

Modification of Vermiculite with Ionic Liquids

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Vermiculite, a layered silicate, was modified with three different ionic liquids *i.e.*, 1-ethyl-3-methyl imidazolium tetrafluoroborate, 1-butyl-3-methyl imidazolium tetrafluoroborate and methyl-1-methylimidazolium-3-acetate tetrafluoroborate. The modified vermiculite was characterized by SEM, FTIR, WXR and TGA. The data shows an overall increase in interlamellar spacing as a result of sodium cation exchange with the imidazolium cations and improved thermal stability *vs.* commercial layered silicates modified with long chain quaternary ammonium salts. Data is also reported on the evaluation of the modified clays in the preparation of composite polymer membranes.

Key Words: Vermiculite, Ionic liquid, Thermal stability, Polymer membrane.

INTRODUCTION

It is a great challenge to reduce the amount of volatile organic compounds in chemical and industrial processes. Room temperature ionic liquids (ILs) are a special class of molten salts composed of organic cations and inorganic or organic anions, which melted at temperatures below 373 K. As a class of potential greener solvents, ionic liquids exhibit many unique physicochemical properties, such as negligible volatility and nonflammability under ambient conditions, large liquid range, high thermal stability, wide electrochemical window and strong ability to dissolve many chemicals. Thus, ionic liquids have found wide applications in chemical synthesis¹⁻³ and electrochemistry^{4,5}.

Ionic liquid can be produced with a variety of cations and anions. The most common organic cations containing nitrogen are imidazolium and pyridinium derivatives. Other compounds are based on phosphonium or tetra-alkylammonium cations while commonly used anions include $[\text{BF}_4]^-$, $[\text{PF}_6]^-$ and $[\text{CF}_3\text{SO}_3]^-$, *etc.* Their properties can usually be 'coarse-tuned' either by changing the chemical nature of the cation or that of anion. The "fine-tuned" of their characteristics is usually achieved by slightly changing the cations size, typically by altering the alkyl chain length of its organic residue, while preserving its chemical nature.

One of the most interesting (and potentially most useful) properties of ionic liquid is its higher thermal stability and non-flammability. This can be used to advantage to overcome the lower thermal stability of conventional organic modifiers that are used to enhance dispersion, wetting and compatibility of nanoparticles in organic media.

Layered minerals are layered aluminosilicates in which isomorphous substitution generates a permanent negative charge, which arises from material to material and which is balanced in the national state by inorganic cations. Compared to montmorillonite, hydrous mica, vermiculite (VMT) is abundant and has a larger cation exchange content (CEC) as listed in Table-1. Vermiculite, a mica-type silicate, possesses a layered structure. Each layer consists of octahedrally coordinated cations (typically Mg, Al and Fe) sandwiched by tetrahedrally coordinated cations (typically Si and Al). The isomorphous substitution of Si^{4+} by Al^{3+} leads to a net negative surface charge that is compensated by an interlayer of exchangeable hydrated cations (Ca^{2+} , Mg^{2+} , Cu^{2+} , Na^+ and H^+). Adjoining layers are held together by a combination of electrostatic and vander Waals forces.

TABLE-1
SUMMARY OF CLAY MINERAL PROPERTIES

Secondary mineral	Type	Interlayer condition/bonding	Specific surface area (m^2/g)	Basal spacing (nm)	CEC (cmol/kg)
Vermiculite	2:1 expanding	Weak bonding, great expansion	500-700	1.0-1.5+	100-150
Montmorillonite	2:1 expanding	Very weak bonding, great expansion	700-800	0.98-1.8+	80-150
Hydrous mica	2:1 non-expanding	Partial loss of K, strong bonding	50-200	1.0	10-40

*The data cited from the work of Sabine Grunwald, University of Florida, USA. See <http://grunwaldifas.ufl.edu>

In the modification of vermiculite by ion exchange, the interlayer accessible compensating cations can be exchanged with a variety of hydrated inorganic cations or organic cations including those of amines or quaternary ammonium salts and also oxonium, sulfonium and more complex cationic species. Commercially organophilic vermiculite used in polymer composites are usually hydrophilic and when used to fill non-polar polymers, its surface must be modified. The mostly used modification methods is the exchangeable metal ions present between vermiculite platelets into alkylammonium ions or aromatic heterocyclic amines^{6,7}. However, the use of alkylammonium is limited in two ways: because of health concerns the allowable concentration of alkylammonium compounds should not exceed 5 ppm and most importantly, these compounds are characterized by low thermal stability and most of them are thermally degraded at the temperature not higher than 220-250 °C, which reduces their applicability to certain polymeric materials only⁸.

