A conductive mechanism of PVA (Mowiol 10-98) filled with ZnO and MWCNT nanoparticles

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Abstract. Polyvinyl alcohol (PVA) hybrid nanocomposites are prepared *via* an *ex situ* approach with ZnO and MWCNT nanoparticle fillers and their conductive mechanisms have been investigated. The tailored hybrid nanocomposite conformation and their microstructural disparities for different filler concentrations were studied using an X-ray diffractometer. The direct current (DC) conductivity studies show an increase in the conductivity from 1.0528×10^{-11} to $2.1514 \times 10^{-8} \text{ S cm}^{-1}$ up to a percolation threshold filler concentration of $x = 7.5 \text{ wt\%}$. The dielectric constant substantially indicates a decreasing trend with increasing frequency. The exaggerated dielectric constant values of 11.8 at 5 kHz, 6.3 at 100 kHz, 5.86 at 500 kHz and 2 at 1 MHz are observed for 7.5 wt% filler hybrid nanocomposites, which indicates their potential application as a gate material in metal-oxide-semiconductor field-effect transistors (MOSFETs). The alternating current (AC) electrical conductivity demonstrates an increasing behaviour up to $x = 7.5 \text{ wt\%}$ filler concentration. The smaller values observed in the real part of the electric modulus (M') indicates a riddance in electrode polarization. The observed higher frequency shift in the imaginary part of the electric modulus for increasing the filler concentration up to $x = 7.5 \text{ wt\%}$, decreases the relaxation time of the dipole orientation thereby increasing the conductivity mechanism of the hybrid nanocomposites. Apart from these, its small relaxation time with high electrical conductivity favours this material PVA/(x)MWCNT($15 - x$)ZnO to have prospective application in microwave absorption appliances. The increase in the surface roughness of the film seen from the AFM images up to $x = 7.5 \text{ wt\%}$ concentration supports an enhancement in the crystalline nature of the filler. Differential scanning calorimeter studies show an enhancement in glass transition temperature (T_g), melting temperature (T_m) and decomposition temperature (T_d) for PVA filled with MWCNTs and ZnO composites for optimum filler concentration $x = 7.5 \text{ wt\%}$.

Keywords. Nanocomposite; filler; PVA.

1. Introduction

Nowadays, the addition of metal oxide nanoparticles into a polymer matrix has become a unique metal–oxygen combination to enhance the physical and structural properties of polymer nanocomposites. These metal–oxygen bonds as the main backbone consisting of side chains, such as organic groups, hydrides or halogens revolutionize the nanocomposites for the fabrication of optical, dielectric, electrical and opto-electronic devices [1–4]. In this contemporary era, zinc oxide (ZnO) nanoparticles, which is the combination of zinc and oxygen metal-oxide atoms, have proved to be the best filler in terms of optical and electrical properties for polymer hybrid nanocomposites. These ZnO metal oxide nanoparticles have less energy gap and some outstanding properties, such as antibacterial and anticorrosive with high chemical stability [5–7]. On the other hand, multi-walled carbon nanotubes (MWCNTs) were also proved to be ideal filler candidates inside a polymer matrix. The potential applications are due to their high aspect

ratio with length having tremendous mechanical strength and conducting behaviour. These gifted characteristics of MWCNTs in the polymer matrix aid in the formulation of electrical, opto-electronic and dielectric commercial devices [8–10].

