

Dielectric Behavior of Some Vinyl Polymers/Montmorillonite Nanocomposites on the Way to Apply Them as Semiconducting Materials

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ABSTRACT

Some vinyl polymers/montmorillonite nanocomposites were prepared via *in-situ*-atom transfer radical polymerization (ATRP) in presence of clay. Methyl methacrylate, styrene and n-butyl methacrylate were involved in the formation of such polymeric nanocomposites. Their dielectric properties were extensively studied to invest them in the a.c. power applications. Several dielectric parameters such as dielectric constant loss (ϵ'') and a.c. conductivity (σ) were measured at both different frequencies (0.1 Hz to 100 KHz) and temperature ranged from (20°C to 90°C). From the dielectric results, it was realized that the dielectric a.c. conductivity was enhanced by increasing the temperature for the four prepared polymer nanocomposites.

Keywords: Nanocomposites; Atom Transfer Radical Polymerization; Insulation; Dielectric Measurements; Intercalation; Polarization

1. Introduction

At the last decades, polymers/clay nanocomposites (PCNs) became an interesting area of research where PCNs have evoked an intense industrial and academic research, due to their outstanding mechanical, thermal, chemical and electrical properties over the pure polymers [1]. Several kinds of nanofillers were used such as layered silicates which include montmorillonite as the widely used nano-clay [2,3]. Organic polymers, loaded with small amounts of montmorillonite (MMT) clay produce polymer-clay nanocomposites (PCNs) having a good resemblance in dielectric properties with respect to their structural properties [4]. Generally, the research work on novel polymeric materials in the field of power engineering and high voltage technology is of great significance both nationally and internationally due to the increasing demands of more cost effective and environmentally better materials for high voltage equipment [5]. Traditionally, additive agents and fillers are often used for improving dielectric and mechanical properties of materials [6]. Nowadays, polymeric nanocomposite materials are attracting attention of many researchers in the field of dielectric [7] where polymeric nanocomposites are thought

to be the state of the art of dielectric materials with improved dielectric performance [8]. Polymeric semiconducting materials are widely applied to power apparatuses and cables [9]. Therefore, recent preliminary work has been already done to investigate the dielectric performance of polymeric nanocomposite materials regarding the reduction of space charge, variation of conductivity and increase of electric strength where these studies were carried out in case of various polymeric materials, doped with nanofillers [10-12]. Generally, three methods are commonly used for the synthesis of PCNs including *in-situ* polymerization [13], solvent intercalation [14] and polymer melt intercalation [15]. For *in-situ* technique, free radical polymerization is likely the most important process [16]. However, conventional free radical polymerization methods lack the control due to chain transfer and termination reactions. Therefore, living controlled polymerization techniques (LCR) appeared as the vital alternative including nitroxide mediated polymerization (NMP) [17], reversible addition fragmentation process (RAFT) [18] and metal mediated atom transfer radical polymerization (ATRP) [19]. ATRP appeared as the most attractive living controlled polymerization tech-

niques tolerant to various monomers, solvents, temperatures and catalytic systems. The aim of the current work was to prepare some vinyl polymeric/montmorillonite clay nanocomposites via *in-situ*-atom transfer radical polymerization where their dielectric behavior was successively studied by measuring different related parameters such as dielectric constant (ϵ'), dielectric constant loss (ϵ'') and a.c. conductivity (σ) [20-22].

2. Experimental Section

2.1. Materials

Montmorillonite (CEC = 88 meq/100 g) was received from Sigma-Aldrich chemical company (USA). Other chemicals-otherwise mentioned were used as received from Sigma-Aldrich without further purification. The monomers such as styrene (St), methyl methacrylate (MMA), and n-butyl methacrylate (n-BuMA) were purified by filtration through an activated basic alumina column and then stored under argon in the fridge.

