

NSPM 2006  
VIth National Symposium on Polymeric Materials 2006  
13-14 December 2006, Subang Jaya, Malaysia

## TOUGHENING POLYAMIDE 6 NANOCOMPOSITES WITH MALEIC ANHYDRIDE GRAFTED POLYETHYLENE OCTENE

*M.U. Wahit, A. Hassan, Y.F. Koay, N. Othman and M.Mokhtar  
Department of Polymer Engineering,  
Faculty of Chemical and Natural Resources Engineering  
Universiti Teknologi Malaysia, 81310 Skudai, Johor Malaysia*

### ABSTRACT

Rubber toughened nanocomposites consisting of ternary blends of polyamide 6 (PA 6), maleic anhydride grafted polyethylene octene (POEgMAH) and organoclay montmorillonite (MMT) were prepared by melt compounding followed by injection moulding. The organoclay content was kept constant at 4 wt% while the POEgMAH content was varied between 5 to 20 wt%. The mechanical properties were studied through tensile, flexural and impact properties. The scanning electron microscope (SEM) and X-ray diffraction (XRD) were used to examine the morphology of the nanocomposites. The results showed that, the incorporation of 4 wt% organoclay significantly increased the stiffness and strength but at the expense of the toughness. Izod impact measurement indicated that the addition of POEgMAH led to a significant improvement in the impact strength of the nanocomposites. X-ray diffraction analysis (XRD) revealed that an intercalation organoclay silicate layer structure was formed in rubber-toughened PA6 nanocomposites. SEM study revealed a two-phase morphology where POE, as droplets was dispersed finely and uniformly in the PA6 matrix..

### Keywords:

Nanocomposites, polyamide 6, maleic anhydride grafted polyethylene octane, monmorillonite.

### INTRODUCTION

The use of organoclay particularly montmorillonite (MMT) as reinforcing filler for thermoplastic to produce polymer nanocomposites has attracted great interest. These nanocomposites often exhibit remarkable improvement in material properties comparison to virgin polymer and microcomposites [1-4]. In recent years, there has been increasing interest in the development of polyamide nanocomposites. Among all, there were several researches that have been carried out related to PA6 layered silicate nanocomposites in order to investigate the morphology characteristic, thermal, mechanical and other properties of the material [1-11]. The improvement can include high modulus, increased strength and heat resistance. However, incorporation of organoclay at high loading usually resulted in a severe embrittlement manifested in a drop of the impact strength and elongation at break.

In order to compensate the low impact resistance due to the incorporation of organoclay into the polymer matrix, elastomeric impact modifier was used as a toughening agent to form rubber-toughened PA6/PP nanocomposites in this study. The POEgMAH had better compatibility with nylon-6 as compared to unmodified POE which had hardly contributed to the toughness of PA6 [12-13].

The aim of the research is to study the effectiveness of organoclay as reinforcing filler and POEgMAH as impact modifier for PA6. The structural and mechanical properties of the formed nanocomposites will be investigated using X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and mechanical analysis.

## EXPERIMENTAL

### **Materials and Preparation of Blends**

The blends used in this work are described in Table 1. The PA6 (Amilan CM 1017) was a commercial product from Toray Nylon Resin AMILAN, Japan. The MFI at 230°C and 2.16 kg load was 35 g/10 min and the density was 1.14 g/cm<sup>3</sup>. The impact modifier, POEgMAH grade Fusabond N MN493D was supplied by DuPont Dow Elastomers with the following specification: density – 0.87 g/cm<sup>3</sup>, medium MAH graft level, MFI (g/10 min, 190°C/2.16 kg) – 1.6. The organoclay (Nanomer 1.30TC) was a commercial product from Nanocor Inc., USA. It was a white powder containing montmorillonite (MMT) (70 wt%) intercalated by octadecylamine (30 wt%).

