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Ionic Conductivity of Poly(ethylene oxide) (PEO)-Montmorillonite (MMT) Nanocomposites Prepared by Intercalation from Aqueous Medium

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Solid electrolyte systems, especially solid polymer electrolyte systems have been widely used as potential technological applications in secondary energy sources and electrochromic devise nowadays. The ion-transport behavior of these systems is to be well understood to enhance electronic properties. It is apparent that these materials show ionic conductivity when ionic salts are dissolved in them. The mechanism of ionic mobility is still controversial. We have made an attempt to address these problems by choosing montmorillonite/poly(ethylene oxide)(PEO)/cation as a model system and systematically understanding the bonding, intercalation and ionic conductivity by Fourier Transformed Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD) and AC-Impedance Spectroscopy respectively. The systems of Na^+-montmorillonite, Li^+-montmorillonite, and Li^+-montmorillonite-PEO are characterized. The XRD data showed that the Na^+-montmorillonite has a d-spacing of 15.49 Å attributing to the presence of Na^+ and two water layers within interlayers of MMT at room temperature. The removal of water brings the d-spacing to 9.97 Å. Solution intercalation of PEO into Li^+-montmorillonite results in the enhancement of d-spacing up to 18.73 Å which readily takes up water, enhancing the d-spacing to 23.33 Å. These results show clearly that PEO is readily intercalated in montmorillonite at a composition of 6 wt% PEO, and leaching of PEO at successive washing takes place below 6 wt% of PEO. In the FT-IR spectrum of montmorillonite two types of ν (OH) are seen; isolated ν (OH) groups and those involved in hydrogen bonding. The Li^+ exchange decreases the extent of isolated hydroxyl groups, but the extent of H-bonding increases. This suggests that Li^+ is coordinated by the octahedral unit of the clay, through the O atoms (ions) of free Al-O-H groups. The ionic conductivity figures measured using AC-impedance analyzer is in agree with this bonding arrangement.

It has been found that the intercalation of PEO in Li^+-montmorillonite reverses the above process by the coordination of Li^+ ions with O atoms of PEO. The amount of free O-H then increases and the extent of hydrogen bonded O-H decreases.

Keywords: montmorillonite-polyethylene oxide nanocomposites, intercalation

1. INTRODUCTION

The inevitable studies of Wright and Armand on ionically conducting polymers, called "polymer electrolytes" in the late 1970s have opened an innovative area of materials research with potential applications in the power industry. The main applications of these polymer electrolytes were in rechargeable lithium batteries as an alternative to liquid solution electrolytes [1,2]. The inventions of conducting polymers together with the extensive studies on intercalation chemistry helped to understand the microscopic structure-property relationship of nanocomposite materials based on polymer-layered silicate in the development of nanotechnology [3]. These hybrid materials with features on the scale of nanometers exhibit characteristics properties superior to conventional composites [4]. The conductivity enhancement of cation exchanged montmorillonite have been reported afore by many researchers, using clay samples from different origins [5,6]. Six typical montmorillonite clays from different locations in China have shown that the ionic conductivity of smectite intercalation compounds (SIC) depends on the original structure and compositions of smectite minerals. Samples with high cation exchange capacity (CEC), and less substitution has higher ionic conductivity and vise versa, in addition, the conductance increases with the migration of ions in the interlayer galleries [7,8]. The relative humidity also plays a significant role on the conductivity of the modified montmorillonite, other than the location of the montmorillonite. The effect of relative humidity on the conductivity of sodium (Na-montmorillonite) and lithium-montmorillonite (Li-montmorillonite) have been reported, where similar values of increased conductivity have been observed for both samples at higher humidity, whereas at low humidity zone the Li-montmorillonite has exhibited higher conductivity than that of Na-montmorillonite [9]. The inventions of two families of fast ion conductors; a series of complex compounds based on silver iodide and β-alumina, and montmorillonite with the support of latest sophisticated physical techniques such as X-ray, neutron scattering and NMR provided considerable development in the fast ion conductors. The X-ray diffraction, X-ray fluorescence, the ionic conductivity and electronic conductivity measurements were observed for Li^+, Na^+, Mg^{2+}, Ca^{2+} and Zn^{2+}-montmorillonite composites respectively. However, in this finding the influence of the relative humidity or the water content on conductivity of cations intercalated montmorillonite showed remarkable changes as compared to previous investigation [10,11]. The composite mixtures of alkali salts/MMT (NaCl, NaI, NaSCN and LiI/MMT) have shown an enhancement in solid-state ionic conductivity than the two constituents. The mixing of different alkali salts mentioned above has been carried out by solution intercalation method and powder mixing method, and their conductivities have been measured by ac impedance technique in the temperature region of RT to 400 °C in a dry atmosphere. The ac conductivity Na^+- or Li^+-montmorillonite has shown low conductivity of 10^{-7} to 10^{-6} S cm^{-1} at 200 °C, and the NaSCN-montmorillonite has shown the highest conductivity of 10^{-4} S cm^{-1} at 200 °C [9].

