Investigation of correlation between dielectric parameters and nanostructures in aqueous solution grown poly(vinyl alcohol)-montmorillonite clay nanocomposites by dielectric relaxation spectroscopy

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Abstract. Poly(vinyl alcohol) (PVA)-montmorillonite (MMT) clay nanocomposite films up to 10 wt% clay concentration were synthesized by aqueous solution grown technique. The relative complex dielectric function, alternating current electrical conductivity, electric modulus and impedance properties of these organic-inorganic nanocomposites were investigated in the frequency range from 20 Hz to 1 MHz at ambient temperature. The PVA-MMT clay nanocomposite films show a large decrease in the real part and loss of relative dielectric function at 1 wt% MMT clay loading compared to pure PVA film and anomalous behaviour is observed with further increase of clay concentration in PVA matrix. Two dielectric relaxation processes were observed in these nanocomposites; a high frequency relaxation associated with PVA segmental motion and a low frequency relaxation resulting from PVA/dispersed MMT clay interfacial polarization (Maxwell-Wagner relaxation). Dielectric relaxation times corresponding to these processes were determined by fitting dc conductivity corrected complex dielectric function data to the Havriliak-Negami expression. A correlation between change in dielectric relaxation strength, relaxation time and hindrance to the PVA-chain dynamics with the degree of exfoliated structures of dispersed nanoscale MMT clay filler in the PVA matrix were explored. Results confirm the application of dielectric relaxation spectroscopy as a potential tool in the confirmation of nanocomposite formation and their structure characterization.

Keywords: nanocomposites, dielectric spectroscopy, dielectric properties, PVA dynamics, MMT clay

1. Introduction

Synthesis and structural characterization of polymer-clay (organic-inorganic) nanocomposites (PCNs) are of technological interest due to significant improvement in the useful properties of composite materials over those of the pure polymer [1–12]. For the preparation of poly(vinyl alcohol) (PVA)-layered silicate nanocomposite, montmorillonite (MMT) clay is the most commonly used, which has hydrophilic property, and 2:1 phyllosilicate laminar structure. Synthesis of PVA-MMT clay nanocomposites by solution casting technique and their structural characterization have been sub-

ject of several investigations [13–17]. Structural and morphological studies of PVA-MMT clay nanocomposite materials investigated by X-ray diffraction (XRD), Fourier transform infra-red (FTIR) spectroscopy, differential scanning calorimetry (DSC), atomic force microscopy (AFM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) have established the high degree intercalation and exfoliation behaviour of MMT clay in the PVA matrix, which improves their thermal, mechanical and permeability properties. Due to the transparent nature of PVA-MMT clay films, these nanocomposites have established

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their potential use in paper coating. Survey of literature exhibits that, the structure-dielectric properties relationship in PVA-MMT clay nanocomposites has not yet been studied in detail, which is needed for their technological and microelectronic applications, and as electrolyte materials in solid-state batteries.

In the present paper, the dielectric relaxation spectroscopic study of aqueous solution grown PVA-MMT clay nanocomposite films up to 10 wt% MMT clay concentration was carried out to characterize the dielectric properties and their correlation with PVA local chain dynamics in view of low dielectric constant materials as passivation layers in modern microelectronic devices. The complex dielectric function, alternating current (ac) electrical conductivity, impedance properties and electric modulus spectra of the PVA-MMT clay nanocomposite films were investigated over the frequency range 20 Hz to 1 MHz. An attempt is made to correlate the values of various dielectric parameters with structural behaviour of these nanocomposite materials to establish the use of dielectric relaxation spectroscopy as diagnostic tool for the development of on-line testing and monitoring of the nanocomposite formation in PCNs materials [18–33].

