

EFFECT OF TRIISOBUTYL (METHYL) PHOSPHONIUM ION MODIFIED MONTMORILLONITE TO THE TENSILE PROPERTIES OF POLY(METHYL METHACRYLATE) COMPOSITES

SITI AISYAH RUSLI, MOHD AIDIL ADHHA ABDULLAH* AND MAZIDAH MAMAT

School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia.

*Corresponding author: aidil@umt.edu.my

Abstract: Sodium montmorillonite (Na^+ -MMT) is one of the natural clays used worldwide in producing polymer nanocomposite. Commercially available modified-MMTs which are based on alkyl ammonium modified Na^+ -MMT is not thermally stable above 200°C . Considering its high thermal degradation temperature, triisobutyl (methyl) phosphonium (TBMP) surfactant was used in this research as an organic modifier in the modification of Na^+ -MMT via an ion exchange process forming organo montmorillonite of TBMP-MMT. The TBMP-MMT was then used as a filler in poly(methyl methacrylate) (PMMA) via melt intercalation technique which required high processing temperature. The successful modification of Na^+ -MMT to TBMP-MMT was assessed by X-ray diffractometer (XRD), Fourier transform Infrared spectrophotometer (FTIR), thermogravimetric (TGA) and elemental analyzers. The PMMA chain was successfully intercalated into TBMP-MMT galleries as confirmed by XRD analysis. The TBMP-MMT loading was significantly improved the tensile strength and Young's modulus of PMMA composites.

Keywords: Montmorillonite, alkylphosphonium, poly(methyl methacrylate), melt intercalation technique, nanocomposites

Introduction

Modification of clay by organic modifier has been attracted worldwide in both industrial applications and researches (Hernández-Hernández *et al.*, 2016) due to excellent thermal stabilities of the organoclay itself (Chalderon *et al.*, 2008). In addition, surface modifications of clay create new materials with new applications such as cosmetics, paint and adsorbents of organic pollutant in water. Montmorillonite (MMT) or also known as clay is actually part of soil having size less than $2\ \mu\text{m}$. MMT composes of many stacks of layers with nanometer in thickness. MMT is modified with cationic surfactant (Chalderon *et al.*, 2008; De Paiva *et al.*, 2008) and usually used as nanofiller in the preparation of polymer nanocomposite (Malucelli *et al.*, 2007; Chalderon *et al.*, 2008; Haerudin *et al.*, 2010; Kiliaris & papaspyrides, 2010). Naturally, MMT has hydrophilic character and only compatible with hydrophilic polymer. By exchanging sodium cation with

organic modifiers such as surfactant, the surface energy of MMT will decrease and the basal spacing will increase (Chalderon *et al.*, 2008) as well as improve their compatibility with hydrophobic polymers. The properties of organoclay such as thermal stability, surface energy and basal spacing usually depend on surfactant in which type of cation head that embedded into the surface of the clay (Chalderon *et al.*, 2008). The clay mineral will be successful exfoliated in the polymer matrix if they have a proper organophilization process (De Paiva *et al.*, 2008).

There are a number of surfactant used in the industry such as imidazolium surfactant, ammonium surfactant (Vazquez *et al.*, 2008; Singla *et al.*, 2012), phosphonium surfactant (Xie *et al.*, 2002; Chalderon *et al.*, 2008; Suin *et al.*, 2013) and many more. The most common surfactant has been introduced into the modification of clay is alkylammonium (De Paiva *et al.*, 2008). However, this type of

surfactant has low thermal stability and raised a problem in polymer nanocomposite processing where high processing temperature exceeding 200 °C is preferred (Chalderon *et al.*, 2008).

In this study, the potential of alkylphosphonium ion which have a higher thermal stability than ammonium surfactant (Xie *et al.*, 2002) is utilized in developing a new generation of thermally stable organo-montmorillonite which is critical for synthesis and processing of a wide range of polymer layered silicate nanocomposites. The modified MMT was used as filler for poly(methyl methacrylate) (PMMA) via melt intercalation method. The effect of organoclay on the tensile properties was investigated.

Materials and Method

Sodium montmorillonite (Na⁺-MMT) with cation exchange capacity (CEC) of 119 meq/100g was supplied by Kunimine Inc, Japan. Triisobutyl (methyl) phosphonium tosylate, Cyphosil106 (TBMP) was purchased from Iolitec, USA.

