



Research paper

# Structure and properties research on montmorillonite modified by flame-retardant dendrimer



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## ABSTRACT

A novel approach to highly branched polymer chains for making advanced flame-retardant organoclays (OC) was presented. In this effort, a series of dendrimer based montmorillonite (Mt) were synthesized by tetrahydroxymethyl phosphonium chloride (THPC), N, N-dihydroxyl-3-aminomethyl propionate, and boric acid. Mt was first modified by THPC, and organic Mt (OMt) was obtained. Three generations of dendrimer modified organic clay minerals, DOMt-1, DOMt-2, and DOMt-3, were successfully prepared by OMt and the monomer prepared. Their chemical structures were characterized by FTIR, <sup>1</sup>H NMR, elemental analysis, XRD, and TGA. These DOMts had expanded interlayer space and possessed good thermal stabilities. With an increase of generations, the thermal stability was not further enhanced for highly branched polymers due to the increasing content of C–H bonds. These DOMts were terminated by boric acid, and a flame-retardant and dendrimer modified OMT (FR-DOMt) was successfully prepared. Experiments demonstrated that this FR-DOMt had better thermal stability and larger d-value due to steric hindering and thermal stability of the surfactant. The chemical structure and properties of FR-DOMt were valuable for its further applications.

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## 1. Introduction

Montmorillonite, a 2:1 clay mineral is a member of the smectite group. Its layer consists of two tetrahedral sheets sandwiching a central octahedral sheet (Brigatti et al., 2013). Due to substitutions of structural cations in the layers by cations of lower valency, a negative charge of the layers arises. This charge is compensated by cations (sodium ions in case of Na<sup>+</sup>-Mt) in the interlayer space and on the external surface. These cations are exchangeable, which is the reason for the high adsorption capacity of Mt for cations (cation exchange capacity, CEC). In addition to the exchangeable cations, the interlayer space of Mt contains a varying amount of water. The variation of interlayer water content results in variations of d001-value and swelling pressure of the clay mineral. Although the adsorption capacity of Mt for cations is very high, its adsorption capacity for anions is generally very low. This can be altered through an exchange of the inorganic cations with organic cations resulting in so-called organically modified clay mineral (Bergaya et al., 2011; Lambert and Bergaya, 2013). This organically modified clay mineral has a high adsorption capacity for anions but a decreased swelling pressure.

Different surfactants have been used to prepare organoclays (OC). These include single and dual cationic surfactants (Wang et al., 2004; Yilmaz and Yapar, 2004), anionic–cationic surfactants (Zhu and Chen, 2000), and nonionic surfactants (Shen, 2001). Cationic surfactants are commonly used to render the clay mineral surface hydrophobic prior

to its being used for the preparation of clay polymer nanocomposite (CPN) (Carrado and Bergaya, 2007; Nalwa, 2004). In practice, the use of OC prepared by alkyl ammonium salts to manufacture CPN is limited by the clay properties. For instance, the alkyl ammonium salts decompose about 170–180 °C and are not suitable for high temperature melt processing techniques. The decomposition products impart an undesirable color, odor, and taste. Efforts have been made to synthesize thermally stable OC based on stibonium (Wang and Wilkie, 2003), phosphonium (Arroyo et al., 2006), or imidazolium surfactants (Bourbigot et al., 2003).

Recently, a new class of macromolecules, dendrimers, has received more attention due to their special structures, such as porous and three-dimensional networks, plenty of functional end groups, difficult to crystallize, and high compatibility with other polymers (Tan and Luo, 2002). Dendrimers exhibit characteristics features of both molecular chemistry and polymer chemistry. Molecular chemistry like properties are due to their step by step controlled synthesis while it shows polymer chemistry like properties as it is made up of monomers (Dasgupta et al., 2002; Malik et al., 2012). Chen et al. (2010) prepared PAMAM dendrimers with different generations. Two generations of PAMAM dendrimers, D-0 and D-2, were used to intercalate Na<sup>+</sup>-Mt. Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) indicated that all PAMAM had exchanged with Na<sup>+</sup> ions in Na<sup>+</sup>-Mt. Then, Mt polycarbonate (PC) nanocomposites were prepared by melt intercalation process. The XRD curves showed that the molecular chains of PC had successfully intercalated into the interlayer space of Na<sup>+</sup>-Mt and DOMt. Azzouz et al. (2010) reported that microporous OMT bearing weak base OH sites were prepared through Mt intercalated with

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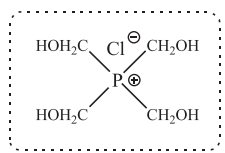
polyol dendrimers at different proportions (0.5, 1.0, and 3.0 mass%). These materials turned out to be suitable for the reversible capture of carbon dioxide, inasmuch as high amount (0.5–2.5 mmol/g OMT) of CO<sub>2</sub> can be retained, and easy regeneration can be achieved upon heating up to 100 °C. Garea et al. (2013) developed some new hybrid hosts based on dendrimers and Mt designed for 5-Fluorouracil drug encapsulation. These hybrid systems combined the advantages of polymers with the features of inorganic component. The UV–vis results showed that the dendrimer involved in the hybrid hosts influenced the drug release.

To date no one has reported the use of flame-retardant polymer for the fabrication of dendrimer modified clays. Here, the present study described preparation and characterization of dendrimer modified OC. The dendrimer containing phosphorus and boron elements behaved like a surfactant for surface modification. The flame-retardant and smoke inhibition effects of phosphorus, boron, and silicon elements in Mt and dendrimers can be used to fabricate a new type of enhanced CPN. First, THPC modified Mt (OMt) was prepared by ion exchanging between phosphonium ions in THPC and Na<sup>+</sup> ions in Mt. Then, three generations of DOMt were prepared by condensation polymerization between OMT and the monomer synthesized. Last, the intermediate reacted with boric acid, and a novel flame-retardant and dendrimer modified OMT (FR-DOMt) was thus obtained. The structure and properties of OMT, the intermediates, and FR-DOMt were evaluated by FTIR, <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR), elemental analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), XRD, and thermogravimetric analysis (TGA). Results revealed that the use of dendrimers can increase the d001-value and thermal stability of OC.