Ionic liquid containing long chain cations (mostly imidazolium based) have been recently evaluated as MMT modifiers⁸. Important incentives were the improvement of the thermal stability of the organoclays and the preparation of nanocomposites with enhanced flame retardant characteristics. However, there is few literature about the modification vermiculite with ionic liquid.

In this paper, we modified vermiculite with different ionic liquids with an objective to develop a related data base. The primary objective of this work is to compare the degree of modification of the vermiculite interlayer spacing. The second aim is to discuss the thermal stability. In order to assess the potential of using the imidazolium molten salts as a substitute for the conventional alkyl ammonium surfactant, a detailed study was carried out using thermogravimetry (TGA), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The thermal stability of composite polymer membrane were also discussed.

EXPERIMENTAL

The vermiculite used in this work was purchased from Aldrich with grade number 3 and was treated at 300 °C for 12 h before use. Methylimidazole was purchased from KaiLe Chemical Company and distilled under reduced pressure before use. Organic-Vermiculite (O-VMT) was prepared in our laboratory using benzyltrimethyl ammonium bromide. PVDF ($M_w = 900,000$) was obtained from Shanghai 3F New Material CO., Ltd. and dried under vacuum oven at 100°C for 48h before use. PEG ($M_w = 10,000$) was purchased from Shanghai Pudong Chemical Company. Other chemicals were obtained from commercial suppliers and used without further purification.

Preparation of methylimidazolium salts: Imidazolium salts were typically prepared as follows: The methylimidazole (distilled, 0.2 mol), alkylbromide or chloride (0.23 mol) and acetonitrile (200 mL) were combined in a round-bottom flask equipped with a reflux condenser. The mixture was refluxed for 8 h under nitrogen at 60 °C. After the reaction was complete, a large excess of ethyl acetate was added to precipitate the imidazolium salt. This solid was filtered and washed several times with ethyl acetate to remove the methylimidazolium. Residual solvent was removed from the resulting methylimidazolium salt under vacuum, at 80 °C for 12 h. The solid was redissolved in minimum amount of acetonitrile and precipitated with ethyl acetate. The white solid was filtered and washed with ethyl acetate and solvent was removed under vacuum at 80 °C. Salts with BF_4^- anions can be attained by exchanging the halide ion for the desired anion. For a typical reaction, in a 1 l reaction flask 1 mol of the substituted imidazolium salt was added to 5 % molar excess of the NaBF_4 in 500 mL acetone. The flask was then sealed and allowed to stir at room temperature for 7 days under nitrogen atmosphere. After which, the flask was removed for the last purification steps. The prepared ionic liquids are: 1-ethyl-3-methyl imidazolium tetrafluoroborate (IL-1), 1-butyl-3-methyl imidazolium tetrafluoroborate (IL-2) and methyl-1-methylimidazolium-3-acetate tetrafluoroborate (IL-3).

Modification of vermiculite with different ionic liquid: Standard ion-exchange procedures were employed for the preparation of the organic-treated layered silicates⁹. In this work, the inorganic cations in the vermiculite crystals were first ion exchanged with sodium ions as follows: vermiculite crystals (200 mesh, 5 g) were refluxed in

about 100 mL aqueous solution containing 1 g NaCl for 72 h at 60 °C. The slurry was washed with distilled water until no Cl⁻ was detected, which was performed using 0.1 mol/L AgNO₃. The alkyl-imidazolium salt was first dissolved in 50:50 mixture of ethanol and deionized water at 70 °C. Aqueous suspension of vermiculite (1 wt %) was added to the alkyl-imidazolium solution and the mixture was stirred for 24 h at 70 °C. The imidazolium exchanged vermiculite was collected by filtration and washed with a mixture of hot ethanol and deionized water to remove all the residual anions. The final product was dried at room temperature and then under vacuum at 100 °C for 5 h. For comparison purposes the Na-exchanged VMT modified with imidazolium salts (EMIm-VMT) was prepared with and without distilled water washed. The prepared complexes are: 1-ethyl-3-methylimidazolium vermiculite (VMT-1), 1-butyl-3-methylimidazolium vermiculite (VMT-2) and methyl-1-methylimidazolium-3-acetate vermiculite (VMT-2).

