

INFLUENCE OF MOLECULAR STRUCTURE OF QUATERNARY PHOSPHONIUM SALTS ON THAI BENTONITE INTERCALATION

CHUREERAT PRAHSARN^{1,*}, NANJAPORN ROUNGPAISAN¹, NATTAPHOP SUWANNAMEK¹, WATTANA KLINSUKHON¹, HIROMICHI HAYASHI², KAZUNORI KAWASAKI², AND TAKEO EBINA²

¹ National Metal and Materials Technology Center, 114 Paholyothin Rd., Klong 1, Klong Laung, Pathumthani 12120, Thailand

² Research Center for Compact Chemical Process, National Institute of Advanced Industrial Science and Technology, 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan

Abstract—A comprehensive study of the intercalation of organo-phosphonium salts into Thai bentonite (Mt) was conducted to investigate the influence of the molecular structures of organic moieties, including chain types (alkyl vs. aryl), chain length, and structural symmetry, on their intercalation. A series of quaternary phosphonium salts with systematically varied molecular structures (tetraphenyl phosphonium, TPP-Br; tetrabutyl phosphonium, TBP-Br; tetraoctyl phosphonium, TOP-Br; methyl triphenyl phosphonium, MTPP-Br; and butyl triphenyl phosphonium, BTPP-Br) was intercalated into Mt *via* an ion-exchange reaction. From thermogravimetric analysis results, tetrabutyl phosphonium-modified Mt (TBP) with shorter alkyl chain length began to decompose at a slightly lower temperature (263 vs. 351°C), yet showed comparable thermal stability (*i.e.* maximum decomposition temperature) at 470°C, compared to tetraoctyl phosphonium-modified Mt (TOP). Aryl phosphonium-modified Mt (TPP) showed a higher thermal decomposition temperature (576 vs. 470°C) than those of alkyl phosphonium-modified Mts (TBP and TOP). Introducing short alkyl chains into the aryl phosphonium moiety (MTPP, BTPP) caused a slight decrease in thermal decomposition temperature, but an increase in cation loadings of their modified Mts (71 and 73%, respectively). X-ray diffraction analysis showed that the flexibility of alkyl chains in TBP yielded smaller increases in basal spacing, *i.e.* lower degree of intercalation, compared to the rigid aryl structure in TPP. Increasing chain length resulted in greater basal spacing in alkyl phosphonium-modified Mts (1.67 nm. in TBP vs. 2.46 nm. in TOP). Such an effect, however, was less significant in aryl phosphonium-modified Mt.

Key Words—Intercalation, Molecular Structure, Montmorillonite, Organo-clay, Phosphonium Salts.

INTRODUCTION

Organo-clays have been studied extensively in terms of their roles in enhancing thermal and mechanical properties of clay-polymer nanocomposites (Leszczynska *et al.*, 2007a, 2007b; Paiva *et al.*, 2008; Avalos *et al.*, 2009; Feng *et al.*, 2012; Garcia-Lopez *et al.*, 2013; Suin *et al.*, 2014). Many studies have been conducted on the modification of montmorillonite-rich clay to obtain organo-clay with high thermal stability, *i.e.* high decomposition temperature, using different types of organic modifiers such as ammonium salts, phosphonium salts, and imidazolium salts (Xie *et al.*, 2002; Hedley *et al.*, 2007; Leszczynska *et al.*, 2007a, 2007b; Patel *et al.*, 2007; Calderon *et al.*, 2008; Paiva *et al.*, 2008; Avalos *et al.*, 2009; Feng *et al.*, 2012; Garcia-Lopez *et al.*, 2013; Suin *et al.*, 2014). Organic modifiers helped to reduce the hydrophilic nature of the clay, resulting in better compatibility with organic polymers (Paiva *et al.*, 2008). Properties of clay-polymer nanocomposites are mainly dependent on the dispersion of

organo-clay in polymer matrix as well as interaction between organo-clay and polymer (Feng *et al.*, 2012; Garcia-Lopez *et al.*, 2013; Suin *et al.*, 2014). Garcia-Lopez *et al.* (2012) reported different improvements in the thermomechanical properties of polyamide6/organo-sepiolite nanocomposites, which depended on modifier structures and contents. From their results, strong interaction between PA6 and the Diamin T modifier led to homogeneous dispersion of sepiolite-Diamin T in the nanocomposite, thus increasing the elastic modulus and heat deflection temperature.