In this current work, we report on the preparation of PVA hybrid nanocomposites using polyvinyl alcohol (PVA, Mowiol 10–98) as the host polymer matrix. PVA has an ability to form a broad range of hydrogen bonds and this helps the PVA to bind with the added fillers for the preparation of novel hybrid nanocomposites [11–13]. Furthermore, the basic host PVA matrix is filled with MWCNTs and ZnO nanoparticles. This mixed filler combination (ZnO and MWCNTs) inside a single PVA matrix leads to the formation of unique organic–inorganic hybrid nanocomposites having the effects of both the fillers in the solitary polymer matrix. Thus, by mixing two fillers in a single polymer matrix, we can anticipate improvements in their physical characteristics promoting new applications in materials science. The PVA hybrid nanocomposites are traditionally prepared using the

solvent casting method at room temperature. Furthermore, these PVA/(x)MWCNT(15 – x)ZnO nanocomposites for $x = 0, 1, 5, 7.5, 10, 14$ and 15 wt% concentration hybrid nanocomposites are characterized to study their structural, dielectric relaxation, relaxation time for dipole orientation, electric conductivity and thermal conductivity behaviour.

2. Experimental

2.1 Materials

The basic host PVA (Mowiol 10–98) fully hydrolysed to 97–100 mol% grade was provided by Sigma Aldrich, Germany. The procured PVA has a molecular weight, $M_w = 61,000 \text{ g mol}^{-1}$, degree of polymerization, $P_w = 1400$ and bulk density ranging from 0.4 to 0.6 g cm^{-3} . The reagents for the production of ZnO nanoparticles were provided by Merck, India. The additional filler MWCNTs (75 mg) were obtained from Sigma Aldrich, Germany (CVD, 95% purity). The chemicals used for the preparation of PVA hybrid nanocomposites were procured from Merck, India.

2.2 Preparation of PVA hybrid nanocomposites

Initially, ZnO nanoparticles are synthesized by the precipitation method to act as a filler [14]. The additional filler MWCNTs (carbon nanotube, multi-walled >98% carbon 6–8 tube walls) are functionalized with the carboxyl group by treating with sulphuric acid (H_2SO_4) and nitric acid (HNO_3) taken in a 3:1 volume ratio solution and sonicated by using a probe ultrasonicator for 2 h. Using the nanofillers of ZnO and MWCNTs, the PVA/(x)MWCNT(15 – x)ZnO hybrid nanocomposite solvents are prepared by sonication of the composite solvent for $x = 0, 1, 5, 7.5, 10, 14$ and 15 wt% filler concentrations. The each filled composite solvent mixture was stirred and sonicated until the hybrid composite solvent was bubble free, homogeneous and highly viscous. The obtained solvent composite for various filler concentrations is casted on a Petri dish glass. This solvent is allowed to evaporate at room temperature for 3 days and peeled off. The average thickness of the prepared PVA hybrid nanocomposites was measured using a dial thickness gauge (Mitutoyo, Japan) and was found to be 100–130 μm .

2.3 Measurements

X-ray diffraction (XRD) data of PVA/(x)MWCNT(15 – x)ZnO nanocomposites were chronicled using a Bruker D8 Advance X-ray diffractometer with Ni filtered, $\text{CuK}\alpha$ radiation of wavelength $\lambda = 1.5406 \text{ \AA}$, with a graphite monochromator and a scanning speed of 2° min^{-1} in the 2θ range of 10 – 110° . From the I – V characteristics, the direct current (DC) conductivity studies of the prepared PVA nanocomposites were analysed using a Keithley 4200-SCS parameter analyser through the computer interface by the two-probe method at room temperature. The I vs. V (current vs. voltage)

measurements were performed in the voltage range of 0–5 V in multiple steps of 0.1 V. The frequency-dependent parameters such as dielectric properties and capacitance were analysed using a Keithley 4200-SCS parameter analyser at room temperature in the frequency range of 1 kHz–1 MHz. The composite surface topography related to roughness and particle size was investigated using a Bruker (Nano) atomic force microscope (AFM). Thermal studies were performed using a differential scanning calorimeter (DSC) Q2000 from TA Instruments.