2. Materials and methods

2.1. Materials

The PVA of average molecular weight $77\,000\text{ g}\cdot\text{mol}^{-1}$ of laboratory grade was obtained from Loba Chemie, Mumbai, India. Polymer grade hydrophilic montmorillonite (MMT) clay (Nanoclay, PGV), a product of Nanocor® was purchased from Sigma-Aldrich. The MMT clay is white in colour, and has 145 meq/100 g cation exchange capacity (CEC), 150–200 aspect ratio, 2.6 g/cc specific gravity, and 9–10 pH value on 5% dispersion. This is the best MMT clay for the preparation of nanocomposites with the PVA matrix recommended by the manufacturer.

2.2. Preparation of PVA-MMT clay nanocomposite by solution-grown technique

For the 0, 1, 2, 3, 4, 5 and 10 wt% MMT clay concentration (weight fraction concentration for a total

3 g of PVA-MMT clay), 0.00, 0.03, 0.06, 0.09, 0.12, 0.15 and 0.30 g amounts of MMT clay powder were colloiddally suspended each in 5 ml double distilled deionized water in separate glass bottles with airtight caps by vigorous stirring with Teflon® coated magnetic stir bar on a magnetic stir plate for 24 hrs at room temperature. The balance weight 3.00, 2.97, 2.94, 2.91, 2.88, 2.85 and 2.70 g of PVA corresponding to the 0 to 10 wt% clay concentration were dissolved each separately in 22 ml double distilled deionized water at 90°C in separate glass bottles. After that, the respective concentration clay colloidal solutions were mixed with the PVA solutions. For proper intercalation and exfoliation of the clay, these mixtures were again stirred vigorously with Teflon® coated magnetic stir bar on a magnetic stir plate each for 24 hrs. PVA-MMT clay nanocomposite films were cast by pouring the PVA-MMT clay hydrocolloidal suspensions of varying clay concentration into 60 mm diameter stainless steel rings directly onto optically smooth glass plates and were left to dry at room temperature for one week. Room dried films of thickness ~0.4 mm were further dried under vacuum for 24 hrs before their dielectric/electric measurements. All the prepared PVA-MMT clay nanocomposite films were found optically clear to the eyes.

2.3. Measurements

Agilent 4284A precision LCR meter and Agilent 16451B solid dielectric test fixture having a four terminals nickel-plated cobalt (an alloy of 17% cobalt + 29% nickel + 54% iron) electrodes of diameter 38 mm, were used for the measurement in the frequency range 20 Hz to 1 MHz. Frequency dependent values of parallel capacitance C_p , parallel resistance R_p and loss tangent $\tan\delta$ (dissipation factor D) with sample, were measured for the determination of dielectric/electrical functions of the PVA-MMT clay nanocomposite films at ambient temperature (30°C). Prior to the sample measurements, the open circuit calibration of the cell was performed to eliminate the effect of stray capacitance. The details of the evaluation of complex dielectric function $\epsilon^*(\omega) = \epsilon' - j\epsilon''$, complex alternating current (ac) electrical conductivity $\sigma^*(\omega) = \sigma' + j\sigma''$, complex electric modulus $M^*(\omega) = M' + jM''$ and complex impedance $Z^*(\omega) = Z' - jZ''$

of the solid PCNs films are described by us elsewhere [29–31, 34].

3. Results and discussion

3.1. Complex dielectric function

Figure 1a shows that the real part ϵ' of the complex dielectric function of PVA-MMT clay nanocomposites decreases with the increase in frequency of applied alternating electric field from 20 Hz to 1 MHz, which confirms the dielectric dispersion in these materials. The ϵ' values of the nanocomposite films are found to be lower than that of the pure PVA film and have anomalous variation with increase of MMT clay concentration. These observations reveal that the intercalated and exfoliated MMT clay structures in PVA matrix change dramatically with the increase of MMT clay concentration in aqueous solution grown PVA-MMT clay nanocomposite films. Such anomalous variation was also observed in ϵ' values with the increase of MMT clay concentration in PVA-MMT clay hydro-

colloids over the same frequency region [23]. This behaviour is not surprising, because in aqueous solutions the flexible PVA chain and dispersed clay exist with a variety of hydrogen bonded structures. Recently, Wang *et al.* [20, 21] investigated the dielectric properties of solution intercalated polystyrene-MMT clay and poly(methyl methacrylate)-MMT clay nanocomposite films within the frequencies of 100 Hz–1 MHz and found that loading of 1 wt% MMT clay significantly reduces the ϵ' values as compared to the pure polymer film, which is mainly due to reduction in the number of aligned dipolar groups in the presence of randomly distributed exfoliated clay nanoplatelets in the polymer matrix.