It is apparent in the literature that the researches have not been confined only to the studying of montmorillonite based nanocomposites or conductivity but extended to cover certain other applications. One such contribution is the formation of well-dispersed metal oxides over montmorillonite matrix, which shows enhanced reactivity with gaseous reactants. Increased absorption of H_2S by ZnO supported on montmorillonite matrix can be cited as an example [12]. In addition to the widespread researches, which are being carried out to understand the structure-property of modified montmorillonite, the cation diffusion coefficient studies have given a light in elucidation of conductivity mechanism in montmorillonite. The diffusion coefficients of Li^+ and Na^+ intercalated montmorillonite have been measured by potentiostatic and galvanostatic step techniques. The investigation has showed comparatively that the presence of interlayer water molecules or other polar molecules always enhances the ionic conductivity and diffusion coefficient. Moreover, the diffusion coefficients of MMTLi and MMTNa are proportional to the water content less than 20% [13]. In addition to diverse researches of the properties of layered minerals, the transport properties in layered Vermiculite have also gained a great interest in many researchers. In these studies, the ionic conductivity of magnesium and calcium ion-exchanged Vermiculite has been reported from 5 °C to 90 °C. They have comparatively presented from the results of sodium conductivity data with tracer sodium and proton NMR studies that the dominant migrating species in Vermiculite are counter ions and not protons [14]. It is not much attributed fact, that in the literature of the mixtures of two model clays. However, an investigation of physical property tests of a mixture of kaolinite and montmorillonite has filled this vacuum. It has shown that these properties are influenced by exchangeable cations (Ca, Na) and specific surface (S) [15].

In this publication, we describe the preparation of MMT-PEO nanocomposites via aqueous solution phase intercatation of PEO within the intergalleries of MMT, their characterization and ionic conductivity studies.

2. EXPERIMENTAL PART

2.1 Materials

The clay, sodium montmorillonite (Bentonite) was purchased from (Aldrich Chemicals, Milwaukee, WI). The crystalline poly(ethylene oxide) (PEO) (Aldrich Chemicals) with a weight-average molecular weight of 400,000, and lithium chloride (LiCl) (Hopkin & Williams, G. P. R), were used as received. Generally, the PEO, and salts are highly hygroscopic, therefore it is required to ensure the dryness of these materials prior to sample preparation. Normally, the salt is dried at 80-150 °C for 24 h and then at room temperature for 24 h under dynamic partial vacuum (10^{-5} Pa). The PEO is dried at 40 °C for 24 h under high vacuum.

2.2 Methods

The clay sample (montmorillonite) may consist of organic and inorganic impurities Therefore, it is desirable to eliminate them as much as possible. The centrifuging and washing method were employed, which will have a least effect to the structure and chemical composition. The montmorillonite (50 g) was suspended in excess de-ionized water and stirred magnetically for about 48 h at room temperature. The suspension was centrifuged at 5000 rpm for two minutes, and the clear supernatant was decanted. The resultant slurry was re-dispersed in excess of de-ionized water and the above procedure continued. This procedure was repeated several times until the supernatant was free of any impurity. The clear supernatant observed, confirmed the absence of organic impurities in the montmorillonite. This slurry thus obtained kept in the normal environment to air-drying and used in other applications.

The Li^+ ion intercalation has been carried out by suspending 15.0 g of purified montmorillonite slurry in 200 cm^3 of 1.0 mol dm^{-3} LiCl (aq) solution. The suspension was then stirred for 48 h continuously. The resultant mixture was then centrifuged at 5000 rpm for two minutes, and the supernatant was decanted. This was followed by a series of washings with de-ionized water and centrifugation until complete removal of chloride ions in supernatant was achieved [tested using $AgNO_3$ (aq)]. The slurry thus obtained is MMTLi.

15.0 g of MMTLi was suspended in 200 ml of de-ionized water and stirred for few minutes and then added 1.0 of PEO into that solution. The suspension was stirred for 48 h continuously until a homogeneous mixture was obtained. The suspension was centrifuged and supernatant was decanted. This procedure was carried out several times. The slurry thus obtained is the MMTLiPEO.

Another 15.0 g of purified montmorillonite was suspended in 200 cm^3 de-ionized water and stirred for few minutes, and then 1.0 g of PEO was added and allowed to stir for 48 h continuously. The suspension was centrifuged and washed as mentioned above. The slurry thus obtained is the MMTPEO.

2.3 Instrumentation and Characterization

The ac impedance measurements of the MMT and it's intercalated systems were carried out using a computer-interfaced SI 1260 IMPEDANCE/GAIN-PHASE ANALYSER over the frequency range of 8-10 MHz at the voltage of 20 mV. The samples were sandwiched between two stainless steel blocking electrodes (1.27 cm diameter.) and the temperature changed from 25 °C to 80 °C. At each temperature the conductivity value was calculated using the resistance value from the real axis intercept of the semicircle in the complex impedance plane plot and the sample dimensions.

In this work the X-ray diffraction patterns were conducted by SIEMENCE X-ray diffractometer (SIEMENCE, German). The slurries of each of above composite were suspended in a small volume (~ 5.00 cm^3) of distilled water, and the suspension was poured onto glass plates allowing to dry in air for a few days. The samples of each of above type was X-rayed after a various treatments including air-drying, moisturizing, and heating in a furnace at 100 °C, 150 °C, 200 °C, 250 °C and 300 °C for 1 hour.

