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# Preparation and characterization of phosphonium montmorillonite with enhanced thermal stability

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## Abstract

Quaternary phosphonium cations (hexadecyl tributyphosphonium; tetradecyl tributylphosphonium; tetraphenylphosphonium; methyl triphenylphosphonium; ethyl triphenylphosphonium and propyl triphenylphosphonium) were intercalated into montmorillonite (MMT) rich bentonite of Indian origin, by ion exchange reaction. The phosphonium MMT were characterized by Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction analysis (PXRD), particle size distribution (PSD) and thermogravimetric analysis (TGA). The phosphonium cations significantly influenced the particle size distribution. With longer alkyl chain finer particles were formed. The tetrabutylphosphonium and tetraphenylphosphonium MMT showed enhanced thermal stability (300–400 °C) and may be potentially useful materials for melt processing of polymer/layered silicates nanocomposites.

*Keywords:* Montmorillonite; Organoclays; Nanocomposites; Thermal stability; Phosphonium; Intercalation

## 1. Introduction

Organoclays have attracted substantial attention both in fundamental research and industrial applications because of their superior reinforcement properties (Carrado, 2001; Deniss et al., 2001; Lee and Lee, 2004). Compared to conventional filled polymers, clay/polymer nanocomposites can have enhanced mechanical properties, increased heat distortion temperature, improved thermal stability, decreased gas/vapour permeability and reduced flammability (Hasegawa et al., 1998; Takekoshi et al., 1998; Garces et al., 2000; Meier et al., 2001; Maguy et al., 2005). Several methods have been reported to synthesize clay/polymer nanocomposites; however, three methods (in situ polymerization, intercalation in solutions and melt processing) developed during the early stages of this field are widely applied (Garces et al., 2000). The melt processing technique is mostly used because this process played an important role in speeding up the progress of the commercial production of clay/polymer nanocomposites. Most of the commercially available organoclays are produced by exchange of alkali or alkali earth cations in the interlayer space of clay minerals with alkyl ammonium salts (Hasegawa et al., 1998; Garces et al., 2000; Klapyta et al., 2001; Maguy et al., 2005). Other cations, such as phosphonium, pyridinium and imminium have also been used due to their higher thermal stability (Takekoshi et al., 1998). Alkyl ammonium modified clays are thermally not very stable above 250 °C and start to degrade at nanocomposites processing temperature (200–300 °C). Therefore,

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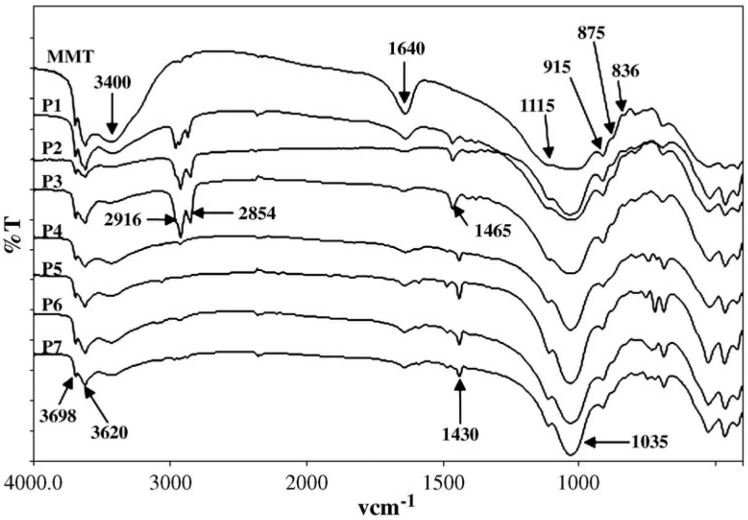

Fig. 1. FTIR spectra of upgraded bentonite and phosphonium MMT (P1, P2, P3, P4, P5, P6 and P7).

organoclays prepared using quaternary alkyl ammonium salts are less suitable for most engineering plastics with high processing temperature (Wu and Lerner, 1993; Wei et al., 2001a,b; Gao, 2002; Li and Ishida, 2002; Wang and Wilkie, 2003). The thermal stability of organoclays is improved by intercalating quaternary phosphonium salts (Wei et al., 2002). Degradation pathways and thermal stability depend on molecular structure. Nevertheless, the stability of phosphonium MMT is substantially decreased (70–80 °C) with regard to the parent phosphonium salt, necessitating future studies of the specific influence of the interlayer environment and aluminosilicate surface on reaction pathways.

In the present paper, we report the preparation and characterization of phosphonium MMT by the interaction of quaternary phosphonium salts with MMT rich bentonite clay of Indian origin with an objective to prepare organoclays with higher thermal stability. The thermal stability of the phosphonium MMT were correlated with different parameters of the phosphonium salts. We have selected three quaternary phosphonium salts similar to those reported by Wei et al. (2002) and compared them with four other quaternary phosphonium salts, which are not reported so far.

## 2. Experimental

### *2.1. Materials and methods*

The montmorillonite rich bentonite clay was collected at Akli mines, Barmer, Rajasthan, India. The bentonite was purified by sedimentation technique. The clay fraction was obtained by dispersing 150 g of bentonite in 10 l de-ionized water and collecting the supernatant dispersion of particles <2 µm after the calculated time (10 h) at a height of 15 cm at 30 °C according to the Stokes law of sedimentation. The slurry was then dried at 90 °C. The cation exchange capacity (CEC) of purified bentonite, measured by the standard ammonium acetate method, was 91 meq/100 g on dry basis (dried at 110 °C). The chemical composition of the purified bentonite was: 55.9% $SiO_2$, 20.9% $Al_2O_3$, 9.15% $Fe_2O_3$, 2.1% MgO, 2.8% CaO, 0.71% $K_2O$ and 0.73%$Na_2O$ with loss on ignition of 7.7%, and the ionic formula: $(Si_{3.7}\ Al_{0.3})\ (Al_{1.33}\ Mg_{0.21}\ Fe_{0.46})\ O_{10}\ (OH)_2 nH_2O \cdot Na_{0.094}$, $K_{0.06}$, $Ca_{0.20}$. The purified bentonite was rich in montmorillonite with $Na^+$ and $Ca^{+2}$ as exchangeable cations. The purified bentonite contained minor

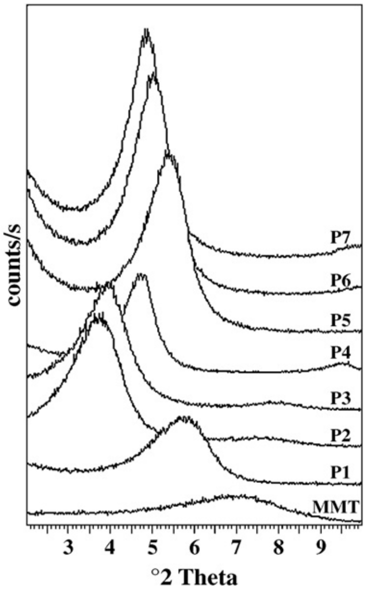

Fig. 2. PXRD of upgraded bentonite and phosphonium MMT (P1, P2, P3, P4, P5, P6 and P7).