Characterization of polymer/nanoclay composites via direct pyrolysis mass spectrometry

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ABSTRACT

In this work, direct probe mass spectrometry, DP-MS, method was applied to investigate the characteristics of polymer/organoclay composites. For this purpose organically modified montmorillonites involving four different alkyl quaternary ammonium salts were incorporated into polylactide, poly(methyl methacrylate) and polyethylene matrices. The morphology of the composites were first analyzed by x-ray diffraction, XRD, and transmission electron microscopy, TEM, measurements. The temperature regions at which the organic modifier was lost during the pyrolysis of the organoclays and the polymer/organoclay composites were correlated with inter-layer spacing of the clay layers. It has been determined that the loss of organic modifier shifted to lower temperatures as the interlayer-spacing increased. As a consequence of broader inter-layer spacing, the extent of intercalation was improved leading to an increase in thermal stability of the matrix polymer. The results clearly showed that the DP-MS technique supplies strong evidences for the extent and type of dispersion of clay layers in the polymer matrices. In addition the technique allows identification of possible interactions between the polymer and the organic modifier.

1. Introduction

With the emergence of the nanotechnology, the polymer/layered silicate nanocomposites have received significant attention, owing to their remarkable mechanical, thermal, and physical-chemical properties, compared to virgin polymer and conventional composites [1–7]. Montmorillonite, known as clay, has two tetrahedral sheets of silica sandwiching a central octahedral sheet of alumina. The stacks of clay platelets are held tightly together by electrostatic forces leading to galleries. The galleries are occupied by cations, typically Na^+ and/or Ca^{2+}. By exchanging the ions present in between the layers with various organic cations, montmorillonite clay can be compatibilized with a wide variety of polymers generating intercalated and exfoliated structures. The properties of clay nanocomposites depend on the dispersion of the nanoparticles in the polymer matrix which is affected by several factors such as nature of the clay, the organic cation and the characteristics of the polymer.

The most commonly used techniques for characterization of the morphology are Transmission Electron Microscopy (TEM) and X-Ray Diffraction (XRD) methods [8–11]. Solid-state NMR [10–15] and Melt Rheology [15–17] techniques are also used by some research groups. Small-angle and ultra-small-angle neutron scattering (SANS and USANS), small-angle X-ray scattering (SAXS), Fourier Transformed-Infrared (FT-IR), and high-resolution transmission electron microscopy (HR-TEM), atomic force microscopy (AFM) are also applied for the purpose [18–20]. However, although each method provides some information about the dispersion, each possesses some limitations and drawbacks [8,11,13]. TEM is a direct way to visualize dispersion of nanoclay, yet, for statistical view of the morphology of the whole sample large number of images at different magnifications has to be obtained. In case of XRD method, the characteristic peak of the clay shifts to lower angles, indicating larger d-spacing, for intercalated structures and disappears for exfoliated structures. But the disappearance of the peak due to dilution, peak broadening, mixed-layer morphology and preferred orientation may lead to misinterpretation. SAXS, can be more informative, yet, similar problems exist. Melt rheology and solid state NMR are bulk analyses, thus, the sample is representative of the material. Melt rheology has the advantage to be a semi-quantitative method enabling to compare the dispersion of different samples. Solid state NMR quantifies both the degree of separation of the platelets and the homogeneity of the dispersion, yet, the level of information about dispersion depends on polymer and clay characteristics.

On the other hand, the thermal stability of the polymer may

decrease due to presence of catalytic sites such as hydroxyl groups. In general, finer dispersion of the clay nanoparticles leads to thermal stabilization. Thus, it may be thought that the temperature at which the organic modifier is evaporated or the thermal stability of the organic modifier should increase upon incorporation into clay galleries, and the elimination or decomposition of the organic modifier is supposed to be shifted to low temperatures as the inter-layer spacing between the clay layers increases. In a recent study on pyrolysis of organically modified montmorillonites involving various quaternary ammonium salts as the organic modifier, the loss of organic modifier was determined to be shifted to lower temperatures as the interlayer-spacing of the clay increased [21].

This paper presents the application of direct probe mass spectrometry, (DP-MS), method to investigate the characteristics of organically modified montmorillonites and their polymer nanocomposites. DP-MS has been shown as a valuable tool for analyses of complex polymer matrices as components are separated as a function of their volalities and/or thermal stabilities [22–24]. In this work, various quaternary ammonium salt modified natural montmorillonites were incorporated into poly(lactic acid), poly(methyl methacrylate) and polyethylene matrices and analyzed via DP-MS technique. The temperatures at which the organic modifier lost were correlated with inter-layer spacings calculated from XRD analyses. Furthermore, the interactions between the organic modifier and the matrix polymer were investigated. The significantly higher sensitivity of mass spectrometers compared to other spectrometric techniques that are based on measurement of intensity of photons allows detection of even very low amounts of organic modifier.