3. Results and discussion

3.1 XRD studies

XRD spectra of the PVA loaded with different concentrations of MWCNTs and ZnO show intense peaks at $2\theta = 32.33, 35.15, 36.93, 48.49, 57.66, 64.23, 67.67, 69.35, 70.46$ and 74.29° signposts for filled ZnO nanoparticles (ICSD collection code: 154490 and International Center for Diffraction Data, JCPDS 5-0664) and a small peak of the loaded MWCNT at $2\theta = 26.52^\circ$ (JCPDS file no: 48-1449). The broad prominent peaks of PVA are observed between $2\theta = 19$ and 20° [15]. The enhancement in the filler concentration leads to deviations in shifts and intensity of the crystalline peaks of PVA spectra around $2\theta = 19^\circ < 2\theta < 22^\circ$. The observed shifts and variations in the intensity suggest the changes in the actual degree of order or crystalline phases of the PVA nanocomposites. Figure 1 shows that the increase in the concentration of fillers up to $x = 7.5$ wt% intensifies the crystalline peaks of PVA and the peaks shift towards the lower angle. The crystallizability of the PVA nanocomposites is found for $x = 7.5$ wt% filler. These facts suggest that the PVA chains during solidification take up the conformation leading to highly ordered and oriented chain aggregates with the added nanoparticles. This strong interfacial interaction occurring between the added filler up to $x = 7.5$ wt% with the host PVA transforms the polymer nanocomposites to gain a high impact on physical properties. For $x > 7.5$ wt%, the crystalline peaks of PVA shift nearer to the higher angle with a decrease in the intensity resulting in a low crystalline phase in the PVA matrix. This happens because the increase in carbon atoms and the decrease in oxygen vacancies of the fillers reduce the hydrogen bonding and ionic bonding and co-ordination interactions with the host PVA matrix. As a result, the nanoparticles cause less agglomeration in PVA nanocomposites thereby decreasing the physical properties [16,17].

3.2 DC conductivity

The following relationship provides the measurements of DC conductivity of the PVA nanocomposites tailored with MWCNTs and ZnO nanofillers,

$$\sigma_{\text{DC}} = \frac{d}{RA}, \quad (1)$$

Figure 1. XRD peaks of PVA/(x)MWCNT($15-x$)ZnO nanocomposites: (a) pure PVA, (b) $x = 0$ wt%, (c) $x = 1$ wt%, (d) $x = 5$ wt%, (e) $x = 7.5$ wt%, (f) $x = 10$ wt%, (g) $x = 14$ wt% and (h) $x = 15$ wt%.

Table 1. Variations of DC conductivity for different filler concentrations of PVA/(x)MWCNT($15-x$)ZnO.

S. no.	Sample (wt%)	Resistance (Ω)	Conductivity (σ in S cm^{-1})
1	Pure PVA	9.4984×10^6	1.0528×10^{-11}
2	0	3.7617×10^6	4.6583×10^{-10}
3	1	2.3528×10^4	4.2502×10^{-9}
4	5	1.264×10^4	7.9063×10^{-9}
5	7.5	0.4648×10^4	2.1514×10^{-8}
6	10	3.7895×10^5	2.6388×10^{-10}
7	14	11.895×10^5	8.406×10^{-11}
8	15	2.7486×10^4	3.6382×10^{-9}

where d is the thickness of the sample, A the cross-sectional area of the electrode used and R the resistance offered by the sample, which is assessed from the I - V data.

Table 1 shows the measurements of DC conductivity of PVA/(x)MWCNT($15-x$)ZnO nanocomposites. The DC conductivity is found to increase with the increase in the filler concentration up to $x = 7.5$ wt% and above $x = 7.5$ wt%, the values show a decreasing trend. The increase in the filler concentration up to the threshold level reduces the entanglement length thereby reducing the volume fraction of nanoparticles. The threshold ratio of carbon and oxygen molecules receding in the interstitial position of PVA molecules assists them to form charge transfer complexes through hydrogen bonding between the filled nanoparticles and host PVA molecules. The increase in the filler concentration up to the threshold limit causes the increase in charge transfer complexes. This reduces the barrier height and provokes the hopping of charges from one charge complex to other, significantly increasing the conductivity [18]. Thus, the formation of the percolate network of the conducting filler inside the PVA/(x)MWCNT

Figure 2. Variations of (a) real and (b) complex dielectric constants with an increase in the frequency of PVA/(x)MWCNT($15-x$) ZnO nanocomposites for different ' x ' filler concentrations.

