

## Research paper

## Pre-exfoliated nanoclay through two consecutive reaction systems: Silane functionalization followed by grafting of amino acid monomers



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## ABSTRACT

This work presents a novel way to produce a thermally stable nanoclay with an increased interlayer space, which are the essential requirements in fabricating clay-polymer nanocomposites. Sodium montmorillonite (Na-Mt) was functionalized through two separate, consecutive reaction systems. Functionalization with an aminosilane was first performed, in order to produce reactive groups at the silicate nanolayers. In the second step, amino acid monomers were employed for a further reaction with silane-modified nanoclay. X-ray diffraction results demonstrated an increased  $d_{001}$ -value (24 Å) using 10 mmol  $\gamma$ -aminobutyric acid. The 001 reflection peak disappeared when 5 mmol  $\omega$ -aminoundecanoic acid/g Mt was used as the second type of amino acid. Transmission electron microscopy images of modified Mt with 10 mmol  $\omega$ -aminoundecanoic acid exhibited a well separated or exfoliated structure of nanolayers. Thermogravimetric measurements indicated a trend of increasing thermal stability of the modified nanoclays (350 °C to 400 °C) with increasing amounts of initial  $\omega$ -aminoundecanoic acid. Based on these results, optimizing the modifiers and synthesis conditions can control the properties of modified nanoclay. Tensile modulus and strain at break of HDPE/2 mass% modified Mt showed 10% and 14% enhancements, respectively, due to the increased  $d_{001}$ -value of the nanofiller, which results in greater filler-polymer interaction.

## 1. Introduction

Over the last 20 years, researchers have investigated modifications of layered silicates as reinforcements for polymers (Pavlidou and Papaspyrides, 2008). The unique layered structure, high aspect ratio, and nanoscale distribution of nanoclays provide enhanced mechanical, thermal, and gas barrier properties in polymer nanocomposites (Sinha Ray and Okamoto, 2003). This has sparked numerous companies to conduct research and analyze the efficacy of nanosilicates compared to other nanofillers. Currently, one of the most commonly used nanofillers in the production of polymer nanocomposites is montmorillonite (Mt) from the smectite family. A regular arrangement of two silicon tetrahedral ( $\text{SiO}_4^{4-}$ ) and one aluminum octahedral ( $\text{Al}(\text{OH})_3^{6-}$ ) layer forms the unit cell structure of the Mt, with oxygens forming the corners and cations residing in the center (Zanetti et al., 2000). The tetrahedral coordination contains smaller metal ions such as  $\text{Si}^{4+}$ , while the octahedral coordination possesses larger metal ions such as  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Mn}^{2+}$ . Clay minerals can have a deficit of positive charges, which is usually due to the substitution of  $\text{Si}^{4+}$  for  $\text{Al}^{3+}$  (Deer et al., 1992; Alexandre and Dubois, 2000; Gopakumar et al., 2002; Hotta and Paul, 2004; Zhang et al., 2006; Park et al., 2009; Piscitelli et al., 2010).

The negative charge is, in fact, neutralized with the placement of cations such as  $\text{Li}^+$ ,  $\text{Na}^+$  or  $\text{Ca}^{2+}$  within the interlayer spaces of nanosilicates (Alexandre and Dubois, 2000; Zanetti et al., 2000; Fornes et al., 2002; Hotta and Paul, 2004; Mehrabzadeh and Kamal, 2004; Chen et al., 2005; Bergaya and Lagaly, 2006; Zhang and Sundararaj, 2006; Di Gianni et al., 2008; Lakshminarayanan et al., 2009; Huskić et al., 2013). Silanol groups, which reside most commonly at the edges of the nanoclay, can act as reactive sites when other reactive moieties are present in the system (Herrera et al., 2005; Choi et al., 2009; Alvi et al., 2013).