For organo-clays modified with ammonium salts, which have low thermal stability, thermal degradation begins to occur when the polymer processing temperature exceeds 200°C (Patel *et al.*, 2007; Calderon *et al.*, 2008). Other complex salts such as phosphonium, pyridinium, imminium, and imidazolium salts were later employed to achieve greater thermal stability of modified clays (Xie *et al.*, 2002; Hedley *et al.*, 2007; Leszczynska *et al.*, 2007a; Patel *et al.*, 2007; Calderon *et al.*, 2008; Paiva *et al.*, 2008; Avalos *et al.*, 2009; Suin *et al.*, 2014). Several factors including chemical structure, packing density, and type of cation in the organic modifier, as well as silicate layer thickness in the clay, were found to influence the space between the silicate layers and thermal stability of the organo-clays. Calderon *et al.* (2008) employed four alkylphosphonium

* E-mail address of corresponding author:

chureerp@mtec.or.th

DOI: 10.1346/CCMN.2014.0620102

salts with different molecular structures to investigate the effects of chemical composition and molecular weight of phosphonium salts on the thermal stability and basal spacing of modified clays. An organo-clay with tetra *n*-octyl phosphonium salt, which had the shortest chain length and smallest molecular weight of those examined, showed the smallest basal spacing compared to those with additions of higher molecular weight salts. The thermal stability and degradation mechanisms of modified montmorillonites of alkyl and aryl quaternary phosphonium salts (dodecyltriphenyl phosphonium, tetradecyltributyl phosphonium, hexadecyl tributyl phosphonium, octadecyltributyl phosphonium, tetraphenyl phosphonium, and tetraoctyl phosphonium) were investigated by Xie *et al.* (2002) and compared to clay modified with ammonium salt (tetraoctyl ammonium bromide). Unlike the ammonium salt system, the thermal stability of phosphonium-modified clay depended on the molecular structures of the organic salts. The symmetric tetraoctyl phosphonium-modified clay showed an increase in decomposition temperature of 30°C, compared to that of asymmetric tributyl alkyl phosphonium-modified clay. The increased decomposition temperature was explained to result from an increase in steric resistance around the P center of the tetraoctyl phosphonium ion, thus reducing the susceptibility of the alkyl chains to β -elimination. For triphenyl alkyl phosphonium-modified clay, steric hindrance from phenyl groups contributed to the increased thermal stability. In addition, π – π interactions between the P center and phenyl groups led to delocalization of the positive charge, thus inhibiting the alkyl chain from β -elimination. Patel *et al.* (2007) prepared modified montmorillonites (Mt) with different quaternary phosphonium cations (hexadecyl tributyl phosphonium, tetradecyl tributyl phosphonium, tetraphenyl phosphonium, methyl triphenyl phosphonium, ethyl triphenyl phosphonium, and propyl triphenyl phosphonium). Tetraphenyl phosphonium-modified Mt exhibited the highest decomposition temperature (350–400°C). Substitution of the phenyl group with alkyl chains (methyl, ethyl, or propyl group) resulted in lower decomposition temperatures (300–350°C). The thermal stability or decomposition temperature was found to increase with alkyl chain length. Tetraoctyl phosphonium-modified Mt, despite having relatively short chain length, showed an unexpectedly high decomposition temperature (up to 350°C) due to the high thermal stability of the tetrabutyl phosphonium cation.

Though these earlier studies provided informative experimental data, they had been reported individually and their results had not been correlated. To develop a comprehensive understanding of the influence of organic modifiers on organo-clay, the present study employed a series of quaternary phosphonium salts with systematically varied molecular structures to intercalate into

the Thai bentonite *via* a cation exchange reaction. The influence of molecular structures of organic modifiers on basal spacings and decomposition temperatures of phosphonium-modified Mts was investigated and discussed in relation to those reported by other research groups.

MATERIALS AND METHODS

Materials

Thai bentonite was provided by the Thai Nippon Co. Ltd (Thailand). The bentonite was further purified, using a method modified from Thuc *et al.* (2010): 10 g of bentonite was dispersed in 2 L of deionized water and stirred for 24 h, followed by sonication for 20 min. The resultant bentonite slurry was then left to settle for 50 h. The upper fraction of slurry with dispersed clay particles (~1500 mL) was collected and oven dried slowly at 90°C. The cation exchange capacity (CEC) of the purified bentonite, determined by the standard ammonium acetate method, was 80 meq/100 g. Phosphonium bromide salts purchased from Aldrich were used as received. Their molecular structures as well as the molecular mass of the cations are shown in Table 1.