FTIR spectra were collected on a JASCO FT/IR-410 spectrometer from 400 to 4000 cm^{-1}. The samples were prepared by mixing the well-dried sample with dry KBr powder, having the ratio 1:13. The mixture was pressed into a disc of 13 mm in diameter and thick < 1 mm. Prior to the analysis of FTIR each pellet was kept in the desiccator for several days to avoid the disturbances from water molecules.

3. RESULTS AND DISCUSSION

3.1 XRD Studies

Figure 1 (a), (b), and (c) show the XRD spectra of natural montmorillonite, kept in ambient laboratory environment, after heat-treating at 150 °C for 2 hrs, and moisturising with water respectively. In MMT the layers are stacked along a line perpendicular to (001) basal plane. Generally, the interlayer of pure MMT contains two planes of water molecules compensated with inter gallery exchangeable cations. These interlayer water molecules are loosely bound by weak van der Walls forces as such they can be removed easily at higher temperature. When the same samples were oven dried at 150 °C for 2 hours, the (001) layer spacings reduced to 9.96 Å, which attributed to the absence of water molecules within the MMT, however the layer spacing increases up to 13 Å when the cations are surrounded by one water-layer [16]. The layer spacing increases up to 18.9 Å when the surface of pure MMT was wet with moisture. This indicates that the interlayers contain three water layers in this condition [17,18]. Hence, it can be concluded that the montmorillonite samples used in the present work with d-spacing of around 10 Å contain fully dehydrated cations, samples with d-spacings of 13.0 Å contained a single water layer, samples with d-spacings of 15 Å contained two water layers, and samples with d-spacings of 18.0 Å contained three water layers within interlayer spaces.

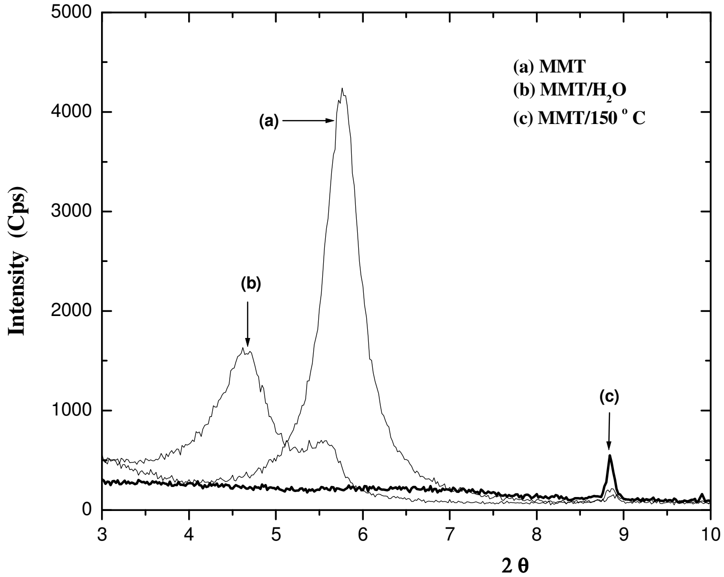

Figure 1: The d-spacing profile for (a) pure montmorillonite (MMT), (b) with moisturizing (MMT/H_2O) and (c) heated at 150 °C for 2 h (MMT/150 °C)

The d value of pure montmorillonite will not with the intercalation of Li^+ cations, and it seems remained at 15.57 Å almost unchanged. The hydration power of Li^+ cations are high, therefore it can be assumed that the Li^+ cations present in the interlayer gallery would be hydreated, in addition to the weakly bonded water molecules within the layers. The intercalation of Li^+ ions within the interlayer spacing of MMT has a significant effect on water uptake that the MMT becomes hydrophobic, see figure 2. The speculation is that Li^+ ions migrate into the octahedral sheet and neutralize the layer charge if the charge is due to octahedral substitution. The elimination of charge converts MMT to a pyrophyllite-like mineral that does not expand upon treatment with water, glycerol, or ethylene glycol [17]. However, at higher temperatures the water gets removed as that of pure MMT.

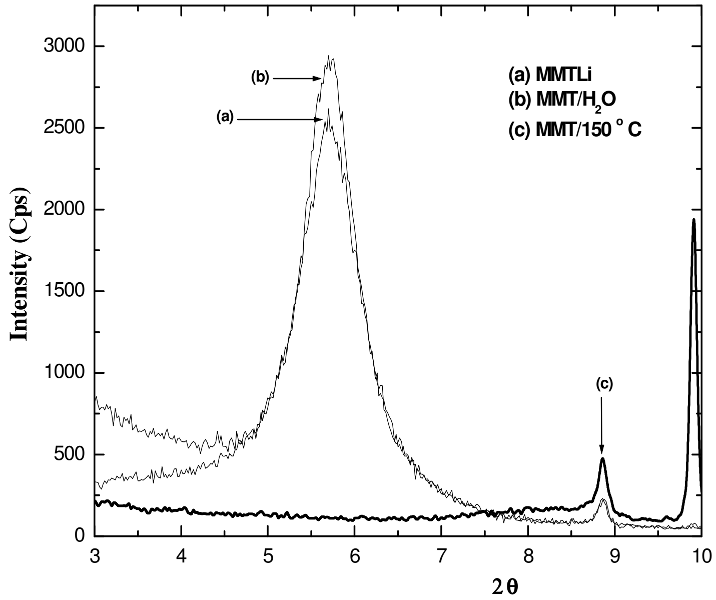

Figure. 2: The d-spacing profile for (a) Li^+ cations intercalated montmorillonite (MMTLi), (b) with moisturizing (MMTLi/H_2O) and (c) heated at 150 °C for 2 h (MMTLi/150 °C)