Preparation of polymer membranes: The PVDF-PEG/VMT-3 composite microporous membranes were prepared by a phase inversion method. Desired amount of PVDF, PEG and VMT-3 were dissolved in a mixture of DMF (solvent) and glycerin (non-solvent) (v/v = 10/1). After stirring for 4 h at 80 °C, the resulting homogeneous solution were cast onto a glass plate and then placed in an oven at 120 °C for 36 h. This procedure yielded mechanically stable, free standing films of thickness ranging from 100 to 300 μm. TG analysis confirmed that both solvent and non-solvent evaporated completely during above preparing process. The composite microporous membranes used in this study were denoted as PVDF-PEG/6 % VMT-3, in which the weight ratio of PEG to PVDF is 0.5. The alkyl-ammonium treated vermiculite (O-VMT) was also used to prepare polymer membrane.

Characterization: FTIR spectra of Na-VMT, ionic liquid and EMIm-VMT were obtained using a Dig lab FTS3000. Thermal property was studied by TGA (Perkin-Elmer instruments TG/DTA 6300) from room temperature to 400 °C, at a heating rate 10 °C/min in a nitrogen atmosphere. Wide angle X-ray diffraction (WXR) with a Rigaku D/max-2400 diffractometer (CuK_α radiation = 0.15 nm, generator voltage = 40 kV, current = 60 mA) was used to calculate *d*-spacing of Na-VMT and EMIm-VMT. The layer structure was studied by scanning electron microscopy (SEM) using field emission scanning electron microscope (JSM-6701F) with gold sputtered coated films.

RESULTS AND DISCUSSION

Figs. 1-3 show the FTIR spectra of Na-VMT, pure ionic liquid IL-1, IL-2, IL-3 and the VMT-1, VMT-2 and VMT-3, respectively. The infrared spectrum for vermiculite (Fig. 1a) showed a peak at 1064 cm⁻¹ associated to asymmetric stretching vibrations of Si-O-Si and Si-O-Al. The bending vibration of Al-OH appeared at 814 cm⁻¹ while the OH stretching vibration was observed at 3416 cm⁻¹ related to OH hydroxyl groups of interlamellar water and the silanol groups. Absorption at 1640 cm⁻¹ was attributed to the characteristic bend deformation of the O-H group of water.