Na⁺-MMT had been swollen by adding 25 g of Na⁺-MMT with 2 litre of warm distilled water and mixed well by using a mechanical mixer with speed of 60-70 rpm about 1 hour. An aqueous solution of TBMP which is equivalent to CEC in the ratio of 1:1.2 was slowly added to swollen Na⁺-MMT and left for an hour. The produced organophilic montmorillonite (TBMP-MMT) precipitate was filtered and washed by hot distilled water. The precipitate was then dried in an oven at 110 °C for two days. This dried precipitate was ground to fine powder.

Various MMT loadings with PMMA have been prepared by using melt intercalation technique in the Haake Polydrive internal mixer. PMMA was melt-mixed with TBMP-MMT at different filler loadings (1– 5 wt %) at 185 °C, 130 rpm, and 15 minutes mixing time.

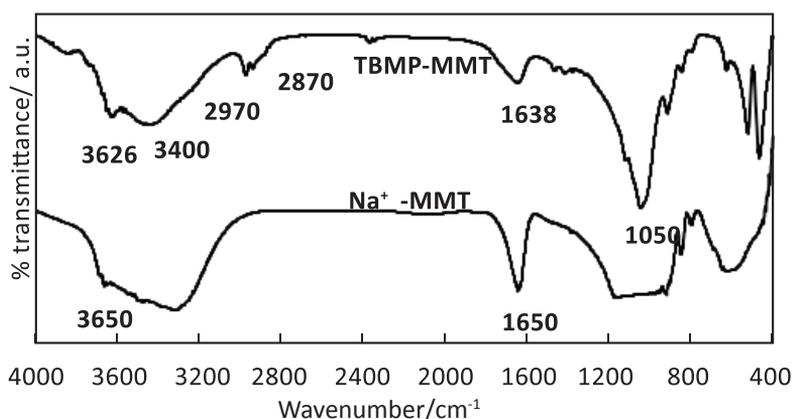
The tensile test specimens were prepared by injection molding according to ASTM D638. Tensile test of composites was carried out on Instron 3366 universal material testing machine.

Fourier transform infrared (FTIR) (Perkin Elmer Spectrum 100) analysis was performed by using a KBr disk method. Thermo gravimetric analysis (TGA) was recorded under nitrogen gas atmosphere at a heating rate 10 °C/min. On the other hand, elemental analyzer CHNS-932 instrument was used to investigate the carbon content in Na⁺-MMT and TBMP-MMT. X-ray diffractograms were recorded by using CuK α radiation with wavelength, λ of 1.540562 Å at a scan rate of 2 °C/min.

Results and Discussion

The percentage of carbon present in TBMP-MMT was recorded by the CHNS elemental analyser. As expected, carbon element percentage increased dramatically from 0 to 9.2% after the ion exchange process took place. This observation indicates the successful modification process as Na⁺-MMT clay does not contain carbon, hence carbon content detected in TBMP-MMT originated from TBMP. Based on this result, the calculated amount of TBMP presence in TBMP-MMT was 53.68mmol/100g.

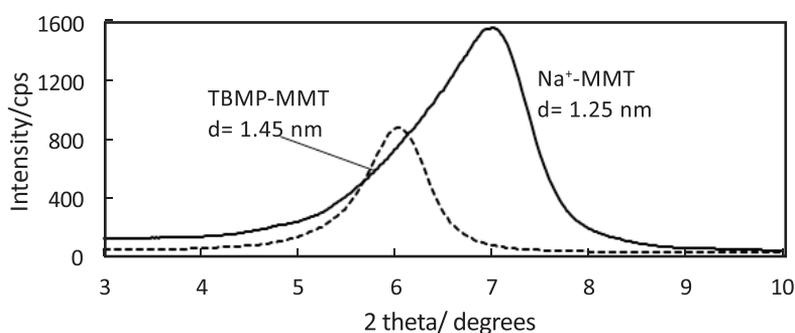
The existence of TBMP ion in TBMP-MMT was in agreement with FTIR analysis (Figure 1). The characteristic band of Na⁺-MMT at 3626-3650 cm⁻¹ is due to –OH stretching mode of MMT structure. The broad band near 3400 cm⁻¹ is due to –OH stretching mode of interlayer water while peak at 1638-1650 cm⁻¹ is attributed to –OH bending mode of adsorbed water. The presence of organic modifier of alkylphosphonium in TBMP-MMT can be observed in the range of 2970 – 2870 cm⁻¹ represent by asymmetric and symmetric vibration of methylene group (CH₂)_n of the aliphatic chain (Xie *et al.*, 2002).

