparticles are uniformly diffused and connected to pyrrole. The semi-crystalline structure of the PPy/PCM nanocomposites is seen in the SAED pattern. SAED pattern of Pure PPy shows no ring structure or diffraction spots, indicating its amorphous nature. As PCM concentration increased from 10 to 50 wt%, distinct structural changes were made to PPy.



Fig. 7. SAED patterns for PPy and PPy/PCM nanocomposites.

3.3. FTIR analysis

The functional groups in polypyrrole and its nanocomposites were confirmed by using Perkin Elmer FTIR spectrum two in KBr medium. The FTIR spectra of Pure PCM, PPy and all PPy/PCM nanocomposites are displayed in Fig. 8. FTIR spectra was studied from 4000 to 400 cm^{-1} which was observed to be the considerable range for organic materials [12] for chemical characterization. A distinctive peak at 657 cm1 for the pure PPy indicates ring deformation. The O-H bend and C-H out-of-plane deformation, respectively, cause the peaks at 916 cm⁻¹ and 785 cm⁻¹ in nanocomposites. The =C-H plane deformation vibration and N-C stretching band are indicated by the peaks maxima at 1095 cm⁻¹ and 1178 cm⁻¹, respectively. The bands at 1293 cm⁻¹ and 1206 cm⁻¹ are, respectively, the =C-H in plane vibration band and the N-C stretching band. Bands at 1542 cm⁻¹ refers to pyrrole ring (C–N) vibration and 1458 cm⁻¹ refers to ring stretching mode (C=C, C–C). The peak at 1365 cm⁻¹ is due to the vibrations of polypyrrole ring. The stretching frequencies of C=C and N-H are indicated by the peaks at 1557 cm⁻¹, 1458 cm⁻¹ and 3434 cm⁻¹ [18]. The detected bands in this analysis match those in the scholarly literature quite well [19]. In comparison with pure PPy, the PCM nanocomposites have shown that

the shift of stretching frequencies is towards the higher frequency side. This confirms homogeneous distribution of PCM particles along the polymeric chain and the existence of Vander Waal's interaction between the polymeric chain and PCM nanoparticles [20].



Fig. 8. FTIR Spectra of pure PPy and PPy/PCM nanocomposites.

3.4. AC conductivity

Total conductivity is given by the relation

$$\sigma_{tot}(\omega, T) = \sigma_{dc}(T) + \sigma_{ac}(\omega, T)$$
(1)

where σ_{dc} (T) is the non-dispersive DC component of the conductivity and σ_{ac} (ω , T), is a dispersion region that increases with frequency according to [21,22] Jonscher's power law,

$$\sigma_{ac}(\omega, T) = A(T)\omega^{s(\omega, T)}$$
⁽²⁾

here A(T) is the pre-factor that depends on temperature, and s is the exponent with values in the range of 0 to 1. Fig. 9 depicts the total conductivity fluctuation with frequency for pure PPy and all PPy/PCM nanocomposites at 303K, except for PPy/PCM-20 (inset).



Fig. 9. AC conductivity vs frequency with nonlinear fitted curves.

All the conductivity graphs obey Jonscher's power law and the solid lines in these plots represent fitted curves. At lower frequencies direct current (dc) plateau region (from 100 Hz to 10^6 Hz) was observed where the conductivity was found to be almost constant.

At critical frequency, the ac conductivity starts to increase. Higher frequencies cause the production of polarons and bipolarons, which tend to jump across grain and grain boundary barriers and cause AC conductivity to reach its maximum value [23]. This is a characteristic of disordered materials where charge carriers hop to favorable sites increasing conduction. The maximum conductivity was observed for PPy/PCM 20 at 1 MHz frequency. This could be explained by charge carriers hopping over grain boundaries and barriers, resulting in high conductivity.

Table 3. The DC conductivity (σ_{dc}) and the power law exponent (s) evaluated for pure PPy and PPy/PCM composites.