**Table 1: Blend formulations**

Sample Code	PA6 (%)	POEgMAH (%)	Organoclay (%)
PA6	100	0	0
PA6/F4	96	0	4
PA6/E5/F4	91	5	4
PA6/E10/F4	86	10	4
PA6/E15/F4	81	15	4
PA6/E20/F4	76	20	4

Following pre-designed compositions ratios, PA6, POEgMAH and organoclay were dry blended in a tumbler mixer, prior to compound in a Berstoff co-rotating twin-screw extruder. The barrels temperature was maintained at 200, 220, 230 and 240°C and the rotating screw was fixed at 50 rpm. The extrudate was then air-cooled and palletized using pelletizer.

The extruded materials were injection molded into ASTM standard tensile, flexural and Izod impact specimens using Hai Tian injection-molding machine with barrel temperature of 210-240°C. All test specimens were conditioned under ambient temperature about 27±2°C in desiccators for prior to testing.

### **Mechanical Testing**

Tensile and flexural tests were carried out according to ASTM D638 and ASTM D790 respectively, using an Instron 5567 Universal Testing Machine under ambient conditions. The crosshead speeds of 50mm/min and 3mm/min were used for tensile and flexural test, respectively. The Izod impact test was carried out on notched impact specimens using a Toyoseiki Impact Testing Machine under ambient conditions. Five specimens of each formulation were tested and the average values were reported.

### **Microscopy Examination**

The morphology of the blends was examined using a Philips scanning electron microscope (SEM). Samples were cryogenically fractured in liquid nitrogen and etched in heptane at 50°C for 3 hours to extract the elastomeric POEgMAH phase. Samples were coated with gold prior to examination under the electron beam. An operating voltage of 10kV and a magnification of 2000x were used. The particles sizes of the particles were calculated from the diameter of the particles which were approximated to spheres. The POE dispersed phase size (number average diameter,

$D_n$ ) was measured using image analysis software package (Zeiss KS 300 Imaging System Release 3.0 software).

### **X-Ray Diffraction (XRD)**

X-ray diffraction (XRD) was performed with the Siemens XRD. The XRD were recorded with a step size of  $0.02^\circ$  from  $2\theta = 1.5$  to  $10^\circ$ . The interlayer spacing of organoclay was derived from the peak position ( $d_{001}$ -reflection) in XRD diffractograms according to Bragg equation.

## **RESULTS AND DISCUSSION**

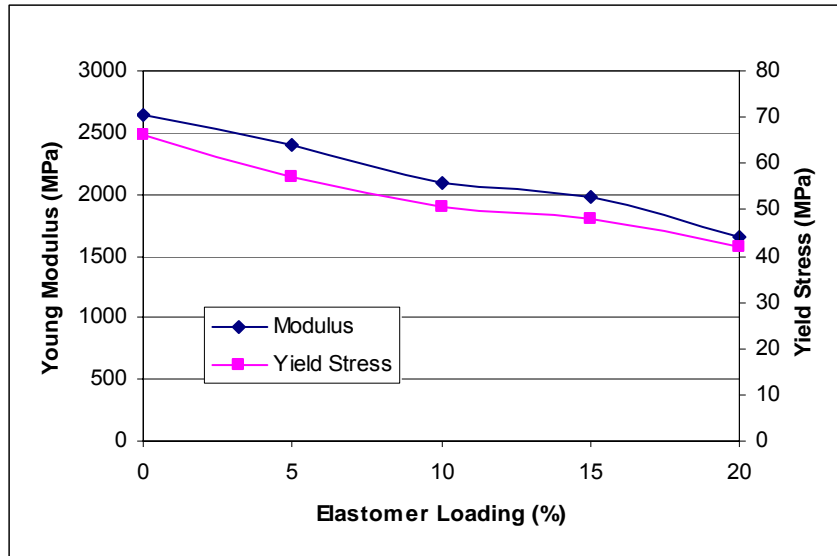
### **Mechanical Properties**

Table 2 show the tensile strength, flexural strength, elastic modulus (E-modulus) and flexural modulus for the pristine PA 6 and PA 6/organoclay. As shown in Table 2 the E-modulus and flexural modulus of the neat PA6 increased with the incorporation of 4 wt% organoclay. A significant improvement was also evident in the tensile and flexural strength. However, it is also noted that the addition of 4 wt% organoclay has deteriorated the Izod impact strength of the nanocomposites. The Izod impact strength was reduced from 18.9 to 16.1 kJ/m<sup>2</sup>.

