

# Improved polypropylene / clay nanocomposites

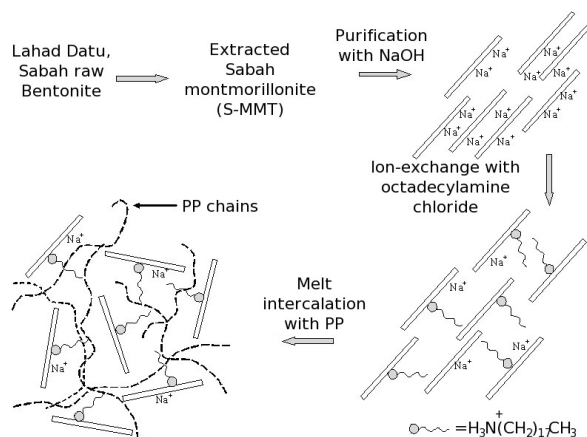
Mat Uzir Wahit, Harintharavimal Balakrishnan,  
Muthmirah Ibrahim, and Azman Hassan

*Malaysian montmorillonite can be incorporated into a polymer nanocomposite with comparable performance to existing commercial forms.*

Polypropylene/montmorillonite (PP/MMT) nanocomposites are popular with researchers and industry due to their high aspect ratio and nanoscale filler distribution, which improves the composite properties at low content compared to conventional microfillers (<5wt% rather than >30wt%). However, to disperse well, the naturally hydrophilic MMT has to be organically modified with quaternary alkyl ammonium ions (such as an octadecylamine group). This modification increases the interlayer spacings and leads to the formation of intercalated or even exfoliated structures.<sup>1</sup> Previously, researchers have explored the properties of these nanocomposites with various established and commercially available grades of MMT.<sup>2–5</sup> However, more recently, Araújo and co-workers<sup>6</sup> and also Barbosa and co-workers<sup>7</sup> investigated novel polyethylene nanocomposites with Brazilian clay and reported that newly developed forms of MMT might perform as well as the established ones.

In the last decade, Malaysia's natural bentonite—an impure clay mainly made up of montmorillonite<sup>8,9</sup>—from Lahad Datu, Sabah has been found to be an excellent drilling mud/additive in the petroleum industry<sup>8–10</sup> and also used as activated clay to decolorize crude palm oil in the agricultural sector.<sup>11</sup> Despite previous efforts to widen the applications of this natural resource, its prospects in polymer technology remain unexplored. MMT extracted from Sabah bentonite contains ionic impurities and purification by cation exchange is the most viable method to obtain sodium-based MMT.<sup>8,12</sup> We have investigated a new PP/MMT nanocomposite incorporating organically modified Sabah MMT (S-OMMT) to see whether its unique structure and properties result in a better performance than commercially available forms of MMT.

We extracted so-called S-MMT from Sabah bentonite obtained from Lahad Datu, Sabah in Malaysia, and purified it with sodium hydroxide. We then exchanged the sodium ions with octadecylamine chloride to prepare S-OMMT, which we incorporated into PP to

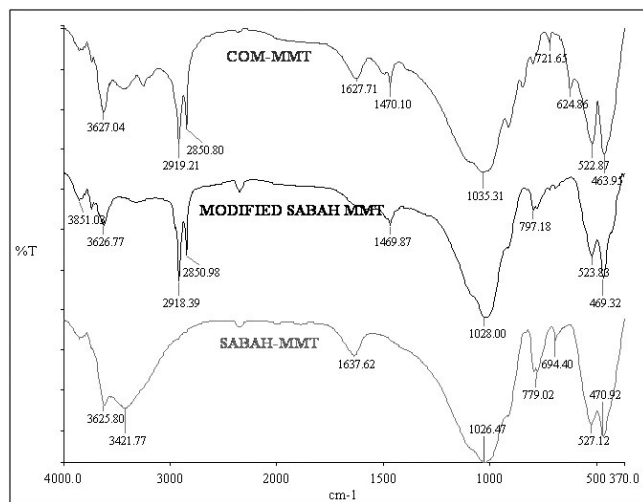


**Figure 1.** Extraction, purification, and modification of Sabah montmorillonite (S-MMT) followed by preparation of polypropylene/organically modified Sabah montmorillonite (PP/S-OMMT) nanocomposites.  $\text{Na}^+$ : sodium ions; NaOH: sodium hydroxide.

form nanocomposites (see Figure 1). We also investigated the mechanical, thermal, and morphological properties of the new PP/S-OMMT nanocomposites. We then studied unmodified S-MMT, filled PP/S-MMT, and PP/Nanomer 1.30P nanocomposites for comparison. Nanomer 1.30P is a commercial grade MMT, which is widely used in polymer/clay nanocomposites.