Superior properties in clay-polymer nanocomposites are usually generated by the homogeneous dispersion of silicate layers throughout the matrix (Gopakumar et al., 2002; Burgentzlé et al., 2004; Zhang and Sundararaj, 2006; Choi et al., 2009). However, poor interfacial interactions between the hydrophilic layers of nanosilicates and the hydrophobic organic polymer matrix hinder the dispersion of individual nanolayers throughout the polymer (Sinha Ray and Okamoto, 2003; Hotta and Paul, 2004; Zhao et al., 2005; Zhang and Sundararaj, 2006). This problem can be resolved, at least in part, by adding a swelling agent, functionalizing the clay mineral, or both, in order to achieve organically modified Mts prior to adding it into the polymers (Hotta and Paul,

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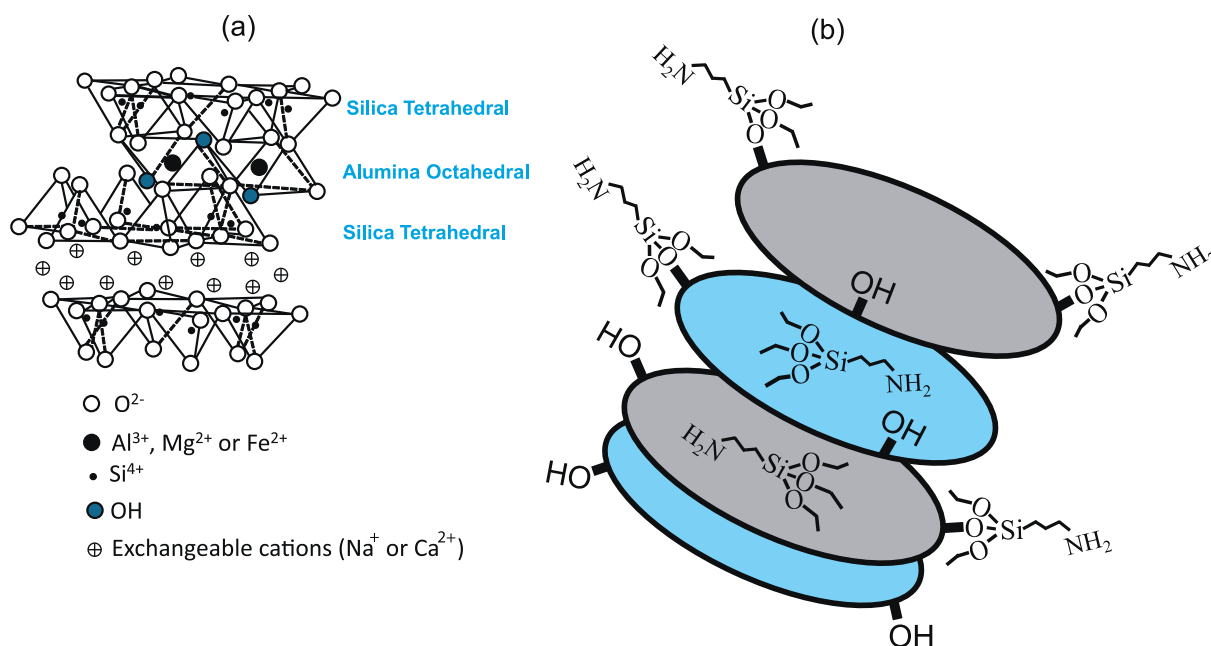


Fig. 1. a) Crystalline structure of Na-Mt, and b) silane-functionalized nanoclay.

2004; Mehrabzadeh and Kamal, 2004; Chen et al., 2005; Negrete-Herrera et al., 2006; Park et al., 2009).

The conventional method used to prepare organophilic Mt is the cation exchange reaction with quaternary ammonium or phosphonium salts. However, this type of surface modification does not provide an efficient or thermally stable bond with nanoclay particles (Calderon et al., 2008). To address this gap, the functionalization of Mt with silane coupling agents has attracted great interest in the last few years (Shanmugharaj et al., 2006; Alvi et al., 2013; Huskić et al., 2013; Bertuoli et al., 2014). The organosilanes have an organic part and three hydrolysable substituents that can be hydrolyzed on the nanolayer surfaces, as shown in Fig. 1.