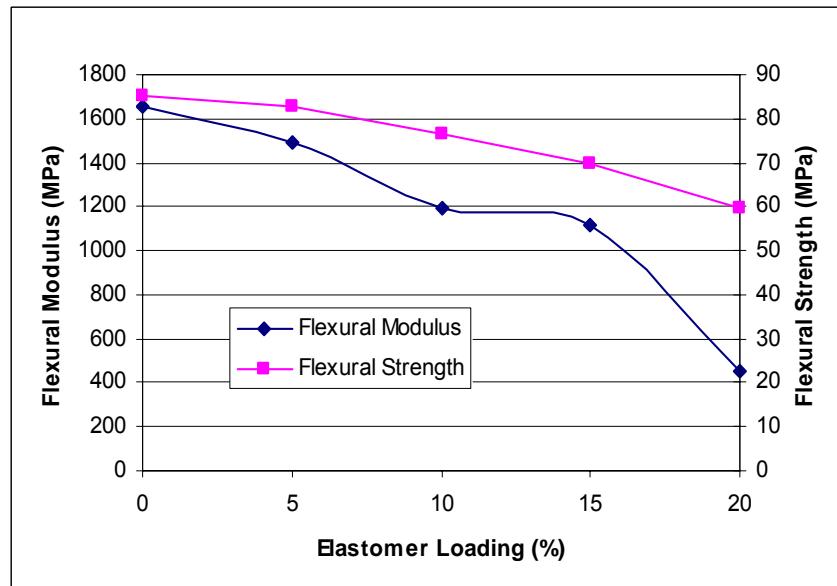
**Table 2: Mechanical properties of pristine PA 6 and PA 6/organoclay**

<b>Properties / sample</b>	<b>PA6</b>	<b>PA6/organoclay</b>
E-modulus (MPa)	1947 ± 164	2636 ± 119
Flexural modulus (MPa)	1251 ± 32	1660 ± 251
Tensile Strength (MPa)	56 ± 1.0	66.2 ± 1.9
Flexural strength (MPa)	77.2 ± 0.9	85.2 ± 2.0
Impact strength (kJ/m <sup>2</sup> )	18.9 ± 0.7	16.1 ± 0.6

The effect of POEgMAH contents on the mechanical properties of rubber-toughened PA6 nanocomposites (RTPA6NC) are indicated in Figure 1 to 3. Based on Figure 1 and 2, it can be seen that by adding POEgMAH content on the PA6 nanocomposites (PA6NC) up to 20 wt% POEgMAH has caused a steady decline in the stiffness of RTPA6NC. Figure 1 and 2 show the reduction in Young and flexural modulus up to 37% and 72%, respectively relative to the PA6NC. The incorporation of POEgMAH content into PA6NC matrix had also resulting in the reduction of yield stress and flexural strength. Similar finding was also reported by Cho and Paul [1], Laura *et al.* [15] and Tjong *et al.* [16]. These observations are generally found in various blends and have been reported to be due to the softening or diluting effect of the incorporation of a soft elastomeric phase into the matrix.