PEO gets easily intercalated by solution intercalation method into the interlayer spacing of montmorillonite. The d-spacing observed for MMTPEO at the room temperature is 18.73 Å. It is assumed that PEO molecules get coordinated to interlayers perpendicular to the (001) basal plane and not to the external surface of the montmorillonite as XRD patterns revealed the expansion of interlayer spacing even with washing and centrifuging for many times. As evidenced the water molecules within the interlayer spacing of montmorillonite can be removed at higher temperature (above 120 °C). The MMTPEO gave a d value of 17.17 Å at 150 °C. This implies that the interlayer spacing are occupied all most all by the PEO molecules. The d-spacing further increases readily to a value of 23.33 Å when moisturizing the MMTPEO samples (see fig. 3). We have observed that the intercalation of PEO can be done at 6 wt% PEO with water as the solvent that has not been reported previously elsewhere.

It has been reported previously that Li^+ cations intercalated montmorillonite shows some reluctance to up take water or glycerol, or ethylene glycol within the interlayer gallery. However, in contrast to that the MMTLi shows great tendency to intercalate PEO within the interlayers. But in this system it was observed that the d-spacings of the respective conditions such as at room temperature and with moisturizing show slightly lower value than those in the case of MMTPEO. The d-spacing of MMTLiPEO at room temperature is about 18.66 Å, with the moisturizing it increases to the value of about 22.62 Å (see fig. 4). This may have been due to the fact that some regions within the interlayer spacings have been occupied by hydrated Li^+ cations therefore now the rooms that were available in pure montmorillonite became less. Similar to the MMTPEO system this system also shows expanded d-spacing at higher temperatures. As observed the d-spacing at 150 °C is about 17.08 Å. This confirms that PEO molecules are bonded to the layers of MMT, and Li^+ cations, and not to the external surface of the clay particles. The d-spacing values of MMT, MMTLi, MMTLiPEO, and MMTPEO determined at room temperature (RT/ °C), 100 °C, 150 °C, 200 °C, 250 °C, and 300 °C are summarized in table 1. The d-spacing temperature profiles of each of above system are shown in fig. 8 to have a better comparison.

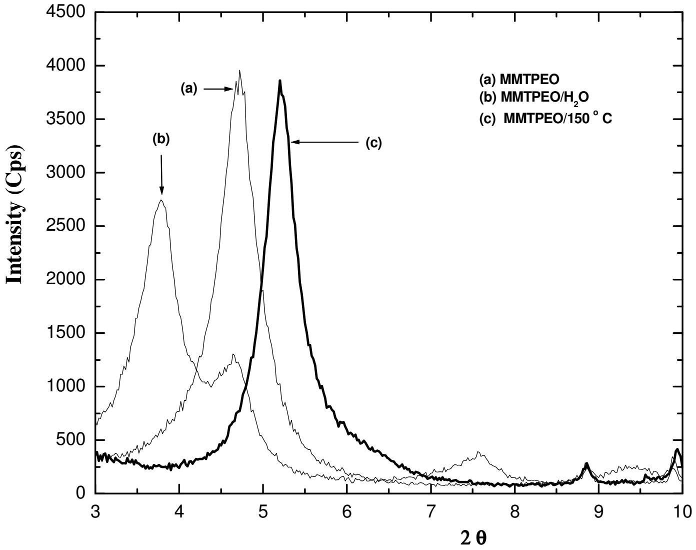

Figure 3: The d-spacing profile for (a) PEO intercalated montmorillonite (MMTPEO), (b) with moisturizing (MMTPEO/H_2O) and (c) heated at 150 °C for 2 h (MMT/150 °C)

Table 1: The d-spacing of the Na-montmorillonite, MMTLi, MMTPEO, and MMTLiPEO at RT (26 °C), 100 °C, 150 °C, 200 °C, 250 °C and 300 °C

Sample Name	**Change of inter gallery spacing d/Å**						
	RT °C	**Addition of water at RT (26 °C)**	**100 °C**	**150 °C**	**200 °C**	**250 °C**	**300 °C**
Montmorillonite	15.19	18.97	14.85	9.96	9.97	9.58	9.96
BLi	15.57	15.68	15.27	9.97	9.95	9.97	9.97
BPEO	18.73	23.33	18.55	17.17	17.09	13.52	14.49
BLiPEO	18.66	22.62	18.16	17.08	17.40	13.45	13.38