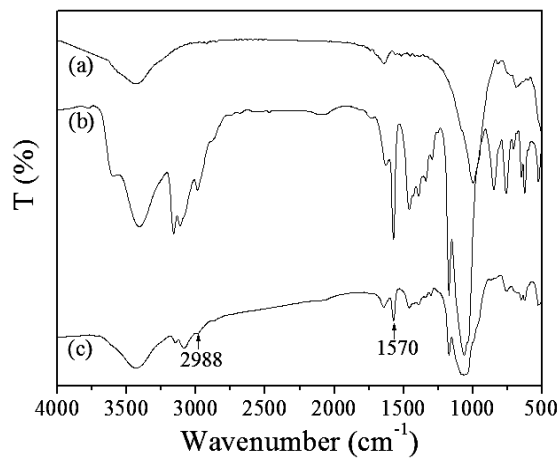


Fig. 1. FTIR spectra of (a) Na-VMT (b) IL-1 (c) VMT-1

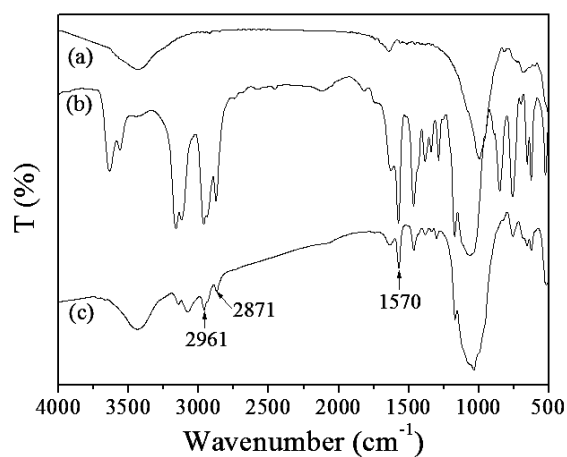


Fig. 2. FTIR spectra of (a) Na-VMT (b) IL-2 (c) VMT-2

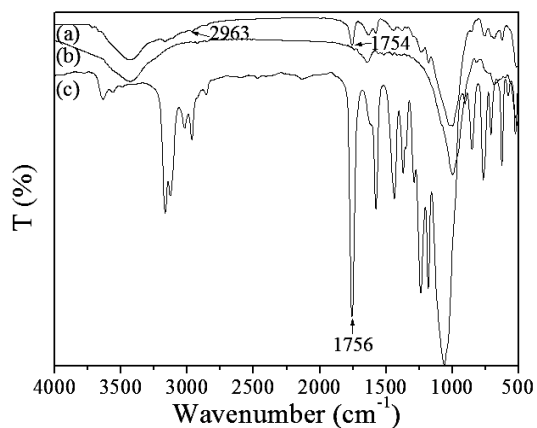


Fig. 3. FTIR spectra of (a) Na-VMT (b) IL-3 (c) VMT-3

Fig. 1b shows the peaks for the imidazolium functional group in the range between 1650 and 1000 cm^{-1} . It can be seen that the peaks in the range of 1600-1320 cm^{-1} are due to carbon-carbon and carbon-nitrogen vibrations. The conjugated strong peaks around 1630 and 1570 cm^{-1} are due to carbon-nitrogen-carbon or carbon-carbon bonds. It is also worth to note that the spectra of VMT-1 shows a resemblance with peaks due to VMT and IL-1 at 1570 cm^{-1} and weak bands in the range of 3160-2870 cm^{-1} .

Fig. 2 shows the spectrum of IL-2 and VMT-2. A longer hydrocarbon chain in IL-2 gives significantly stronger peaks in the ranges of 3100-2800 cm^{-1} and 1640-1465 cm^{-1} . The spectrum of VMT-2 shows peaks due to VMT, which are also found in the spectrum of IL-2. These peaks occur at 1470 cm^{-1} , 1570 cm^{-1} and in the range of 3060-2860 cm^{-1} , indicating the presence of IL-2 in the modified VMT-2.

The infrared spectrum of IL-3 and VMT-3 shows the C=O bands appeared at 1756 and 1754 cm^{-1} , respectively. In this work, after treating VMT with IL-3, the C=O band shifts to lower energy. It is postulated that this may be due to chemical interaction of C=O with structural hydroxyl of vermiculite or linking IL-3 to an exchangeable metal cation of VMT through water bridge or cationic hydroxyl group¹⁰.

SEM and XRD analysis: Fig. 4 shows the SEM image of Na-VMT. The structure of Na-VMT exhibits a more ordered character. It can be seen that the flakes are remarkably compact and gaps between them are smaller and not torn on the edges. Due to the fine particle, the low crystallizability and the complicated chemical components of clays, detailed information about the interlayer structure and the atomic local environment in organoclay is rarely available from experimental measurements. So far, X-ray diffraction (XRD) is the most widely used technique to determine the structure of organoclays¹¹.

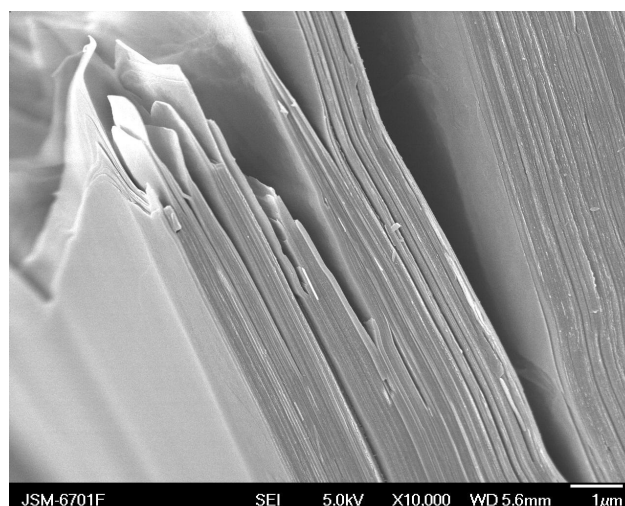


Fig. 4. SEM image of Na-VMT

The X-ray diffraction patterns for the Na-VMT, VMT-1, VMT-2 and VMT-3 are presented in Fig. 5. In principle, the guest molecules can interact either at the external surface or in the interlayer space of clay. In the latter condition, the intercalation inside the interlayer space can change the basal spacing. As reported earlier, when d_{001} peak shift to a lower angle, the interlayer of the VMT or O-VMT will be widened¹². The interlayer spacing can be calculated according to the Bragg equation. Increase in d -spacing vs. the Na-VMT follows the order VMT-3 > VMT-2 > VMT-1. The higher extent of intercalation corresponding to the largest interlayer distance of 1.187 nm in VMT-3 (compared with 1.107 nm for Na-VMT), which has a relatively larger cation. The d -spacing of EMIm-VMT was found to be significantly smaller than the alkyl-ammonium treated VMT¹³.