Figure 1: FTIR spectra of Na⁺-MMT and TBMP-MMT

Replacement of existing sodium (Na⁺) cation in the interlayer of MMT by larger TBMP cation resulting in an expansion of basal spacing of MMT. The d001 diffraction plane was shifted towards lower 2θ angles together with the increased in basal spacing value (Figure 2). Na⁺-MMT shows a characteristic diffraction peak at 2θ of 7.08° with basal spacing 1.25 nm. The insertion of TBMP into the interlayer increased the basal spacing to 1.45 nm which appeared at 2θ value of 6.01°. The expansion indicates that Na⁺ cation had successfully been exchanged by long alkyl chain of ammonium/phosphonium

cation in the interlayer of MMT thus expanded the interlayer distance.

The initial weight loss observed in both MMT's thermograms (Figure 3) was related to dehydration of physically adsorbed water and water molecules located around metal cations in the interlayer (Xi *et al.*, 2007; Lenza *et al.*, 2012). Na⁺-MMT and TBMP-MMT experienced significant weight loss due to dehydration process (Stage I). It was due to naturally existing minerals in Na⁺-MMT interlayer being highly hydrated owing to the large

Figure 2: XRD patterns of Na⁺-MMT and TBMP-MMT

internal surface of hydrophilic Na⁺-MMT thus releasing free water molecules at low temperature (40 – 150°C). The weight loss occurs from 150 to 200°C due to the interlayer water that coordinate with Na⁺ cation has been removed. The cation exchanged between Na⁺ and TBMP cation altered the natural character

of MMT from hydrophilic to hydrophobic thus reducing the amount of hydrated water in/on TBMP-MMT from 15% in Na⁺-MMT to 7% in TBMP-MMT. The second degradation is due to dehydroxylation of structural water (bonded OH) (Stage II) in the temperature range 500-1000°C (Greeny-Kelly, 1957).

TBMP-MMT experienced another thermal decomposition (Stage III) at temperature between 200-500°C which begins at $T_{\text{onset}} = 291^{\circ}\text{C}$ due to organic substance starts to decompose. The degradation of organic substance in TBMP-MMT is higher compared to alkyl ammonium cation (below 200°C) (Abdullah, 2008; Chalderon *et al.*, 2008) due to the high stress tolerance of phosphorus atom as well as the participation of its low energy d-orbitals in the making and breaking bonds processes, thus making it capable of undergoing a wide range of reactions (Xie *et al.*, 2002). The thermal decomposition of tetra-alkyl

phosphonium salts proceeds through 4 possible types of reaction; nucleophilic substitution at the α -carbon (SN(C)); β -elimination; nucleophilic substitution at the phosphorus atom (SN(P) and α -elimination (Mittal, 2011). TGA analysis suggested TBMP-MMT potentially used as filler in PMMA composites due to its hydrophobic character as well as the degradation temperature of TBMP is higher than the injection molding processing condition of PMMA (240-280°C). The composition structure of TBMP as an organic modifier is important which may affect the thermal degradation of polymer clay nanocomposites (Unnikrishnan *et al.*, 2011).

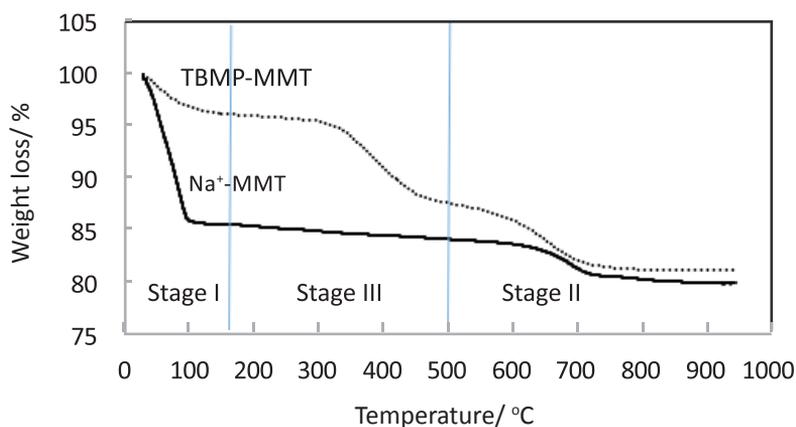


Figure 3: TGA analysis of Na⁺-MMT and TBMP-MMT

Morphological properties of PMMA composites

X-ray diffraction analysis was carried out to evaluate the interlayer distance of clay platelets in polymer matrix. The intercalation or insertion of polymer matrix into clay interlayer commonly represent by increasing value of d001 and shifting diffraction plane to the lower 2θ angles than Na⁺-MMT.

