



Preparation and characterization of melt intercalated poly(ethylene oxide)/lithium montmorillonite nanocomposites



M. Erceg^{a,*}, D. Jozić^b, I. Banovac^a, S. Perinović^a, S. Bernstorff^c

^a Department of Organic Technology, Faculty of Chemistry and Technology, University of Split, Teslina 10/V, 21000 Split, Croatia

^b Department of Inorganic Technology, Faculty of Chemistry and Technology, University of Split, Teslina 10/V, 21000 Split, Croatia

^c Elettra-Sincrotrone Trieste S.C.p.A., Strada Statale 14, km 163.5 in AREA Science Park, 34149 Basovizza, Trieste, Italy

ARTICLE INFO

Article history:

Received 14 October 2013

Received in revised form 24 January 2014

Accepted 27 January 2014

Available online 8 February 2014

Keywords:

Poly(ethylene oxide)

Nanocomposites

Crystallinity

Thermal degradation

Kinetic analysis

ABSTRACT

The structure, crystallinity, thermal properties, kinetic analysis of thermal degradation and ionic conductivity of poly(ethylene oxide)/lithium montmorillonite (PEO/LiMMT) nanocomposites prepared by melt intercalation were investigated. An intercalated structure of PEO/LiMMT nanocomposites was found by small angle X-ray scattering (SAXS). Differential scanning calorimetry (DSC) shows that an addition of LiMMT decreases the crystallinity of PEO which completely disappears above 80 wt.% of LiMMT and decreases PEO melting temperature. The influence of LiMMT on the PEO crystallinity was also observed by SAXS and Fourier Transform Infrared Spectroscopy (FTIR). Thermogravimetric analysis (TGA) indicates that LiMMT significantly lowers the thermal stability of PEO and changes its degradation mechanism what is confirmed by kinetic analysis using isoconversional method and deconvolution procedure. Electrochemical impedance spectroscopy reveals the significant increase in ionic conductivity at room temperature with addition of LiMMT and optimum LiMMT content concerning conductivity was defined.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Lithium ion secondary batteries are currently the best portable energy storage device for the consumer electronics market [1]. However, due to the usage of liquid organic solvents as electrolytes safety and ecological issues arise and manufacturers are turning to technology where liquid electrolyte is replaced with solid polymer electrolyte (SPE), i.e. to lithium polymer batteries. Lithium polymer batteries can be up to 20% lighter than lithium ion ones, they are much more flexible and can be as thin as a credit card. But, they are more expensive, lose capacity faster and the efficiency of their recycling is not satisfactory. Using biodegradable polymers, like poly(ethylene oxide) (PEO) as SPE can be advantageous from the ecological point of view. PEO based SPEs are among the most studied polymer ionic conductors [1–9]. Since ionic conductivity primarily takes place in the amorphous phase, the high crystallinity of PEO limits the lithium ion transport resulting in a poor ionic conductivity of PEO based electrolytes at room temperatures. Useful conductivity can be reached at temperatures above PEO melting point [10]. Some investigators tried to reduce PEO melting point by adding plasticizers, but this approach leads to a deterioration of

the mechanical properties of PEO [11]. Incorporation of nanoclays in the PEO matrix may reduce the crystallinity of PEO and thus increase its ionic conductivity. This investigation is focused on the preparation and characterization of PEO nanocomposites with lithium montmorillonite (LiMMT) as nanoclay in order to establish the influence of LiMMT on the structure, crystallinity, thermal stability, thermal degradation mechanism of PEO as well as on its ionic conductivity.