Elemental analysis of S-OMMT showed that carbon was present, indicating that octadecylamine is an intercalant group in the inter-gallery of S-MMT platelets, having replaced sodium cations. Potassium was also present, which is characteristic of S-MMT. Fourier transform IR analysis of S-MMT, S-OMMT, and Nanomer 1.30P provided further evidence of the organic modification process with the appearance of three new peaks (see Figure 2). The band at  $\sim 1470\text{cm}^{-1}$  is assigned to ammonium salt whereas bands at  $2918\text{cm}^{-1}$  and  $2850\text{cm}^{-1}$  are attributed to the C-H asymmetric and symmetric stretching vibrations of octadecylamine, respectively. The bands at  $3421\text{cm}^{-1}$  and  $1631\text{cm}^{-1}$  originate from stretching and bending vibrations of O-H groups from water molecules in the interlayer. The reduced intensities of these

*Continued on next page*

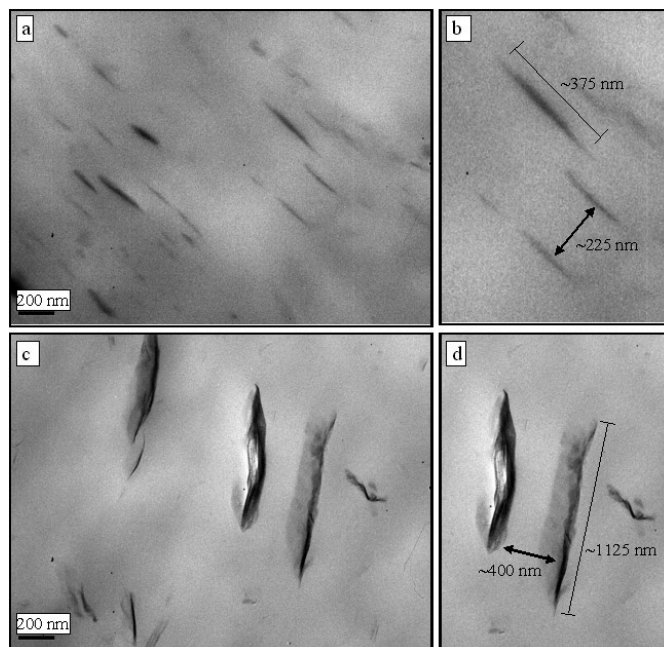


**Figure 2.** Fourier transform IR spectra of Sabah-MMT (S-MMT), Modified Sabah MMT (S-OMMT), and Com-MMT (Nanomer 1.30P).

bands in S-OMMT and Nanomer 1.30P suggest that the octadecylamine group reduces MMT's hydrophilic nature. Thermogravimetric and derivative thermogravimetric analysis of S-OMMT suggest that S-OMMT has more octadecylamine molecules in the edges of its galleries than its interior. This merits further investigation.

X-ray diffraction patterns of PP nanocomposites with S-MMT, S-OMMT, and Nanomer 1.30P reveal that the  $d_{001}$  peak at  $2\theta = 4.9^\circ$  disappears in PP/S-OMMT nanocomposites, which shows a good dispersion of S-OMMT after organic modification with octadecylamine. It is proposed that the remarkable performance of S-OMMT might be due to its much shorter layers in its nanocomposite with PP, as revealed by transmission electron microscopy images (see Figure 3). The shorter length of S-OMMT platelets enables better distribution compared to Nanomer 1.30P platelets.

We also found that the tensile and flexural modulus (stiffness) of all PP nanocomposites improved significantly with increasing MMT content. We believe that the size of platelets—as observed in Figure 3—contributes to better performance of Nanomer 1.30P, compared to S-MMT and S-OMMT platelets. The larger platelets impose higher chain restriction during deformation and provide a larger surface area for stress transfer from polymer matrix to MMT. We also found that PP/S-OMMT nanocomposites have higher tensile and flexural strength compared to PP/Nanomer 1.30P nanocomposites, which might be due to the better dispersion of MMT platelets. Reduction of impact strength and elongation at break values for PP/S-MMT, PP/S-OMMT, and PP/Nanomer 1.30P nanocomposites indicate that introducing MMT into PP makes it more brittle.



**Figure 3.** Transmission electron micrograph of (a) PP/S-OMMT (2wt%), (b) a magnified portion of S-OMMT, (c) PP/Nanomer 1.30P (2wt%), and (d) a magnified portion of Nanomer 1.30P.

Thermogravimetric analysis curves of neat PP, PP/S-MMT, PP/S-OMMT, and PP/Nanomer 1.30P nanocomposites revealed that PP/S-OMMT nanocomposites had higher thermal stability than PP nanocomposites with other types of MMT. We think that this might also be due to its characteristic structure and dispersion. Differential scanning calorimetry analysis revealed that the crystallization temperature ( $T_c$ ) and the degree of crystallinity ( $X_c$ ) of PP increased with the introduction of MMT. MMT platelets act as nucleating agents, promoting the growth of crystals.

In summary, we found that the new PP/S-OMMT nanocomposites showed comparable performance with PP/Nanomer 1.30P nanocomposites, which might lead to increasing use of S-MMT in polymer/MMT nanocomposites. In future work, we might focus on the use of S-OMMT in other commodity and engineering plastics. In addition, we are keen to improve the S-MMT extraction process for commercial purposes.