($15-x$)ZnO nanocomposites up to the optimized filler concentration ($x = 7.5$ wt%) increases the electrical conductivity.

The incorporation of nanoparticles above the threshold filler ($x > 7.5$ wt%) causes the variation in the ratio of carbon and oxygen molecules in the PVA molecule. The small variation in the filler concentration leads to a significant change in the tethered zone and tether chain conformation. This leads to the creation of agglomeration in PVA nanocomposites reducing the charge transfer complexes thereby reducing conductivity.

3.3 Dielectric studies

The dielectric studies were carried out in the frequency range of 1 kHz–1 MHz isothermally at room temperature. Figure 2a and b represents the significant variation of dielectric constant (ϵ') and dielectric loss (ϵ'') with the increase in the frequency range of 1 kHz–1 MHz.

The defect density in the forbidden gap is responsible for the variation in the real and imaginary parts of the dielectric constant of the hybrid nanocomposite films [19–21]. The observed higher values of the real part of the dielectric constant at a lower frequency range signposts the greater

Figure 3. AC conductivity values of PVA/(x)MWCNT($15 - x$) ZnO for different filler concentrations.

energy storage capacity of the hybrid PVA nanocomposites. On the other hand, the decrease in the dielectric constant with the increase in the frequency indicates the polar molecular nature of nanocomposites. This strange behaviour is due to the interfacial effect observed in the grain boundaries caused by the immovability of charges which hampers the molecular motion. As a result, the dipoles themselves start to orient in the applied field direction. With the increase in the frequency, the movement of bound charges is promoted and the dipole orientation in the applied field direction is reduced. Thus, the transport of bound charges encourages the enhancement in conductivity with the increase in the frequency [18,22].

3.4 AC conductivity

The following relationship is utilized to determine the AC conductivity performance of the synthesized polymer nanocomposites,

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon'', \quad (2)$$

where f is the applied frequency, ε_0 the permittivity of free space and ε'' the dielectric loss.

Figure 3 shows the AC electrical conducting mechanism of the filled PVA nanocomposites. The frequency dependence of the electrical behaviour of materials is explained by:

$$\sigma_{AC} = \sigma_{DC} + \sigma_1(\omega), \quad (3)$$

or

$$\sigma_{AC} = \sigma_{DC} + A\omega^n, \quad (4)$$

where σ_{DC} is the frequency independent DC conductivity, $\sigma_1(\omega)$ the typically assigned to the hopping conduction, A the pre-exponential factor dependent on the temperature and n the exponent ($n < 1$, the hopping motion is a translational one whereas $n > 1$, the motion is a localized one).

According to the law, the following effects that contribute to the AC conductivity are:

- (1) electrode effect (active low frequencies),
- (2) DC plateau (at intermediate frequencies),
- (3) defect process (which can be explained by the term $A\omega^n$) viz., quantum mechanical tunnelling through the barrier separating the localized state or correlated barrier hopping over the same barrier.

The improvement in the AC electrical conductivity was found up to $x = 7.5$ wt% filler concentration. It has also been observed that the conductivity increases with frequency and is characteristic of the ω^n (n is the exponential). Furthermore, the Jonscher power law is applied for all the prepared composites and is confirmed by the non-linear fit. It was observed that at low frequencies, there is a slight deviation for all the composites. The non-linear fit also suggested that the value of $n < 1$ corresponds to the diffusion limit. Hence, the transport mechanism is explained by the hopping process between the two sites separated by an energy barrier.