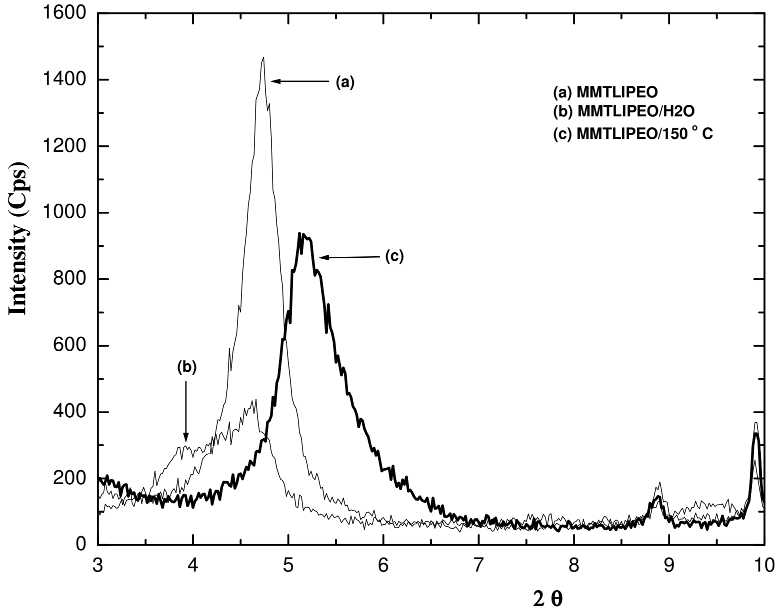

Figure 4: The d-spacing profile for (a) Li^+ cations intercalated within MMTPEO (MMTLiPEO), (b) with moisturizing (MMTLiPEO/H_2O) and (c) heated at 150 °C for 2 h (MMTLIPEO/150 °C)

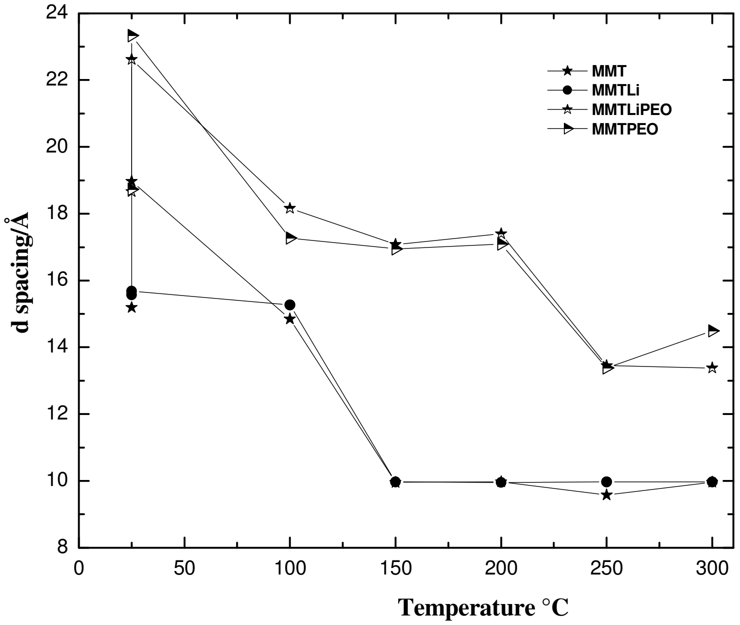

Figure 5: The d-spacing temperature profiles for MMT, MMTLi, MMTLiPEO and MMTPEO. Note that points are connected only for clarity. The lines may not show continuous variation.

3.2 Ionic Conductivity Studies

The typical temperature dependent conductivity Arhenius plots measured for MMT, MMTLi, MMTPEO, and MMTLiPEO in the range of 25 °C - 80 °C are shown in fig. 6. The corresponding conductivity values obtained at various temperatures are listed in table 2.

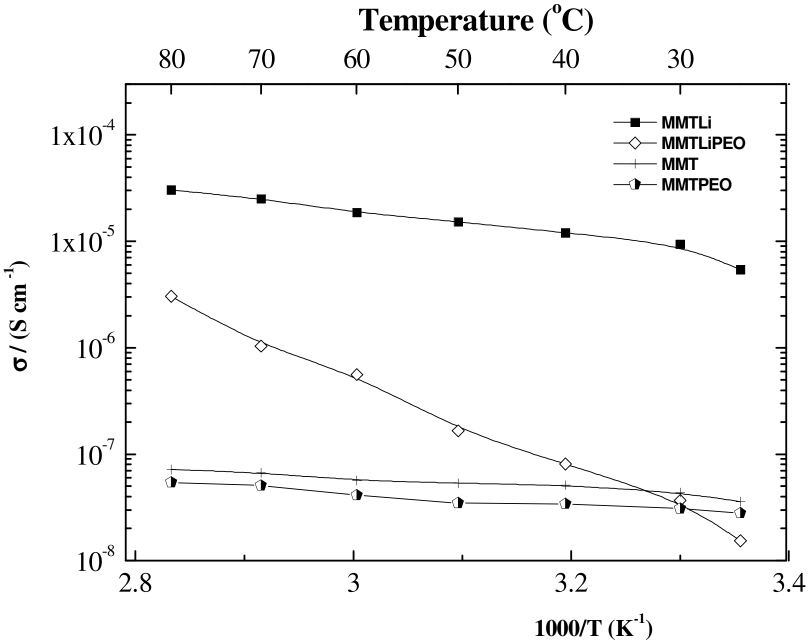

Figure 6: Temperature dependence of conductivity for MMT, MMTLi, MMTPEO, and MMTLiPEO.