2.2. Characterization

Gel permeation Chromatography (GPC) was used to determine number-average molecular weight (\bar{M}_{nGPC}) and polydispersity (\bar{M}_w/\bar{M}_n) of the polymers by using Agilent-1100 GPC-technologies-Germany. The refractive index detector was G-1362 A with $100\text{-}10^4\text{-}10^5$ Å°, using polystyrene (PS) as a standard and tetrahydrofuran (THF) as the eluent. The structures of the formed polymers were determined via proton nuclear magnetic resonance spectrometry ($^1\text{H-NMR}$) which was carried out with Jeol-ECA 500 MHz, using tetramethylsilane (TMS) as internal standard and CDCl_3 as the main solvent. X-ray Diffraction (XRD) measurements were carried out by using Phillips X Pert X-ray generator with Cu K α radiation at 40 kV. Dynamic mechanical thermal analyses (DMTA) were carried out with a diffractometer (type PW 1390) with employing Ni-filtered CuK. A typical sample weight was about 8 - 10 mg and the analyses were performed at a heating rate of $10^\circ\text{C}/\text{min}$ from 50 to 600°C under Helium atmosphere. Transmission electron microscopy (TEM) was used to determine the morphology of the formed polymers/clay nanocomposites by using transmission electron microscopy (TEM-JEOL JX 1230) with micro-analyzer electron probe and magnification up to 600 kx, giving a resolution down to 0.2 nm. The measurements were performed at an accelerating voltage of 100 kV. The dielectric measurements were performed using Computerized LRC-bridge (Hioki model 3531 zHi Tester). The dielectric constant ϵ' for the investigated samples was studied at both different temperatures and frequencies ranging from (20°C to 90°C) and (0.1 Hz up to 100 KHz). The samples used in the

dielectric measurements were in disc form, having 10 mm in diameter and 3 mm in thickness, pressed using a pressure of 10 ton at room temperature. Then, silver paste was coated to form electrodes on both sides of the sintered ceramic specimens in order to ensure good contacting. The electric measurements were carried out by inserting the sample between two parallel plate conductors forming cell capacitor. Then, the whole arrangement was placed in non-inductive furnace for heating the samples with constant rate. The relative dielectric permittivity was calculated using the relations:

$$\epsilon' = Cd/\epsilon_0 A \quad (1)$$

$$\epsilon'' = \epsilon' \tan \delta \quad (2)$$

where, ϵ' is the permittivity, ϵ'' is the dielectric loss and $\tan \delta$ is the loss tangent and A is the area of the electrode. The a.c. resistivity of the prepared samples was estimated from the dielectric parameters. As long as the pure charge transport mechanism is the major contributor to the loss mechanism, the resistivity (ρ) can be calculated using the following relation:

$$(\rho) = 1/(\omega \epsilon_0 \epsilon' \tan \delta) \Omega \text{Cm} \quad (3)$$

where $\omega = 2\pi f$, ω is the angular frequency and f is the frequency of the applied electric field in Hertz.

$$\sigma = 2\pi f d C \tan \delta / A \quad (4)$$

where σ is the a.c. conductivity, f is the operating frequency, d is the thickness of the dielectrics, $\tan \delta$ is the dielectric loss, C is the capacitance and A is the area of the electrode.

2.3. General Polymerization Procedure

2.3.1. Organic Modification of Clay with Cationic Surfactant (CTAB) [23]

The montmorillonite clay (MMT, 20 gm) was dispersed in 500 ml distilled water containing certain amount of cationic surfactant, as cetyltrimethyl ammonium bromide (CTAB) (6 gm, 0.0165 mol) at room temperature. The temperature was increased to 80°C with vigorous stirring for 6 - 8 h. The clay was separated by filtration and washed several times with distilled water where the filtrate was tested with AgNO_3 solution (1 gm AgNO_3 in 100 ml distilled H_2O) to obtain the modified clay without CTAB residuals. The resulting modified clay with CTAB (MMT-CTAB) was dried under vacuum at 60°C for 24 h. MMT-CTAB was grinded and characterized via XRD and TEM.

2.3.2. Preparation of the MMA or St Homopolymers/ Montmorillonite Nanocomposites [24]

MMT-CTAB (0.15 g, 4%filler) was placed in a test tube, then bipyridine (bpy) (0.15 g, 4.9×10^{-4} mol) and CuBr (I)

(0.07 g, 4.9×10^{-4} mol) were added. The tube was closed and purged with argon for 15 minutes. 5.2 ml of MMA or 5.6 ml of St (4.9×10^{-2} mol) were successively injected into the reaction mixture under argon atmosphere. The tube was immersed in an oil bath with continuous stirring at 90°C. The reaction mixture was left for 10 minutes, then, 1 ml (4.9×10^{-4} mol) of ethyl-2-bromoisobutyrate was added to the reaction mixture as a sacrificial initiator. After 6 h, the vial was opened and the polymerization was terminated by adding THF to the reaction mixture. The polymers/clay nanocomposites were washed with aqueous solution of disodium salt ethylene-diamine-tetraacetic acid (EDTA-disodium salt) to remove the catalysts and dried in vacuum at 40°C. For GPC measurements, the free polymer was separated by precipitation of THF solution in n-hexane, then filtration, re-dissolving it in THF and passing through alumina column to get the free polymer.