Apart from these, two mix fillers i.e., ZnO and MWCNT nanoparticles are filled on the host PVA matrix. The conduction may also occur by the formation of MWCNT and ZnO nanoparticle networks. This can be explained based on the primary particle model. The conductive mechanism shows a discrepancy by means of the electron tunnelling mechanism as explained above. This quantum tunnelling is a governing mechanism around the percolation threshold. The quantum mechanical tunnelling represents the wave function of the electron that is not restricted completely within a potential box, but also contains a small tail prolonging beyond the potential barrier. This small tail helps the stream of conduction electrons (10^{-5} – 10^{-10}) having kinetic energy below the potential barrier to penetrate the barrier and reach the next aggregate [18,24]. The increase in the filler concentration gradually reduces the distance between the filled nanoparticles and enhances the carbon and oxygen molecules encouraging the conductance in the nanocomposites. At a threshold ratio of $x = 7.5$ wt% filler concentration, the distance between the nanoparticles is < 10 nm and the conductivity escalates owing to the tunnelling effects. Furthermore, increase in the filler concentration above $x = 7.5$ wt% decreases the carbon and oxygen vacancy ratios and also when the content of the filled particles is above the percolation threshold, the conducting mechanism decreases by the overlapping of wave functions and ohmic instead of the tunnelling process. The decrease in the filler ratio reduces the free ion concentration and assists in the less agglomeration process of fillers leading to a larger particle having a reduced surface area. These factors lead to the reduction in the conductivity for the filler concentration above $x = 7.5$ wt% [10,25].

Figure 4 shows the intensification in the AC electrical conductivity with frequency due to dielectric transition. These

Figure 4. Variations of AC conductivity with frequency of PVA/(x)MWCNT(15 - x)ZnO nanocomposites for different ‘x’ nano-filler concentrations.

transitions generate chemical changes in each PVA molecule improving the AC conducting behaviour of nanocomposites [10,25–29].

3.5 Electric modulus

The electric modulus (M) in the frequency domain is determined by the reciprocal of the complex dielectric [10,25,29]

$$M = \frac{1}{\varepsilon' + i\varepsilon''} = M' + iM'', \quad (5)$$

where $M' = \varepsilon' / (\varepsilon'^2 + \varepsilon''^2)$ epitomizes the real part and $M'' = \varepsilon'' / (\varepsilon'^2 + \varepsilon''^2)$ symbolizes the imaginary part of the electric modulus.

The imaginary part of the electric modulus represents the measure of distribution of ion energies and determines the value of dipole relaxation time (τ_p) using the following equation:

$$\tau_p = \frac{1}{\omega_p}, \quad (6)$$

where ω_p is the angular frequency obtained from asymmetric peaks of the imaginary part of electric modulus (M'') vs. frequency graph.

The observed small values of the real part of the electric modulus at a lower frequency in figure 5a epitomize the high dielectric constant [19].

These small values of the real part of the electric modulus (M') represent the restricted orientation of dipoles and the elimination of electrode polarization [10,29]. Figure 5a shows an S-shaped curve indicating the increased values of M' with the increase in frequency. This asymptotic value of M' results from short-range mobility of charge carriers during conduction [30].

Figure 5. Variations of (a) real and (b) complex electric moduli with an increasing frequency of PVA/(x)MWCNT(15 - x)ZnO nanocomposites for various ‘x’ nano-filler concentrations.

Figure 5b represents the variation of the imaginary part of the electric modulus (M'') with the increase in the applied frequency. The observed distinct asymmetric peaks in M'' are obtained from the heterogeneous polymeric system having a different dielectric constant. A noticeable shift in the maximum asymmetric peaks with the increase in filler concentration up to 7.5 wt% reveals Maxwell–Wagner–Sillars (MWS) polarization [31].

This polarization restricts the relaxation time of the dipole orientation and promotes the hopping of charges from one site to other. These favourable facts authorize the local chain dynamics of the PVA hybrid nanocomposites and enhance their conductivity on the filler.