Table 2: Ionic conductivity for MMT, MMTLi, MMTLiPEO, and MMTPEO at some selected temperatures.

Sample	25 ° C	30 ° C	40 ° C	50 ° C	60 ° C	70 ° C	80 ° C
MMT	3.58E-8	4.38E-8	5.12E-8	5.33E-8	5.64E-8	6.68E-8	7.19E-8
MMTLi	5.43E-6	9.33E-6	1.20E-5	1.52E-5	1.87E-5	2.50E-5	3.04E-5
MMTLiPEO	1.53E-8	3.69E-8	8.09E-8	1.66E-7	5.62E-7	1.03E-6	3.03E-6
MMTPEO	2.80E-8	3.07E-8	3.40E-8	3.48E-8	4.13E-8	5.07E-8	5.41E-8

The montmorillonite used in our study showed a conductivity of 3.58×10^{-8} S cm^{-1} at room temperature. The water content in MMT used for conductivity measurement was found to be 15%, see table 3. However, the maximum conductivity arrived at higher temperature (80 °C) is around 7.19×10^{-8} S cm^{-1}. Prior to the ac impendence measurements we have carried out dc polarization test on each system; however, it shows that the ionic conductivity of purified montmorillonite could not be observed due to low sensitivity of the apparatus. But in the case of ac characterization plot small ionic conductivity can be observed. It has been reported previously that the interlayer absorbed water molecules in montmorillonite has a considerable impact on its ionic conductivity and diffusion coefficient: the higher the water content, the lower the activation energy, and greater the ionic conductivity and diffusion coefficient [13]. A hypothesis has been developed describing that the compensated cations in MMT are in thermal disturbance [11]. In addition to that a NMR study of MMT and vermiculite has shown two relaxation processes. One reveals the motion of free water and the other contributes to the hydrated Na^+ cations [19, 20, 21]. It was assumed from the available data that with the increase of temperature the mobility of interlayer exchangeable cations in this case Na^+ is enhanced. This gives rise to the conductivity increment with varying temperature in montmorillonite. This conductivity of purified MMT is much less with compare to other materials and composite systems.

Table 3: Conductivity values of montmorillonite and its derivatives in relation to the water content observed at room temperature.

Sample name	Cond. (σ/S cm^{-1}) at 298K	Water content (% by mass)
MMT	3.58×10^{-8}	15
MMTLi	5.43×10^{-6}	13
MMTPEO	2.80×10^{-8}	3
MMTLiPEO	1.53×10^{-8}	1.7

The table 3 gives the conductivity values with their water content measured at room temperature. Our objective here is to develop a high conductivity material, which satisfies the in situ requirements enhancing the applications in opto-electronic devices and high-energy secondary batteries. It has been observed that Li^+ ions intercalated montmorillonite has an enhanced conductivity i.e. about 5.43×10^{-6} Scm^{-1} at room temperature at 13 % water content. We could observe a gradual increase of conductivity with the increases of temperature up to 80 °C. The conductivity observed at 80 °C is 3.04×10^{-5} S cm^{-1}. In this case the mobility of Li^+ increases as the temperature increases, and it can hop through water network. Samples with high cation exchange capacity (CEC), and less substitution has higher ionic conductivity and vise versa, in addition, the conductance increases with the migration of ions in the interlayer galleries [22,23]. The MMT used in this study has the cation exchange capacity of 100 meq/100 g. As confirmed by the XRD studies the MMTLi has the hydrophobic nature, therefore water absorption could be less. As shown in the table 3, the water content in MMTLi is reduced with compare to the pure MMT. Therefore, the protonic conductivity due to the presence of water molecules could be minimized. The overall results thus showed that the conductivity of MMTLi is mainly due to the Li^+ cation than water molecules.

Due to the screening effect of the interlayer bonded water, the Coulombic attraction of the layers to the exchanged cation becomes weaker [11,13]. Therefore, the activation energy of Li^+ cations decreases. This phenomenon also contributes to the increase of ionic conductivity with the increase of temperature. The MMTPEO showed a lower conductivity at room temperature. The increase of conductivity with the temperature increase can be seen parallel to that of MMT, but this lies below the MMT behavior. This can be attributed that the PEO molecules arranges in a disordered manner within the clay structure restricting the free hydroxyl groups and coordinates with interlayer cations making a net structure [3]. The change of asymmetric CH_2 stretching and bending vibrations confirmed this phenomenon. The XRD data showed that the interlayers of MMT are mainly occupied by PEO molecules, thus reducing interlayer water content. The water content at the conductivity measurement was found to be 3 %. This causes the lowering of both protonic conductivity and mobility of interlayer exchangeable cations. In the system of MMTLiPEO the conductivity behavior is somewhat different. At room temperature the ionic conductivity is reduced to 1.53×10^{-8} S cm^{-1}. But it increases rapidly with the increase of temperature and reached to a value of 3.03×10^{-6} S cm^{-1}. The intercalation of PEO within MMTLi prefers the interaction of Li^+ cations with ether oxygen of PEO. Thus it reduces the mobility of Li^+ cations. Similar to MMTPEO system the interlayers in MMTLiPEO are occupied by PEO molecules, forming a net like structure within the clay layers. The water content at the conductivity measurement was found to be 1.7 %. In addition to that PEO within the montmorillonite increases the amount of free O-H, thus reducing the extent of hydrogen bonded O-H. Therefore the conductivity at room temperature is reduced. However, the increase of temperature enhances the Li^+ mobility favorably. As such now the conductivity increases as the increase of temperature.