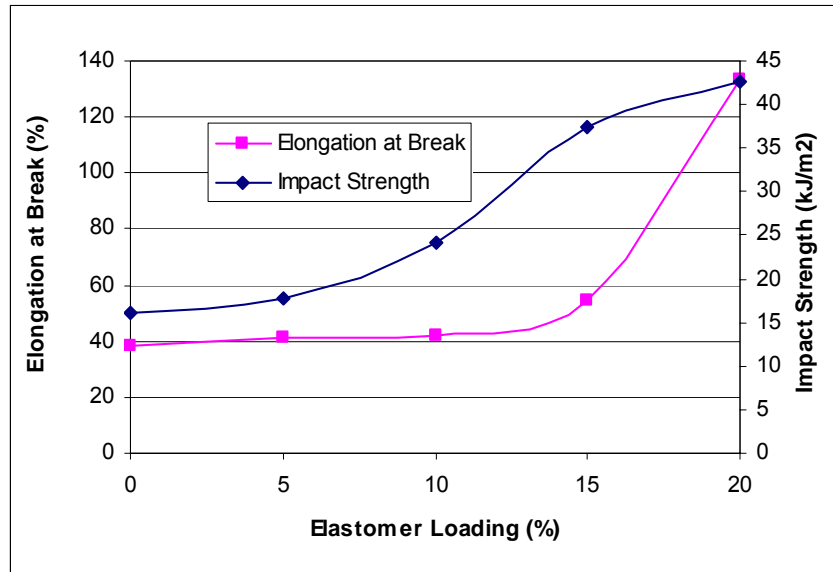


**Figure 1: Effect of organoclay POEgMAH content on tensile modulus and yield stress of RTPA6NCs**



**Figure 2: Effect of organoclay POEgMAH content on flexural modulus and flexural strength of RTPA6NCs**

The effect of adding POEgMAH to the PA6 matrix on the impact strength and elongation at break are shown in Figure 3. The results revealed that the incorporation of POEgMAH has upgraded the toughness and elongation at break of PA6NC. As shown, the impact strength increased greatly from 16.1 kJ/m<sup>2</sup> in untoughened PA6NC to 42.5 kJ/m<sup>2</sup>, nearly a three-fold improvement after 20 wt% POEgMAH were added to the PA6NC. The effective toughening was achieved probably due to the optimum particle size and good interfacial bonding between polymeric matrix and its dispersion [17].

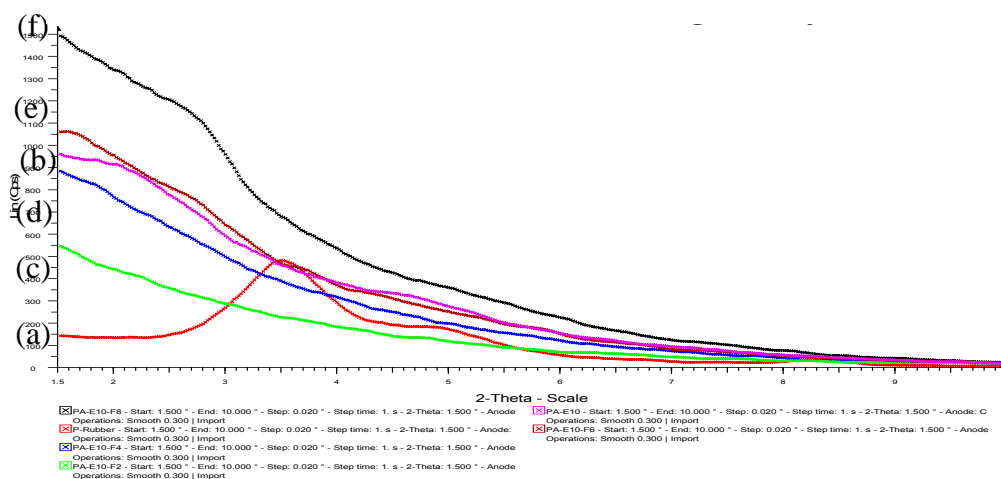


**Figure 3: Effect of organoclay POE-g-MAH content on elongation at break and impact strength of RTPA6NCs**

**X-Ray Diffraction (XRD)**

The XRD patterns of pristine organoclay (Nanomer 130TC), untoughened PA6 nanocomposites and RTPA6NC with different POEgMAH loading (5-20 wt%) were shown in Figure 4. The mean interlayer spacing of the (001) plane peak for the neat organoclay calculated from the XRD measurements is 2.53 nm ( $2\theta = 3.50^\circ$ ).

Figure 4 also shows XRD patterns for the POE toughened PA6/PP nanocomposites (containing 5-20 wt% of POEgMAH). It can be seen that for all POEgMAH toughened PA6 nanocomposites, no characteristic basal diffraction peak of the organoclay appears in the range  $2\theta = 1-10^\circ$ . This suggests that the organoclay is exfoliated and dispersed in the PA6/POEgMAH matrix during melt compounding. Similar pattern was also observed for all systems. These results imply that POEgMAH concentration was not playing a significant role in the formation of the intercalated or exfoliated structure.