Furthermore, the increase in the filler concentration above $x = 7.5$ wt% allows the asymmetric peaks to shift towards a lower value. This fact supports the presence of localized sites consisting of short-range motion of charge carriers with increasing relaxation time. The increase in the relaxation time reduces the transition of charge carrier mobility plummeting the electrical conductivity of the prepared hybrid nanocomposites.

Figure 6. AFM 2-D images of (a) pure PVA and (b) MWCNT- filled PVA for 7.5 wt% concentration.

Figure 7. AFM 3-D image of PVA/(x)MWCNT($15 - x$)ZnO for $x = 7.5$ wt%.

3.6 Film topography

Figure 6a and b represents the AFM two-dimensional images of pure and $x = 7.5$ wt% filled hybrid nanocomposites. Figure 7 shows the three-dimensional AFM topography of the tailored PVA hybrid nanocomposites for the optimum percolation threshold filler concentration ($x = 7.5$ wt%). The AFM photographs of the pure PVA film show a smooth surface having reduced grain size. The addition of fillers into the PVA matrix changes the grain size and obviously roughens the surface of the hybrid nanocomposites due to the presence of undulation between valleys and peaks that are present. The transport properties and fouling potential also depend on the composite surface roughness. The difference among the highest peak ($Z_{\max}$) and lowest valley ($Z_{\min}$) on the composite surface provides the peak to valley roughness. The average peak to valley roughness (R_{avg}) for the obtained AFM image is 54.9 nm. This observation is due to the adsorption of PVA molecules tightly on the surface of nanoparticles. These primary complex particulate formations are due to the result of

the particle–particle interactions, as the added nanoparticles are completely encapsulated by PVA, which impressively shields or interdicts the strong interactions between the filled nanoparticles. Thus, the adsorption of polymer main chains with loaded nanoparticles results in complex formation i.e., host PVA molecular chains may adsorb mixed nanoparticles to form the nano-sized hybrids [32]. This wrapping shell of PVA covering the whole nanofillers changes the root mean square (rms) values [33]. Thus, change in the filler concentration attributes the variations to the rms value, which indicates the fluctuations in the crystallinity of the prepared hybrid nanocomposites. On the other hand, the AFM data represented in table 2 regarding the complex particle parameters support the fact that the prepared hybrids are of nano-size in nature.

3.7 DSC studies

Figure 8 presents the effects of thermal behaviour of unfilled and filled PVA for optimized filler concentration $x = 7.5$ wt% in the temperature range of 30–350°C. The recognizable increase in the T_g from 49.10 to 56.17°C for $x = 7.5$ wt% concentration indicates the formation of the complex through the interaction of fillers with the hydroxyl group of the PVA backbone.

The influence of other functional groups also supports the hydrogen bonding and enhances the value of T_g to a maximum for the optimum filler concentration $x = 7.5\%$. The width of the T_g for the filled concentration of the polymer nanocomposites is almost identical to that of the unfilled PVA components signifying the single-phase behaviour of the polymer nanocomposites. The endothermic peak occurring at 220.66°C was accredited to the melting point of the PVA nanocomposites [34]. The increase in the value of T_m for $x = 7.5$ wt% filler concentration signifies the increase in the crystallite size in the crystalline phase or the increase in the order of the molecular packing in the crystallites. On the other hand, the dispersion of nanoparticle fillers into the PVA main

Table 2. AFM particle size parameters of PVA/(x)MWCNT($15 - x$)ZnO for $x = 7.5$ wt% filler concentration.