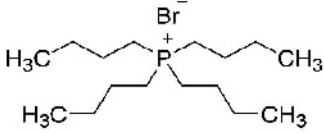
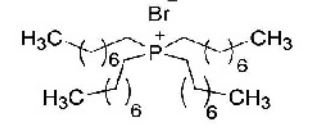
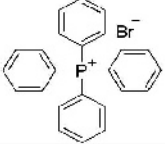
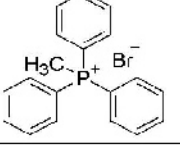
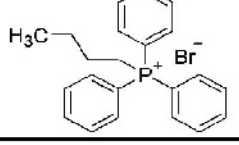
Preparation of phosphonium-modified montmorillonite

A 5 g portion of purified bentonite (Mt) was dispersed in 1 L of deionized water and stirred continuously for 30 min at room temperature, using a disperser (Ultra-Turrax® T50, IKA, Stauffen, Germany). Excess phosphonium salt (5 g) was added slowly to the bentonite slurry and stirred at high speed (~6000 rpm) for 30 min to allow intercalation of phosphonium cations into Mt *via* ion exchange before further stirring at medium speed (~3000 rpm) for another 3 h. The phosphonium-modified Mt was filtered and washed with deionized water until no residual bromide remained and then dried at 110°C for 24 h. The modified Mts obtained (identified as in Table 1) were prepared as powder samples for analysis by X-ray diffraction (XRD) and thermal analysis.

Characterization

The thermal properties of purified Mt, organic phosphonium salts, and phosphonium-modified Mts were characterized by thermogravimetric analysis (TGA) using a Mettler Toledo (Leicester, UK) instrument (SDTA 851^e). Samples were heated to 1200°C (except for the phosphonium salts which were heated to 900°C) at a heating rate of 10.0 °C/min under a N₂ flow of 20 mL/min. The structures of Mt and phosphonium-modified Mts were characterized, using a wide-angle X-ray diffraction apparatus (JEOL, JDX3530) with CuK α source. Intensity distributions for diffraction angles (2θ) ranging from 3 to 80° 2θ at a scanning rate of 0.02° 2θ /min were recorded. The corresponding *d* values were then derived from the first-order reflections.

Table 1. List of phosphonium salts and their structures.

Phosphonium salts	Molecular structure	Cation MW (g/mol)	Organo-modified clay labeling
Tetrabutyl phosphonium bromide		259	TBP
Tetraoctyl phosphonium bromide		491	TOP
Tetraphenyl phosphonium bromide		339	TPP
Methyltriphenyl phosphonium bromide		277	MTPP
Butyltriphenyl phosphonium bromide		319	BTPP

RESULTS AND DISCUSSION

Thermogravimetric analysis

Derivative TGA mass-loss curves (Figure 1a) showed that the parent Mt maintained thermal stability, *i.e.* was not thermally decomposed, through the range of temperatures studied. The derivative mass-loss peaks which occurred below 200°C were due to loss of interlayer water and the adsorbed gases such as N₂ (Xie *et al.*, 2002). Phosphonium-modified Mts exhibited greater thermal stabilities than their corresponding phosphonium salts (Figure 1a,b) such that decomposition temperatures occurred over the ranges 470–576°C and 285–419°C, respectively. Overall, the modified Mts showed gradual mass loss before a significant loss of mass occurred at a single particular temperature, except for tetraphenyl phosphonium-modified Mt (TPP) and tetraoctyl phosphonium-modified Mt (TOP) each of which showed two decomposition steps.

