Structure, Interaction and Thermal Behavior in Electrolytes of Polyethylene oxide/Sodium thiocyanate/Montmorillonite Nanocomposites

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บทคัดย่อ ได้ศึกษาโครงสร้าง อันตรกิริยา และสมบัติเชิงความร้อนของพอลิเมอร์อิเล็กโตรไลท์แบบนาโนคอมพอสิตระบบ PEO/NaSCN/MMT โดย PEO, MMT และ NaSCN ทำหน้าที่เป็นพอลิเมอร์ตัวกลาง สารเติมแต่งอนินทรีย์และประจุไอออน ตามลำดับ ระบบที่ศึกษาคือ (PEO)$_8$NaSCN/yMMT และมีอัตราส่วนระหว่าง PEO:NaSCN คงที่เท่ากับ 1:8 โดย y มีค่าตั้งแต่ 0 ถึง 20 wt% เตรียมตัวอย่างโดยการเคลือบสารละลายเป็นฟิล์มบางบนแผ่นกระจก จากนั้นนำมาวิเคราะห์ด้วย XRD, FTIR และ DSC เพื่อ ศึกษาผลของการเติมเกลือและดินเหนียวต่อโครงสร้าง อันตรกิริยา และสมบัติเชิงความร้อน จากข้อมูลของ DSC และ XRD พบว่าร้อยละความ เป็นผลึกของพอลิเมอร์มีค่าลดลงเมื่อเติมดินเหนียวและเกลือ การเกิดสารประกอบระหว่างพอลิเมอร์กับเกลือสามารถพิสูจน์ได้โดยการเกิดแถบการ ดูดกลืนของ FTIR ใหม่ที่ไม่พบใน PEO และทำให้แถบการสั่นของ C-O-C กว้างขึ้นเมื่อปริมาณเกลือเพิ่มขึ้น การเติม MMT มีส่วนทำให้ เกลือแตกตัวได้ดีขึ้นและเพิ่มจำนวนไอออนในระบบ การจับกันระหว่าง PEO/NaSCN และ PEO/MMT สามารถเปรียบเทียบได้โดยดู จากข้อมูล FTIR

ABSTRACT The structure, interaction and thermal behavior of polymer electrolyte nanocomposites has been investigated. The system of interest is the mixture of PEO/NaSCN/MMT where PEO, MMT and NaSCN act as polymer host, inorganic filler and ionic charge, respectively. We present the results from the system (PEO)$_8$NaSCN/yMMT, where the molar ratio of PEO:NaSCN is fixed at 1:8 and y varies from 0 to 20 wt%. All samples were prepared by solution casting on glass surface. XRD, FTIR and DSC were employed to investigate the effect of clay and salt addition on structure, interaction and thermal behavior of these materials. From DSC and XRD results, the percent of polymer crystallinity was decreased upon addition of clay and salt. Complexation of salt to polymer was substantiated by an appearance of new bands not present in pure PEO and also broaden the C-O-C vibrations as the salt content increased. Adding MMT seems to enhance salt dissociation and increase the carrier concentration. Competitive interaction between PEO/NaSCN and PEO/MMT can also be illustrated by FTIR data.

Introduction :

The rapid development of portable electronic devices and electric/hybrid vehicles has increased the demand for compact, lightweight, high capacity batteries. Polymers are widely studied due to their significant potential for an application as a medium in rechargeable batteries. One of the earliest example involved complexes of alkali salts with poly(ethylene oxide) (PEO) studied in details by *Wright* [1, 2]. However, it was particularly *Armand* who pointed out and explored the usefulness of ion-conducting polymer electrolytes in high energy storage materials [3]. Since then, an application of this polymer-salt complex or Solid Polymer Electrolyte (SPEs) to solid state batteries has been much interest. Poly(ethylene oxide)/alkali metal salt-based solid electrolytes is the most interesting base material because of its high chemical and thermal stability. PEO is a semicrystalline polymer, possessing both an amorphous and a crystalline

phase at room temperature. It can also solvate a wide variety of salts, even at very high salt concentrations. The solvation of salts occurs through the association of the metallic cations with the oxygen atoms in the backbone. Considerable efforts have been devoted to the development of solid polymer electrolytes (SPEs) with high ionic conductivity ($\sim10^{-4}$ S/cm) and dimensional stability. The multi-phase nature of PEO is most often regarded as a major problem in real working systems, since the ionic conduction has been shown to take place mainly in the amorphous phase. Many investigations have been done to reduce the crystalline content, via various approaches such as using blends, copolymers, comb-branch polymers and cross-linked polymer networks [4, 7-9].

Our interest here is to overcome these problems by the incorporation of mineral clay which is an inorganic filler with intercalation property. Intercalating polymer in layered clay host can produce huge interfacial area to sustain the mechanical property of polymer electrolyte system and imparts salt-solvating power to dissolve the salts. In this work, we present a novel polymer electrolyte nanocomposite consisting of $(PEO)_8NaSCN/MMT$ at various clay (Montmorillonite, MMT) content. The role of clay addition on structures and properties of SPEs will be investigated via differential scanning calorimetry (DSC), X-Ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy.