In PVA-MMT clay nanocomposites, the intercalation of PVA in clay galleries and exfoliation of MMT clay nanoplatelets occur simultaneously [13–17]. The XRD, TEM and DSC studies established that in aqueous solution grown PVA-MMT clay nanocomposites up to 10 wt% MMT clay loading have well dispersed MMT nanoplatelets throughout the PVA matrix, i.e., nanocomposites formed are mostly exfoliated hybrids [14]. The exfoliation of layers is attributed to the water casting method used, since the water suspended layers become kinetically trapped by the polymer and cannot re-aggregate. Further, the formation of the hydrogen bonds between the PVA vinyl alcohol group and silicate oxygen force the PVA chains to create long adsorbed trains due to the atomically smooth dispersed MMT surfaces. The large reduction in ϵ' value at 1 wt% MMT clay concentration in PVA-MMT clay nanocomposites also suggests that the amount of exfoliated structures is very high as compared to that of the PVA intercalated clay structures [14, 15], which is the common characteristics of solution grown PCNs at very low clay concentration [18–34].

The loss part ϵ'' spectra of complex dielectric function (Figure 1b) reflects the presence of two relaxation processes in the PVA-MMT clay nanocomposite films over the frequency range 20 Hz–1 MHz, which can be seen in their complex plane plots (ϵ'' vs. ϵ') (Figure 2). The frequency values of the experimental data points increases on going from right to left side on these plane plots. The higher frequency arc in Figure 2 is corresponding to the PVA local chain motion, whereas the lower frequency arc represents the contribution of direct

Figure 1. Frequency dependent real part ϵ' and loss ϵ'' of complex dielectric function of solution grown PVA-MMT clay nanocomposite films of varying MMT clay concentration [wt%]. The solid lines are smooth joining of the experimental data points, as guides for the eyes.

Figure 2. Complex plane plots (ϵ'' vs. ϵ') of solution grown PVA-MMT clay nanocomposite films of varying MMT clay concentration [wt%]

current (dc) conductivity and Maxwell-Wagner (MW) interfacial polarization relaxation process. To explore the dispersed MMT clay nanoplatelets structures and their effects on the PVA molecular local chain dynamics, the higher frequency dielectric data (above 10^4 Hz) were fitted by the Havriliak-Negami (HN) expression [35]. The fit parameters namely limiting real part of dielectric function ϵ_s at lower frequencies and ϵ_∞ at higher frequencies, the dielectric relaxation strength $\Delta\epsilon = \epsilon_s - \epsilon_\infty$, the mean relaxation time τ , and the symmetric and asymmetric broadening parameters α and β , respectively, are recorded in Table 1 and also plotted in Figure 3.

The static dielectric constant ϵ_s (limiting lower frequency ϵ' value) of the 1 wt% MMT clay loaded PVA-MMT clay nanocomposite film decreases nearly by 1 as compared to that of the pure PVA film (Figure 3a and Table 1). The decrease in ϵ_s value confirms the formation of PVA-MMT clay nanocomposites with large amount of exfoliated MMT clay structures in the PVA matrix, as revealed by the dielectric studies of different PCNs materials [1, 2, 18–24, 33, 34]. The $\epsilon_s \sim 2.4$ at the

Figure 3. MMT clay concentration [wt%] dependent static dielectric constant ϵ_s , dielectric relaxation strength $\Delta\epsilon$ and mean relaxation time τ of PVA molecular polarization dispersion and, dielectric relaxation strength $\Delta\epsilon_{MW}$ and relaxation time τ_{MW} of MW interfacial polarization process of solution grown PVA-MMT clay nanocomposite films. The solid lines are B-spline fit of the experimental data points, as guides for the eyes.