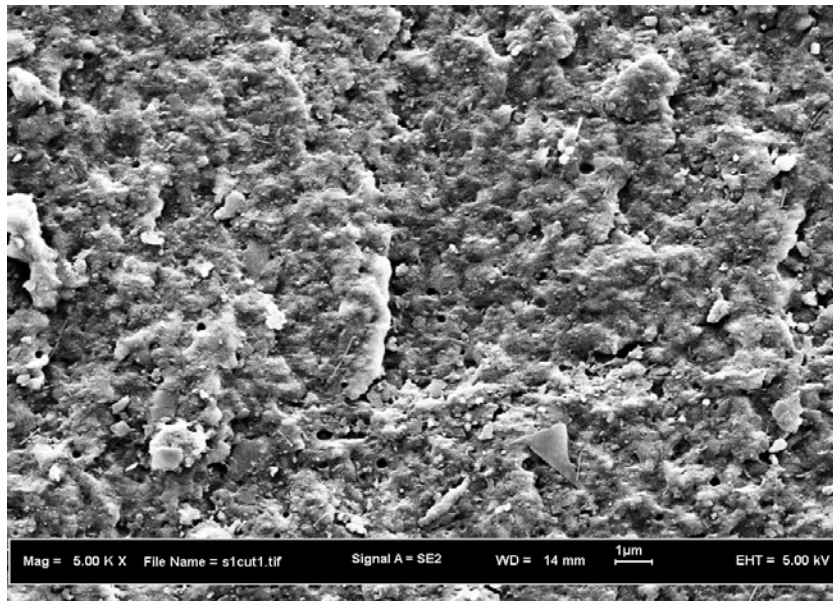
**Figure 4: XRD pattern for (a) pristine organoclay and RTPA6NC containing different POEgMAH loading (b) 0 wt%, (c) 5 wt%, (d) 10 wt%, (e) 15 wt%, (f) 20 wt% POEgMAH content**

### **Scanning Electron Microscopy (SEM)**

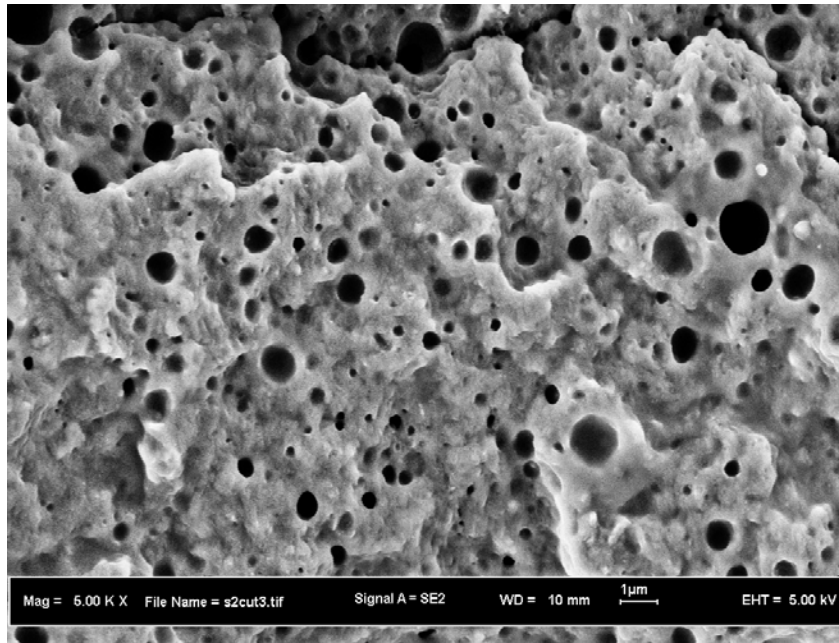
The effect of varying the concentration of POEgMAH from 0 - 20 wt% on the morphology of RTPA6NCs are discussed qualitatively based on the SEM micrographs of POE-g-MAH elastomer in RTPA6NC as shown in Figure 5 to 9.