Parameter	Mean	Minimum	Maximum	Sigma
Total count	12.000	12.000	12.000	0.000
Density (μm^{-2})	0.030	0.030	0.030	0.000
Height (nm)	108.003	23.181	224.744	77.661
Area (nm^2)	779215.500	158691.406	3808593.750	992543.563
Diameter (nm)	869.520	449.502	2202.102	485.863

Figure 8. DSC thermograph of (a) pure PVA and (b) PVA with MWCNTs and ZnO for $x = 7.5$ wt% filler concentration.

chain causes a tendency of local ordering in the PVA structure. This occurrence of local ordering might be due to the intra-molecular and inter-molecular interactions existing between the nanoparticle fillers and PVA structure. Thus, these factors increase the size of the crystallite in the composite film. Figure 8 also shows that the addition of nanoparticle fillers also enhances the decomposition temperature (T_d) and further on heating the PVA nanocomposites above the T_d , the polymer composite initiates a rapid chain-stripping elimination of H_2O causing colour changes and crosslinking to yield insoluble yellow to black rigid foam-like residues as it decomposes [35,36].

4. Conclusions

The fascinating results of the conductive mechanism of the novel PVA/(x)MWCNT($15 - x$)ZnO hybrid nanocomposites for different percolation filler concentrations are studied. The

XRD studies confirm the hybrid PVA chain entanglements, variation in the crystalline properties and other microstructural disparities with the increase in the filler concentration. It is found that for percolation threshold, filler concentration $x = 7.5$ wt%, the enhancement in the crystalline properties is achieved. The hybrid nanocomposites featured for up to $x = 7.5$ wt% percolation filler concentration show a steep increase in DC conductivity from 1.0528×10^{-11} to $2.1514 \times 10^{-8} \text{ S cm}^{-1}$. The high dielectric constant values at low frequency indicate the electrode polarization and with the increase in frequency, the dielectric shows a decreasing trend. At a threshold ratio for $x = 7.5$ wt% filler concentration, due to the presence of oxygen and carbon molecules and also due to tunnelling effects, the conductivity of the hybrid nanocomposites increases. The exaggerated dielectric constant values of 11.8 observed at 5 kHz, 6.3 at 100 kHz, 5.86 at 500 kHz and 2 at 1 MHz are noticed for 7.5 wt% filler hybrid nanocomposites indicating their potential application as a gate material in metal-oxide-semiconductor field-effect transistors (MOSFETs). The smaller values of the real part of the electric modulus (M') signify the elimination of electrode polarization. The observed higher frequency shift in the imaginary part of the electric modulus (M'') for an increasing filler concentration up to $x = 7.5$ wt% decreases the relaxation time of the dipole orientation, thereby increasing the conductivity of the nanocomposites. Apart from these, its small relaxation time with high electrical conductivity favours this material PVA/(x)MWCNT($15 - x$)ZnO to have prospective application in microwave absorption appliances. The addition of fillers into the PVA matrix changes the grain size and enhances the surface roughness of the hybrid nanocomposites which supports the enhancement in the crystalline nature of the PVA nanocomposites up to $x = 7.5$ wt% percolation threshold, which are analysed by AFM. The DSC studies show an enhancement in T_g , melting temperature (T_m) and T_d for PVA filled with MWCNTs and ZnO composites for optimum filler concentration $x = 7.5$ wt%.