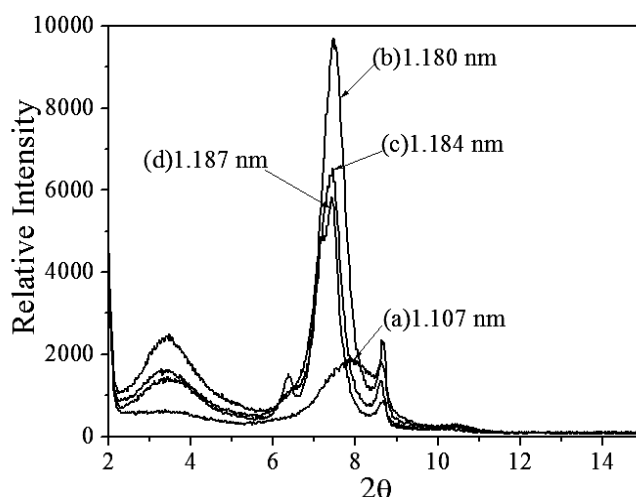
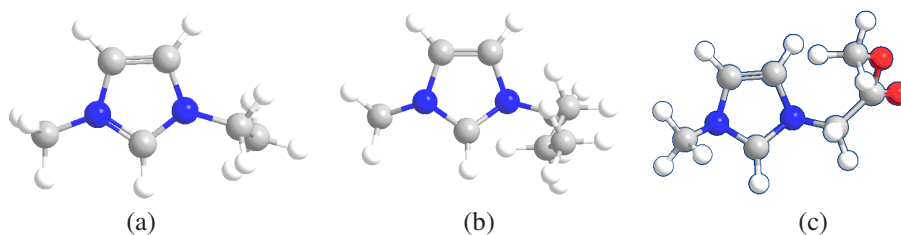


Fig. 5. XRD results of: (a) Na-VMT; (b) VMT-1; (c) VMT-2; (d) VMT-3

Therefore, it may conclude that the guest molecule intercalated into the VMT gallery and the VMT modified with different ionic liquid form an intercalated structure. The molecular shape of the different ionic liquids was determined using molecular modeling software (**Scheme-I**). It is reported that the surfactant (*n*-dodecyltrimethylammonium bromide) takes spherical or elliptical shape in the aqueous solution, which changes into flat elliptical shape at the hydrophobic silica surface¹⁴. In this experiment, it is expected that imidazolium cations will occupy configuration inside the interlayer space so that the positively charged imidazolium is closer to the negatively charged silicate to maximize electrostatic interaction. It is worth to note that the d -spacing of unwashed VMT is slightly bigger than the washed one (Fig. 6). It may be assumed that the alkyl chains are holding the structure in an ordered arrangement and during the washing process the structure collapses¹⁵. Information on the probable packing and orientation arrangement of the molecules can be obtained by combining spacing measurements and consideration of molecular geometry. The resulting

imidazolium modified vermiculite has lower surface energy than Na-vermiculite and hence has the important property of being able to swell and disperse in organic polymers.



Scheme-I: Minimized energy structures of: (a) 1-ethyl-3-methyl imidazolium cation; (b) 1-butyl-3-methyl imidazolium cation; (c) methyl-1-methylimidazolium-3-acetate cation. (ChemOffice 2004, Chem3D ultra 8.0)

