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The modification of Na-montmorillonite by salts of fatty acids: An easy intercalation process

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ABSTRACT

The organic modification of Na-montmorillonite (Na-MMT) clay by a reaction with the sodium salts of octadecanoic acid (SOD) and dodecanoic acid (SDD) was studied for the production of effectively intercalated and organophilic clays. The results of X-ray diffractometer (XRD) analysis reveal that the interlayer spacing of Na-MMT increased from 1.38 nm to 3.37–1.44 nm, 3.56–1.45 nm, 3.61–1.44 nm and 3.56–1.44 nm in the organoclays containing 393 mM SOD, 787 mM of SOD, 540 mM SDD and 1080 mM SOD, respectively.

In the Fourier transform infrared spectrometer (FTIR) analyses, the stretching and bending vibrations of the hydroxyl groups of Na-MMT at 3619,3407 and 1634 cm^{-1} 15 as well as the Si–O and Al–O vibrations of silica–alumina layers at 1039–534 cm^{-1} 16 respond to the structural changes from hydrophilic to hydrophobic character. Thermogravimetric (TG) analyses results also suggest that the intercalation of SOD and SDD were achieved in the organoclays samples and the samples had permanent structural modifications, although they retained their inorganic character. The TEM-EDS and SEM results show that the SOD and SDD were well dispersed and intercalated throughout the interlayer spaces or adsorbed onto the clay surface. The suggested organic modification of Na-MMT is an easily applicable process in which the chemically stable, low cost and widely available SOD and SDD are used as intercalating agents.

1. Introduction

The physical and chemical interactions of expandable clays with organic molecules have been studied extensively since the introduction of organically modified clays by Mac Ewen and Jordan [1,2]. As a result of these studies, a substantial industry has been established to utilize organoclays. The majority of applications for organoclays involve the use of their rheological and adsorbent properties in various systems such as oil well drilling fluids, paint, grease, cosmetics, personal care products, wastewater treatment and hydrocarbon cracking [3–6].

A considerable amount of research has also addressed the preparation and properties of the polymer-clay nanocomposites. Because of their organophilic character, organoclays are preferentially used in these nanocomposites. Organoclays exhibit pronounced improvements in the properties of nanocomposites compared with virgin polymer or conventional micro- and macro-composites. These improvements include increased elastic modulus and mechanical strength, improved heat and flame resistance, reduced gas permeability and increased biodegradability. These properties have led to the application of polymer clay nanocomposites in many industrial fields, e.g. the automotive, packaging, medical and technical textile industries [7–15]. The most commonly used organoclays for polymer-clay nanocomposites are prepared by the organic modification of montmorillonite (MMT). The crystal structure of MMT consists of layers made up of two tetrahedral silica sheets fused to an edge-shared octahedral sheet of alumina. The central atoms ($A1^{3+}$ and Si^{4+}) in the interior crystal lattice have been substituted for lower valance ions such as Mg^{2+} and Fe^{2+}. These isomorphic substitutions within the layers create a charge imbalance on the outer and interlayer surfaces of the clay platelets. The negative charge is neutralized by the adsorption of hydrated cations (usually Na^{+1} and Ca^{+2}) inside the interlayer spacing (gallery) and on the surface. Thus, the clay platelets are inherently hydrophilic. To render MMT miscible with polymer matrices, the hydrophilic silicate surface must be modified to an organophilic surface. This change makes the clay platelets compatible with the organic polymer matrices. The modification of MMT with different molecules has been investigated previously [14–21]. Generally, organic modification of MMT can be accomplished by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkyl ammonium or alkyl phosphonium salts. Several studies about the

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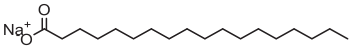
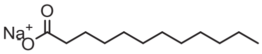
Table 1
The types of organoclay samples produced and the properties of intercalating agents used.

Sample	Intercalating agent				
	IUPAC Name	Molecular and structural formulas, molar mass	Amount		
			$mmol.g^1$ Na-MMT	mM	Multiples of CEC of Na-MMT
OMMT-SOD1	Na salt of octadecanoic acid (SOD)	$C_{18}H_{35}OO^-Na^+$  (306.47 gmol^{-1})	3.3	393	2.3
OMMT-SOD2			6.6	787	4.5
OMMT-SDD1	Na salt of dodecanoic acid(SDD)	$C_{12}H_{23}OO^-Na^+$  (222.32 gmol^{-1})	4.5	540	3.1
OMMT-SDD2			9.0	1080	6.2

modification of MMT with different organic products have been reviewed in the literature [13,22–24].