1 wt% MMT clay concentration in PVA-MMT clay nanocomposite suggests its possible use as low dielectric constant material of improved thermal and mechanical properties in microelectronic devices [1, 2]. At 2 and 3 wt% MMT clay concentration, the ϵ_s values of these nanocomposites are found to be close to that of the 1 wt% MMT clay loaded nanocomposite film, which suggest that the degree of exfoliated MMT clay structures remains

Table 1. Dielectric parameters of PVA–MMT clay nanocomposites of varying MMT clay concentration [wt%]

MMT clay [wt%]	PVA molecular polarization process dielectric parameters					MW interfacial polarization process dielectric parameters					$\sigma_{dc} \cdot 10^{11}$ [S/m]	s
	ϵ_s	$\Delta\epsilon$	τ [ns]	α	β	ϵ_{sMW}	$\Delta\epsilon_{MW}$	τ_{MW} [μ s]	α_{MW}	β_{MW}		
0	3.42	1.89	35.7	0.92	0.78	3.97	3.79	4.1	0.97	0.78	1.68	0.30
1	2.39	0.74	63.9	0.90	0.76	2.82	2.60	18.1	0.97	0.82	1.34	0.30
2	2.75	1.27	44.6	0.91	0.78	3.30	2.57	10.4	0.62	0.76	2.79	0.35
3	2.53	1.04	52.0	0.91	0.80	3.11	2.25	13.0	0.95	0.74	2.28	0.32
4	3.17	1.50	33.5	0.94	0.78	3.60	3.18	5.5	0.98	0.83	0.63	0.22
5	3.19	1.67	35.6	0.93	0.81	3.85	2.89	7.9	0.95	0.72	1.36	0.23
10	2.53	0.91	43.8	0.90	0.75	2.97	2.63	9.0	0.98	0.82	0.51	0.19

nearly the same up to 3 wt% MMT clay loading in PVA matrix. At 4 and 5 wt% MMT clay concentration, the ϵ_s values are found to be slightly less than that of the pure PVA film, which reveals that exfoliated MMT clay structures at these concentrations still dominate over the PVA intercalated clay structures. This finding confirms that at 4 to 5 wt% MMT clay loading in PVA matrix brings critical changes in its mechanical and thermal behaviour without affecting the dielectric constant. At 10 wt% MMT clay concentration the exfoliated structures again increase as compared to the intercalated structures of the MMT clay and their ratio is nearly equal to the 1 to 3 wt% MMT clay concentrations, because the ϵ_s at 10 wt% MMT clay concentration is of the order of 1 to 3 wt% MMT clay loaded nanocomposites. Recently, Pluta *et al.* [27] also confirmed that in polylactide/MMT nanocomposites, large exfoliated nanostructures are formed up to the 3 wt% MMT clay loading due to combined interactions of MMT surfactant with polymer chains, whereas at the 10 wt% MMT clay loading, mixed intercalated and exfoliated nanostructures are formed, which is in agreement with the nanostructures discussed in PVA-MMT clay nanocomposites. Figure 3b also shows that the MMT clay concentration dependent values of dielectric relaxation strength $\Delta\epsilon$ of these nanocomposites vary according to the variation in their ϵ_s values.

