



Research paper

Study of the modification of montmorillonite with monofunctional and trifunctional vinyl chlorosilane



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ABSTRACT

Montmorillonite (Cloisite®Na⁺) was modified with dimethylchlorovinylsilane (DMCVS) and trichlorovinylsilane (TCVS), in order to replace the silanol groups of clay mineral with silane vinyl groups (silylation reaction). The grafting reaction was studied using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). Variation of the grafted amount and the grafting yield was evaluated as a function of the initial silane concentration. The grafted amount was increased with both mono- and trichlorosilane concentrations; where, the reaction yield decreased. Since the reaction will liberate HCl, the effect of the presence of NaHCO₃ in the reaction media, was studied. Silylation with monofunctional silane leads to higher grafting amount compared to silylation with trifunctional one. The mechanism of silylation reaction was determined and the effect of the number of silane functional groups on the reaction mechanism was studied. The highest grafted amount and grafting yield were achieved with the initial silane concentration of ~4 mmol/g of DMCVS. The basal spacing of the silylated montmorillonites (Mt) was observed to be more than the basal spacing of pristine Mt.

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1. Introduction

Surface modification of clay minerals has been studied extensively since the produced clay minerals exhibit appropriate properties for many material science applications (He et al., 2013), such as clay polymer nanocomposites (CPNs), environmental materials and drug delivery systems (Isoda et al., 2000; Su et al., 2013). Recently, CPNs have received a widespread attention by scientists. Among all nanostructured materials, natural or synthetic layered silicates have been focused by several researchers to produce CPN (Carrado and Bergaya, 2007; Shanmugharaj et al., 2006). In general, the interface structure affects the properties of CPN. Therefore, controlling the interactions between inorganic and organic moieties is vital for the construction of CPN used for specific applications (Shimojima et al., 2001). In general, two main methods have been used for the modification of clay mineral surfaces: physical and chemical (He et al., 2013). Modifying clay minerals with various surfactants is the most widely used physical method to prepare inorganic/organic hybrid materials such as CPN (Greesh et al., 2008). In this method, surfactants enter the interlayer spaces and replace the initial inorganic cations. In this case, electrostatic force is the main linkage between the surfactant cations and clay

mineral. However, there are two main problems during the service life of CPN prepared with physically modified clay minerals. First is the pollution of the surrounding solutions due to leaching of the intercalated surfactant when the CPN is used as an adsorbent (He et al., 2013) and second is that the weak electrostatic interaction may lead to a distinguished interface between hydrophilic clay and hydrophobic organic material, which can result in a negative influence on the mechanical properties of CPN. Meanwhile, the edges of organoclays are still hydrophilic and hinder the intercalation of hydrophobic organic molecules. Therefore, aggregation and segregation of clay particles in the matrix would occur (Ray and Okamoto, 2003). During the last decade, great efforts have been made to develop novel methods like the modification or functionalization of clay mineral surfaces in order to solve the abovementioned problems (Avila et al., 2010). Silylation, also known as silane grafting, is proven to be an efficient method to modify the surfaces of clay mineral. In the modified clay minerals, the linkage between organic components and layered silicates via covalent bonds enables a long lasting immobilization of the reactive organic groups, preventing their leaching when the silane grafted clay minerals are applied in solutions (e.g. clay water soluble polymer nanocomposites) (He et al., 2013; Su et al., 2012). Moreover, when polymer chains are attached to the clay mineral surface via covalent bonds, the dispersion of modified clay minerals in the matrix improves (Roghani-Mamaqani et al., 2012).

One of the most extensively used layered silicates in CPN is montmorillonite (Mt), since it displays high in-plane strength, stiffness, and high

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aspect ratio. Mt is a member of smectite (2:1) family (Brnardic et al., 2008; Ruiz-Hitzky and Van Meerbeek, 2006; Utracki, 2004). In fact, 2:1 type layered silicates have a “sandwiched” structure as a $\text{Al}(\text{Mg})-\text{O}_4(\text{OH})_2$ octahedral sheet is enclosed by two Si–O tetrahedral sheets (Brigatti et al., 2006). Therefore, 2:1 clay minerals contain only two siloxane surfaces, which are the least reactive surfaces on clay mineral under ambient conditions (Schoonheydt and Johnston, 2006). In the previous studies, it was shown that hydroxyl groups act as the reactive sites on the silica surface in the grafting reaction between silane and silica. Although siloxane surfaces are the least reactive, similar to Si atom of silica, the structural defects in Si–O tetrahedral sheets (e.g., isomorphous substitution and vacancy) and the “broken” bonds of layer edges will obviously increase the reactivity of the siloxane surface and react with silane during the grafting reaction. Therefore, until now three basic types of interactions (interlayer, external surface, and “broken” edge grafting) between silane and swelling clay minerals such as Mt, under mild conditions (e.g., room temperature and no need of pre-intercalation) have been proposed (He et al., 2005, 2013). Organosilanes would be bonded onto clay mineral surfaces through a condensation reaction between the silanol groups of clay mineral surfaces and hydroxyl groups of hydrolyzed silanes (Su et al., 2013). Therefore, the organosilane should contain $\equiv\text{Si}-\text{X}$ groups (in which X could be OR, Cl, etc.) in order to participate in condensation reactions. Hence, these organoclays are very stable and the attached groups would be eliminated only after heating under combustion or pyrolysis conditions, in the presence and absence of oxygen, respectively (Ruiz-Hitzky and Van Meerbeek, 2006). The most common organosilane used in the recent studies for layered silicate silylation has been 3-aminopropyltriethoxysilane (Piscitelli et al., 2010; Shanmugharaj et al., 2006; Shen et al., 2009) and silylation with chlorosilanes has been rarely studied.