Composite	σ_{dc} (S/m)	S
Pure PPy	4.316E-4	0.3867
PPy/ PCM-10	9.406E-4	0.5436
PPy/ PCM-20	0.004178	0.2489
PPy/ PCM-30	2.574E-4	0.4868
PPy/ PCM-40	0.001433	0.5328
PPy/ PCM-50	3.092E-4	0.5721
-		



Fig. 10. Temperature-dependent total conductivity (σ_{tot}) versus frequency graph for pure PPy and PPy/PCM composites.



Fig. 11. s vs temperature for PPy and PPy/PCM nanocomposites.

The other higher wt % nanocomposites showed very less conductivity which can be attributed to the Jahn Teller distortion. From SEM and TEM images the particle size increased as the PCM particles are agglomerated and coated with the PPy matrix forming bigger size particles and breaking the effective conduction band (24). Fig. 10 shows Temperature-dependent total conductivity (σ_{tot}) versus frequency graph for pure PPy and PPy/PCM nanocomposites from 303K to 453K. The NTCR behavior of the materials is confirmed by the rise in conductivity with rising temperature. The Arrhenius plots also take this aspect into account. Therefore, it suggests that space charge conduction is the cause of the conduction process in the material. The variation of s with temperature for PPy and PPy/PCM nanocomposites is shown in fig.11 . The dc conductivity (σ_{dc}) and the power law exponent (s), evaluated by fitting with the nonlinear curve, are shown in table 3. The exponent "s" has changed as a function of temperature at a constant frequency (f = 1MHz) and has reduced as frequency increases. Hence 's' varies following CBH (correlated barrier hopping) conduction model.

3.5. Permittivity

The dielectric constant as a function of frequency given as, $\epsilon^*(\omega) = \epsilon' - j \epsilon''$ where ϵ' and ϵ'' relates to real (dielectric constant) and imaginary (dielectric loss) parts of complex permittivity correspondingly.



Fig. 12. Dielectric constant and dielectric loss vs frequency for PPy and PPy/PCM nanocomposites at 303K

3.5.1. Dielectric constant and tangent loss as a function of frequency

Figure 12 displays the dielectric constant and dielectric loss as a function of frequency for PPy and PPy/PCM nanocomposites at 303K. The synthetic composites show highest dielectric constant and maximum dispersion at lower frequencies. The localised or immobile dipoles aid long range migration and are polarised resulting in a high dielectric constant.



Fig. 13. Temperature dependant Dielectric constant as a function of frequency for PPy and PPy/PCM nanocomposites.

Dielectric constant decreases at a higher frequency due to the relaxation process and is almost constant [25, 26] which is common nature exhibited by ceramics. Dielectric relaxation phenomena depend on polarisation mechanisms. At low frequencies, all types of polarisation mechanisms are active while at high frequencies major contribution is due to space charge/ Interfacial polarisation. The dielectric constant is minimal at high frequencies because dipoles cannot follow the applied field. The orientational polarization leads to the rotational displacement of the dipoles. It becomes impossible for charge carriers to move freely within the crystal [27, 28].

The tangent loss is given by ε^{l} tan δ . At increasing concentrations, permittivity decreases as a result of nanoparticle aggregation and an ensuing reduction in surface area. The temperature dependence of dielectric constant (ε^{l}) and dielectric loss (tan δ) of PPy/PCM nanocomposites with the frequency of the applied electric field at higher temperatures is as shown in Fig. 13 and Fig. 14 respectively. It has been noted that all nanocomposites have high dielectric constant and dielectric loss values at low frequencies. This can be attributed to Maxwell Wagner interfacial polarisation due to which a large number of localised dipoles orient themselves along the applied field and grain boundary resistance dominates. As a result, the dielectric constant and dielectric loss becomes frequency independent at higher frequencies and fall to almost constant levels [29]. The rapid periodic reversal of the electric field prevents the extra charge from diffusing along the direction of the field. As a result, the charges accumulate less, which reduces tangent loss.



Fig. 14. Temperature dependant dielectric loss as a function of frequency for PPy and PPy/PCM nanocomposites.