The MMT clay concentration dependent mean relaxation time τ of PVA-MMT clay nanocomposites (Table 1 and Figure 3c) confirms that the PVA local chain dynamics is governed by the amount of exfoliated structures of the MMT clay nanoplatelets in the PVA matrix. As discussed above by considering their ϵ_s values, the exfoliated clay structures dominates at the 1 wt% clay loading, which is also favoured by the large increase in τ value at this concentration as compared to that of the pure PVA. The silanol (Si–O) groups of exfoliated clay structures have large range H-bonded interactions with –OH groups of PVA chain, which results in the adsorption of PVA on exfoliated clay surfaces and hence produces large hindrance to its local chain dynamics, thus enhancing the corresponding relaxation time. Kanapitsas *et al.* [18] also observed that for the PCNs, when ϵ' decreases the overall mobility of the polymer chain decreases, as compared to the pure polymer matrix. The decrease in polymer chain segmental mobility relaxation time in nano-

composite provides an explanation for the increased thermal and mechanical stability in the PCNs. Davis *et al.* [24], Kim *et al.* [28], and Sengwa *et al.* [34] also concluded that the increase of τ value represents an increase in clay exfoliation in the PCNs. At varying MMT clay concentrations, good resemblance is observed between the change in the ϵ_s and τ values (Figure 3). The MMT clay concentration at which ϵ_s decreases, τ increases and vice versa is in good agreement with the above discussed correlation between the ϵ_s values and the amount of exfoliated clay structures in the solution grown PVA-MMT clay nanocomposites.

Recently, Bandi and Schiraldi [17] have investigated the glass transition temperature T_g of solution intercalated PVA-MMT clay films as a function of clay size, concentration and dispersion in the PVA matrix. They observed that T_g exhibits a maximum value at 1 wt% concentration of MMT clay and for higher concentration its value decreases anomalously. Further, they explained that at 1 wt% MMT clay concentration, there is the existence of large amount of exfoliated MMT clay nanoplatelets with greater interfacial area, which favours the coupling of PVA chains to the clay surfaces through the adsorption and hydrogen bonding, and simultaneously strengthen the disordered interfaces leading to an increase of the T_g value and the reduce of PVA chain dynamics. The present dielectric study also confirms that a large reduction of the ϵ_s and also the increase of τ value at 1 wt% MMT clay loading results in the formation of large range crosslinked hydrogen bonded structures between exfoliated MMT clay sheets and the randomly coiled and flexible PVA chains, which reduces the net dielectric polarization and increases the hindrance to the PVA local chain dynamics. Wang *et al.* [20] also concluded that a large amount of exfoliated MMT clay structures in PCNs enhances the T_g value and simultaneously reduces the ϵ_s value. The increase in τ value is also related to the increased amount of layered silicate surface area as a result of the increased degree of exfoliation [24, 28]. Above 1 wt% MMT clay loading both the interfacial area and intercalation are enhanced and more PVA chains are confined between the MMT clay sheets. Under confinement the PVA molecules inside the MMT clay galleries are aligned mechanically, resulting from fewer entanglements and bringing enhanced relaxation dynamics within the

composite and reduces its T_g values [17]. The anomalous decrease in τ values (Figure 3c) with the increase in MMT clay loading above 1 wt% are in good agreement with the structural properties of solution intercalated PVA-MMT clay films as explored from their T_g values [17].

The SEM, TEM, FTIR and XRD study of these nanocomposites established that the exfoliated structures in PVA matrix have mixed nanomorphology [16]. Individual silicate layers, along with two, three and four layer stacks (tactoids) exfoliate in the PVA matrix in addition to some large intercalated tactoids. Further, crystalline morphology of pure PVA approaches to amorphous state as the MMT clay concentration increases in PVA matrix. The anomalous decrease in the τ value of nanocomposites above 1 wt% clay loading (Figure 3c) suggests that the mixed nanomorphology of the exfoliated clay tactoids randomly changes with the increase in MMT clay concentration in the aqueous solution grown PVA-MMT clay nanocomposite films, since the water suspended silicate layers becomes kinetically trapped by the randomly coiled and flexible PVA chains. The atomic force microscopy (AFM) of these nanocomposites also revealed that the PVA has a tendency to cover completely the tactoids, which is driven by strong specific interactions between the hydroxyl groups of PVA monomer units and the silanol groups of silicates and causes a strong wetting of PVA on the delaminated clay surfaces [15].