To investigate the influence of the alkyl chain length of organic moieties in phosphonium salts on the thermal stability of modified Mt, tetrabutyl phosphonium-modified Mt (TBP) and tetraoctyl phosphonium-modified Mt (TOP) were compared. In order to compare the resulting

data with previous studies, the decomposition temperature was reported as the temperature range between two temperature points; the temperature at 5% mass loss (T_5) and the temperature at maximum rate of mass loss (T_{max}). The TBP underwent thermal decomposition over a temperature range of 263–471°C whereas that of TOP occurred at a temperature range of 351–470°C (Table 2). Although TBP began to decompose at a lower temperature than did TOP ($T_5 = 263$ vs. 351°C), both showed comparable decomposition temperatures for maximum rate of mass loss (T_{max}) up to 470°C. The lower initial temperature of decomposition was thought to be due to the shorter alkyl chain length in TBP, but the molecular symmetry of tetrabutyl- and tetraoctyl-phosphonium moieties ensured that for the thermal stabilities observed in their modified Mts that the T_{max} temperatures were still at 470°C.

When alkyl groups (tetrabutyl; TBP) were replaced by aryl groups (tetraphenyl; TPP) for organic moieties in phosphonium salt, an increase in decomposition temperature was observed (263–471°C vs. 418–576°C, respectively). A similar observation was reported by Xie *et al.* (2002), who found that tetraphenyl phosphonium-Mt showed a greater decomposition temperature

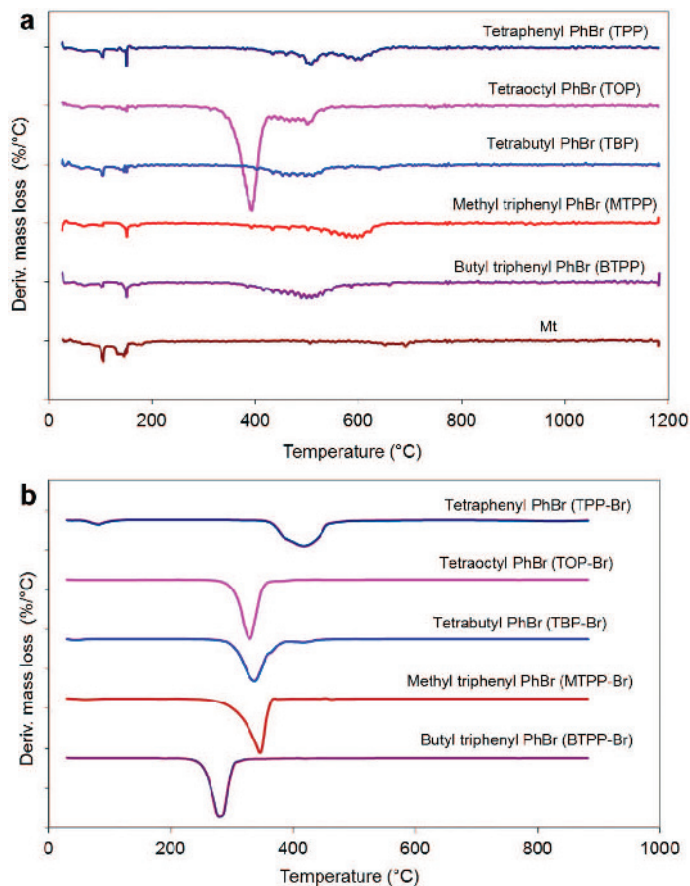


Figure 1. Derivative mass-loss curves of parent Mt (a), modified Mts (a), and phosphonium salts (b).

than tetraoctyl phosphonium-Mt (309–407°C vs. 262–362°C, respectively), despite the longer chain of the octyl group. According to Xie *et al.* (2002), this was due to steric hindrance from the phenyl substituents as well as the absence of α -hydrogen in phenyl groups,

which inhibited α - and β -eliminations and led to different decomposition pathways, resulting in greater thermal stability. Kawasaki *et al.* (2010) prepared transparent clay film by cation exchange reaction of synthetic saponite (SA) with tetraphenyl phosphonium

Table 2. Basal spacing and thermal properties of modified Mts and phosphonium salts.

Sample	Basal spacing (nm)	Temperature (°C) (@ 5% wt. loss)	Temperature (°C) (@ max. wt. loss rate)	Cation loading (%)
Mt	1.53	131*	n/a	n/a
TBP	1.67	263	471	65.5
TOP	2.46	351	470	32.5
TPP	1.79	418	576	30.5
MTPP	1.75	431	543	73.74
BTPP	1.83	405	499	71.2
Organic phosphonium salts				
TBP-Br	—	—	340	—
TOP-Br	—	—	332	—
TPP-Br	—	—	419	—
MTPP-Br	—	—	355	—
BTPP-Br	—	—	285	—

* Mainly water loss

bromide (TPP-Br). From TG-differential thermal analysis (DTA) measurement, the resultant tetraphenyl phosphonium saponite (TPP-SA) film showed good thermal stability such that decomposition occurred at 380–600°C and its DTA peak occurred at 550°C, which is in good agreement with the observation made on TPP in the current study.

