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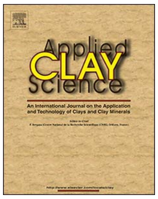

Research paper

Silane functionalization of sodium montmorillonite nanoclay and its effect on rheological and mechanical properties of HDPE/clay nanocomposites

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ABSTRACT

The present research reveals novel results about the silane functionalization of sodium montmorillonite (Na-Mt) by comparing the interlayer space and thermal stability of the nanofiller at different initial silane concentrations. XRD and TGA results indicate an increased d_{001} and a high thermal stability for the silane-modified Na-Mt, which makes it a promising nanofiller for polymer nanocomposites. The amounts of intercalation and chemical grafting are estimated from TGA results using equations developed in this work; the silane intercalation is found to be the highest (0.504 mmol/g clay) for 9 mmol/g clay initial silane concentration, which is consistent with the d_{001}-value (22.6 Å). Intercalation increases with increase in initial silane concentration up to 9 mmol (intercalated amount ≈ 0.504 mmol/g clay), then decreases at higher concentrations, e.g., 15 mmol silane have an intercalated amount of 0.405 mmol/g clay. However, the chemical grafting value for 15 mmol silane is greater (0.18 mmol/g clay) relative to that of the 9 mmol silane initial concentration (0.15 mmol/g clay). This can be explained by the occurrence of the side reactions at the edges for 15 mmol silane, which reduces the intercalation amount. The rheological and tensile properties of HDPE/silane functionalized clay suggest that the storage modulus, damping factor and mechanical behavior of the composites depend on the clay nanofiller, as well as the nanocomposite preparation procedure (i.e. masterbatch technique). The tensile modulus showed ~15% enhancement for 85%HDPE/15%PEMA/2% modified clay over the pure polymer. TEM images revealed a well-dispersed clay structure for the HDPE/2 wt% modified-clay/PEMA nanocomposite that is prepared through the masterbatch technique.

1. Introduction

The unique layered structure of silicate nanofillers has drawn attention in the past few decades for their outstanding structural properties due to their nanoscale plate-like geometry (Bergaya and Lagaly, 2001; Zhang and Sundararaj, 2006). Accordingly, polymer nanocomposites consist of a polymer matrix embedded with nanosilicate particles and can exhibit significant improvement in final properties over the pure polymer (Mehrabzadeh and Kamal, 2004; Bergaya et al., 2011). A trace (< 2 vol%) of these nanoparticles can potentially increase the mechanical, thermal, and gas barrier properties due to their exceptionally high surface area (Pavlidou and Papaspyrides, 2008). Montmorillonite (Mt) silicates have been extensively utilized in the synthesis of polymer nanocomposites (Lew et al., 2004; Calderon et al., 2008; Lee et al., 2010; Piscitelli et al., 2010; Ghasemi et al., 2012). Mt is a 2:1 clay, with 2 silicon tetrahedral [SiO_4^{4-}] sheets sandwiching a central aluminum octahedral [$Al(OH)_6^{3-}$] sheet. Due to the substitutions of Mg^{2+} for Al^{3+}, the Mt surface has a negative charge, which is usually counterbalanced by locating first-group cations, such as sodium, on the surface of the interlayer space (Fornes et al., 2002; Gopakumar et al., 2002; Wang et al., 2002; Hottal and Paul, 2004; Bergaya et al., 2006; Lakshminarayanan et al., 2009; Piscitelli et al., 2010). As a result, counterbalanced clays such as Na-Mt possess a highly polar structure due to these charges, which makes them incompatible with the vast majority of organic polymers (Zanetti et al., 2000; Zhang et al., 2006). The formation of polymer-clay nanocomposite necessitates an extensive delamination, exfoliation, and dispersion of clay platelets throughout the polymer matrix (Zhang and Sundararaj, 2006; Lee et al., 2010). In order to accomplish this, a strong interfacial interaction between the hydrophilic reactive sites of Na-Mt and the hydrophobic polymeric matrix molecules, is required to obtain enhanced properties (Ray and Okamoto, 2003; Piscitelli et al., 2010).

Therefore, modification of the internal and external platelets of nanoclays is critical to design and to produce polymer-clay nanocomposites that have appropriate properties for the final material application. Numerous studies have attempted to decrease the

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hydrophilicity of Na-Mt, particularly by modifying with surfactants (e.g., alkyl ammonium salts) via the cation exchange process (Zanetti et al., 2000; Xie et al., 2001; Ray and Okamoto, 2003; Zhao et al., 2005; Zhang et al., 2006; Xidas and Triantafyllidis, 2010). Nonetheless, in spite of producing a satisfactory hydrophobic structure, surfactants are not thermally stable because of their weak electrostatic attachment to the platelets (Zhang and Sundararaj, 2006; Calderon et al., 2008; Piscitelli et al., 2010; Ghasemi et al., 2012). Recently, chemical functionalization, such as silylation, has been used to form chemical bonds at the surface of platelets. Silylation includes the grafting of Na-Mt with highly thermal-resistant silane coupling agents. Silane grafting occurs on internal and external surfaces of platelets, and more significantly, at the broken edges of platelets, by silanes reacting with available hydroxyl groups (Mercier and Detellier, 1995; Shimojima 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). This type of modification produces an organophilic environment, and also yields higher thermal stability when compared to surfactants (Zhao et al., 2004; Chen et al., 2005; Herrera et al., 2006; Piscitelli et al., 2010). The organosilanes have an organic part and three hydrolyzable substituents. The hydroxyl groups existing at the damaged edges of the clay platelets are capable of reacting with multifunctional silane coupling agents through a hydrolysis reaction. The alkoxy groups of the trialkoxysilanes are hydrolyzed to form a silanol-containing species (Pavlidou and Papaspyrides, 2008). Either the formed SiOH groups in silane molecules, or the non-hydrolyzed $-SiOCH_2CH_3$ segments of silane coupling agents can condense with $-OH$ groups present at the edges to form $Si-O-Si$ bonds at the clay surface (Fig. 1) (Piscitelli et al., 2010).