3.5.2. Dielectric constant and dielectric loss as a function of temperature

Variation of dielectric constant for PPy and PPy/PCM nanocomposites at specified frequencies (10 kHz, 50 kHz, 100 kHz, 500 kHz, 1 MHz as a function of temperature is shown in Fig. 15.). The phase transition temperature is the temperature at which the dielectric constant begins to grow and reaches its maximum value (Tc). The interfacial polarisation is affected by a distinct temperature due to which the dielectric constant increases quickly with an increase in temperatures at low frequencies. Due to the presence of ionic and electronic polarizations, the dielectric constant is low at higher frequencies. The conductivity of most polar dielectrics increases smoothly with temperature, although it significantly changes at the changeover temperature.



Fig. 15. Dielectric constant vs temperature for PPy and PPy/PCM nanocomposites.

The fluctuation of dielectric loss for PPy and PPy/PCM nanocomposites over the same range of frequencies is shown in Fig. 16 as a function of temperature. Tangent loss decreases with an increase in frequency. Interfacial dipole orientation is hampered by the high resistance and low frequency activity of grain boundaries. While at higher frequencies conduction takes place by the

PPy/PCM-10 PPy 10 kHz 10 kHz 60 50 kHz 50 kHz 8 100 kHz 100 kHz 500 kHz 500 kHz 1 MHz ∞6 40 1 MHz tan 0 tan 4 20 0 320 360 400 Temperature (K) 440 320 360 400 440 Tor PPy/PCM - 20 PPy/PCM - 30 10 kHz 10 kHz 13 80 50 kHz 50 kHz 100 kHz 10 100 kHz 500 kHz 60 40 tan 0 500 kHz 1 MHz tan 8 1 MHz 20 0 400 450 300 350 350 400 Temperature in K 450 300 Temperature (K) PPy/PCM - 50 PPy/PCM - 40 10 kHz 10 kHz 50 kHz 50 kHz 100 kHz 100 kHz 500 kHz 500 kHz 0 1 MHz 1 MHz tan tan 8 300 350 400 450 300 400 350 Temperature (K) Temperature (K)

hopping mechanism of grains. This results in low dielectric loss. Increased tangent loss is caused by an increase in thermal energy of charge carriers as a result of temperature rise.

Fig. 16. Dielectric loss vs temperature for PPy and PPy/PCM nanocomposites.

4. Impedance studies for PPy and PPy/PCM nanocomposites

The formula for complex impedance Z in a circuit is $Z = \overline{Z'} + iZ'' = Z\cos\theta + iZ\sin\theta$ where Z' and Z'' are the real and imaginary parts of the complex impedance and $i = \sqrt{-1}$. |Z| and θ are the modulus and complex angle of the complex impedance, respectively.

4.1. Real (Z') and imaginary (Z") Impedance as a function of frequency

Figure 17 illustrates the fluctuation of real impedance (Z') and imaginary impedance (Z'') as a function of frequency for pure PPy and all PPy/PCM composites. At lower frequencies, for PPy, the real impedance of polypyrrole was high which decreased with an increase in frequency gradually. This reveals that PPy behaves as a capacitive type. Till a peculiar cut-off frequency, (f_c) for all nanocomposites the impedance was frequency independent or resistive type. But after f_c the impedance falls with an increase in frequencies showing capacitive nature. At high frequencies, we

observe frequency dispersion for all nanocomposites hence reflecting the short-range charge carrier transport. Of all the nanocomposites PPy/PCM 20 shows the least impedance exhibiting the highest conductivity. Doping PPy with PCM particles helps create granular-shaped particles, boosts compactness, and lowers resistance. Pure PPy forms larger clusters that are less compact and have weaker linkages, as observed in SEM pictures. In PPy/PCM composites, the oxide particles help a better coupling across the grain boundary, increasing the interconnected routes between the polymers and so boosting the composites' compactness [30].

The disappearance of the interfacial polarisation is indicated by the impedance spectrum merging at a very high frequency range. Maxwell-Wagner-Sillars (MWS) polarisation [31] makes a significant contribution to the dielectric characteristics of PPy/PCM composites.