When one aryl chain in tetraphenyl phosphonium-modified Mt (TPP) was substituted by alkyl chains (methyl triphenyl phosphonium- and butyl triphenyl phosphonium-), the decomposition temperature was altered. Methyl triphenyl phosphonium-modified Mt (MTPP) showed a slight decrease in decomposition temperature compared to TPP (431–543°C vs. 418–576°C, respectively). With increasing alkyl chain length, butyl triphenyl phosphonium-modified Mt (BTPP) showed a further decrease in decomposition temperature (405–499°C). Increasing the chain length of the substituted alkyl chain in the aryl phosphonium moiety caused the molecular structure to be more asymmetric, which tended to decrease decomposition temperature of the modified montmorillonite. A similar trend was observed in their corresponding phosphonium salts in that BTPP-Br showed a lower decomposition temperature than MTPP-Br and TPP-Br (285°C, 355°C, and 419°C, respectively). Despite their asymmetric structures, alkyl-substituted aryl phosphonium-modified Mts (MTPP and BTPP) still showed greater decomposition temperatures than those of alkyl phosphonium-modified Mts (TBP and TOP). Similar observations have been reported by other studies. The influence of molecular symmetry on decomposition temperature of phosphonium-modified Mt was examined by Patel *et al.* (2007), who reported that the symmetric tetraphenyl phosphonium-modified Mt showed the highest decomposition temperature at 350–400°C (at T_5), while substitution of the phenyl group by a methyl, ethyl, or propyl group resulted in lower decomposition temperature ($T_5 = 300–350^\circ\text{C}$). Xie *et al.* (2002) reported that the short chains having symmetrical structures showed higher decomposition temperature than non-symmetrical longer-chain structures. Tetraoctyl phosphonium Mt (P-4C8), which has a symmetrical structure, exhibited degradation temperatures which were $\sim 30^\circ\text{C}$ higher than those of asymmetric tributyl alkyl phosphonium Mts (where alkyl = tetradecyl (C14), hexadecyl (C16), and octadecyl (C18)).

To investigate incorporation of organic phosphonium cations in Mt interlayers, organic cation loading of modified Mts was evaluated by comparing measured mass loss (from TGA) with the theoretically completely exchanged Mt (based on CEC of 80 meq/100 g). As mentioned previously, tetraphenyl phosphonium-modified Mt (TPP) and tetraoctyl phosphonium-modified Mt (TOP) showed two decomposition steps. In comparison with their respective phosphonium salts, the first decomposition step occurred in a temperature range

comparable to that of the phosphonium salt. The decomposition at the second step should relate to the organic phosphonium moiety contained in the Mt interlayer. Organic mass losses which occurred during this second step were, thus, employed to determine the organic cation loadings for TPP and TOP, and these were found to be 30.5 and 32.5%, respectively (Table 2). For the others, tetrabutyl phosphonium-modified Mt (TBP), methyl triphenyl phosphonium-modified Mt (MTPP), and butyl triphenyl phosphonium-modified Mt (BTPP), decomposition of which occurred in a single step, had calculated cation loadings of 65.5, 73.7, and 71.2%, respectively. Increases in cation loading of MTPP and BTPP, compared to that of TPP, implied that introducing flexible alkyl chains assisted in the incorporation of the rigid aryl phosphonium moiety into the montmorillonite interlayer. Good mixing of the clay-polymer nanocomposite while maintaining heat stability could, thus, be achieved.