2. Experimental

2.1. Materials

Polylactide, (Mn ∼ 190,000) was provided by Cargill Dow. PMMA with the trade name SUMIPEX® Clear 011 (Mn ∼ 105,000) was purchased from Sumitomo Chemical Co., Ltd. Low density polyethylene, LDPE, with a commercial name, Petilen F2-12, was supplied from Petkim Petrochemical Holding. The organically modified natural montmorillonites, Cloisite 15 A, Cloisite 20 A, Cloisite 25 A, Cloisite 93 A and Cloisite 30B were provided by Southern Clay Products Inc. The characteristics of the organically modified montmorillonites, cation exchange capacities in units of milliequavalents per 100 g, and layer spacings (d_{001}) are given in Table 1. Cloisite 15 A having a cation exchange capacity of 125 and 95 meq/100 g, respectively involves dimethyl dihydrogenated tallow (∼ 65% C18; ∼ 30% C16; ∼ 5% C14) ammonium, whereas Cloisite 25 A (C25 A) and Cloisite 93 A (C93 A) involve dimethyl, hydrogenated tallow, 2-ethylhexyl ammonium and methyl, dihydrogenated tallow ammonium salts respectively. Finally, Cloisite 30B involves methyl, tallow, bis-2-hydroxyethyl, ammonium salt. Dimethyl hydrogenated ditallow (∼ 65% C18; ∼ 30% C16; ∼ 5% C14) ammonium chloride and the solvent, CHCl₃ (99%) were purchased from Sigma Aldrich. All materials were used without further purification.

Polymers and clays were dried at 60 °C overnight under reduced pressure prior to mixing processes. PLA-clay composites (3 or 5 wt% inorganic content) were melt-compounded using a DSM Xplore twin screw micro compounder at 190 °C, with a screw speed 100 rpm for 8 min, whereas, PE composites with 5 wt% inorganic content were melt-compounded at 185 °C, with a screw speed 100 rpm for 3 min. PMMA composites involving 5 wt% organically modified montmorillonites were solution mixed in CHCl₃ by magnetic stirring.

2.2. Characterization

Rigaku X-ray diffractometer (Model, Miniflex) with CuK$_\alpha$ (30 kV, 15 mA, λ = 1.54051 Å) was used to obtain 2θ XRD patterns of the composites, at 25 °C in the 1°–10° range. Transmission electron

Table 1
Characteristics of organically modified montmorillonites.

Montmorillonite	d_{001} (nm)	OM meq*/ 100 g clay	Organic modifier
Cloisite 15A	3.15	125	dimethyl, dihydrogenated tallow, ammonium $H_3C-\overset{+}{\underset{CH_3}{\overset{TH}{N}}}-TH$
Cloisite 20A	2.42, 1.21	95	dimethyl, dihydrogenated tallow, ammonium $H_3C-\overset{+}{\underset{CH_3}{\overset{TH}{N}}}-TH$
Cloisite 25A	1.86	95	dimethyl, hydrogenated tallow, 2-ethylhexyl ammonium $H_3C-\overset{+}{\underset{CH_3}{\overset{TH}{N}}}-CH_2CH(C_2H_5)C_4H_9$
Cloisite 93A	2.36	90	methyl, dihydrogenated tallow ammonium $H-\overset{+}{\underset{CH_3}{\overset{TH}{N}}}-TH$
Cloisite 30B	1.85	90	methyl, tallow, bis-2-hydroxyethyl, ammonium $H_3C-\overset{+}{\underset{CH_2CH_2OH}{\overset{CH_2CH_2OH}{N}}}-T$

Tallow, (T) (∼65% C18; ∼30% C16; ∼5% C14).

microscopy (TEM) analyses were carried out using a FEI Tecnai G2 Spirit BioTwin CTEM. The specimens cut from the middle portion of the injection molded samples of melt blended composites of PLA and PE were analyzed. On the other hand, very dilute solutions of PMMA nanocomposites in CHCl₃ were poured into carbon coated-copper grid with 3 mm diameter and 400 mesh. Then, the grid was allowed to dry in room temperature for 24 h. After drying, TEM analyses were performed.

Direct pyrolysis mass spectrometry (DP-MS) analyses of PLA were performed on a 5973 HP quadrupole mass spectrometry system coupled to a JHP SIS direct insertion probe pyrolysis system. 70 eV EI mass spectra, at a rate of 2 scan·s⁻¹, were recorded. About 0.10 mg of PLA composites in flared glass sample vials, were heated to 450 °C at a rate of 10 °C min⁻¹. DP-MS analyses of PMMA and PE (0.010 mg) were performed in flared quartz sample vials on a Waters Micromass Quattro Micro GC Mass Spectrometer with a mass range of 15–1500 Da coupled to a direct insertion probe. The samples were heated to 650 °C at a rate of 10 °C/min while recording 70 eV EI mass spectra, at a rate of 1 scan/s. All experiments were repeated at least twice to assess repeatability.

3. Results and discussions

3.1. Transmissions electron microscopy analyses

TEM images of PLA, PMMA and PE nanocomposites involving C15 A, C25 A, C93 A and C30B are presented on Fig. 1. These images were the best ones representing dispersion of nanoclay in polymer matrices, selected among several images obtained. The images showed both intercalated and exfoliated regions in PLA and PMMA matrices. Whereas, for PE composites mainly intercalated platelets can be identified. Thus, it is clear that although TEM is a direct way to visualize dispersion of nanoclay it may be very difficult to obtain appropriate images independent of analyst.

3.2. X-ray diffraction analyses

XRD pattern for C15 A revealed three peaks at 2θ = 3.3, 5.18 and