2.3.3. Preparation of Co- and Ter-Polymers/Montmorillonite Nanocomposites

The co- and ter-polymerization experiments were carried out as previously described in case of homo-polymers but in different amounts as:

2.3.4. In Case of Copolymers

0.3 g of MMT-CTAB, 0.306 g (9.8×10^{-4} mol) of bpy and 0.14 g (4.9×10^{-4} mol) of CuBr (I) were added. 5.6 ml (4.9×10^{-2} mol) of St were added under argon atmosphere with continuous stirring. After 4 h, the vacuum was applied to the reaction mixture to remove the remaining of the first monomer, then, 5.2 ml (4.9×10^{-2} mol) of MMA were added and the reaction was left for additional 20 h.

2.3.5. In Case of Ter Polymerization

0.45 g of MMT-CTAB, 0.45 g (9.8×10^{-4} mol) of bpy and 0.21 g (4.9×10^{-4} mol) of CuBr (I) were added. Then, the vessel was closed for 30 min. Then, the first and second monomers were sequentially added as previously described. St and MMA were added as in case of copolymerization. 7.7 ml of n-BuMA (4.9×10^{-2} mol) were added after 24 h. The reaction was left for additional 24 h and terminated by adding THF as previously described.

3. Results and Discussion

Several polymers/MMT nanocomposites were prepared via *in-situ*-atom transfer radical polymerization (ATRP) of some vinyl monomers. On that way, MMT was modified with CTAB cationic surfactant where the basal spacing (d) increased from 1.210 nm at 2 theta of 7.5 for MMT to 1.837 nm at 2 theta value of 5 for MMT-CTAB. That extension in the interlayer distance between the clay

platelets was referred to the intercalation of the CTAB molecules between the clay layers which caused widening of the interlayer distance. MMA and St/MMT nanocomposites were prepared via *in-situ* ATRP in presence of MMT-CTAB. Block copolymer/MMT nanocomposite was obtained by *in-situ* ATRP of St and applying vacuum to get rid of the monomer residuals, then adding MMA as the second monomer. In case of block terpolymer, n-BuMA was added as the third monomer after successive additions of St and MMA, respectively and by removing the excess of each monomer by vacuum before proceeding in further new polymerization step. The resulting polymers/MMT nanocomposites such as PMMA, PSt, PSt-b-MMA and PSt-b-MMA-b-n-BuMA/MMT were characterized via XRD, TGA, DSC and TEM. As shown in **Figure 1**, XRD indicated d values of 1.174 nm and 1.019 nm for PMMA/MMT and PSt-b-PMMA/MMT at 2 theta values of 7.7 and 8.7, respectively, with lower intensity than recorded for MMT-CTAB. The values of basal spacing d for both PSt/MMT and PSt-b-PMMA-b-P-n-BuMA/MMT were 8.251 and 1.894 nm at 2 theta values of 10.7 and 5.7, respectively. The formed polymers/MMT nanocomposites were characterized via TGA where as shown in **Figure 2**, PMMA lost about 88% from its initial mass where the degradation started at 170°C with slight weight loss (2.0%) till 310°C. Then, it lost 85.55% of its weight from 310 up to 455°C where the sample completely decomposed at 600°C. Pst sample lost about 42.2% from its initial mass where it started to decompose at 120°C and it lost 2.11% of its weight till 150°C then it lost 12.78% up to 260°C followed by weight loss of 17.97% up to 410°C where the complete decomposition occurred at 600°C. On the other hand, in case of PSt-b-PMMA, the sample stayed unaffected till 200°C where it began to lose about 8 % of its weight up to 340°C, and then gradual decomposition happened where it lost 45.11% up to 440°C and finally complete degradation was recorded at 600°C. Generally, it seemed that PSt-b-PMMA lost about 54% from its initial mass. In case of PSt-b-PMMA-b-P-n-BuMA, it lost about 73.94% from its initial mass where it started to decompose at 30°C up to 130°C with a weight loss 14.6%, and then the sample gradually degraded up to 415°C with weight loss of 47.94% and 11.4% at two stages but the sample completely degraded at 600°C.

