



Research paper

Silane functionalization of sodium montmorillonite nanoclay: The effect of dispersing media on intercalation and chemical grafting

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ABSTRACT

This study investigated the effect of various dispersing media on the silane functionalization of sodium montmorillonite nanoclay (Na–Mt) to evaluate each medium's effectiveness on the intercalation and chemical grafting of silane coupling agent. The amount of intercalation was estimated using the equation that was developed in our previous work based on thermogravimetric analysis. The results showed that the amount of silane intercalation was the greatest for water and glycerol media (≈ 1.582 mmol/g clay and ≈ 1.480 mmol/g clay, respectively), which was in agreement with the d_{001} -values calculated by the XRD analysis (≈ 19.6 Å and ≈ 14.4 Å, respectively). ^{29}Si NMR results showed a new T site in addition to Q peaks for all modified nanoclays in different dispersing media, indicating the occurrence of silane chemical grafting at the surface of the nanolayers. The $\frac{A_{T3}}{A_{Q3}}$ in NMR spectra was used to compare the amount of chemically grafted silane in different dispersing media, a new approach for Mt material. Hydrogen-bonding solvents (water, glycerol and ethanol), and polar solvents (DMF and THF) showed greater T³ peak intensities compared to other dispersing media, indicating higher amounts of chemical grafting of silane molecules. This observation was in agreement with the broadening of FTIR peak at $1130\text{--}1000\text{ cm}^{-1}$ which is explained by the formation of extra Si–O–Si bonds; that is, in turn, due to silane chemical grafting at the surfaces of the nanolayers. The silane-nanofiller interactions were correlated with the Hansen solubility parameters of different dispersing media used for the modification. This research has potential to help design and improve the nanoclay modification processes, which are used in the fabrication of clay-polymer nanocomposites.

1. Introduction

Layered silicate nanofillers have received attention in both academia and the polymer industry over the past few decades due to their unique nanoscale sheet-like structure (Bergaya and Lagaly, 2001; Zhang and Sundararaj, 2006). Numerous efforts have been made to synthesize clay polymer nanocomposites (CPNs) by embedding nanosilicate particles into polymers (Pavlidou and Papaspyrides, 2008). Adding a small amount of this high aspect ratio nanofiller gives rise to improved mechanical, thermal, and gas barrier properties (Mehrabzadeh and Kamal, 2004). This opens new pathways in the design and synthesis of novel and high-performance functionalized nanoclays, which can be used in the production of CPNs (Piscitelli et al., 2010).

Montmorillonite (Mt) is presently one of the most widely used layered silicates in the manufacture of CPNs (Fornes et al., 2002; Gopakumar et al., 2002; Wang et al., 2002; Lew et al., 2004; Hottal and Paul, 2004; Lakshminarayanan et al., 2009). The unit crystal structure of Mt is based on a regular arrangement of two silicon tetrahedral

SiO_4^{4-} sheets and one aluminum octahedral ($\text{Al}(\text{OH})_6^{3-}$) sheet. The surfaces of the Mt layers have negative charges because of the substitution of Mg^{2+} for Al^{3+} . These negative charges are counterbalanced by the first-group cations (e.g., sodium) in the proximity of the clay layers inside the interlayer spaces (Zhang et al., 2006). These charges induce a polarity in the pristine structure (such as sodium Mt [Na–Mt]) consequently making the silicate layers incompatible with the vast majority of organic polymers (Zanetti et al., 2000). Dispersing the unmodified Na–Mt in a polymer matrix will not result in a CPN with enhanced properties compared to the original polymer matrix. This is due to poor interfacial interactions between the hydrophilic Mt and the hydrophobic polymeric matrix (Ray and Okamoto, 2003). Typically, CPN formation requires a wide-ranging delamination or an extensive dispersion of the clay nanosheets throughout the polymer matrix, as well as good interfacial interactions between the two phases (Xidas and Triantafyllidis, 2010). To produce CPNs, then, it is important to modify the clay nanolayers. Numerous studies have investigated reducing the hydrophilicity of Na–Mt, in particular,

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modifying with surfactants (such as alkyl ammonium salts) via a cation exchange process (Zanetti et al., 2000; Zhao et al., 2005; Zhang et al., 2006; Huskić et al., 2009; Xidas and Triantafyllidis, 2010). This type of modification increases the size of the interlayer spaces, and provides a hydrophobic environment (He et al., 2005; Mandalia and Bergaya, 2006). Nevertheless, alkyl ammonium surfactants have only electrostatic interactions with the clay nanolayers. The electrostatic interactions between surfactants and the nanolayers can debond during the processing of polymers under high processing temperatures (Xie et al., 2001; Piscitelli et al., 2010). Therefore, chemical functionalization (e.g., silanization), which encompasses the chemical grafting of thermally stable silane coupling agents onto the clay platelets, have drawn increased interest (Su et al., 2013; Su et al., 2012; He et al., 2013). The chemical modification techniques make inorganic nanolayers and the organic polymer matrix compatible (Shimajima et al., 2001; Herrera et al., 2004; Chen et al., 2005; Gianni et al., 2008; Choi et al., 2009; Park et al., 2009; Ha et al., 2010; Piscitelli et al., 2012; Huskić et al., 2013). Broken bonds at the edges of the platelets are very common in layered silicates, leading to the formation of reactive hydroxyl groups that can be used for the silylation reaction (Herrera et al., 2004; Zhao et al., 2004; Tao et al., 2016; Asgari et al., 2017). A schematic representation of the layered silicate clay structure and the silylation reaction are shown in Fig. 1.