Methodology :

PEO (MW 1 x 10^5 g mol^{-1}, Aldrich) and Na-MMT (SWy-2, Clay Mineral Depository) were used as received. The salts, sodium thiocyanate (NaSCN, Fluka), were dried in the vacuum oven at $\sim$ 140 °C for 48 hours. Stoichiometric amount of PEO, salt and clay were dissolved in methanol and stirred continuously for 24 hours at room temperature. After continuous stirring, the solution was allowed to stand at room temperature for 24 h to facilitate degassing. To obtain thin film of the sample, the gelatinous polymer solution was cast on the glass plate. The films were dried in vacuum oven at 50 °C for 24 hours to remove solvent. The interactions between salt and polymer and salt association in $(PEO)_8NaSCN/MMT$ complexes were investigated by FTIR. The study was carried out with FT-IR spectrometer Perkin-Elmer model: spectrum GX. The numbers of scans were 4 at the resolution of 4 cm^{-1}. The range of measurement was between 4000 cm $^{-1}$ and 400 cm^{-1}. The diffraction patterns were recorded with a Bruker D5005 X-ray generator at room temperature between 2θ values 10 ° to 60 °. DSC data were collected with DSC (Perkin-Elmer Diamond) of 8 − 10 mg from 25 to 100 °C at heating rate of 10 °C min^{-1} under N_2 atmosphere.

Results and Discussions:
X-Ray Diffraction (XRD)

The intercalation of polymer chains usually increases the interlayer spacing of clay, leading to a shift of the diffraction peak towards lower angle values which are related through the Bragg's relation: $\lambda = 2d \sin \theta$. Upon intercalation, the basal spacing was expanded from 1.24 to 2.07 nm indicating the incorporation of large PEO molecules. The magnitude of a shift was not constant but varied with the clay content. The diffractograms of the 8:1 PEO/NaSCN with 0-20 wt% MMT displayed the characteristic crystalline peaks centered around 15°, 19° and 23° and it was ascribed to crystalline PEO. Addition MMT to the sample also gave peaks at the same positions but with lower intensities. It should be emphasized that the crystalline phase of 8:1 PEO/NaSCN with different % weight of MMT still existed but at a lower content than that of 8:1 PEO/NaSCN.

Fourier Transform Infrared Spectroscopy (FT-IR)

For PEO/NaSCN and PEO/MMT system, the new bands were found at 2000-2100 cm^{-1} regions (stretching modes of SCN^- in PEO/NaSCN), indicating the formation of crystalline complex of $P(EO)_8NaSCN$ (the band at 2060 cm^{-1} was ascribed to the contact ion-pairs and solvent-separated dimers). Upon addition of MMT to PEO/NaSCN, the relative intensity of the band at 2060 cm^{-1} was increased at the expense of the band at 2031 cm^{-1}, indicating the disintegration of crystalline PEO phase and resulting in a decrease of crystalline $P(EO)_8NaSCN$ complex. Spectral changes in 1000-800 cm^{-1} region (the characteristics of C-O stretching and CH_2 rocking modes) were related to changes occurring in the local structure of polymer backbone. When NaSCN was added, the bands occured at 860, 834 cm^{-1} which particularly were sensitive to the local conformation of the O-C-C-O torsional angle. The appearance of one mode at a higher frequency and the second mode at a lower frequency than that in pure PEO are originated from the interaction of sodium ion with ether oxygens. For the CH_2 wagging modes at 1360 and 1343 cm^{-1} (the characteristic of crystalline PEO), the intensity of these two peaks was decreased drastically and replaced by sharp band at 1350 cm^{-1} upon addition of NaSCN. These results indicated an amorphous content for $P(EO)_8NaSCN$. The character of 1280 cm^{-1} peak (CH_2 twisting mode in pure PEO) were also changed upon adding of salt as well as clay. Therefore both clay and NaSCN were able to reduce the crystalline phase of pure PEO.

Differential Scanning Calorimeter (DSC)

The effect of adding MMT on the changes of T_m and ΔH_m of PEO and PEO-NaSCN complexes were investigated using DSC technique. The melting temperature of PEO are changed from 69.0 °C to 66.8 °C with MMT addition. There was more amorphous domain in the complex due to the miscibility of MMT with PEO. ΔH_m and the percentages crystallinity of PEO+MMT were lower than that of PEO. In agreement with XRD data, these results suggested that MMT was compatible with PEO and caused a reduction of the crystallinity of the complex.

Conclusions

FTIR, XRD and DSC results showed that the MMT was able to decrease the crystalline content and enhanced salt dissociation of PEO-NaSCN systems. Complexation of salt to polymer was substantiated by an appearance of new bands not present in pure PEO and also broaden the C-O-C vibrations as the salt content increased. Competitive interaction between PEO/NaSCN and PEO/MMT were also illustrated by FTIR data.

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