DSC measurements indicated T_g values of 90°C, 117°C, 156°C and 180°C for PMMA, PSt, PSt-b-PMMA and PSt-b-PMMA-b-P-n-BuMA polymers inside their nanocomposites with MMT. Some of the prepared nanocomposites were characterized by TEM as shown in **Figure 3**. TEM showed that the stacks of the intercalated clay platelets are embedded in the polymer matrices showing good distribution of the MMT particles within the polymer matrices. The structure of the resulting polymers was confirmed by $^1\text{H-NMR}$ [25]. $^1\text{H-NMR}$ of

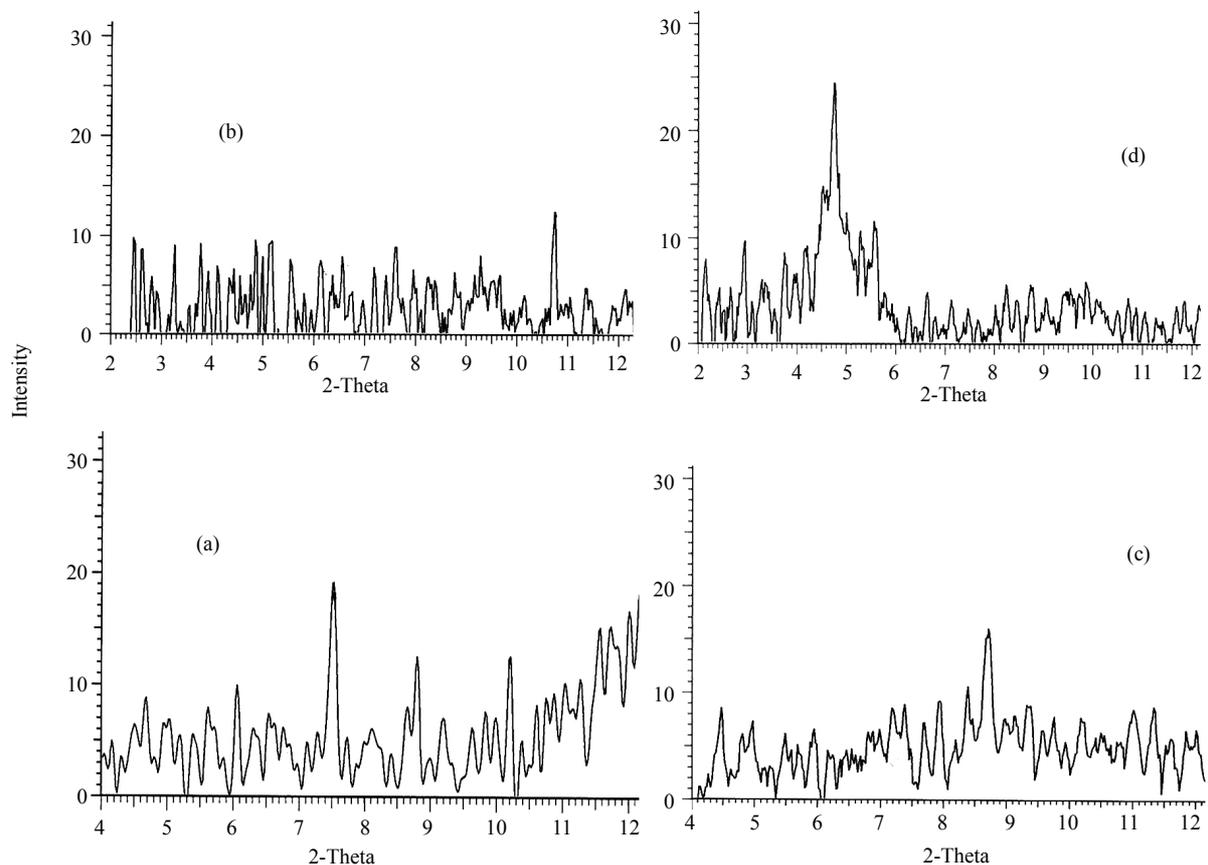


Figure 1. XRD of (a) PMMA/MMT, (b) PSt/MMT, (c) Pst-b-PMMA/MMT, (d) PSt-b-PMMA-b-P-n-BuMA/MMT nanocomposites.