The silylation of layered silicates occurs at three sites: in the interlayer spaces, on the external surfaces, and at the edges (Piscitelli et al., 2010). Unmodified Mt swells in water, forming a suspension. When the clay concentration is high enough, a continuous structure appears due to the propensity of clay platelets to form a network. This leads to a gel-like behavior (Burgentzlé et al., 2004; Herrera et al., 2005; Shanmugaraj et al., 2006). This phenomenon occurs in water more than any other dispersing media, due to the extremely hydrophilic structure of clay. Using water as the dispersing medium leads to greater swelling, intercalation, and also the arrangement of the organic species, and consequently, results in a larger d_{001} -value (Burgentzlé et al., 2004). However, controlling the gel system during the modification is challenging, which necessitates finding an appropriate organic medium to successfully modify the nanoclay. Additionally, increased interlayer space and high chemical grafting of the silane coupling agent are important for the nanofiller in polymer nanocomposite applications. This varies by using different media for the modification process. Despite

many studies in this area, the chemical grafting of coupling agents, such as silane, onto nanoclay is not well understood. When it comes to clay chemical modification, there is no comprehensive study that examines the influence of dispersing media on silane intercalation and chemical grafting, which are two important factors on producing hydrophobic nanoclays with increased d_{001} -values (Asgari et al., 2017). Because the clay structure is very hydrophilic, removing the water from the interlayer spaces in the drying stage is challenging. Clay that is modified in water medium shrinks due to strong water dipoles that remain between nanolayers (Deer et al., 1992). As a result, for the clay modification process, it is essential to find an appropriate organic medium with acceptable grafting efficiency for the silane coupling agent.

This research investigates the chemical modification of Na–Mt using trifunctional γ -aminopropyltriethoxysilane (γ -APTES) in the presence of various dispersing media. To compare the efficiency of various solvents on chemical grafting, different techniques are used to characterize the functionalized clay, such as Fourier transform infrared spectroscopy (FTIR) and solid state ^{29}Si nuclear magnetic resonance spectroscopy (^{29}Si NMR). Comparing the new T sites in the NMR spectra of silane-modified nanoclays shows the amounts of chemically grafted silanes. The $\frac{A_{T-3}}{A_{Q-3}}$ ratio in ^{29}Si NMR spectra allows comparison of these amounts. Thermogravimetric analysis (TGA) is applied to measure the amount of silane intercalation, using an equation that was developed in our previous work (Asgari et al., 2017). The amount of intercalation of silane coupling agents inside the interlayer spaces, which indicates the level of expansion of interlayer spaces, is correlated with d_{001} -values measured by X-ray diffraction (XRD). Additionally, the interactions between silane and the nanofiller are explained by the Hansen's solubility parameters of the dispersing medium.

2. Experiment

2.1. Materials

Sodium montmorillonite (Na–Mt), Cloisite $^{\circ}\text{Na}^+$, with cation exchange capacity (CEC) of 92.6 meq/100 g of clay was purchased from Southern Clay Products Inc., USA. The trifunctional γ -aminopropyltriethoxysilane (γ -APTES) agent obtained from Gelest Inc. was used without further purification. Toluene, ethanol, glycerol, acetone,

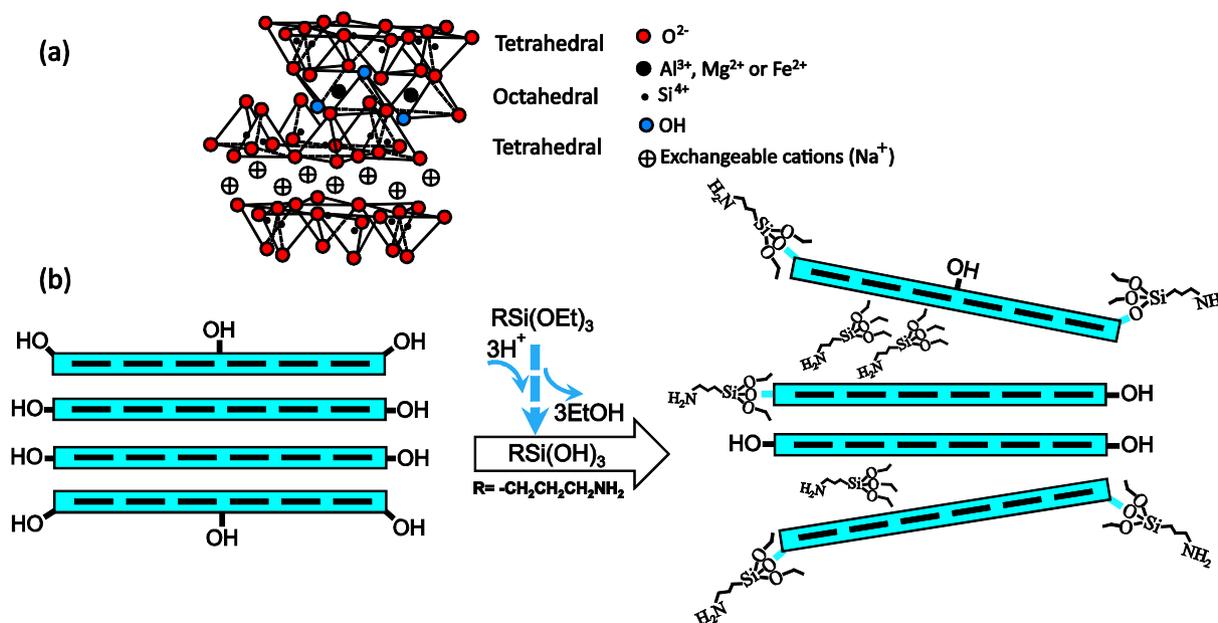


Fig. 1. (a) The structure of a layered silicate (b) Chemical silylation and intercalation of silane coupling agents inside interlayer space of nanosilicate sheets. Up to 3 groups can be reactive depending on the $-\text{OH}$ symmetry.

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