Organization of mixed dimethyldioctadecylammonium and choline modifiers on the surface of synthetic hectorite

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ABSTRACT

Understanding the nature of mixed surfactant self-assembly on the surface of organoclays is an important step toward optimizing their performance in polymer nanocomposites and for other potential applications, where selective surface interactions are crucial. In segmented thermoplastic polyurethane nanocomposite systems, dual-modified organoclays have shown significantly better performance compared to their single-modified counterparts. Until now, we had not fully characterized the physical chemistry of these dual-modified layered silicates, but had hypothesized that the enhanced composite performance arises due to some degree of nanoscale phase separation on the nanofiller surface, which enables enhanced compatibilization and more specific and inclusive interactions with the nanoscale hard and soft domains in these thermoplastic elastomers. This work examines the organization of quaternary alkyl ammonium compounds on the surface of Lucentite SWN using X-ray diffraction (XRD), thermogravimetric analysis (TGA), attenuated total reflectance Fourier-transfer infrared (ATR FT-IR), ^{13}C cross-polarization (CP)/magic angle spinning (MAS) nuclear magnetic resonance (NMR), and small-angle neutron scattering (SANS). When used in combination with choline, dimethyldioctadecylammonium (DMDO) was observed to self-assemble into discontinuous hydrophobic domains. The inner part of these hydrophobic domains was essentially unaffected by the choline (CC); however, surfactant intermixing was observed either at the periphery or throughout the choline-rich phase surrounding those domains.

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1. Introduction

Organoclays are important and versatile commercial additives [1–3]. In the polymer nanocomposite systems, organoclays are one of the most dominant and industrialized class of nanomaterials used [1]. The incorporation of organoclays in polymers has resulted in improvements of mechanical, barrier, thermal, dimensional, and chemical properties as well as reductions in cost and total weight at a relatively low loading [4–6]. Underpinning these property enhancements is the clay's large surface area and aspect ratio, which is achieved when clay layers are well-dispersed or exfoliated in a polymer matrix [5]. In order to exfoliate the clay layers, a favorable entropy interaction between the organoclay and the host polymer is required to facilitate polymer chain intercalation into the clay galleries and their subsequent delamination. The common approach employed to create a favorable organoclay/polymer interaction is to match the polarity of the host polymers and organoclays [7]. A challenge therefore arises when the polymers consist of segments with differing polarity, such as in block co-polymers and segmented polyurethanes. Prior, the literature shows that the chemical structure of surfactants determines the degree of organoclay exfoliation, distribution, and mechanical properties of polyurethane nanocomposites [8,9]. Organoclays which are modified with a single type of surfactant can preferentially associ-

ate with one of the segments, which can detrimentally disrupt the underlying morphology [10–12]. In many cases, the enhancement in properties is accompanied with a loss of resilience and an increase in stiffness and sometimes brittleness [8–10,13,14], which in turn limits the number of potential applications.

Recently, dual-modified organoclays have started to gain interest. A small number of examples in the literature incorporate both cationic surfactants and alkoxysilanes to modify the surface and edges of the clays [15–19]. While the main objectives of these investigations were to improve the thermal stability and clay dispersion, in the two studies where mechanical properties were measured, these dual cationic and silane modified organoclays did not result in enhanced tensile properties [16,19]. Demonstrable benefits of incorporating dual-modified organoclays with alternating polarities in poly(dimethylsiloxane)-based polyurethanes were reported by Osman et al. [20]. These organoclays were prepared by modifying the surface of synthetic fluoromica, Somasif ME100, with 75% octadecyltrimethylammonium bromide (nonpolar), and 25% choline chloride (polar). Compared to those modified with 100% octadecyltrimethylammonium bromide, the dual-modified organoclays exhibited more balanced interactions with both the soft and the hard segments of this polyurethane host. This resulted in improved dimensional stability, tensile, and tear properties, combined with a reduced stiffening effect. To the best of our knowledge, the physicochemical structure and properties of these dual-modified organoclays have not been fully investigated and documented.

In this study, the conformation and organization of DMDO and CC adsorbed on the surface of synthetic hectorite were investigated. The mean orientation of surfactants with respect to the clay surface was investigated using XRD. TGA provided information regarding thermal stability and cationic exchange capacity (CEC) saturation. The surfactant phase separation and mixing was identified from ATR FT-IR and ^{13}C CP/MAS solid-state NMR spectroscopy studies. ^{1}H relaxation time measurements were then carried out to further investigate the degree of phase mixing, while the larger-scale structure and solubility behavior were acquired from SANS.