3.3 FT-IR studies

Figure 7 shows the FTIR spectra obtained for MMT, MMTLi, MMTPEO, and MMTLiPEO in the wavenumber range 400 to 4000 cm^{-1}. In pure MMT a clear broad band in the region 3300-3700 cm^{-1} was observed which, corresponds to the –OH stretching (ν(-OH)) vibration. The band has two features at 3624 cm^{-1} and at 3440 cm^{-1} showing in the presence of two types of O-H groups: isolated OH groups and those involved in hydrogen bonding [24]. The nanocomposite prepared by intercalation of either Li^+ or PEO within the interlayer spacing of MMT shows strategic features in the FTIR spectra than those of pure constituents. In MMTLi system, it is clear that the intercalation of Li^+ cations has a significant impact upon the structure of MMT. The typical bands of 3624 cm^{-1} and 3440 cm^{-1} in MMT are transformed to a new intensed broad band centered at around 3460 cm^{-1} in MMTLi which corresponds to the decrease of isolated hydroxyl groups and the increase of hydrogen bonding –OH groups. This suggests that Li^+ cations interact with the –OH groups of the clay, through the O atoms (ions) of free Al-O-H groups. The peak at 1634 cm^{-1} corresponds to the bending vibrational mode of hydrated water molecules and weakly bonded water molecules. The corresponding band in MMTLi is intensed. It can be suggested that the interlayer Li^+ cations are more hydrated than pure MMT; therefore the presence of -OH groups is abundant. The strong interactions of MMT to the Li^+ cations were further confirmed, as the change of typical vibrational modes in MMT is apparent. The typical bands of 920 cm^{-1} ν(Al–O-H), 796 cm^{-1} ν(Al (Mg)–O-H), 1040-1120 cm^{-1} ν(Si-O) and the bands appear at 525 cm^{-1} and 470 cm^{-1} which correspond to the ν(Al (Mg)–O-Si) were observed in pure MMT [25]. However, a clear observation can be seen in MMTLi, in which the intensities of above modes were affected and reduced. This suggests that Li^+ cations significantly interact with –OH groups in the octahedral layer and coordination with Si-O in tetrahedral layer of the MMT clay. The above results are consistent with the results of conductivity measurements and XRD experiments.