The amount of discrete rubber particles evidently increased with increasing rubber content, but the average dispersed POEgMAH particles size changed slightly with composition. Under the strong shear rate applied to the polymer blends during intense melt mixing using extruder, the extent of dispersion and the probability of particles recombination probably remain independent of composition for low rubber loading.

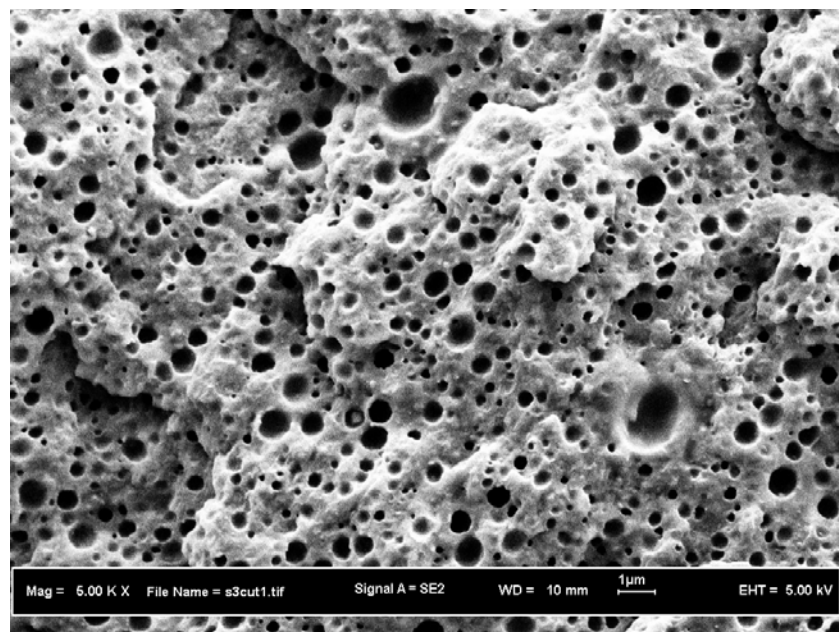
SEM photomicrograph also revealed that for POEgMAH copolymer loading at 15 wt% (Figure 8) and 20 wt% (Figure 9), the rubber particles were well-distributed and dispersed into the overall blends comparison to POEgMAH copolymer loading at 5 wt% (Figure 6) and 10 wt% (Figure 7). These finding agree well with the reported elongation at break results, which reported that the elongation at break increased remarkably at POEgMAH loading more than 15 wt%.