Fig. 17. Real impedance and imaginary impedance vs frequency for PPy/PCM nanocomposites at 303K.



Fig. 18. Temperature dependent imaginary part (Z') of impedance vs frequency for PPy and PPy/PCM nanocomposites

 $Z'' = 1 / j\omega$ C, where j is less than 1, C represents capacitance, and ω is the angular frequency, which defines the imaginary portion of impedance. From the plots, it is observed that at low frequencies for all composites, except PPy/PCM 20 and 10 wt %, the imaginary impedance is constant which steadily takes the form of a broad peak which shifts towards higher frequencies and then decreases further for almost all PPy/PCM nanocomposites at room temperature. This broad peak shows the presence of single dielectric relaxation attributing to grains that contribute to impedance. This indicates non Debye type relaxation. PPy/PCM 20 and PPy/PCM 10 wt% were observed to behave differently due to high mobility charge carriers [32] that showed the least relaxation hence showing the highest conductivity. The overall charge carrier transport was improved due to the addition of PCM nanoparticles to PPy.

4.2. Real and imaginary Impedance as a function of temperature

Fig. 18 displays the temperature-dependent real component (Z') of the impedance vs frequency graph for PPy and PPy/PCM composites. At lower frequencies the real impedance of polypyrrole and all nanocomposites were high which decreased with an increase in frequency gradually. Hence they exhibit typical NTCR behavior. Many more thermally activated charge carriers begin to participate in the transport process. In Fig. 19, the temperature-dependent imaginary portion (Z") of impedance vs frequency for nanocomposites made of PPy and PPy/PCM is displayed.



Fig. 19. Temperature dependent imaginary part (Z") of impedance vs frequency for PPy and PPy/PCM nanocomposites.

The Z" versus temperature shows that the loss peak intensity decreases and there is a shift in relaxation frequency towards higher frequencies. At lower frequencies the real impedance of polypyrrole was high which decreased with an increase in frequency gradually. This reveals that PPy behaves as a capacitive type.

4.3. Nyquist plots

The effects of grains, grain boundaries, and conduction processes are depicted graphically in a Nyquist plot, which shows the real (Z) and imaginary (Z) components of impedance. Temperature-dependent Nyquist plots of pure PPy and nanocomposites of 10–50 wt% PPy/PCM are shown in Fig. 20 for the frequency range of 100 Hz–1 MHz. Just one semicircle was seen in pure PPy and all PPy/PCM composites. This demonstrates that these materials' polarisation has a single relaxation time constant [33].



Fig. 20. Temperature-dependent Nyquist plots for Pure PPy and PPy/PCM nanocomposites.

The resistance of the composites is proportional to the arc radius. Using the equation $\omega \tau = \omega RC = 1$, the value of capacitance may be evaluated, where τ is the relaxation time for a parallel RC circuit and ω is a peak angular frequency [34]. The depressed semicircles show the non-Debye capacitance nature called constant phase element (CPE) [35] denoted by Q.

The Nyquist plots are is simulated with an equivalent circuit [capacitive and resistive components in parallel combination] using ZsimpWin software to evaluate R, Q, and n values as shown in fig. 21 for pure PPy, and all PPy/PCM nanocomposites at room temperature. The graphs show a semicircle arc confirming non Debye type of behavior. The circuit comprises resistance and capacitors in parallel combination along with constant phase element (CPE) and Warburg (W) diffusion elements. The presence of these elements in the equivalent circuit is due to the random position of the doped PCM in the PPy chain which distorts the PPy/doped matrix.

Table 3 summarises the equivalent circuit, grain boundaries, and resistive and capacitive components obtained from the ZsimpWin software for pure PPy and PPy/PCM composites.