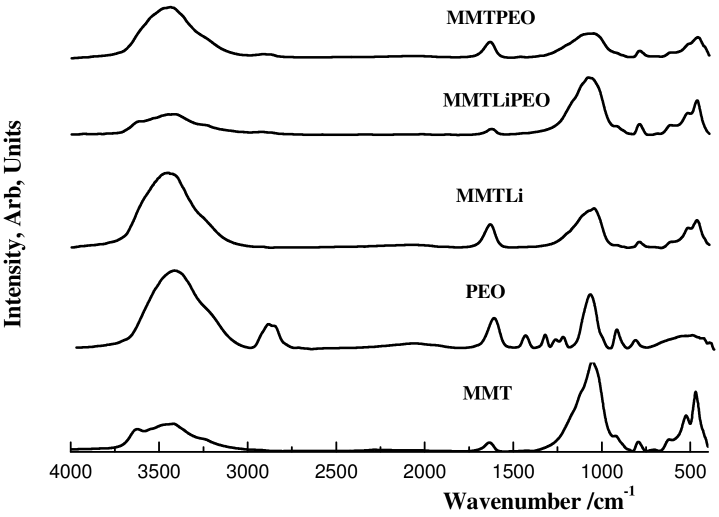

Figure 7: FTIR spectra of MMT, MMTLi, MMTPEO, MMTLiPEO, and PEO

It was observed that the intercalation of PEO within MMT shows the similar type of effect on MMT structure and in return on PEO crystallinity. The band at 3624 cm^{-1} is absent in the MMTPEO. This is due to the interaction between the ether-oxygen of PEO segments and the free –OH groups of clay layers via hydrogen bonding [26]. This can be seen as the disappearing of the band at 3624 cm^{-1} and appearing of well-transformed peak at 3447 cm^{-1}. In the pure PEO spectrum a large broad band appears centered at 3446 cm^{-1}. This is possibly due to the hydration of PEO. It was experienced that the PEO is highly hydrophilic, thus it absorbs water vapor and gets hydrated. Pure PEO shows a large, broad band of CH_2 stretching between 2950 and 2840 cm^{-1}. However, the band is split into two at 2918 cm^{-1} and 2884 cm^{-}1 corresponding to asymmetric CH_2 stretching ($\nu(CH_2)_a$) and symmetric CH_2 stretching ($\nu(CH_2)_s$), respectively. In the intercalated MMTPEO these bands show lower intensity. Most significant changes were observed between 1700 and 800 cm^{-1}. Two clear CH_2 vibrational modes appear in PEO at 1464 cm^{-1} which, correspond to asymmetric CH_2 bending ($\delta(CH_2)_a$) and 1358 cm^{-1} which, corresponds to symmetric CH_2 wagging and some C-C stretching ($w(CH_2)_s + \nu(CC)$) [27]. Thus in MMTPEO hybrid these bands seem almost absent. This phenomenon is due to the ion dipole interactions between the ether-oxygen of oxyethylene groups and the interlayer cations [25]. This was further confirmed as the intensity of the band of (ν(C-O) at 1640 cm^{-1} in pure PEO shifted to lower frequency in MMTPEO and the band of (ν(O-H) at 1636 cm^{-1} in MMT is intensed. It is understood that PEO interacts not only with free –OH of clay layers but with the interlayer cations in a similar manner to conventional PEO-salt complexes. The two bands at 1295 cm^{-1} and 1252 cm^{-1} which are related to twisting vibration $t(CH_2)_a$ and stretching vibration $\nu(C\text{-}O\text{-}C)_a$ [28] are completely absent in MMTPEO. It is worth noted here that a clear band at 1100 cm^{-1} that corresponds to the $\nu(C\text{-}O\text{-}C)_a$ vibration mode in PEO is not to be observed in the hybrid MMTPEO. Instead, a broad distorted band centered at1068 cm^{-1} in MMTPEO was observed. It suggests that significant interactions take place between oxygen and interlayer cations in MMT. The CH_2 rocking modes observed in the ranges of 1000-700 cm^{-1} are sensitive vibrational modes in the conformational arrangements for pure PEO.

To further support the above observation it is clear that the typical modes of $r(CH_2)_s$ appear at 949 cm^{-1} and 844 cm^{-1} also absent in PEO intercalated MMT. It has been reported in a previous study that the presence of two bands at 949 cm^{-1} and 844 cm^{-1} were the characteristic peaks in supporting the gauche conformations of $–CH_2-CH_2-$ groups, as needed for a helical conformation of pure PEO. In addition to that relative lowering of intensities of 920 cm^{-1} ν(Al–O-H), 796 cm^{-1} ν(Al (Mg)–O-H), 1040-1120 cm^{-1} ν(Si-O) and the bands appear at 525 cm^{-1} and 470 cm^{-1} correspond to the ν(Al (Mg)–O-Si) also concede this observation. The overall results confirmed that the crystallinity of PEO has been enormously distorted as the strong interactions with MMT layers and interlayer cations.

The intercalation of PEO within MMTLi showed significant changes in bonding mechanism of the hybrids of MMTLiPEO. It is apparent that intercalated PEO segments tend to interact with Li^+ cations those are coordinated to Al-O- units in the clay layers favorably. As a consequence of this, the amount of free O-H increases as the extent of hydrogen bonded O-H decreases. The appearance of the band at 3624 cm^{-1} ν(OH) stretching mode in MMTLiPEO confirms this assumption. As discussed earlier the typical vibrational modes observed in pure PEO have not been observed in the MMTLiPEO nanocomposite. It is an evident that the PEO also interacts with the relative bonding sites of MMT layers in addition to interlayer cations or Li^+ cations However, this can be assumed with results of the relative intensity changes of typical vibrational modes in both pure PEO molecules and MMT. The FTIR results observed for the above nanocomposite systems are consistent with results of XRD, and conductivity discussed in earlier sections

4. CONCLUSIONS

Montmorillonite (MMT) has been a very promising layered silicate material in the fabrication of nanocomposites. Among many applications of MMT, its use as a conducting material is to be well understood further. The modified MMT showed strategic structure-property relationships as opposed to its unmodified state. It was found that the most easy and simple way to modify the structure of MMT is by intercalation of various cations or molecules within the interlayer spacing. The unique properties of MMT such as self-assembling associate with the ease of production through simple processes make it a very attractive material to be used in electrochemical and electronic devices.

The ionic conductivity observed for the systems of MMT, MMTLi, MMTLiPEO and MMTPEO is rarely enough for practical uses. However, the Li^+ cations intercalated MMT showed an enhanced ionic conductivity of 5.42×10^{-6} S cm^{-1} at room temperature than that of pure MMT, MMTPEO and MMTLiPEO. The XRD results revealed that the MMTLi is hydrophobic in nature in contrast to other systems. The MMTPEO and MMTLiPEO showed an expanded d spacing of ~18.73 Å at room temperature and with moisturing it increase to ~ 23.33 Å. The MMT shows an ability to reduce the crystalline nature of PEO. The XRD spectra obtained for the systems of MMT and MMTPEO clearly showed this phenomenon.

The FTIR analysis of the each of above systems showed typical bonding mechanism in the intercalation of Li^+ cations and PEO within the interlay spacing of MMT, which is in agreement with the corresponding ionic conductivity enhancement. In addition to that it has shown that the crystalline nature of PEO is distorted. Thus it can be suggested that if the structure of the MMT is modified in an appropriate way, significantly enhanced electrical properties can be obtained. Therefore, it is worth pointing out that, a much better understanding of the migration mechanism, transport properties of interlayer cations, the structure of the hybrids and the effect of environmental conditions of each type of systems is a must in order to improve the ionic conductivity in these materials.

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