Table 1 shows that the values of PVA local chain relaxation process shape parameters α and β describing the broadening of the relaxation peak that varies anomalously with increase of MMT clay concentration in the PVA-MMT clay nanocomposites. The α and β values of these nanocomposites are found in the ranges 0.90–0.94 and 0.76–0.82, respectively, which confirms that there is an asymmetric broadening of the relaxation peak corresponding to PVA dynamics.

At frequencies below 10^4 Hz the direct current conductivity contribution in the ϵ'' spectra corresponding to low frequency dispersion was fitted with the power law relation $\epsilon'' = \sigma_{dc}/\epsilon_0\omega^s$, where σ_{dc} is the dc conductivity and s is an exponent fitting parameter. For ohmic contacts and no MW polarization, $s = 1$ holds. In the most practical cases $0 < s \leq 1$ is obtained [25], which confirms the contribution of MW interfacial polarization. The dc

conductivity corrected low frequency ϵ'' data were also fitted to HN expression [35] for the evaluation of MW interfacial relaxation time, τ_{MW} and the corresponding dielectric relaxation strength, $\Delta\epsilon_{MW}$. The observed values of σ_{dc} and s along with the dielectric parameters of MW interfacial polarization relaxation process (ϵ_{sMW} , $\Delta\epsilon_{MW}$, τ_{MW} , α_{MW} and β_{MW}) evaluated from the HN expression of the PVA-MMT clay nanocomposites are recorded in Table 1 with varying wt% MMT clay concentration. The values of $\Delta\epsilon_{MW}$ and τ_{MW} of these nanocomposites are also plotted against wt% MMT clay in Figures 3d and 3e, respectively. Table 1 shows that the σ_{dc} values of PVA-MMT clay nanocomposites vary anomalously within one order of magnitude with the increase in MMT clay concentration. The σ_{dc} value of the pure PVA film was found to be in good agreement with the earlier reported value [36]. The values of exponent parameter s are found less than unity (Table 1), which confirms the contribution of MW polarization with dc conduction in lower frequency dielectric dispersion of these nanocomposites. In the MW phenomena, the free charges build up during the electromigration at the interfacing boundaries of different dielectric constants or conductivities components of the composite materials, which results the formation of nanocapacitors in the composite dielectric material at low frequency alternating current electric field [18]. At sufficiently high frequencies, such short-range movements of free charges can not follow the fast changes developed in the applied ac electric field and thus only molecular polarization occurs. In the investigated PVA-MMT clay nanocomposites, at ambient temperature, the MW phenomena contributed in dielectric properties up to 10^4 Hz and above that the dielectric dispersion is due to the PVA molecular polarization. Further, it is found that the s values vary in the same trend of σ_{dc} values with increase of MMT clay concentration in the PVA-MMT clay nanocomposites (Table 1).

In PVA-MMT clay nanocomposites, the interface between non-intercalated galleries of layered silicate (tactoids) and PVA gives rise to the formation of large dipoles, enhancing the electric inertia of interfacial relaxation phenomena, leading to slower motion or greater relaxation time. On the other hand, the interface between PVA and intercalated layered silicates results in formation of relatively smaller dipoles allowing faster motion. Recently,

Noda *et al.* [19] and Bur *et al.* [22] analyzed the MW interfacial relaxation to correlate it with the clay dispersion and the amount of exfoliation in the PCNs materials for on-line process monitoring and off-line measurements. As exfoliation proceeds, nanosize silicate flakes present an ever expanding polymer/silicate interface area that increases the internal capacitance of the composite where the moving charge can accumulate. Silicate flakes act as the nanocapacitors in a sea of dielectric polymer, and as the capacitance increases with exfoliation the characteristic frequency of the MW relaxation decreases and the relaxation time increases. The MW relaxation time τ_{MW} of a nanocomposite is given by the relation $\tau_{MW} = RC$, where R is the resistance of the polymer matrix and C is the capacitance of the dispersed silicate platelets in the matrix [19]. During exfoliation of silicate platelets the value of R remains constant and C changes. Therefore, the RC time constant (τ_{MW}) is controlled solely by the capacitance of the silicate in the aggregate, intercalated, or exfoliated state or any combination thereof.