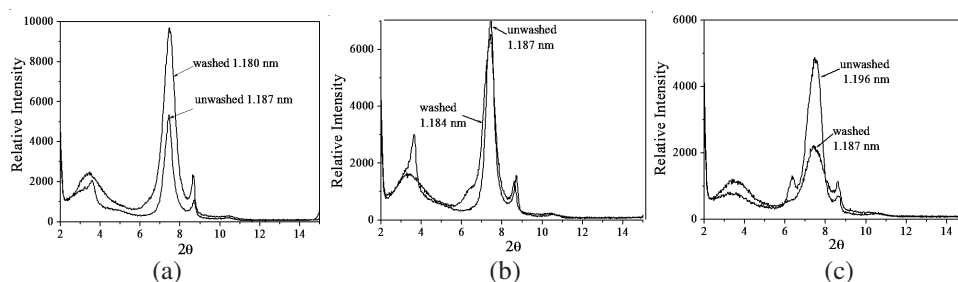


Fig. 6. XRD results of (a) VMT-1; (b) VMT-2; (c) VMT-3, acquired at unwashed and washed stages

TG analysis: Figs. 7 and 8 show the TGA data for pure ionic liquid and for modified clays. It is worth to note that the thermal stability of the ionic liquid is ranked as IL-3 > IL-1 > IL-2. The imidazolium cation is more thermally stable than the alkyl ammonium cation¹⁶. The imidazole is resistant to ring fission during thermal rearrangements of 1-alkyl- and 1-aryl-imidazoles at temperatures above 600 °C. The type of the anion has an effect on the thermal stability of the imidazolium salts. The thermal stability increases in the order: PF₆ > N(SO₂CF₃)₂ > BF₄ > Cl, Br. The imidazolium thermal stability is affected by the type of isomeric structure of the alkyl side group.

It is also of interest to note that the same trends are followed in the stability of the modified clays, *i.e.* VMT-3 > VMT-1 > VMT-2. In an attempt to understand the thermal degradation of the imidazolium-treated vermiculite, the decomposition of pristine Na-vermiculite will be considered first. The temperature range 100-300 °C that corresponds to the loss of adsorbed water. The dehydroxylation of structural hydroxyl groups occurs in the temperature range 500-1000 °C. One of the most interesting findings of this work is the enhancement in the thermal stability of imidazolium compounds after being intercalated into vermiculite. In present

experimental studies, it is important to get rid of the halide residue that may contaminate the intercalated product after ion exchange. The results also indicated that the thermal stability of imidazolium-treated vermiculite decreases as the chain length of the alkyl group attached to the nitrogen atom increases.

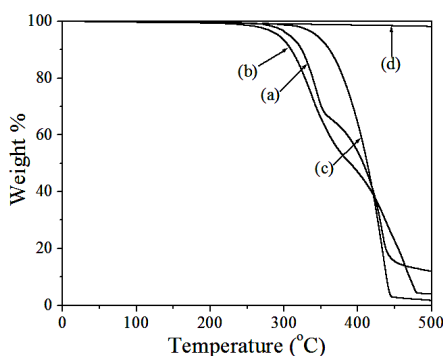


Fig. 7. TGA results of: (a) IL-1; (b) IL-2; (c) IL-3; (d) Na-VMT

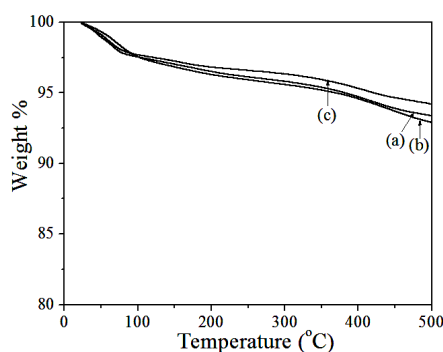


Fig. 8. TGA results of: (a) VMT-1; (b) VMT-2; (c) VMT-3

In the lithium secondary battery series, the polymer electrolyte material combines the functions of both the electrolyte and separator. An exothermic reaction can take place as the battery is charging or discharging. This thermal effect can cause the deformation of the polymer electrolytes, leading to a lower efficiency during charging and discharging. The worst possible case is a short circuit. Therefore, superb thermal stability is essential. Fig. 9 shows the TGA results for the O-VMT, VMT-3, PVDF-PEG/6 % VMT-3 and PVDF-PEG/6 % O-VMT. It can be seen that the use of imidazolium cation to replace the sodium in Na-VMT gives EMIm-VMT a 100 °C improvement in thermal stability (in N₂ atmosphere) as compared to the O-VMT. It