X-ray diffraction

Investigation of the XRD patterns ($3–10^\circ 2\theta$) of purified and phosphonium-modified Mts (Figure 2) revealed that the bentonite (Mt) characteristic reflection occurred at 5.8° , and the corresponding basal spacing was 1.53 nm (Table 2). As organic phosphonium cations were exchanged in the Mt interlayers, the basal spacings of the modified Mts increased and were in the range 1.67–2.46 nm. To investigate the influence of alkyl chain length of organic moieties on intercalation of phosphonium salt into Mt, tetrabutyl phosphonium-modified Mt (TBP) and tetraoctyl phosphonium-modified Mt (TOP) were compared. The basal spacing of TOP, having longer alkyl chain-length moieties, was greater than that of TBP (2.46 vs. 1.67 nm, respectively). This corresponds well with observations reported by Patel *et al.* (2007) that basal spacing increases with alkyl chain length. A similar trend was reported by Xie *et al.* (2002), who found that basal spacing increased from 1.93 nm to 2.04 nm and 2.18 nm for tetradecyl tributyl (C14), hexadecyl tributyl (C16), and octadecyl tributyl (C18) phosphonium-modified Mt, respectively. When aryl groups (tetraphenyl; TPP) were substituted in place of alkyl chains (tetrabutyl; TBP) for organic moieties in phosphonium salt, slight increases in basal spacing were observed (1.79 and 1.67, respectively). The molecular shapes of different phosphonium cations were determined by Patel *et al.* (2007) using molecular modeling software and those authors also calculated their corresponding molecular chain lengths. From their work, using the relationship between basal spacing and chain length, tetraphenyl phosphonium-Mt (P4) showed greater basal spacing than tetrabutyl phosphonium-Mt (P1) (1.76 vs. 1.4 nm) despite having comparable chain length (~ 0.55 and 0.57 nm, respectively). This supports observations made on TPP and TBP in the present work, and indicates that the rigid structure of the aryl group in

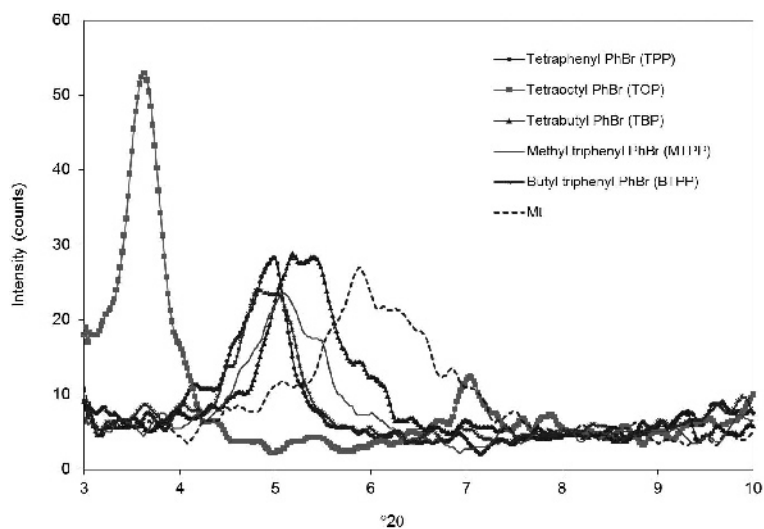


Figure 2. XRD patterns of parent Mt and modified Mts.

the tetraphenyl phosphonium moiety causes a larger increase in basal spacing.

When one aryl group in tetraphenyl phosphonium-modified Mt (TPP) was substituted by alkyl chains (methyl triphenyl, MTPP; butyl triphenyl, BTTP), the basal spacings were slightly different ($d = 1.79$, 1.75 , and 1.83 nm, respectively). Patel *et al.* (2007) reported that basal spacing of tetraphenyl phosphonium-modified Mt and its derivatives of one substituted alkyl chain of different chain lengths (methyl, ethyl, and propyl) were comparable. For longer alkyl chain lengths, Xie *et al.* (2002) also reported slightly smaller basal spacings in dodecyl triphenyl phosphonium-modified Mt, compared to that of tetraphenyl phosphonium counterpart ($d = 1.82$ and 1.88 nm, respectively). These observations on comparable basal spacings in mono-alkyl triphenyl phosphonium-modified Mts, despite their different alkyl chain lengths, imply that the alkyl chains are possibly folded among phenyl groups instead of extending outward. The influence of alkyl chain length in aryl-type moieties is, thus, small compared to that of the alkyl group.