## Author Information

**Mat Uzir Wahit, Harinthaaravimal Balakrishnan,  
Muthmirah Ibrahim, and Azman Hassan**

Department of Polymer Engineering  
Faculty of Chemical Engineering  
Universiti Teknologi Malaysia (UTM)  
Johor Bahru, Malaysia

Mat Uzir Wahit is an associate professor. His research interests include advanced materials, natural fiber composite materials, rubber-toughened polymers, polymer nanocomposites, and polymers for biomedical application. He has published more than 60 research papers and conference proceedings on rubber toughened polymer, polymer blends, and polymer nanocomposites. He has also been appointed as reviewer for more than eight different journals.

Harinthaaravimal Balakrishnan is a PhD candidate. He has worked on various projects involving 'green' polymers, advanced materials, toughness enhancement of polymer nanocomposites, and halogen-free flame-retarded polymer composites. He is the recipient of the National Science Fellowships, Malaysia scholarship award for his PhD studies.

Muthmirah Ibrahim completed her MSc at UTM and has been appointed as a lecturer in the Universiti Malaysia Perlis.

Azman Hassan is a professor and currently serving as a deputy director at the Research Management Center, UTM. He formerly headed the Polymer Engineering Department at UTM. He received his PhD from Loughborough University (UK) in 1997, has approximately 27 years of experience in teaching and research, and has supervised more than 30 postgraduate students. His research interests include polyvinyl chloride technology, polymer blends, thermal characterization, rubber toughened polymers, natural fiber composites, nanocomposites, and flame retardant polymers. He has published over 100 research papers and is currently the editor in chief of the *Malaysian Polymer Journal*. He has also been appointed as reviewer for more than 10 different journals.

## References

1. M. Arroyo, M. A. López-Manchado, and B. Herrero, *Organo-montmorillonite as substitute of carbon black in natural rubber compounds*, **Polymer** **44**, pp. 2447–2453, 2003. doi:10.1016/S0032-3861(03)00090-9
2. L. Jian, C. Zhou, W. Gang, Y. Wei, T. Ying, and L. Qing, *Preparation and linear rheological behavior of Polypropylene/MMT nanocomposites*, **Polym. Comp.** **24**, pp. 323–331, 2003. doi:10.1002/pc.10032
3. J. W. Lee, Y. T. Lim, and O. Ok Park, *Thermal characteristics of organoclay and their effects upon the formation of polypropylene/organoclay nanocomposites*, **Polym. Bull.** **45**, pp. 191–198, 2000. doi:10.1007/s002890070048
4. T. S. Ellis and J. S. D'Angelo, *Thermal and mechanical properties of a polypropylene nanocomposite*, **J. Appl. Polym. Sci.** **90**, pp. 1639–1647, 2003. doi:10.1002/app.12830
5. Z. M. Wang, H. Nakajima, E. Manias, and T. C. Chung, *Exfoliated PP/clay nanocomposites using ammonium-terminated PP as the organic modification for montmorillonite*, **Macromolecules** **36**, pp. 8919–8922, 2003.
6. E. M. Araújo, R. Barbosa, A. W. B. Rodrigues, T. J. A. Melo, and E. N. Ito, *Processing and characterization of polyethylene/Brazilian clay nanocomposites*, **Mater. Sci. Eng., A** **445-446**, pp. 141–147, 2007. doi:10.1016/j.msea.2006.09.012
7. R. Barbosa, E. M. Araújo, T. J. A. Melo, E. N. Ito, and E. J. Hage, *Influence of clay incorporation on the physical properties of polyethylene/Brazilian clay nanocomposites*, **J. Nanosci. Nanotechnol.** **8**, pp. 1937–1941, 2008. doi:10.1166/jnn.2008.030
8. A. Samsuri and H. Abdullah, *Electrolysis treatment study of Sabah bentonite and its applications in petroleum industry*, **Malaysian Sci. Tech. Congr.**, 2002.
9. S. Irawan, C. W. Sum, and K. B. Mohammad, *Formulation of drilling fluids for high temperature well application using Sabah bentonite*, **Proc. World Geotherm. Cong.**, 2010.
10. A. Samsuri, S. Man, R. Junin, and A. Mohamed Osman, *Properties study of a local bentonite as an additive in oil and gas industry*, **Proc. Adv. Malaysian Energy Res. Conf.**, 2000.
11. K. A. Karim and R. Junin, *Mineralogic and physico-chemical studies of Lahad Datu bentonite*, **Geol. Soc. Malaysia Bulletin** **31**, pp. 39–49, 1992.
12. L. B. de Paiva, A. R. Morales, and F. R. V. Diaz, *Organoclays: Properties, preparation and applications*, **Appl. Clay Sci.** **42**, pp. 8–24, 2008. doi:10.1016/j.clay.2008.02.006