## 2. Experimental

### 2.1. Materials

Na<sup>+</sup>-Mt (SMP, cation exchange capacity (CEC) = 100 mmol/g, denoted as Mt), industrial grade, was obtained from Zhejiang Fenghong Clay Company (Zhejiang, China). Its structural formula can be expressed as Na<sub>0.02</sub>K<sub>0.02</sub>Ca<sub>0.32</sub>[Fe<sub>0.41</sub>Mg<sub>1.18</sub>Al<sub>2.50</sub>][Si<sub>6.87</sub>Al<sub>0.08</sub>]O<sub>20</sub>(OH)<sub>4</sub>·nH<sub>2</sub>O, calculated from the chemical analysis. Tetrahydroxymethyl phosphonium chloride, denoted as THPC, chemical pure, was received from Shanghai Pengkai Chemical Industry Company (Shanghai, China). Its chemical formula is expressed as



Hydrochloric acid, chemical pure, 36–38%, was supplied by Yixing Second Chemical Agent Company (Jiangsu, China). Methyl acrylate, diethanolamine, methanol, toluene-*p*-sulfonic acid, and boric acid were supplied by Shanghai Guoyao Chemical Company (Zhejiang, China).

### 2.2. Preparation of OMT

The water solution of THPC (8.57 g) was stirred for 30 min, and the pH value was adjusted to 1.46 using diluted hydrochloric acid (Wang et al., 2013). A 500 ml of round-bottomed and three-necked flask with a mechanical stirrer, thermometer, and condenser with drying tube was used as a reactor. 40 g of Mt was gradually added to the prior prepared THPC solution. The resultant dispersion was vigorously stirred at

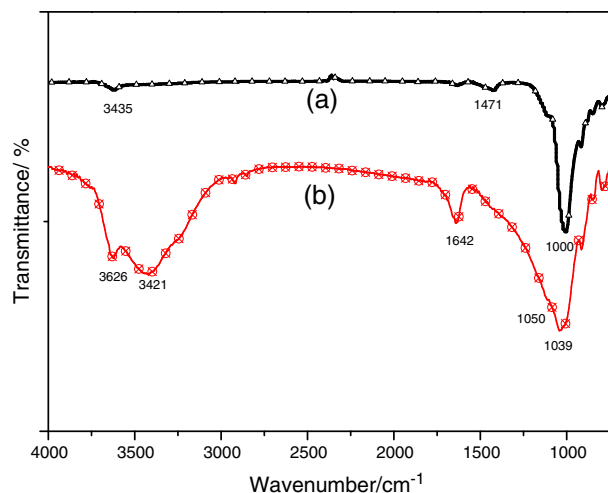
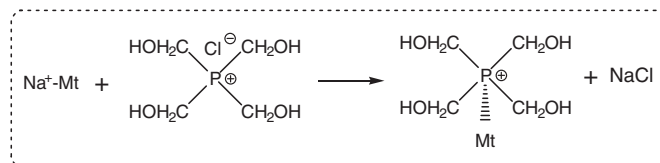


Fig. 1. FTIR spectra of (a) Mt, (b) OMT.

70 °C for 5 h. The treated Mt was repeatedly washed by de-ionized water. The filtrate was titrated with 0.1 N of AgNO<sub>3</sub> until no precipitate of AgCl was formed to ensure the complete removal of chloride ions. The filter cake was then placed in a vacuum oven at 65 °C for 12 h for drying. The dried cake was ground to obtain OMT. Yield: 80–90%.

### 2.3. Preparation of DOMt-1, DOMt-2, and DOMt-3

27.54 g of a prior prepared solvent of N,N-dihydroxyl-3-aminomethyl propionate (Wang et al., 2012) and 0.07 g of toluene-*p*-sulfonic acid were gradually added to above OMT. The resultant dispersion was vigorously stirred for 10 h. The treated clay minerals were repeatedly washed. The filter cake was then placed in a vacuum oven at 80 °C for 6 h for drying. The dried cake was ground to obtain DOMt-1. Yield: ~90%.



Scheme 1. Chemical formula for the reaction between Mt and THPC.

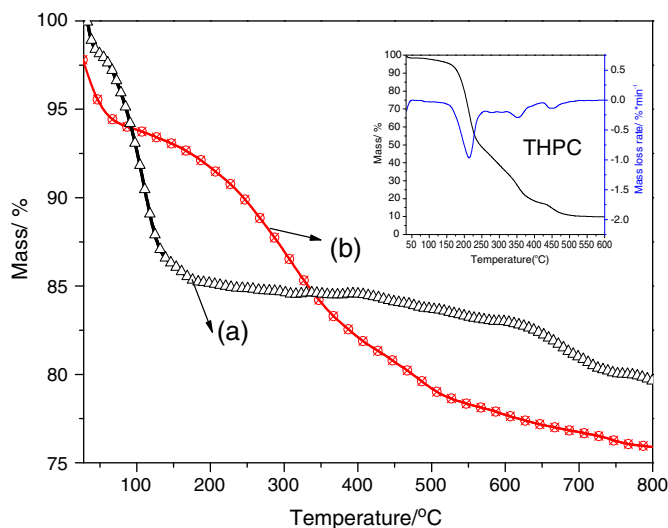


Fig. 2. TGA curves of (a) Mt, (b) OMT.

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