Previous works have found that silane modification has advantages, such as converting the hydrophilic interlayers to an organophilic surface, producing chemical bonds at the interface, and creating higher thermal stability than commonly used commercial surfactants at the polymer processing temperature (Herrera et al., 2005; Ha et al., 2010; Piscitelli et al., 2010; Alvi et al., 2013). In addition, silane coupling agents can increase the interlayer space by intercalating the interlayer spaces, or chemically reacting at the edges (Huskić et al., 2013). However, the interlayer space is still too small for polymer chains to diffuse into that space. Therefore, an additional modification technique combined with silane functionalization is required to increase the interlayer spacing, leading to increased diffusion of the polymer chains into the interlayer spaces.

When aminosilane is chosen, the amine end groups of silane molecules can react with other reactive groups (e.g., carboxylic acid) that are available in other monomers. The reacted monomers act as spacers, further separating the layers. Hydroxy acids and amino acids have reactive carboxylic acid groups that can react with amine end groups of attached silane (Alvi et al., 2013). The grafting procedure is similar to a step growth polymerization system, in which a condensation reaction occurs between amine end groups of silane coupling agents and carboxylic acid moieties.

In this study, silane-functionalized Mt was synthesized using  $\gamma$ -aminopropyltriethoxysilane ( $\gamma$ -APTES) as the first step of the modification. The silane-functionalized nanoclay was purposely synthesized to enable the Mt to have reactive end groups that can react with carboxylic acid end groups of other monomers such as amino acid monomers. In the second step, the silane-functionalized clay reacted

with the amino acid monomers dispersed in the system. Thus, the intercalating effect was stronger and more permanent, due to covalent bonding. This resulted in thermally stable nanoclay with large interlayer spaces.

To the best of our knowledge, this is the first research study that has enhanced the interlayer space of the nanoclay by grafting amino acid monomers onto an aminosilane-functionalized Mt.

## 2. Materials and methods

### 2.1. Materials

Sodium montmorillonite (Na-Mt) was obtained from Southern Clay Products Inc., USA, under the trade name of Cloisite <sup>®</sup>Na<sup>+</sup>, having a cation exchange capacity (CEC) of 92.6 milliequivalent (meq)/100 g clay. The trifunctional  $\gamma$ -APTES silane coupling agent was purchased from Gelest Inc., USA.  $\gamma$ -aminobutyric acid (> 99%),  $\omega$ -aminoundecanoic acid (> 99%), ethanol (denatured, reagent), tetrahydrofuran (THF - ACS Reagent), hydrochloric acid (HCl, 35%), and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95%) were all purchased from Sigma-Aldrich. High density polyethylene (HDPE), an ethylene-octene copolymer, with a density of 0.94 g/cm<sup>3</sup> and a melt index of 3.5 g/10 min (RMs341-U, SURPASS, NOVA Chemicals, Calgary, Canada) was used to produce HDPE/clay nanocomposites. Cloisite 20 (BYK Additives and Instruments, USA) with density = 1.77 g/cm<sup>3</sup> was used as a commercial nanoclay to compare the mechanical results.

### 2.2. Silane functionalization of Na-Mt

The silane functionalization of Na-Mt was carried out in ethanol. Two grams of Na-Mt were dispersed in 200 mL of medium in a 500 mL beaker and sonicated for 1 h at room temperature, allowing the nanosilicates to swell inside the medium by intercalation of solvent molecules into the interlayer spaces. The pH was adjusted to 4 using a 1 M solution of HCl. Next, the dispersion was transferred to a 500 mL three-necked flat bottomed flask at 80 °C. A concentration of 4.5 millimoles of  $\gamma$ -APTES coupling agent per gram of the clay mineral (mmol/g Mt) was introduced drop-wise to the magnetically stirred dispersion using a dropping funnel.

The silane reagent was introduced into the mixture at

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