Fig. 21. Equivalent circuit fitting by ZsimpWin software for pure PPy, and PPy/PCM composites

The complex impedance Nyquist curves are further fitted by equivalent circuits with impedance capacitance and resistance as shown in figure 21 by using ZsimpWin software. For pure PPy the fitted equivalent circuit consists of three series connections of parallel resistance (R) and constant phase elements (CPEs or Q) along with one resistance in series and a parallel combination of resistance and capacitance in series with it. For PPy/PCM-10, PPy/ PCM-20 and PPy/ PCM-30, the equivalent circuit is the same with different values of C, R and Q. The circuit consists of one resistance R in series with a parallel combination of two Q and R connections and one R and L combination.

Compound	Equivalent circuit	R _s	CPE_1/Qg	R_1/R_g	CPE ₂ /Q	R_2/R_{gb}	CPE ₃ and
					gb		$CPE_4(Q_d)$
РРу	R(Q(R(C(R(C(RW))))))(CR)	4.819E3	4.687E-8	3.846E+3	2.798E-9	3.194E+4	3.456E+8
PPy/PCM-10	R(QR)(QR)(CR).	7.281E3	3.182E-9	2.847E+4	3.728E-9	2.914E+2	-
PPy/PCM-20	R(QR)(QR)(CR).	9.579E2	5.231E-9	4.130E+2	2.510E-6	9.784E+2	-
PPy/PCM-30	R(QR)(QR)(CR).	5.351E2	7.912E-9	4.253E+3	2.046E-9	3.235E+3	-
PPy/PCM-40	LR((C(R(QR)))(CR).	7.616E2	4.818E-10	5.124E+4	4.21E-10	9.925E+3	1.784E-5
PPy/PCM-50	R(QR)(QR)(OR).	2.572E3	6.218E-10	7.844E+4	7.38E-10	3.249E+4	-

 Table 4. The equivalent circuit, resistive and capacitive components of grains and grain boundaries for pure PPy, and PPy/PCM composites.

362



Fig. 22. Nyquist plots for pure PPy and PPy/PCM nanocomposites at 303K, along with fitted curves and an equivalent circuit

For PPy/ PCM-40 nanocomposites the equivalent circuit consists of a parallel combination of Q and R in series with R which intern parallel with capacitance. Further, this circuit is in series with L and R with a parallel circuit of L and R. In the case of PPy/PCM-50 nanocomposites the equivalent circuit consists of a parallel combination of four components Q and R and two Q and R in series. The whole combination is in series with Resistance. Fig. 22 displays Nyquist plots, fitted curves, and an analogous circuit for pure PPy and PPy/PCM nanocomposites at 303K. The experimental curves and theoretical values complemented each other well.

4. Conclusion

A series of nanocomposites of PPy / $Pr_{0.75}Ca_{0.25}MnO_3$ were synthesized to study electrical properties. Techniques such as XRD, SEM, EDAX, TEM, and FTIR were used to characterize them. The XRD spectrograph analysis depicts the orthorhombic structure of PCM manganite and the amorphous nature of pure PPy. The SEM indicates that PCM particles are embedded in the PPy chain and the grain size varies from 182 to 266 nm. Compositional analysis done through the EDAX technique showed that the atomic percentage of elements was found to be maximum at

PPy/PCM 50 wt % and no other impurities were detected inside the composites. It was observed from FTIR that the shift in the stretching frequencies for all nanocomposites was towards higher frequencies. Jonscher's power law was followed by AC conductivity, and the fitted curves proved that the CBH model is responsible for the conduction process.

According to studies on AC conductivity, conductivity rises with frequency due to the formation of polarons and bipolarons, which tend to cross grain and grain border barriers. The dielectric constant and dielectric loss showed a strong dependence on frequency and temperature showing the non Debye type of relaxation. The impedance study shows that polarization is constant at low frequencies and the concentration of PCM in PPy is responsible for the variation in impedance (Z). The Nyquist plots confirmed that the conduction is due to the effect of grains. Hence these nanocomposites can be used as electrically tunable material. All the dielectric properties depend on the wt % of the PCM nanomaterial in PPy. PPy/PCM nanocomposites may be used as supercapacitors and applied in designing sensors.

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364

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