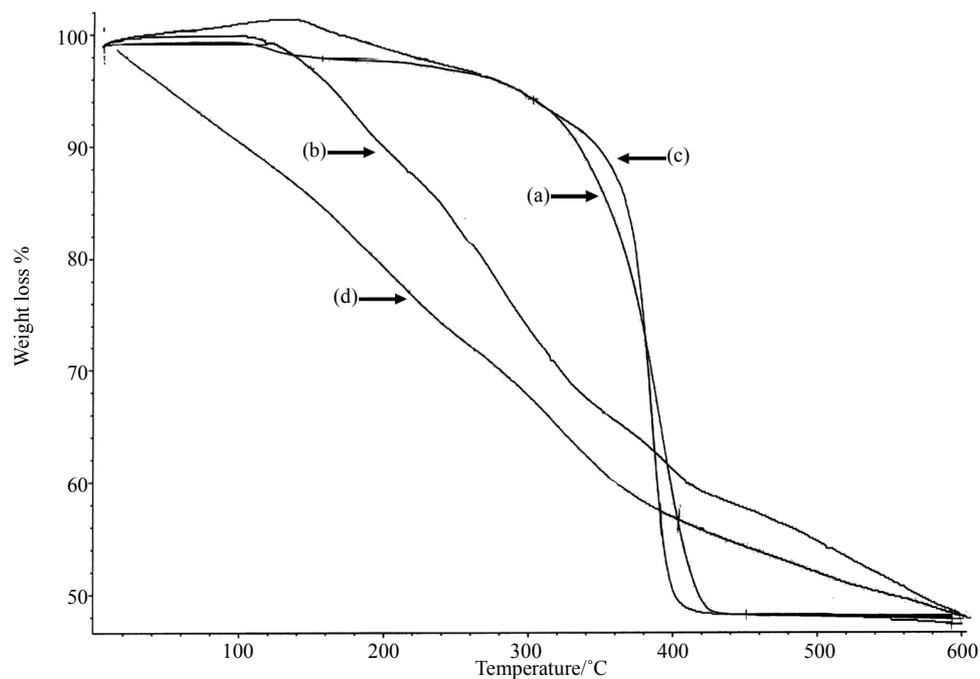


Figure 2. TGA of (a) PMMA/MMT; (b) PSt/MMT; (c) Pst-b-PMMA/MMT; (d) PSt-b-PMMA-b-P-nBuMA/MMT nanocomposites.

