



Research paper

Dynamic of organic species in organo-clay/polypropylene composite by quasi-elastic neutron scattering

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ARTICLE INFO

Keywords:

Quasi elastic neutron scattering
 Polypropylene
 Fluoromica
 Composite
 Molecular motion

ABSTRACT

Dynamics of a fluoromica (ME100) cation exchanged for dioctadecyl dimethyl ammonium ion (DODA⁺)/polypropylene composite was analyzed by quasi elastic neutron scattering (QENS), besides XRD and DSC. The QENS spectra for the DODA-ME100 at low $Q = 2.75 \text{ nm}^{-1}$ were not changed even at temperature higher than 445 K, the melting point of DODA⁺. The results suggested the long range ($> 2 \text{ nm}$) molecular motions in interlayer space are restricted due to the rigid silicate layers and the strong electrostatic interaction between DODA⁺ and the ME100. Elastic intensity scan results suggested that a little amount of motion of the polymer chains in the composite was also restricted in the molten state at 445 K. The QENS is expected to be one of the useful tools for studying the composite materials.

1. Introduction

Clay mineral/polymer nano-composites, in which the silicate layers are dispersed in an organic polymer matrix, have been widely studied. They have notable mechanical (Kojima et al., 1993) and other properties such as heat (Kojima et al., 1993) and burning (Gilman, 1999) resistance, gas-barrier effect (Yano et al., 1997). A grafting of polymer chains on the surface of the silicate was one of the significant factors to control the gas-barrier feature (Gain et al., 2005). The interaction of organic polymer chain with the surface of silicate layers has been one of the most attractive interests for soil scientists (Theng, 1982). Although an attractive interaction of a single segment of $-(\text{CH}_2)-$ with the silicate surface is small (about 7 kJ/mol estimated by Fukushima and Tamura, 2017), the total interaction is large because of a repetitive construction in the polymer chains, which was confirmed by the adsorption isotherms of polymers on clay minerals (Theng, 1982, and Fukushima and Tamura, 2017). An interfacial cohesive surface interaction between silicate layers and polymers was taken into account in atomistic simulation of the mechanical behavior of a polymer nano-composite (Wiedmaier et al., 2016).

The interactions between the organic molecules and the silicate surface have been suggested by NMR (VanderHart et al., 2001; Chen and Evans, 2006) and IR (Fukushima and Usuki, 1992; Deshmanea et al., 2007). Although the interactions should be one of the most important points in the study of clay mineral/organic polymer composites,

there have been only a few approaches to study the interaction. A quasi elastic neutron scattering (QENS) is suitable for observing the local motions on pico- to nano-second timescale and 0.1 to several tens nanometer length scale (Sharma et al., 2015; Springer, 1972). Other techniques such as NMR offer on over micro-meter and nano-second scale information. When the surfactants and organic polymer were co-existed on the silicate surface, they should get some freedom to move at the temperature higher than their melting points. The QENS instrument designed for analyzing a low momentum transfer (Q) scattering with high energy resolution, which is expected to be suitable for study the clay mineral/organic composites, is installed in Materials and Life Science Experimental Facility (MLF) in Japan Proton Accelerator Research Complex (J-PARC).

2. Experimental

2.1. Sample preparation

An organic clay (DODA-ME100) was prepared by using the synthetic expandable fluoromica; SOMASIF ME100[®] obtained from CO-OP Chemicals, Tokyo, Japan, cation exchanged for dioctadecyl dimethyl ammonium ion (DODA⁺). An atactic polypropylene (a-PP, Aldrich 428175-1KG) was purchased from Aldrich Chemical Co. Ltd. The average molecular weight M_w (20,000) and M_n (5000) were determined by gel permeation chromatography (GPC) using polystyrene elution

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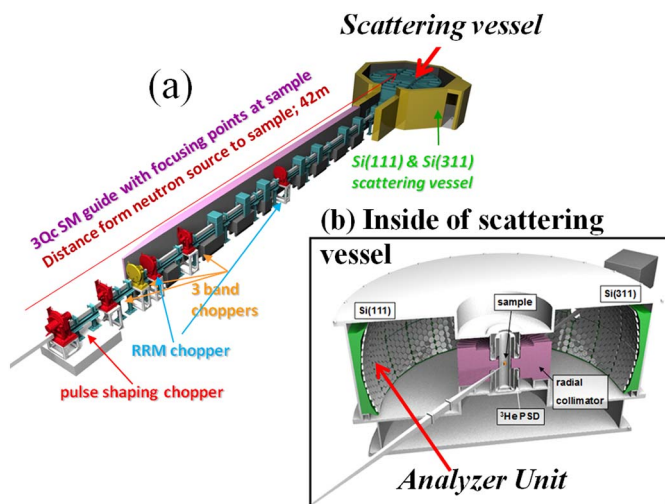


Fig. 1. (a) Overhead view of the Quesi Elastic Neutron Scattering instrument BL02 (DNA) at Japan-Proton Accelerator Research Complex (J-PARC), and (b) Inside the scattering vessel of DNA (Seto et al., 2017).

standards. The a-PP and 33 wt% of the DODA-ME100 was kneaded at 170 °C to get the exfoliation type (Giannelis, 1992) nanocomposite (a-PP/DODA-ME100), followed by hot-press plates forming with about 70 mm × 70 mm × 0.3 mm. The composite and two reference samples; DODA-ME100 and a-PP, were checked by DSC using Hitachi DSC 7020 and XRD using RIGAKU Ultima IV in advance of the QENS measurements. The samples of about 4 mg for DSC were heated to 463 K, followed by cooling 463 K to 203 K and heating to 473 K under 2 K/min of cooling and heating rate under nitrogen flow. The XRD data were collected using by 0.154 nm of Cu-K α 40 kV/30 mA with Ni filter, divergence slit of 0.5°, scattering slit of 0.5° and receiving slit of 3 mm in atmospheric condition.