2. Materials and methods

2.1. Materials

Lucentite SWN was supplied by Kobo Products, Inc (New Jersey, USA). It is a synthetic hectorite with lateral dimensions of ca. 25 nm and layer thickness of ca. 1 nm [21]. Its structural formula is $Na_{0.33}[Mg_{2.67}Li_{0.33}Si_4O_{10}(OH)_2]$ [22]. The CEC of Lucentite SWN is 120 meq/100 g clay, as determined by the methylene blue titration method in our laboratory. Dimethyldioctadecylammonium chloride and choline chloride were purchased from Sigma Aldrich (Castle Hill, Australia) and were used as received.

2.2. Organoclay preparation

Organoclays were prepared via an aqueous ion exchange reaction in which the sodium ions located in the interlayer gallery of clay were replaced with the cationic surfactants. Surfactants were mixed with 1 wt% clay in MilliQ water (resistivity 18.2 MΩ cm) at 60 °C for 24 h. The organoclays underwent a sequential washing (using MilliQ water) and centrifugation step to remove salts (NaCl) and unbound surfactants. This step was stopped when precipitation could not be observed as 0.1 M AgNO₃ was added to the supernatant. The organoclays were subsequently oven dried at 60 °C and then milled using a Micron Master® Jet Pulverizer (The Jet Pulverizer Co., New Jersey, USA). LxD refers to organoclay, which is

modified with x% DMDO and (100-x)% CC. The total surfactant concentration was constant at 120 meq/100 g clay. In addition, 100% CC modification is denoted L100C. The organoclay composition and CEC saturation are summarized in Table S1 in Supplementary information.

2.3. Techniques

XRD data were recorded in a Bruker D8 Advance X-ray diffractometer (Bruker, Germany) with a 0.2 mm exit slit and a parallel beam geometry. Cu Kα radiation was generated at 40 kV and 30 mA. Samples were put in a low background sample holder and scanned over a range of 2θ = 0.5–10° with a step size of 0.02° and a 1 s scan speed. The d-spacing of organoclays was determined using Bragg's equation [23]:

$$n\lambda = 2d_{001} \, \sin \, (\theta)$$

where n is 1, λ is wavelength = 1.54 Å, d_{001} is the d-spacing of the 001 reflection, and θ is a scattering angle.

The presence of surfactant on the synthetic clay surface was confirmed by using ATR FT-IR spectroscopy on a Thermo-Nicolet 5700 FT-IR spectrometer equipped with a Nicolet Smart Orbit single bounce, diamond ATR accessory (Thermo Electron Corp., USA). Spectra were recorded from 4000 cm^{-1} to 400 cm^{-1} at 4 cm^{-1} resolution for 32 scans. Samples were pressed directly onto the diamond internal reflection element of the ATR accessory without further sample preparation. Spectra were normalized to the Si–O peak at 970 cm^{-1}.

A TGA/DSC-1 thermogravimetric analyzer (Mettler Toledo, USA) was utilized to investigate thermal stability of organoclay. Approximately 7–10 mg of sample was put in a 70 μl alumina crucible. The temperature was ramped from 25 °C to 100 °C at a constant rate of 20 °C/min, held isothermally for 15 min, and further ramped to 800 °C at a constant rate of 10 °C/min.

^{13}C magic angle spinning (MAS) NMR spectra were recorded on a Bruker Avance III spectrometer (Bruker, Germany) in a magnetic field of 7.41 T with a ^{13}C frequency of 75.4 MHz. The samples were packed into a 4 mm zirconia rotor, which was spun at 5–7 kHz. ^{13}C spectra were collected using a standard cross-polarization (CP) pulse sequence with a contact time of 1 ms and a recycling delay time of 3 s. ^{1}H spin lattice relaxation times in the rotating frame $T_{1\rho}(^{1}H)$ were measured indirectly via ^{1}H–^{13}C cross-polarization using a standard ^{13}C detected ^{1}H spin-locking pulse sequence. The recycling delay time was 3 s, and the fixed cross-polarization time was 750 μs. Sixteen spectra were collected with an increasing spin-lock pulse lengths ranging from 20 μs to 16,000 μs. The RF field strength was 86 kHz. The ^{13}C NMR spectrum of CC was obtained using a single 90° pulse with a high-power decoupling pulse sequence due to the greater molecular mobility reducing the efficiency of CP in this sample. The decoupling scheme employed was tppm 15. The recycling delay was 5 s.

Sample for SANS experiments was prepared by mixing 1 wt% organoclay in D_2O for 4 h, followed by sonication for 1 h in a sonicating bath and then for 2 min using an ultrasonicating probe to break up any large agglomerates. SANS experiments were performed on the Quokka beamline at the Australian Nuclear and Science Technology Organisation (ANSTO) [24,25]. The scattering intensity as a function of scattering wavevector was obtained from organoclay samples, which were circulated in a 1 mm thick demountable quartz cell connected to a peristaltic pump. The magnitude of the wavevector (q) is related to the scattering angle (2θ) and the neutron wavelength (λ), as follows [26]:

$$q = 4\pi \frac{\sin \, (\theta)}{\lambda}$$