2. Experimental part

2.1. Sample preparation

PEO powder with viscometric average molecular weight of 300,000 was purchased from Sigma–Aldrich. LiMMT was prepared by ion-exchange from natural montmorillonite (Cloisite[®]Na⁺, Southern Clay Products Inc., USA) and lithium chloride (Kemika, Croatia). Ion-exchange has been carried out by suspending 15.0 g of Cloisite[®]Na⁺ in 400 cm³ of 1.0 mol/dm³ LiCl solution in de-ionized water. The suspension was stirred with a magnetic stirrer for 48 h at 40 °C. The mixture was then centrifuged at 5000 rpm until a clear separation was obtained and the supernatant was decanted. A series of washings with de-ionized water and again centrifugation were performed until the chloride ions were completely removed (tested using AgNO₃ solution). The obtained residue is LiMMT.

* Corresponding author. Tel.: +385 21 329 459; fax: +385 21 329 461.

E-mail address: merceg@ktf-split.hr (M. Erceg).

LiMMT was then dried in an oven for 5 h at 120 °C and then in a vacuum oven for 48 h at 100 °C. PEO/LiMMT nanocomposites with compositions 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80 and 10/90 by weight were prepared by melt intercalation. Powders of PEO and LiMMT in the required weight ratios were manually mixed for 10 min using an agate mortar and shaped into pellets using a load of 5 tons produced by a hydraulic press. The obtained samples were 13 mm in diameter, with a thickness of 0.7–0.8 mm. Melt intercalation was performed at 90 °C for 8 h in a vacuum oven.

2.2. Testing methods

2.2.1. Small angle X-ray scattering

Small angle X-ray scattering (SAXS) measurements were performed at the Austrian SAXS beamline at Elettra Sincrotrone Trieste S.c.p.A. The sample to detector distance was 1132 mm and photon energy of 8 keV was used (wavelength of 1.54 Å). Thus the q value range was 0.09–7.58 nm⁻¹, which corresponds to a d range 70.00–0.83 nm. The SAXS data have been collected by a MAR300 (MarResearch) Image plate, with exposition times of 1–2 s. The q range of the scattering setup was calibrated using the AgBeh standard and all SAXS data were corrected for dark current and background. Lorentz correction was applied on the normalized data.

2.2.2. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were performed with a Mettler-Toledo 823° calorimeter in nitrogen atmosphere (30 cm³/min). The apparatus was calibrated with an indium standard. Samples of 11.8 ± 1.5 mg, encapsulated in aluminum pans, were firstly cooled to -90 °C. Then they were heated to 120 °C (heating rate of 20 °C/min – heating scan), kept there for 5 min and then cooled again to -90 °C (cooling rate of 20 °C/min – cooling scan). DSC measurements were performed according to ISO 11357-2 and ISO 11357-3 standards.

2.2.3. Infrared spectroscopy

Infrared spectroscopy was performed with a Perkin-Elmer Spectrum One FT-IR spectrometer. FT-IR spectrograms (average of 40 scans) were recorded using the Horizontal Attenuated Total Reflectance (HATR) technique, with a ZnSe 45° crystal in the wave number range between 650 and 4000 cm⁻¹ and with a spectral resolution of 4 cm⁻¹. The samples were analysed in the form obtained after melt intercalation.

2.2.4. Non-isothermal thermogravimetry

The thermal degradation (sample mass 9.3 ± 0.5 mg) was performed by the non-isothermal thermogravimetry (TGA) in the temperature range 50–500 °C at the heating rates 2.5, 5, 10 and 20 °C/min using a Perkin-Elmer Pyris 1 TGA. The nitrogen flow rate was 30 cm³/min.

2.2.5. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was used for determination of the ionic conductivity of PEO/LiMMT nanocomposites. The measurements were performed at 25 °C in the frequency range from 1 MHz to 1 Hz with the a.c. amplitude ± 20 mV using Solartron frequency response analyser 1255 and Solartron electrochemical interface 1287 controlled by PC. The experimental data were analysed using software Zview. PEO/LiMMT nanocomposites were sandwiched between two stainless steel (SS) blocking electrodes to form symmetrical SS/electrolyte/SS cell.