Figure 3e shows that the MMT clay concentration dependent τ_{MW} values are higher than that of the pure PVA film, which is in good agreement with the formation of large exfoliated clay structures in these nanocomposites, as discussed above on the basis of the comparative change in their ϵ_s and τ values. The MW relaxation process in pure PVA film occurs due to its semicrystalline behaviour. Further, the variation in τ_{MW} values with increase of MMT clay concentration is found to be in good agreement with the trend in the variation of τ values, which reveals that in the PCNs materials the polymer local chain motion relaxation time and MW interfacial polarization relaxation time are coupled processes and provide the same information regarding the nanostructures formation. The τ_{MW} values of these nanocomposites are found to be three to four orders of magnitude higher than that of their τ values. Further, Table 1 and Figure 3d shows that the values of $\Delta\epsilon_{MW}$ are significantly greater than that of the $\Delta\epsilon$ values but the shape parameters values of both the processes vary in the same range with the increase of MMT clay concentration in the investigated nanocomposite films.

Figure 4. Frequency dependent real part of ac conductivity σ' of solution grown PVA-MMT clay nanocomposite films of varying MMT clay concentration [wt%]. Inset shows the σ' spectra of pure PVA film and the 10 wt% MMT clay concentration PVA-MMT clay nanocomposite film.

3.2. AC conductivity

The real part of ac conductivity σ' of PVA-MMT clay nanocomposite films increases with the increase in frequency and shows an anomalous variation with the increase of MMT clay concentration (Figure 4). The turn in slope of frequency dependent σ' values around 10^4 Hz also reflect the presence of two dispersion processes in lower frequency and upper frequency regions of the experimental frequency range, which are corresponding to the MW interfacial polarization and the PVA molecular polarization processes, respectively, as discussed above.

3.3. Electric modulus spectra

Interpretation of relaxation phenomena via electric modulus formalism offers some advantages upon permittivity and conductivity relaxation treatments since large variation in the ϵ' and ϵ'' values at low frequencies and high temperature are minimized [23, 26, 29–31, 37]. Further, difficulties occurring in the analysis of dielectric spectra from the electrode nature (electrode material), the electrode-specimen electrical contact and the injection of space charges and absorbed impurities can be neg-

Figure 5. Frequency dependent real part M' and loss M'' of complex electric modulus of solution grown PVA-MMT clay nanocomposite films of varying MMT clay concentration [wt%]. The solid lines are smooth joining of the experimental data points, as guides for the eyes.

lected in the electric modulus spectra. It is observed that the real part of electric modulus M' of PVA-MMT clay nanocomposite films increases with the increase of frequency at lower frequencies of the M' spectra (Figure 5a), which confirms that the measured dielectric/electrical properties are free from the contribution of EP effect. Generally, the dielectric materials, having the contribution of EP effect in their measured dielectric properties, show a plateau at lower frequencies and an abrupt increase in M' spectra at higher frequencies [26, 29–31, 36, 37]. The M'' dispersion spectra (Figure 5b) of the investigated PVA-MMT clay films also confirms the presence of two relaxation processes in these nanocomposite materials in the experimental frequency range. Figure 6 shows the master-curve representation of ϵ'' , M'' and σ' values of the 1 wt% MMT clay concentration PVA-MMT clay film. The consistency in the dispersion spectra of different formalisms confirms the presence of two relaxation processes in the same frequency

Figure 6. Frequency dependent loss of dielectric function ϵ'' , loss of electric modulus M'' and real part of ac conductivity σ' of solution grown PVA-MMT clay nanocomposite films of the 1 wt% MMT clay concentration. Vertical dotted line shows the turning point in the spectra, which separates two relaxation processes.

range and their suitability in the analysis of nanostructure formation and dynamical behaviour in the PVA-MMT clay nanocomposite materials.