The d001 diffraction plane for composites of PMMA and Na⁺-MMT disappeared at all clay loading except a very small d001 peak for 3 wt% of clay (Figure 4(a)). The disappearance of d001 diffraction plane at low content of clay (1 and 2 wt%) after mixing process is commonly due to formation of exfoliated composites. However, a very

small peak of d001 plane was detected at 3 wt% and disappearance of diffraction plane for 4 to 5 wt% clay loadings indicating no correlation between interlayer spacing with the clay loading suggesting poor distribution of Na⁺-MMT in PMMA matrix.

The diffraction plane d001 which represents the interlayer distance of TBMP-MMT in 1- 4 wt% clay loading disappeared after it was mixed with PMMA suggested highest degree of TBMP-MMT clay dispersion or exfoliated in nanometer scale was formed. However, the d001 diffraction plane appeared and shifted to lower angle ($2\theta=3.76^{\circ}$) at 5 wt% TBMP-MMT loading with the increasing basal spacing from 1.45 to 2.30 nm indicates the insertion of the polymer matrix into the interlayer MMT and confirmed the

formation of intercalated types of polymer-clay nanocomposites (Figure 4(b)). Higher surface interaction between MMT and PMMA reflected by the formation of exfoliated and

intercalated type of nanocomposites suggested the modification of Na⁺-MMT with TBMP has successfully increased the compatibility between MMT and PMMA matrix.

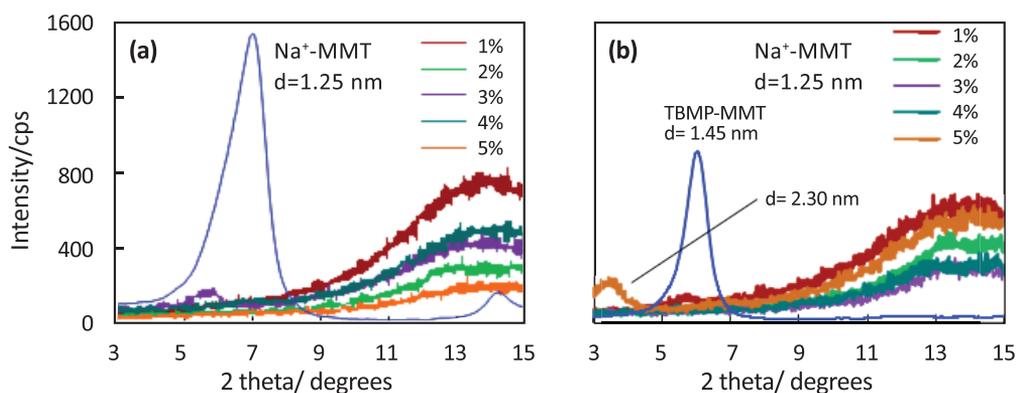


Figure 4: X-ray diffractograms of Na⁺-MMT, PMMA/Na⁺-MMT composites (a) and TBMP-MMT, PMMA/TBMP-MMT composites (b)

Tensile Properties

Generally, PMMA composites experienced increment in the values of tensile strength and Young modulus after Na⁺-MMT and TBMP-MMT was introduced in the polymer matrix (Figure 5). Even though Na⁺-MMT is not compatible with PMMA matrix as shown by the poor distribution of Na⁺-MMT in PMMA matrix, the value of ultimate tensile strength for PMMA/Na⁺-MMT composite illustrates slight

enhancement due to the clay's natural ability to withstand certain amount of load (Dintcheva *et al.*, 2009). PMMA composites with exfoliated and intercalated structure exhibit improvement in ultimate tensile strength compared to conventional composites due to the high surface areas of the clays that are exposed to polymer matrix that enable the platelets to carry applied load when dispersed in polymer matrix. At 5 wt% of clay loading, the tensile strength of TBMP-MMT and Na⁺ MMT composites increased about 14 and 5%, respectively.