CONCLUSIONS

Thai bentonite (Mt) was modified with phosphonium salts of varied structures, and characterized by TGA and XRD. Aryl phosphonium-modified Mts (TPP) showed higher decomposition temperatures, *i.e.* greater thermal stabilities, than those of alkyl phosphonium-modified Mts. The asymmetric structure in methyl triphenyl- and butyl triphenyl phosphonium-modified Mts (MTPP and BTTP), in which one alkyl chain was introduced into TPP, caused slight decreases in their decomposition temperatures. Their cation loadings, however, increased (from 30% for TPP to 71% and 73% for BTTP and

MTPP, respectively), which could favor the use of clay as a filler in polymer composites with improved thermal stability. In alkyl phosphonium-modified Mt, a larger basal spacing was observed with increasing alkyl chain length. In aryl phosphonium-modified Mt, however, the effect of alkyl chain length was less significant such that the basal spacings of alkyl triphenyl phosphonium-modified clays were comparable to those of their TPP counterparts. A fundamental understanding of the influences of organic modifiers on the intercalation of clays as well as on the thermal stabilities of the modified clays obtained can be used as a guide for selection of organo-clays as fillers in polymer-clay composites to achieve effective mixing and high thermal stability.

ACKNOWLEDGMENTS

The present study was supported by the National Metal and Materials Technology Center (Thailand) (grant number: MT-B-53-POL-07-488-I).

REFERENCES

- Avalos, F., Ortiz, J.C., Zitzumbo, R., Lopez-Manchado, M.A., Verdejo, R., and Arroyo, M. (2009) Phosphonium salt intercalated montmorillonites. *Applied Clay Science*, **43**, 27–32.
- Calderon, J.U., Lennox, B., and Kamal, M.R. (2008) Thermally stable phosphonium montmorillonite organo-clay. *Applied Clay Science*, **40**, 90–98.
- Feng, J., Hao, J., Du, J., and Yang, R. (2012) Effects of organoclay modifiers on the flammability, thermal and mechanical properties of polycarbonate nanocomposites filled with a phosphate and organoclays. *Polymer Degradation and Stability*, **97**, 108–117.
- Garcia-Lopez, D., Fernandez, J. F., Merino, J. C., and Pastor, J. M. (2013) Influence of organic modifier characteristic on the mechanical properties of polyamide6/organosepiolite nanocomposites. *Composites: Part B*, **45**, 459–465.
- Hedley, C.B., Yuan, G., and Theng, B.K.G. (2007) Thermal analysis of montmorillonites modified with quaternary

- phosphonium and ammonium surfactants. *Applied Clay Science*, **35**, 180–188.
- Kawasaki, K., Ebina, T., Mizukami, F., Tsuda, H., and Motegi, K. (2010) Development of flexible organo-saponite films and their transparency at high temperature. *Applied Clay Science*, **48**, 111–116.
- Leszczynska, A., Njuguna, J., Pielichowski, K., and Banerjee, J.R. (2007) Polymer/montmorillonite nanocomposites with improved thermal properties I. Factors influencing thermal stability and mechanisms of thermal stability improvement. *Thermochimica Acta*, **453**, 75–96.
- Leszczynska, A., Njuguna, J., Pielichowski, K., and Banerjee, J.R. (2007) Polymer/montmorillonite nanocomposites with improved thermal properties II. Thermal stability of montmorillonite nanocomposites based on different polymeric matrixes. *Thermochimica*, **454**, 1–22.
- Paiva, L.B., Morales, A.R., and Diaz, F.R.V. (2008) Organoclay: Properties, preparation and applications. *Applied Clay Science*, **42**, 8–24.
- Patel, H.A., Somani, R.S., Bajaj, H.C., and Jasra, R.V. (2007) Preparation and characterization of phosphonium montmorillonite with enhanced thermal stability. *Applied Clay Science*, **35**, 194–200.
- Suin, S., Maiti, S., Shrivastava, N.K., and Khatua, B.B. (2014) Mechanically improved and optically transparent polycarbonate/clay nanocomposites using phosphonium modified organoclay. *Materials and Design*, **54**, 553–563.
- Thuc, C.N.H., Grillet, A.C., Reinert, L., and Ohashi, F. (2010) Separation and purification of montmorillonite and polyethylene oxide modified montmorillonite from Vietnamese bentonites. *Applied Clay Science*, **49**, 229–238.
- Xie, W., Xie, R., Pan, W.P., Hunter, D., Koene, B., Tan, L.S., and Vaia, R. (2002) Thermal stability of quaternary phosphonium modified montmorillonites. *Chemistry of Materials*, **14**, 4837–4845.

(Received 6 October 2013; revised 25 January 2014;
Ms. 816; AE: J. Brendlé-Miehè)