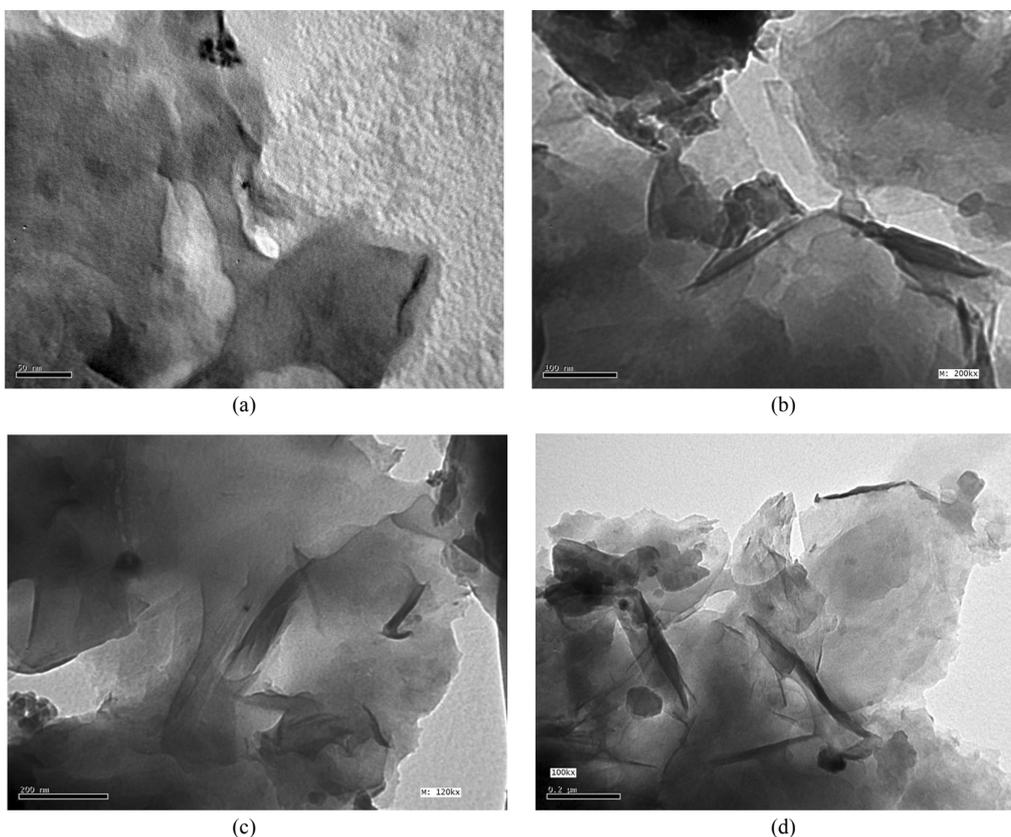


Figure 3. TEM of (a) PMMA/MMT; (b) PSt/MMT; (c) Pst-b-PMMA/MMT; (d) PSt-b-PMMA-b-P-nBuMA/MMT nanocomposites.

MMA polymer, indicated the appearance of characteristic bands at chemical shifts (δ , ppm) at (0.8 - 1.3) for (CH_3CH_2 , C- CH_3), 1.5 - 1.9 for (CH_3CH_2) and at 3.5 for (OCH_3). However, for St polymer, dense bands appeared in high intensity at $\delta = 6.5 - 7.5$ which were referred to the phenyl groups inside the skeleton of the polymer. On the other hand, (Br-CH-ph) appeared at $\delta = 4$ ppm. In case of PSt-b-PMMA copolymer, typical bands for both MMA and St units were observed. Similarly, in case of PSt-b-PMMA-b-P-n-BuMA, characteristic bands for St. and MMA were noticed in addition to several bands at 2 - 2.9 which were attributed to several (CH_2) groups inside the terpolymer skeleton in occasion of the presence of n-BuMA moiety.

Dielectric Measurements of Polymers/Clay Nanocomposites [26,27]

The dielectric constant loss ϵ'' and a.c. conductivity (σ) were studied in the temperature range (20°C - 90°C) and frequency range (0.1 Hz up to 100 KHz) for all polymers/clay nanocomposites samples. **Figures 4(a)-(d)** shows the variation of the dielectric loss ϵ'' of poly (a, PMMA/ MMT), (b, PSt/MMT), (c, PSt-b-PMMA/MMT) and (d, PSt-b-PMMA-b-P-n-BuMA/MMT) nanocomposites samples as a function of frequency at various tempera-

tures. From these graphs, it was noticed that the dielectric loss decreased by increasing the frequency for all investigated samples. This behavior for all polymers/clay nanocomposites prepared samples can be described by the Debye dispersion relation [28],

$$\epsilon'' = \omega\tau \left[\left(\epsilon_s - \epsilon_\infty / 1 + \omega^2\tau^2 \right) \right],$$

where the interfacial polarization dominates [29] at relatively low frequency range which competes the mentioned normal behavior (the rise of ϵ'' with increasing frequency). This leads to diminish the low frequency behavior. Tareev *et al.*, [30] reported that, as the frequency increases, many types of losses get to be reduced because the field frequency begins to exceed their characteristic natural frequency. This is ascribed to the initial high value of dielectric parameters for polar materials, but as the frequency of the field is raised, the value begins to drop which may be due to the fact that the dipoles not being able to follow the field variation at higher frequencies and also due to the polarization effects.