In practice, the use of the organoclays prepared by alkyl ammonium or alkyl phosphonium salts to manufacture polymer-clay nanocomposites is limited by the clay properties. For instance, the alkyl ammonium salts decompose above 170–180 °C and are not suitable for high temperature melt processing techniques. The decomposition products impart an undesirable color, odor and taste. Dissolution of phosphonium salts in water is quite low, so the removal of remainder salts by water is difficult. The commercial availability of quaternary ammonium compounds and phosphonium compounds is limited, mainly because these compounds are used in the detergent and cosmetic industries [25–27].

Another method for modifying the surface of MMT clays involves the use of anionic surfactants. These surfactants contain groups that possess a partial negative charge. Several research papers explain the successful intercalation of various organic anions, including polymeric anions, sulfates, sulfonates, and carboxylates [24,28–32]. The intercalation mechanism of anionic surfactants in MMTs significantly deviates from the conventional cation exchange reactions of MMT with alkyl ammonium salts. The driving forces for the adsorption and intercalation of anionic surfactants in clays occur by ion–dipole attraction to the cations on the surface and by replacing the structural OH groups at the edges and interlayers. This bonding phenomenon was first reported for various glycols by Bradley and later became a standard method for the identification of smectite clays [28].

The interactions of long chain carboxylic acid complexes with divalent montmorillonite (e.g., Ca-MMT) were first reported by Brindley and Moll [33] and were later investigated by many researchers [34–40]. The intercalation of salts of carboxylic acids for divalent MMTs was more successful than the intercalation of monovalent MMTs. The interlayer spacing of the former was measured in the range of 2.5 nm to 4.3 nm, and the interlayer spacing of the latter was 1.50 nm to 1.55 nm [34,36]. This significant difference in the extent of intercalation was explained by the formation of stronger ion-dipole attractions between the divalent cations with the carboxylate compared to the similar attractions with the monovalent cations in Na-MMT. Determination of the optimum intercalating agent-clay combination continues to draw attention as an open-end research topic for developing organoclays that are applicable in various industrial processes.The objective of our study is to modify Na-MMT by reacting it with sodium salts of long chain fatty acids, i.e., a sodium salt of octadecanoic acid (SOD) and of dodecanoic acid (SDD) at two different concentrations, for the production of effectively intercalated and thermally stable organophilic clays. The detailed characterization of the organoclays produced were performed by X-ray diffractometer (XRD), Fourier transform infrared spectrometer (FTIR) and thermogravimetric (TG) analyses. High resolution tunneling electron microscopy with an energy dispersing spectrometer (TEM-EDS) and scanning electron microscopy (SEM) were also used to look for the most convenient precursors for the polymer–clay nanocomposites. In addition to characterization of the organoclays, their applicability in the production of polyurethane nanocomposite foam was also tested.

2. Experimental

2.1. Materials

In the experimental study, Na-MMT clay was organically modified with sodium salts of two fatty acids: octadecanoic acid (common name: stearic acid) and dodecanoic acid (common name: lauric acid). The salts of these fatty acids develop into suitable intercalating agents for MMT type clays because of their long chain molecules with hydrophilic carboxyl heads and organophilic nonpolar alkyl tails (see Table 1). They are stable, cheap and are widely available.

Sodium salt of octadecanoic acid (SOD) and sodium salt of dodecanoic acid (SDD) (see Table 1) were prepared by reacting molten octadecanoic acid or dodecanoic acid with NaOH at a 1:1 molar ratio while stirring the mixture in a beaker at 50 °C and 500 rpm for 30 min. Once the exothermic reaction started, heating was stopped.

The Na-MMT, Nanocor®, was purchased from AMCOL International Corporation, which provided a list of the properties of Na-MMT. The specific gravity was 2.6. The maximum moisture content was 12%, The pH of the 5% dispersion was 9.5–10.5. The aspect ratio (length/width) was 200–400, and the cation exchange capacity (CEC) was 1.45 cmol kg^{-1} (145 meq/100 g). The mean particle size, which was measured by a Malvern Mastersizer 2000 at a beam length of 2.40 μm, was 1.41 μm, where 90% of the particles had a size equal to or less than 2.81 μm.

The rest of the chemicals used in the experiments were technical grade and commercially purchased from Merck Co.

2.2. Preparation and characterization of the organoclay samples

The following organic modification experiments were conducted to alter the character of the surface from hydrophilic to organophilic and to expand the MMT interlayer as much as possible.

To emulsify SOD or SDD and to disperse the clay particles in the colloidal mixture, 150 mL of 0.14 M SDS (aq) (Na salt of 4-dodecylbenzene sulfonic acid; $CH_3(CH_2)_{11}C_6H_4SO_3{}^-Na^+$) was blended with 18 g of dried Na-MMT [33,40]. The colloidal dis-