3.4. Impedance spectra

Complex impedance spectroscopy is commonly used to separate the electrode polarization (EP) effect and bulk material properties, which is distinguished by the appearance of two different arcs in the complex impedance plane plots (Z'' vs. Z') [12, 37, 38–40]. The EP phenomena occur due to formation of electric double layer (EDL) capacitances by the free charges that build up at the interface between the dielectric material and electrode surfaces in plane geometry. This is reflected by the large increase of the complex dielectric function with decreasing frequency in the lower frequency region of the dielectric spectra and an additional arc in the complex impedance plane plots. Figure 7 shows that the Z'' versus Z' plots of PVA-MMT clay nanocomposites have only one arc over the entire experimental frequency range, which is corresponding to the properties of bulk material. The single arc plots confirm that in the frequency range 20 Hz to 1 MHz, the PVA-MMT clay nanocomposites have good electrical contact with nickel-plated cobalt electrodes and there is no formation of EDL capacitances. Further, the large values of imaginary part Z'' as compared to real part Z' of the complex impedance confirm a highly capacitive behaviour of these films [34, 40].

Figure 7. Complex impedance plane plots (Z'' vs. Z') of solution grown PVA-MMT clay nanocomposite films of varying MMT clay concentration [wt%]

4. Conclusions

Earlier studies on the aqueous solution grown PVA-MMT clay nanocomposites materials have established their large enhancement of the Young's modulus, a very moderate decrease of toughness, improved thermal degradation properties, decrease of water permeability, and high melting point at a small amount of MMT clay loading in the PVA matrix and these are also optically clear to eyes [14–16]. In addition to these, the present dielectric relaxation spectroscopy study of these nanocomposite materials confirmed the significant decrease in real part and loss of dielectric function at the 1 wt% MMT clay loading as compared to that of the pure PVA film, which is owing to the formation of a large amount of exfoliated MMT clay nanostructures in the PVA matrix. The anomalous variation in the static dielectric constant values of different processes with the increase of MMT clay in these nanocomposites has good resemblance with the variation in their glass transition temperature [17]. The ϵ'' and M'' spectra of these PCN films confirm the two relaxation processes in the frequency range 20 Hz to 1 MHz. The detailed dielectric study revealed that the static dielectric constant value can be tuned in the magnitude of nearly 1 by loading the 1 wt% MMT clay in PVA matrix for their use as low dielectric constant materials in microelectronic technology and also as electrolytes in solid-state batteries with improved thermal and

mechanical properties. The impedance spectra confirm that in the experimental frequency range there is no contribution of electrode polarization process, but Maxwell-Wagner polarization process and dc electrical conductivity contributed to the lower frequency dielectric dispersion. A strong correlation is observed between the change in static dielectric constant, dielectric relaxation strength and relaxation times of the PVA local chain dynamics and MW interfacial polarization relaxation with the degree of exfoliated clay structures in the PVA matrix. Results suggest that the dielectric relaxation spectroscopy can be applied for the development of testing and monitoring technique in the area of nanocomposite formation, specially confirmation of the amount of exfoliated nanoscale MMT clay platelets in the polymer matrix and their hindrance to the polymer local chain dynamics. At low amount of MMT clay loading the high degree of exfoliated MMT clay structures in polymer matrix significantly reduces the dielectric constant due to the decrease in the number of aligned dipolar groups and simultaneously increases the relaxation time of the polymer local chain motion because of the formation of large range hydrogen bond interactions between exfoliated nanoplatelets of MMT clay and hydroxyl groups of PVA monomer units. The exfoliated MMT clay structures also increase the capacity of PVA/MMT clay interfacial nanocapacitors and enhances the MW interfacial relaxation time, which are responsible for the enhancement in their mechanical and thermal properties.

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