Figures 5(a)-(d) show the dependence of a.c. conductivity on the frequency at different temperatures for (a, PMMA/MMT), (b, PSt/MMT), (c, PSt-b-PMMA/MMT) and (d, PSt-b-PMMA-b-P-n-BuMA/MMT) nanocomposites. The a.c. conductivity behavior of all prepared sam-

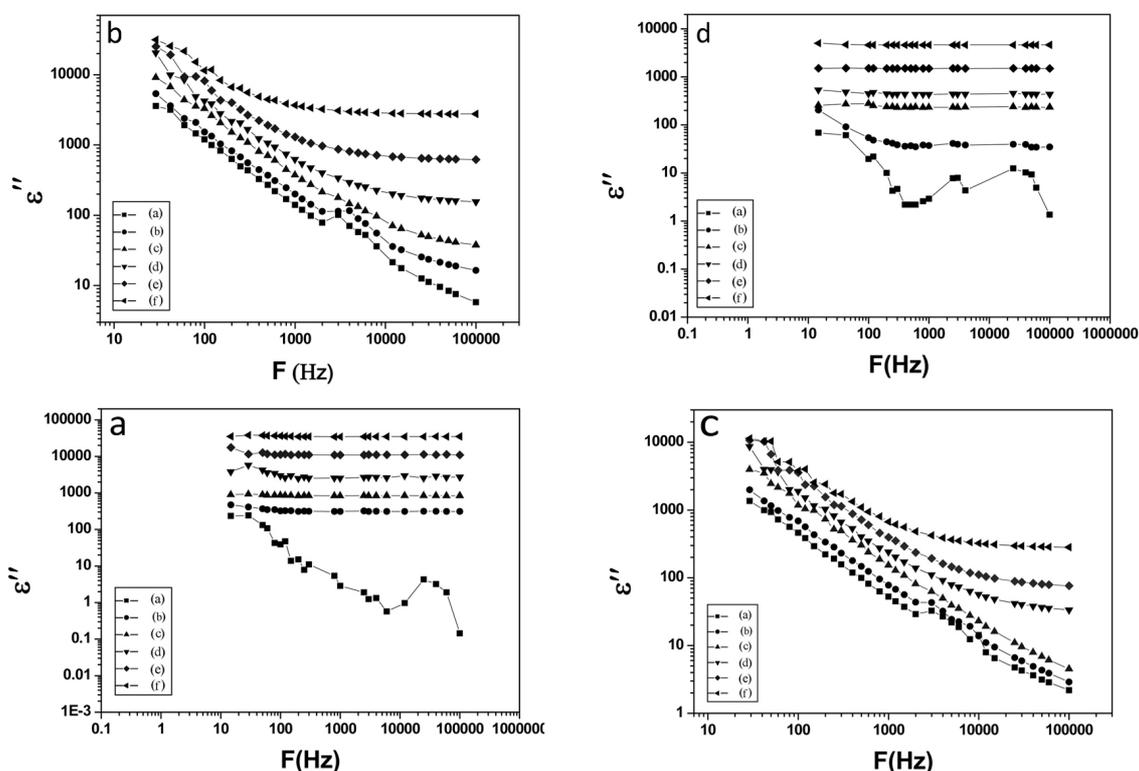


Figure 4. The dielectric constant loss ϵ'' as a function of frequency, (a) PMMA/MMT, (b) Pst/MMT, (c) Pst-b-PMMA/MMT, (d) Pst-b-PMMA-b-P-n-BuMA/MMT, where a = 20°C, b = 40°C, c = 60°C, d = 70°C, e = 80°C, f = 90°C.