References

- [1] Balamurugan A, Ho K C and Chen S M 2009 *Synth. Met.* **159** 2544

- [2] de Barros R A, Martins C R and de Azevedo W M 2005 *Synth. Met.* **155** 35
- [3] Rajeswari N, Selvasekarapandian S, Karthikeyan S, Sanjeeviraja C, Iwai Y and Kawamura J 2013 *Ionics* **19** 1105
- [4] Wang Z L, Kong X Y, Ding Y, Gao P, Hughes W L, Yang R *et al* 2004 *Adv. Funct. Mater.* **14** 943
- [5] Ando M, Kadono K, Haruta M, Sakaguchi T and Miya M 1995 *Nature* **374** 625
- [6] Kumar N B R, Crasta V and Praveen B M 2016 *Mater. Res. Express.* **3** 055012
- [7] Mardare D and Rusu G I 2004 *J. Optoelectron. Adv. Mater.* **6** 333
- [8] Jariwala D, Sangwan V K, Lauhon L J, Marks T J and Hersam M C 2013 *Chem. Soc. Rev.* **42** 2824
- [9] Zhou Y X, Freitag M, Hone J, Staii C, Johnson A T, Pinto N J *et al* 2003 *Appl. Phys. Lett.* **83** 3800
- [10] Suman M, Tomara A K and Shyam K 2010 *J. Alloys Compd.* **508** 406
- [11] Bhajantri R F, Ravindrachary V, Harisha A, Ranganathaiah C and Kumaraswamy G N 2007 *Appl. Phys. A* **87** 797
- [12] Khanna P K, Singh N, Charan S, Subbarao V, Gokhale R and Mulik U P 2005 *Mater. Chem. Phys.* **93** 117
- [13] Seira M, Takashi N and Takuya G 2012 *Polym. J.* **44** 1056
- [14] Nejati K, Rezvani Z and Pakizevand R 2011 *Int. Nano Lett.* **1** 75
- [15] Zidan H M 2003 *J. Appl. Polym. Sci.* **88** 1115
- [16] Bhajantri R F, Ravindrachary V, Harisha A, Crasta V, Suresh Nayak P and Poojary B 2006 *Polymer* **47** 3591
- [17] Rithin Kumar N B, Vincent C, Praveen B M and Mohan K 2015 *Nanotechnol. Rev.* **4** 457
- [18] Sherman R D, Middleman L M and Jacobs S M 1983 *Polym. Eng. Sci.* **23** 36
- [19] Dutta A, Sinha T P, Jena P and Adak S 2008 *J. Non-Cryst. Solids* **354** 3952
- [20] Kumar M, Tiwari T, Chauhan J K and Srivastava N 2014 *Mater. Res. Express* **1** 049601
- [21] Pradhan D K, Choudhary R N P and Samantaray B K 2009 *Mater. Chem. Phys.* **115** 557
- [22] Ruschau G R, Yoshikawa S and Newnham R E 1992 *J. Appl. Phys.* **72** 953
- [23] Mahendia S, Tomar A K and Kumar S 2011 *Mater. Sci. Eng. B* **176** 530
- [24] Janzen J 1975 *J. Appl. Phys.* **46** 966
- [25] Gonzalez-Campos J B, Prokhorov E, Sanchez I C, Luna-Barcenas J G, Manzano-Ramirez A, Gonzalez-Hernandez J *et al* 2012 *J. Nanomater.* **1** 925750
- [26] Paul E W, Riccio A J and Wrighton M S 1985 *J. Phys. Chem.* **89** 1441
- [27] Chanmal C V and Jog J P 2008 *Express Polym. Lett.* **2** 294
- [28] Thomas P, Satapathy S, Dwarakanath K and Varma K B 2010 *Express Polym. Lett.* **4** 632
- [29] Jitendra T, Khushbu Rahangdale K and Balasubramanian K 2016 *RSC Adv.* **6** 69733
- [30] Dutta P, Biswas S and De S K 2002 *Mater. Res. Bull.* **37** 193
- [31] Bhadra S, Singha N K and Khastgir D 2009 *Curr. Appl. Phys.* **9** 396
- [32] Zheng P, Ling X K, Si-Dong L and Pavel S 2006 *J. Nanosci. Nanotechnol.* **6** 3934
- [33] Jun-Feng Z, Zhong-Zhen Y, Yu-Xun P, Xiao-Ping F and Yu-Chun O 2002 *J. Polym. Sci.: Part B: Polym. Phys.* **40** 954
- [34] Rachna M and Rao K J 2000 *Ceram. Intl.* **26** 371
- [35] Cullis C F and Hirschler M M 1981 (Oxford: Clarendon Press)
- [36] Anders H and Zimmerman H 1987 *Polym. Degrad. Stab.* **18** 111