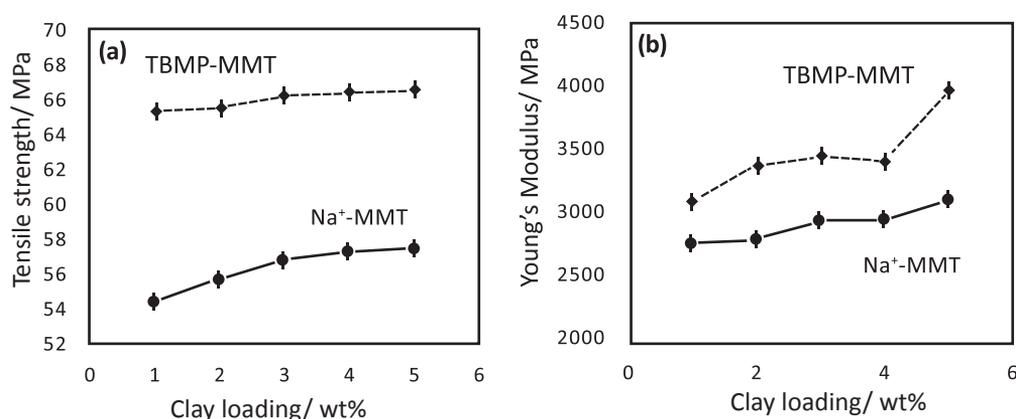


Figure 5: Tensile strength (a) and Young's Modulus (b) of PMMA composites

The similar trend showed in Young Modulus for PMMA composites. Young's modulus increased up to 58.69% with the addition of clay content. At the same clay loading, PMMA with TBMP-MMT loading showed higher Young's modulus than Na⁺ MMT (Figure 5(b)).

Improvement of Young Modulus properties is strongly related to the degree of clay dispersion in polymer matrix.

Incorporated clay platelets into the PMMA matrix cause the brittleness in PMMA. A better dispersion of clay will enhance the ability of clay platelets to carry the major portion of the load applied to the polymer matrix thus increase the composite tensile strength. High tensile strength should cause a decrease in the value of elongation at break as material that requires a large amount of force to be stretched will not elongate further. Na⁺-MMT and TBMP-MMT decreased the elongation at break of the composites for all clay loadings (Figure 6). The dispersion of clay throughout the PMMA matrix prevents PMMA chains from free motions thus reduce the elongation ability. The aggregation of MMT layer with the increasing of clay loading was another factor that cause the composite

to be more brittle (Abdullah, 2007). TBMP-MMT shows higher value of elongation break compared to Na⁺-MMT as expected regarding to the tensile strength.

Conclusion

Organoclay with hydrophobic characteristic was successfully prepared by exchanging the naturally occurred Na⁺ cation with TBMP via cation exchange process. Modification of MMT increases the compatibility with PMMA by forming intercalated and exfoliated structure composites. Thermally stable TBMP-MMT during mixing process contributes to the enhancement of tensile properties due to its ability of MMT platelets, which can carry certain loads applied to PMMA composites.

Acknowledgments

The authors are grateful to Ministry of Higher Education Malaysia for the fundings (FRGS 59171 and ERGS 55082), Universiti Malaysia Terengganu for providing research facilities and Research Management and Innovation Centre, Universiti Malaysia Terengganu for publication fee.