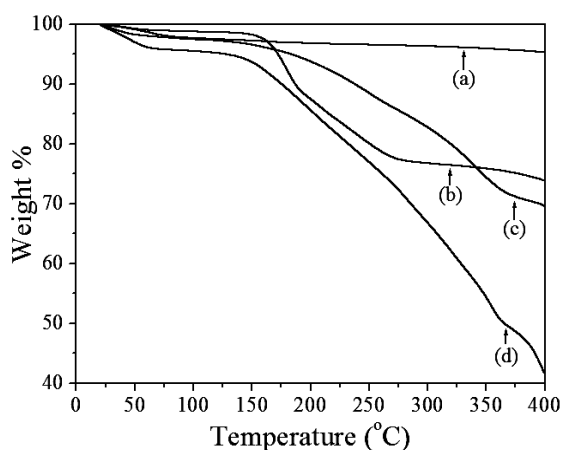


Fig. 9. TGA results of (a) VMT-3; (b) O-VMT; (c) PVDF-PEG/6 % VMT-3; (d) PVDF-PEG / 6 % O-VMT

is worth to note that the microporous polymer electrolyte membranes PVDF-PEG/6 % VMT-3 show better thermal stability (400 °C, the residual is 69.73 %) compared to PVDF-PEG/6 % O-VMT (400°C, the residual is 40.76 %), which can improve the safety of battery.

Conclusion

In this work, we modified vermiculite with three ionic liquids. The FTIR was used to detect functional groups in the exchanged cations in the ionic liquids. The WXRd was used to detect the degree of expansion of the interlayer spacing in the modified VMT. The TGA was used to detect the differences in thermal degradation behaviour between untreated VMT, modified VMT and polymer membrane. It can be concluded that the imidazolium can be successfully intercalated into the interlayer spacing of VMT, which led to high thermal stability as compared to the alkylammonium treated VMT. The imidazolium treated VMT can extremely enhance the thermal stability of polymer electrolyte membrane, which can improve the safety of lithium battery. These results seem to be promising in terms of the potential application of these imidazolium molten salts for the preparation of high temperature polymer-layered silicates. Further investigation will be focused on the interlayer structure and the orientation of imidazolium cations in the interlayer spacing.

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REFERENCES

1. J. Dupont, R.F. de Souza and P.A.Z. Suarez, *Chem. Rev.*, **102**, 3667 (2002).
2. T. Welton, *Chem. Rev.*, **99**, 2071 (1999).
3. P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed.*, **39**, 3772 (2000).
4. N. Matsumi, K. Sugai, M. Miyake, H. Ohno, *Macromolecules*, **39**, 6924 (2006).
5. Y. Yoshida, O. Baba, C. Larriba and G. Saito, *J. Phys. Chem. B*, **111**, 12204 (2007).
6. M.G. da Fonseca, C.M. Cardoso, A.F. Wanderley, L.N.H. Arakaki and C. Airoidi, *J. Phys. Chem. Solids*, **67**, 1835 (2006).
7. S. Williams-Daryn and R.K. Thomas, *J. Colloid. Interf. Sci.*, **255**, 303 (2002).
8. J.W. Gilman, W.H. Awad, R.D. Davis, J. Shields, R.H. Harris Jr., C. Davis, A.B. Morgan, T.E. Sutto, J. Callahan, P.C. Trulove and H.C. DeLong, *Chem. Mater.*, **14**, 3776 (2002).
9. R.A. Vaia, R.K. Teukolsky, E.P. Giannelis, *Chem. Mater.*, **6**, 1017 (1994).
10. J.R. Sohn and S.I. Lee, *Langmuir*, **16**, 5024 (2000).
11. T. Yui, H. Yoshida, H. Tachibana, D.A. Tryk and H. Inoue, *Langmuir*, **18**, 891 (2002).
12. S.D. Wanjale and J.P. Jog, *J. Appl. Polym. Sci.*, **90**, 3233 (2003).
13. X.S. Du, M. Xiao, Y.Z. Meng, T.F. Hung, A.V. Rajulu and S.C. Tjong, *Eur. Polym. J.*, **39**, 1735 (2003).
14. K. Shah, P. Chiu, M. Jain, J. Fortes, B. Moudgil and S. Sinnott, *Langmuir*, **21**, 5337 (2005).
15. G. Shima Martynková, M. Valášková, P. Capková and V. Matejka, *J. Colloid. Interf. Sci.*, **313**, 281 (2007).
16. L.P. Krul, *Thermochim. Acta*, **97**, 357 (1986).

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