**Figure 5: SEM photomicrographs of RTPA6**



**Figure 6: SEM photomicrographs of RTPA6NC with 5 wt% POE-g-MAH**



**Figure 7: SEM photomicrographs of RTPA6NC with 10 wt% POE-g-MAH**

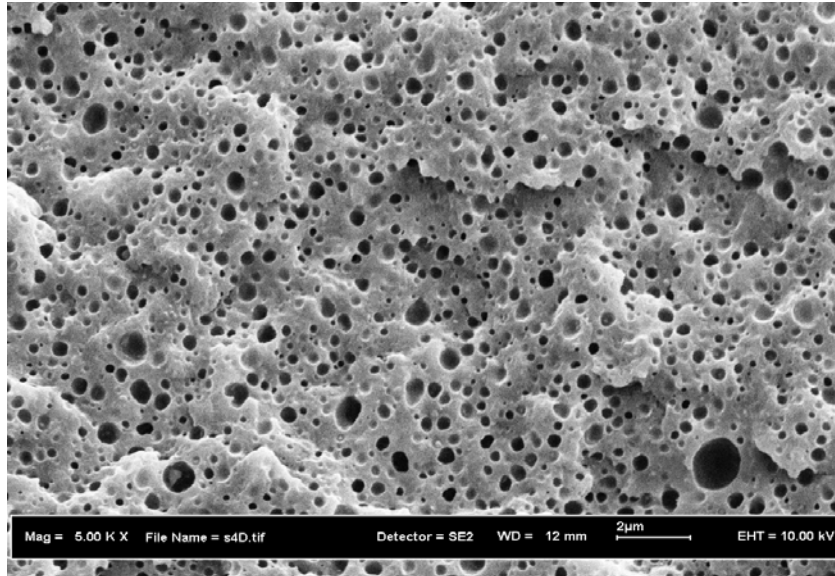


Figure 8: SEM photomicrographs of RTPA6NC with 15 wt% POE-g-MAH

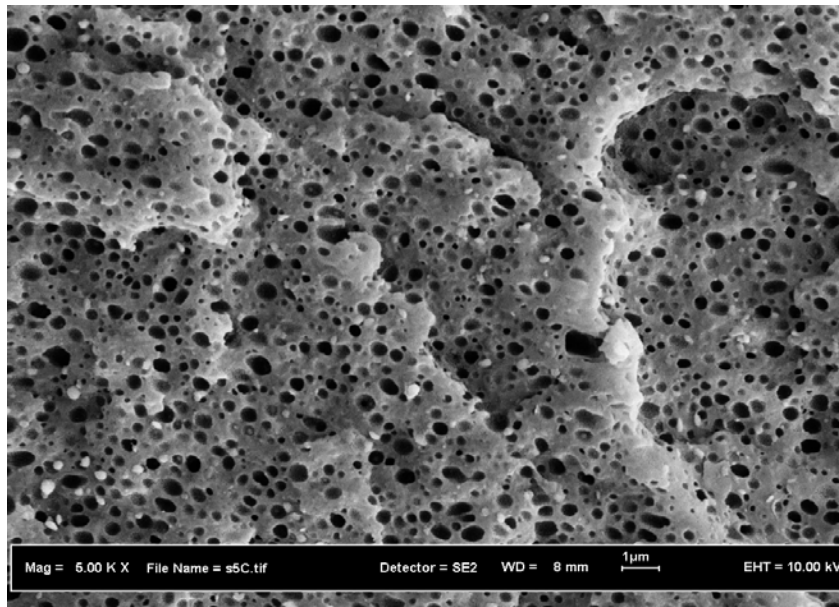


Figure 9: SEM photomicrographs of RTPA6NC with 20 wt% POE-g-MAH

## CONCLUSIONS

In this study, the mechanical and morphological properties of an injection-molded rubber toughened polyamide 6 reinforced with organophilic layered clay was investigated. The following conclusions can be drawn:

1. A good improvement in stiffness and strength has been discovered. Addition of MMT content has led to tremendous improvement in the stiffness of RTPA6NC blends. This is because the PA6 polymer chains have been exfoliated into the organoclay galleries.
2. The incorporation of POEgMAH showed that both toughness and elongation at break of PA6NC were being upgraded. A three fold improvement of the impact strength was observed after 20 wt% POE-g-MAH was added to PA6NC, due to the optimum particle size and good interfacial bonding between polymeric matrix and the dispersed particles.



3. XRD results indicated that the organoclay interlayer has been separated. This assumption is made due to no disappearance of (001) peak of pristine organoclay within the test range from 1.5 - 10°.
4. The SEM photomicrographs showed that two-phase morphology is clearly visible for all system investigated. The rubber particles were well distributed and dispersed in the RTPA6NCs