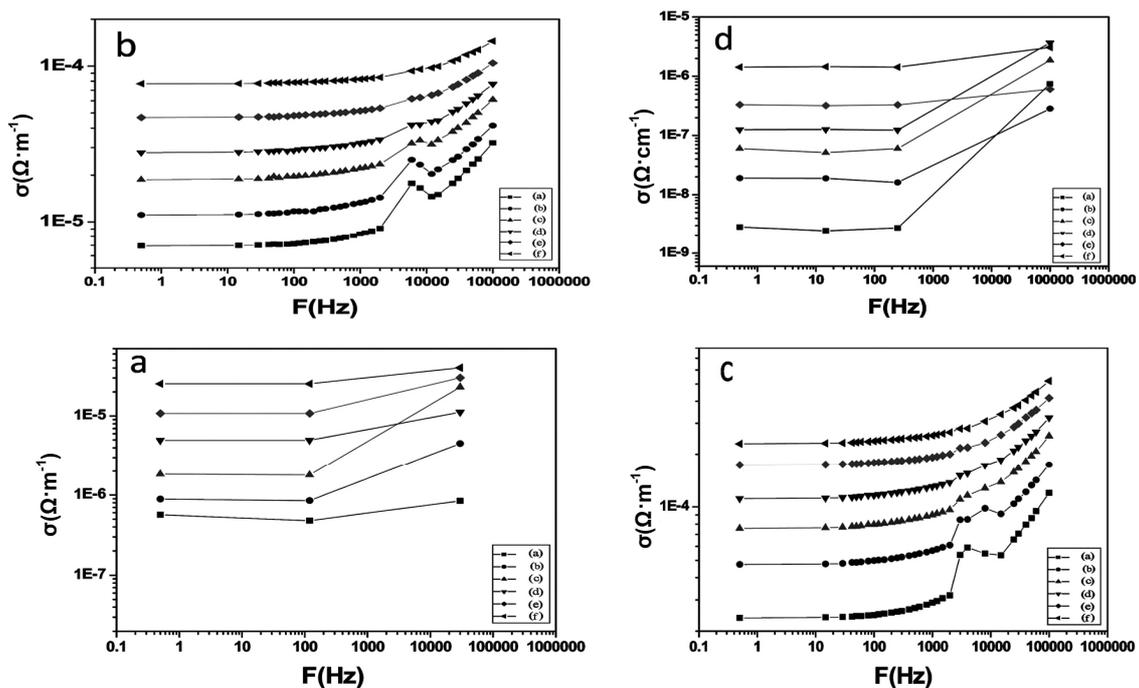


Figure 5. σ as a function of a.c. conductivity $\sigma_{a.c.}$ of (a) PMMA/MMT, (b) Pst/MMT, (c) Pst-b-PMMA/MMT, (d) Pst-b-PMMA-b-P-nBuMA/MMT, where a = 20°C, b = 40°C, c = 60°C, d = 70°C, e = 80°C, f = 90°C.

ples was investigated at both frequency and temperature ranges from (0.1 Hz up to 100KHz) and (20 up to 90°C),

respectively. It was found that the a.c. conductivity for all the prepared samples remarkably increased by in-

creasing the frequency, exhibiting nearly similar behavior. The maximum values of the a.c. conductivity of (b, PSt/MMT) and (c, PSt-b-PMMA/MMT) exhibited higher conductivities when compared with (a, PMMA/MMT) and (d, PSt-b-PMMA-b-P-n-BuMA/MMT) nanocomposites, as shown in **Figures 5(b)** and **(c)** as a result of good intercalation of PSt and PSt-b-PMMA in montmorillonite clay and tremendous increase of the mobility of charge carriers. For the four systems, the a.c. conductivities were enhanced by increasing the temperature from 20 up to 90°C. The samples exhibited better a.c. conduction at high temperature where the intercalation of polymers within clay interlayers was advantageous to the movement of Li⁺ ions inside these interlayers which, resulted in the increase of a.c. conductivity. The lower values of a.c. conductivities at lower temperatures were attributed to two reasons [31]; 1) a few of un-intercalated polymers remained in the grain boundary of montmorillonite clay in addition to the excessive polymer in the exterior of montmorillonite which caused decrease in the a.c. conductivity at low temperature and 2) the number of charge carriers, had high relaxation time due to higher energy barrier at lower temperature and might be less in number with low barrier at higher temperature causing an increase in the a.c. conductivity [32].

4. Conclusion

Vinyl polymers/montmorillonite clay nanocomposites were prepared via in-situ-atom transfer radical polymerization (ATRP). Their dielectric properties were extensively studied to invest them in the a.c. power applications. Intercalated vinyl polymers/MMT nanocomposites gave enhanced values of the dielectric parameters such as a.c. conductivity (σ), and dielectric constant loss (ϵ''). For the four systems, the a.c. conductivities were enhanced by increasing the temperature from 20°C up to 90°C. The samples exhibited better a.c. conduction (σ) at high temperature where increasing temperature facilitated the intercalation of polymers inside clay layers which was advantageous to Li⁺ ions movement inside these layers which results in the increase of a.c. conductivity.

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