In the silylation process, several parameters such as the initial amount of organosilane, reaction duration, solvent type and number of active functional groups of organosilanes would affect the reaction procedure as well as the product properties. Some of these effects have been studied so far. However, getting a foregone conclusion is still a challenging task and some results are contradictive (Herrera et al., 2005; Shanmugharaj et al., 2006; Shimojima et al., 2001; Su et al., 2012, 2013). Accordingly, studying the effects of these parameters on the silylation reaction of different organosilanes seems essential.

In this work, the chemical modification of Mt using dimethylchlorovinylsilane (DMCVS) and trichlorovinylsilane (TCVS), respectively as monofunctional and trifunctional silanes, is investigated. Additionally, the effects of silane concentration and also the presence of

sodium hydrogen carbonate in the reaction media on the basal spacing and grafting amount of clay mineral are studied. A comprehensive study is also conducted on the effect of silane functionality on the silylation reaction, the clay mineral basal spacing and grafting. Chemical grafting of Mt has been clearly confirmed by FTIR and TGA curves. Interestingly, the product of silylation is a vinyl-modified clay which can easily be applied in in-situ polymerization reactions of different polymers.

2. Experimental

2.1. Materials

The commercial clay mineral, Cloisite®Na⁺ (Mt) (Southern Clay Products Inc., Texas, USA), is a natural Mt. trichlorovinylsilane (TCVS) (Alfa Aesar Company, UK), sodium hydrogen carbonate (NaHCO_3), acetone (Merck Co., Germany), and dimethylchlorovinylsilane (DMCVS) (Sigma-Aldrich Co., USA) used in this study were reagent grades and were used without further purification. Molecular structure of the silanes and Mt is shown in Fig. 1.

2.2. Grafting process

Before silylation, Mt was dehydrated under vacuum at 130 °C for 2 h. The grafting reaction was carried out in acetone media with the necessary amount of mono- or trichlorosilane in the presence and absence of NaHCO_3 . In a typical run, 1.5 g of Mt and 6.3 g (75 mmol) of NaHCO_3 were dispersed in 90 mL of acetone in a 200 mL three-neck round bottom flask. The mixture was vigorously stirred for 15 min under nitrogen. Then, the required amount of the coupling agent (i.e. [silane] = 4 mmol/g) was instantly added to the dispersion and the mixture was refluxed for 24 h at room temperature. To avoid the risk of the decomposition of NaHCO_3 at 50 °C, the temperature was not allowed to go above 50 °C. The product was centrifuged and then successively washed with acetone and acetone/ H_2O mixture (50/50 v/v%) in order to remove the unreacted silane and sodium hydrogen carbonate, respectively. Afterward, the mixture was centrifuged and dried under vacuum at room temperature. All samples were named according to the silane type, silane content and presence of sodium hydrogen carbonate, as reported in Table 1.

2.3. Characterization

FTIR spectra of samples prepared as KBr pellets were recorded on a Bruker/Alpha FTIR spectrophotometer, within a range of 500–4000 cm^{-1} using a resolution of 4 cm^{-1} . An average of 32 scans has been reported for each sample. Cell path length was kept

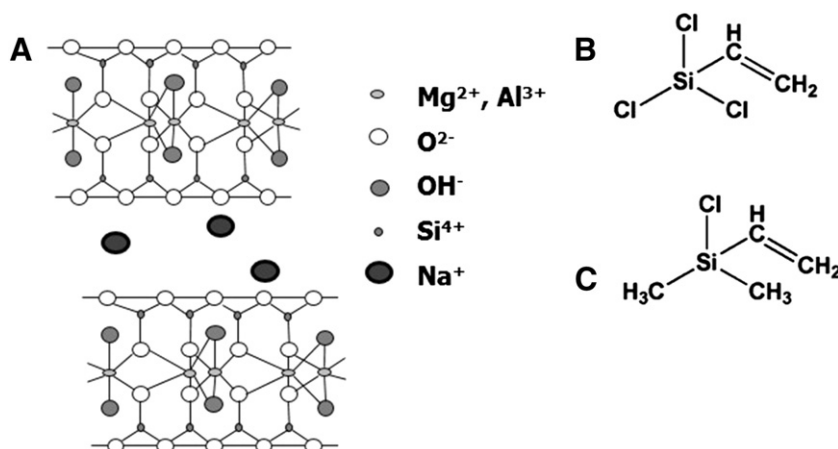


Fig. 1. Schematic of a) Mt, b) trichlorovinylsilane and c) dimethylchlorovinylsilane.

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