## REFERENCES

1. Cho, J.W. and Paul, D.R. (2001). Nylon 6 Nanocomposites by Melt Compounding. *Polymer*. 42: 1083-1094.
2. Chow, W.S., Mohd Ishak, Z.A., Karger-Kocsis, J., Apostlov, A.A. and Ishiaku, U.S. (2004). The effect of organoclay on the mechanical properties and morphology of injection molded polyamide 6/polypropylene nanocomposites. *Journal of Applied Polymer Science*. 91: 175-189.
3. Chavarria, F. and Paul, D.R. (2004). Comparison of nanocomposites based on nylon 6 and nylon 6,6. *Polymer*. 45: 8501-8515.
4. Yang, F., Ou, Y. and Yu, Z.J. (1998). *Applied Polymer Science*, 69, 335.
5. Fornes, T.D. and Paul, D.R. (2003). Crystallization Behavior of Nylon 6 Nanocomposites. *Polymer*. 44: 3945-3961.
6. Hasegawa, N., Okamoto, H., Kato, M., Usuki, A. and Sato, N. (2003). Nylon 6/Na-Montmorillonite Nanocomposites Prepared by Compounding Nylon 6 with Na- Montmorillonite slurry. *Polymer*. 44: 2933-2937.
7. Lincoln, D.M., Vaia, R.A., Wang, Z.G., Hsiao, B.S. and Krishnamoorti, R. (2001). Temperature Dependence of Polymer Crystalline Morphology in Nylon 6/Montmorillonite Nanocomposites. *Polymer*. 42: 9975-9985.
8. Ou, Y., Yang, F. and Yu, Z.Z. (1998). A new Conception on the Toughness of Nylon 6/Silica Nanocomposites Prepared via In Situ Polymerization. *Journal of Polymer Science: Part B: Polymer Physic*. 36: 789-795.
9. Wu, T.M. and Chen, E.C. (2002). Polymorphic Behavior of Nylon 6/Saponite and Nylon 6/Montmorillonite Nanocomposites. *Polymer Engineering and Science*. 42: 1141-1150.
10. Gloaguen, J.M. and Lefebvre, J.M. (2001). Plastic Deformation Behaviour of Thermoplastic/Clay Nanocomposites. *Polymer*. 42: 5841-5847.
11. Ji, X.L., Jing, J.K., Jiang, W. and Jiang, B.Z. (2002). Tensile Modulus of Polymer Nanocomposites. *Polymer Engineering and Science*. 42: 983-992.
12. Yu, Z.Z., Ou, Y.C. and Hu, G.H. (1998). Influence of Interfacial Adhesion on Toughening of Polyethylene-Octane Elastomer/Nylon 6 Blends. *Journal of Applied Polymer Science*. 69: 1711-1718.
13. Yu, Z.Z., Ke, Y.C, Ou, Y.C. and Hu, G.H. (2000b). Impact Fracture Morphology of Nylon 6 Toughened with a Maleated Polyethylene-Octane Elastomer. *Journal of Applied Polymer Science*. 76: 1285-1295.
14. Moczo, J. (2004). *Particulate filled polymer; intercalation, structure and micromechanical defarmation*. University of Budapest: Doctor of Philosophy.
15. Laura, D.M., Keskkula, H., Barlow, J.W. and Paul, D.R. (2003). Effect of rubber particle size and rubber type on the mechanical properties of glass fiber reinforced, rubber-toughened nylon 6. *Polymer*. 44: 3347-3361.
16. Tjong, S.C., Xu, S.A., Robert, K.Y.L. and Mai, Y.W. (2002). Short glass fiber-reinforced polyamide 6,6 composites toughened with maleated SEBS. *Composites Science and Technology*. 62: 2017-2027.
17. Gonzalez-Montiel, A., Keskkula, H. and Paul D.R. (1995). Impact-modified nylon 6/polypropylene blends: 1. Morphology-property relationships. *Polymer*. 36: 4587-4603.
18. Xie, S., Zhang, S., Liu, J. Chen, G. Feng, M., Qin, H., Wang F. and Yang, M.

- (2005). Effects of processing history and annealing on polymorphic structure of nylon-6/montmorillonite nanocomposites. *Polymer*. 46: 5417-5427.
19. Liu, T.X., Liu, Z.H., Ma, K.X. Shen, L., Zeng, K.Y. and He, C.B. (2003a). Morphology, Thermal and Mechanical Behavior of Polyamide 6/Layered-Silicate Nanocomposites, *Composites Science and Technology*. 63: 331-337.
  20. Shelley, J.S. (2000). *Mechanical Reinforcement and Environmental Effects on A Nylon-6/Clay Nanocomposite*. The University of Utah: Doctor of Philosophy
  21. Shah, R.K. and Paul, D.R. (2004). Nylon 6 nanocomposites prepared by a melt mixing masterbatch process. *Polymer*. 45:2991-3000.
  22. Somwangthanaroj, A. (2003). *Melt-State Rheology, Solid-State Mechanical Properties and Microstructure of Polymer-Clay Nanocomposites*. University of Michigan: Doctor of Philosophy.