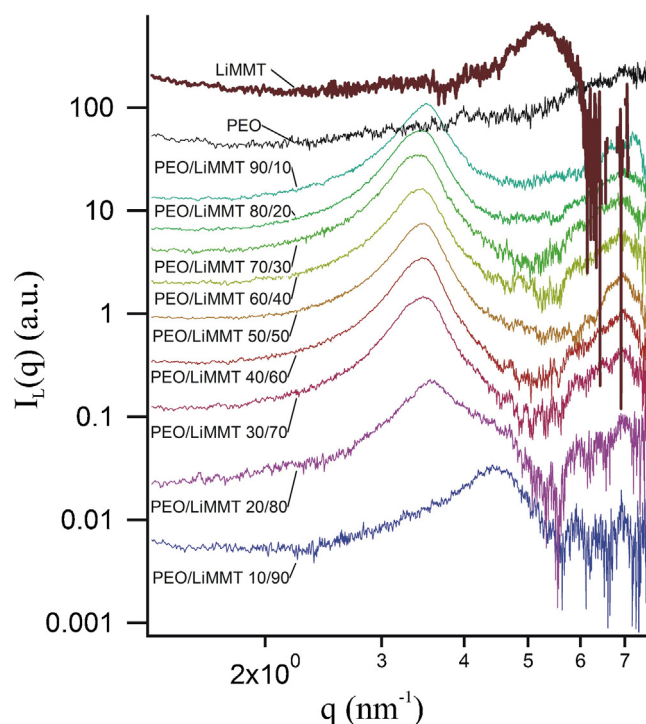


Fig. 1. SAXS patterns for PEO, LiMMT and PEO/LiMMT nanocomposites.

3. Results and discussion

3.1. Small angle X-ray scattering

The Lorentz-corrected SAXS profiles of PEO/LiMMT nanocomposites, pure LiMMT and PEO are shown in Fig. 1.

Pure LiMMT consists of alumina silicate layers stacked along a line perpendicular to the (001) basal plane where interlayers of pure LiMMT contain two planes of water molecules. The negative charge of the aluminosilicate layers is compensated with exchangeable cations (Li⁺) located in the interlayer gallery. The scattering peak of the pure LiMMT at the position $q = 5.21 \text{ nm}^{-1}$ corresponds to the interlayer distance of 1.20 nm (12.0 Å) (d_{001}). For pure PEO, the scattering peak which corresponds to the interlayer distance of 0.88 nm (8.8 Å) appears at $q = 7.15 \text{ nm}^{-1}$. The intercalation of polymers into layered inorganic compounds is generally unfavorable due to the high activation energy associated with the deformation of the crystal structure of the inorganic host. Thus, the intercalation requires the expansion of the interlayer spacing of layered compound. SAXS results show that PEO increases the interlayer distance of LiMMT (Fig. 2a).

In the sample with 10 wt.% of PEO the interlayer distance of LiMMT increases to 1.47 nm (14.7 Å) what is 22.5% expansion compared to pure LiMMT. Samples with higher amounts of PEO show higher but mutually similar values of LiMMT interlayer distances. The maximum value of 1.88 nm (18.8 Å) is observed for PEO/LiMMT 70/30 sample, where the increase amounts 56.7% of LiMMT original value. The scattering peak of LiMMT is present in the scattering curves of all samples, what suggests that exfoliation does not occur. The shift of the LiMMT scattering peak is a consequence of the PEO intercalation into its gallery. Intercalated PEO can be either in helical conformation or in a zigzag conformation what can be further analysed by infrared spectroscopy.

At the same time, the interlayer distance of PEO in nanocomposites increases by the addition of LiMMT up to a maximum value of 0.93 nm (9.3 Å) for nanocomposite assigned as PEO/LiMMT 70/30 (Fig. 2b). This suggests the conformational differences

Download English Version:

<https://daneshyari.com/en/article/7062393>

Download Persian Version:

<https://daneshyari.com/article/7062393>

[Daneshyari.com](https://daneshyari.com)