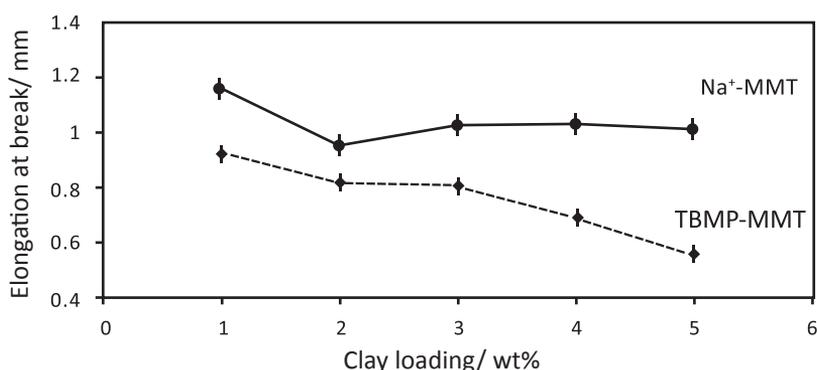


Figure 6: Elongation at break of PMMA composites

References

- Abdullah, M. A. A., Mamat, M., Awang, M., Kusriani, E., Mubin, F. A. N., & Sudin, N. H. (2013). Effect of Trihexyltetradecylphosphonium on thermal degradation properties of Low Linear Density Polyethylene/Montmorillonite nanocomposites. *International Journal of Technology*, 2 : 129-135.
- Abdullah, M. A. A. (2007). Preparation and characterization of natural rubber-, polyethylene- and natural rubber/polyethylene-clay nanocomposites. PhD Thesis, Universiti Putra Malaysia, Serdang.
- Chalderon, J. U., Lennox, B., & Kamal, M. R. (2008). Thermally stable phosphonium-montmorillonite organoclays. *Applied Clay Science*, 40: 90-98.
- De Paiva, L. B., Morales, A. R., & Diaz, F. R. V. (2008). Organoclays: Properties, preparation and applications. *Applied Clay Science*, 42(1-2): 8-24.
- Dintcheva, N. T. Z., Al-Malaika, S., & La Mantia, F. P. (2009). Effect of extrusion and photo-oxidation on polyethylene/clay nanocomposites. *Polymer Degradation and Stability*, 94: 1571-1588.
- Greene-Kelly, R. (1957). *The montmorillonite minerals*, in: R. C. Mackenzie (Ed.), the differential thermal investigation of clays, Mineralogical society. London.
- Haerudin, H., Pramono, A., Kusuma, W., Jenie, D. S., Voelcker, A., & Gibson, C. (2010). Preparation and characterization of chitosan/montmorillonite (mmt) nanocomposite systems. *International Journal of Technology*, 1: 65-73.
- Hernández-Hernández, K. A., Illescas, J., Díaz-Nava, M. D. C., Muro-Urista, C. R., Martínez-Gallegos, S., & Ortega-Aguilar R. E (2016). Polymer-Clay nanocomposites and composites: structures, characteristics, and their applications in the removal of organic compounds of environmental. *Interest Medicinal Chemistry* (Los Angeles), 6(3): 201-210.
- Kiliaris, P., & Papaspyrides, C. D. (2010). Polymer/layered silicate (clay) nanocomposites: An overview of flame retardancy. *Progress in Polymer Science*, 35(7): 902-958.
- Lenza, J., Merkel, K., & Rydarowski, H. (2012). Comparison of the effect of montmorillonite, magnesium hydroxide and a mixture of both on the flammability properties and mechanism of char formation of HDPE composites. *Polymer Degradation and Stability*, 97: 2581-2593.
- Malucelli, G., Ronchetti, S., Lak, N., Priola, A., Tzankova, N., Paolo, F., & Mantia, L. (2007). Polymer Intercalation effects in LDPE / o-montmorillonites nanocomposites. *Macromolecular Nanotechnology*, 43: 328-335.
- Mittal, N. (2011). *Thermally stable and flame retardant polymer nanocomposites*. Cambridge University Press, Cambridge.
- Suin, S., Shrivastava, N. K., Maiti, S., & Khatua, B. B. (2013). Phosphonium modified organoclay as potential nanofiller for the development of exfoliated and optically transparent polycarbonate/clay nanocomposites: Preparation and characterizations. *European Polymer Journal*, 49(1): 49-60.
- Singla, P., Mehta, R., & Upadhyay, S. N. (2012). Clay modification by the use of organic cations. *Green and Sustainable Chemistry*, 2: 21-25.

- Unnikrishnan, L., Mohanty, S., & Ali, A. (2011). Preparation and characterization of poly(methyl methacrylate)-clay nanocomposites via melt intercalation: Effect of organoclay on thermal, mechanical and flammability properties. *Materials Science and Engineering: A*, 528(12): 3943-3951.
- Vazquez, A., López, M., Kortaberria, G., Martín, L., & Mondragon, I. (2008). Modification of montmorillonite with cationic surfactants: Thermal and chemical analysis including CEC determination. *Applied Clay Science*, 41(1-2): 24-36.
- Xi, Y., Zhou, Q., Frost, R. L., & He, H. (2007). Thermal stability of octadecyltrimethylammonium bromide modified montmorillonite organoclay. *Journal of Colloid and Interface Science*, 311: 347-353.
- Xie, W., Xie, R., Pan, W., Hunter, D., Koene, B., Tan, L. S., & Vaia, R. (2002). Thermal stability of quaternary phosphonium modified montmorillonites. *Chemistry of Materials*, 14(11): 4837-4845.