It has been widely recognized that Mt swells in water and forms a stable suspension. If the clay concentration is high enough, the association of clay platelets induces a continuous structure with a gel-like behavior that assists the silylation reaction, leading to a higher grafting efficiency. However, controlling the gel-like behavior of nanosilicates in a water medium is challenging, especially on an industrial scale (Burgentzlé et al., 2004; Shanmugharaj et al., 2006). Some researchers have used a combination of ethanol and water, where the ethanol moderates the gel structure of suspended nanoparticles, and water increases the grafting efficiency by promoting the hydrolysis of silane molecules and their attachment to the silicate platelets (Burgentzlé et al., 2004; He et al., 2005; Herrera et al., 2005; Shanmugharaj et al., 2006). There is still much unknown about the optimum procedure for this process. Therefore, a comprehensive study of silane functionalization that examines the chemical grafting and intercalation of silane molecules in ethanol-water dispersing medium is required. In addition, the grafting of silane coupling agents onto silicate platelets must be performed to understand the effect of different initial silane concentrations.

In this work, the functionalization of Na-Mt nanoclay with trifunctional γ-aminopropyltriethoxysilane (γ-APTES) in ethanol/water was investigated. Different characterization techniques, such as Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), ^{29}Si nuclear magnetic resonance spectroscopy (^{29}Si NMR) and X-ray diffraction (XRD) were used to investigate the grafting process. We successfully developed two new equations to calculate the amounts of intercalation and chemical grafting. The amounts of intercalated and chemically grafted silane molecules were calculated based on thermal analysis. We also found out that there is an optimal amount of initial silane concentration to achieve desired thermal and clay interlayer spaces. The silane intercalation calculated using the developed equation was successfully correlated with the d-values measured via XRD. Polyethylene (PE) nanocomposites with 2 wt% of optimally modified nanoclay in presence and absence of a maleated PE with two different procedures were prepared and their rheological and mechanical properties were investigated.

2. Experimental

2.1. Materials

Sodium montmorillonite (Na-Mt) was obtained from Southern Clay Products Inc., USA, under the trade name of Cloisite® Na$^+$, and has a cation exchange capacity (CEC) of ~92.6 meq/100 g of clay. A trifunctional γ-aminopropyltriethoxysilane (γ-APTES) silane coupling agent was purchased from Gelest Inc., USA. Ethanol was obtained from Sigma Aldrich. A hydrochloric acid (HCl) solution (1 M) was used to adjust the pH (VWR, Edmonton, Canada). Methanol was also purchased from VWR. All chemicals were used as received, unless stated. High density polyethylene (HDPE) used in this study is a homopolymer (SCLAIR 19G, Nova Chemicals, Calgary, Canada). A maleic anhydride grafted HDPE (PEMA) with density of 0.95 g/cm^3 and a melt index of 12 g/10 min (DuPont Fusabond® E265, Ontario, Canada) was used as a compatibilizer.

2.2. Functionalization of Na-Mt

Na-Mt modification was performed using γ-APTES in a solution with volume ratio of 3:1 EtOH:Deionized water (DIW). 1 g of Na-Mt was dispersed in 100 ml of this medium in a 500 ml beaker, then sonicated for 1 h at room temperature with the aim of breaking clay tactoids and making the solvent molecules intercalate into the interlayer space. Afterwards, the pH of the suspension was reduced to 4 by means of a 1 M solution of HCl. Then, the suspension was transferred to a 500 ml three-neck flat-bottom flask, and the temperature was adjusted to 80 °C. The silane coupling agent was diluted in 50 ml of ethanol. The solution was added drop-wise to the Na-Mt suspension using a dropping funnel, and stirred in the flat-bottom flask within a time span of 5 h. Six different initial silane concentrations (1.4, 2.7, 3.6, 4.5, 9, and 15 millimoles γ-APTES per 1 gram clay (mmol/g clay)) were used. The reaction was carried out for 24 h at 80 °C. The grafting of γ-APTES molecules on the edges of platelets and the intercalation of the aminosilane inside the clay mineral structure produce hydrophobicity in the nanoclay. The intercalation of the silane molecules mainly occur by penetrating the interlayer space and forming a physical interaction between silanol

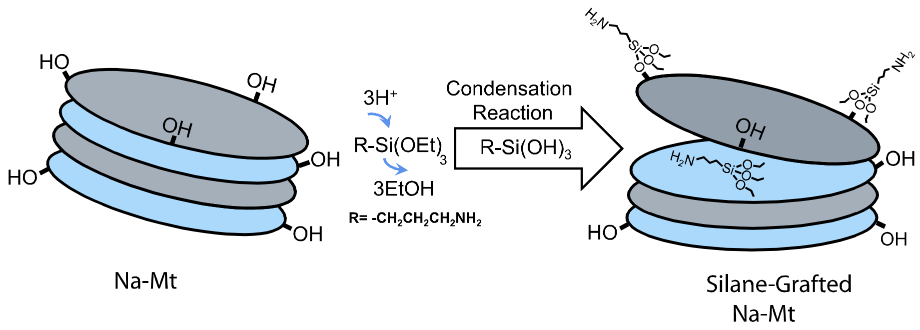

Fig. 1. Schematic representation of grafting of aminosilane onto the clay platelets.