2.2. Neutron scattering

A backscattering QENS instrument (Shibata et al., 2015; Seto et al., 2017); Biomolecular Dynamics Spectrometer (DNA), shown in Fig. 1 (a), installed at Materials and Life Science Experimental Facility (MLF) in Japan Proton Accelerator Research Complex (J-PARC) was designed for measuring the dynamics of several μ eV; corresponding nanosecond, order in sub-nano to nanometer order spaces.

The curled sheet samples were inserted between an aluminum inner cylinder and an aluminum outer holder shown in Fig. 2, followed by sealing in He gas environment.

A spallation pulsed neutron is shaped by high speed disc chopper, shown in Fig. 1 (a), to sharp time distribution white neutron pulses. Neutrons scattered by a sample are analyzed by spherically arrayed Si crystals and detected by ^3He gas position sensitive detectors (^3He PSD) shown in Fig. 1 (b). A momentum transfer; Q , and an energy transfer; ΔE , are analyzed by the Bragg angle ($\theta_b = 87.5$ deg.) of the Si 111 reflection analyzer, and the time of flight between the spallation neutron source and the detector (Shibata et al., 2015; Seto et al., 2017). The QENS spectra were collected with the momentum transfer of $0.8 \text{ nm}^{-1} < Q < 18.7 \text{ nm}^{-1}$, that is corresponding $0.17 \text{ nm} < r < 3.9 \text{ nm}$ in real space, and the energy transfer of $-40 \mu\text{eV} < \Delta E < 100 \mu\text{eV}$ with 3.6 μeV of energy resolution (Shibata et al., 2015).

3. Results

3.1. X-ray diffraction (XRD) and differential scanning calorimetry (DSC)

XRD result shown in Fig. 3 confirmed that the obtained a-PP contained a small amount of crystalline polypropylene. The DODA-ME100

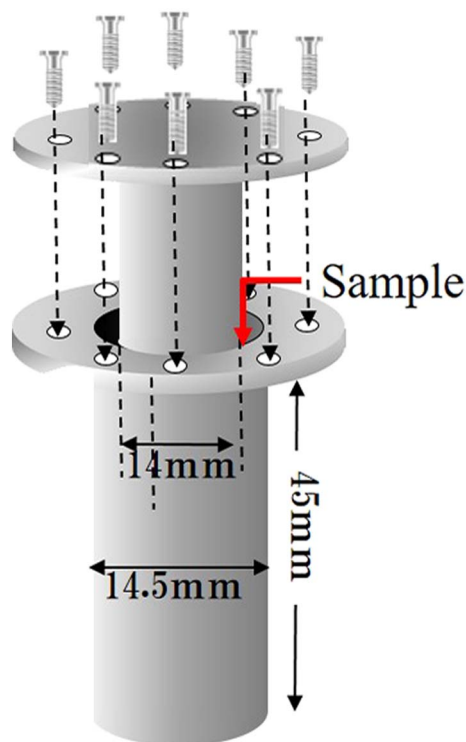


Fig. 2. Schematic sketch of the aluminum sample vessel for QENS experiments at J-PARC.

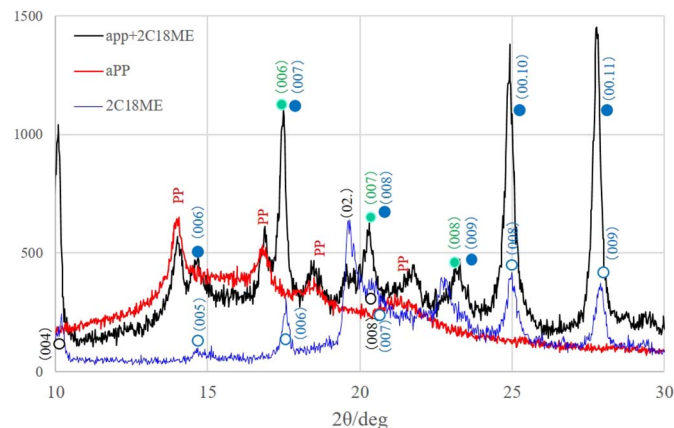


Fig. 3. Results of X-ray diffraction for the a-PP (red), the cation-exchanged DODA-ME100 (blue) and the aPP/DODA-ME100 composite (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

showed a typical layered structure with about 3 nm of the interlayer spacing. The a-PP/DODA-ME100 composite shows peaks corresponding to both a-PP and DODA-ME100. Although XRD pattern from the a-PP in the a-PP/DODA-ME100 composite were not significantly changed by the mixing process comparing, (00L) peaks of the a-PP/DODA-ME100 composite corresponding to the silicate layer stacking in the high angle region were different from the raw DODA-ME100.

Fig. 4 shows DSC heating curves of the a-PP, the DODA-ME100 and the a-PP/DODA-ME100. The a-PP showed a glass transition at about 260 K and the melting of crystalline polypropylene at about 420 K. The crystallinity estimated from the melting enthalpy was ca. 14%. Melting of the DODA⁺ in the interlayer region at about 330 K was observed for both the DODA-ME100 and the a-PP/DODA-ME100. Although the melting temperature of the a-PP was not changed by the mixing, melting temperature of the DODA⁺ increased about 10 K and the melting enthalpy of the DODA⁺ increased and that of the a-PP crystal decreased in the composite.

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