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EFFECTS OF POE AND POE-G-MA ON IMPACT AND TENSILE PROPERTIES OF POLYAMIDE NANOCOMPOSITES

N. Othman, A. Hassan , A.R. Rahmat, M.U. Wahit,

Department of Polymer Engineering, Faculty of Chemical and Natural Resources Engineering,
Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia
Email: hayani_othman@yahoo.com

The incorporation of nanoclay in polyamide 6 (PA6) may increase the strength and water resistance of hygroscopic PA6. However impact strength of PA6 was reduced upon the addition of nanoclay. Blends of polyamide 6 nanocomposites (PA6NC) with either unmodified polyethylene octene elastomer (POE) or reactive polyethylene octene elastomer grafted with maleic anhydride (POE-g-MA) were prepared to overcome the brittleness. The blends were prepared using co-rotating twin screw extruder followed by injection molding into tests samples. The results show that the impact strength of PA6NC containing POE-g-MA is significantly higher than samples containing POE. The plausible reason is that of the better compatibility between PA with POE-g-MA compared to POE with PA6 due to formation of POE-g-PA6 copolymer during the melt processing. POE-g-MA also caused in higher tensile strength values compared to when POE is used. The SEM study show that the rubbery disperse phase is smaller when POE-g-MA is used, making it more effective as impact modifier.

Key words: *PA6 nanocomposites, polyethylene-octene elastomer, compatibilization, impact properties, tensile properties, polyethylene octene elastomer grafted with maleic anhydride*

INTRODUCTION

In recent years, polymer clay nanocomposites consist of layered silicates has received considerable attention. This nanometer-sized dispersion usually exhibit superior properties e.g. increased in stiffness and strength, improved barrier properties and better dimension stability to those of pristine polymer and conventional mineral fillers at very low concentration [1-5].

There are several potential approaches for the preparation of polymer clay nanocomposites. They are in-situ polymerization, polymer intercalation from solution and direct polymer melt intercalation. Direct polymer melt intercalation is the most attractive because of its low cost, high productivity and compatibility with current polymer processing techniques [1-3, 6].

Nylon 6 has been widely used in injection molding and extrusion material due to their easy processing, low friction, wear resistance, and high melting temperature. However, PAs are limited by high affinity for water. Usually its mechanical properties are often significantly affected by the absorption of water. Therefore incorporation of impermeable filler formed a tortuous path that may increase the resistance to both water and gas permeation [7].

Even though dramatic improvement was observed in strength, modulus and water resistance, the PA6 nanocomposite (PA6NC) was more brittle than PA6. Therefore an appropriate rubber that can function as an impact modifier is required. Ternary phase polymer composites containing rigid filler and soft elastomer have become the subject of an increasing number of studies that aim to achieve an optimum balance of impact strength and stiffness. Commonly used elastomers are ethylene-propylene rubber (EPR), styrene ethylene butylenes styrene block copolymer (SEBS) and polyethylene octene elastomer (POE) [8-12].

For three component system such as PA6/elastomer/filler, mutual miscibility and adhesion of the constituents are the crucial factors influencing the structure and the property relationships in ternary composites. Two families of morphologies are assumed in PA6 ternary composites: (i) elastomer and filler particles are separately dispersed in PA6 matrix; (ii) elastomer encapsulates filler particles to form core shell inclusions [8-9]. Morphological structure was controlled by the interfacial adhesion of PA6/filler, PA6/elastomer and filler/elastomer. One of the successful method of improving the interfacial adhesion of ternary composites is by introducing maleic anhydride grafting elastomer such as EPR-g-MA, SEBS-g-MA, POE-g-MA [8-11,13-16]. These functionalized polymers copolymerize 'in situ' by grafting with PA6, giving rise to the interfacial adhesion between the rubber and the PA6 matrix, which are believed to be essential for promoting toughness by reduced the dispersed rubber particles size in the blends,

whereas some of maleic anhydride group of functionalized polymers may also react with octadecylamine group from organoclay [16-17].

The work described in this paper aimed at determining the effects of POE and maleated POE on the mechanical and morphology of PA6NC.

EXPERIMENTAL

Materials

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 of PA6 was 35g/10 min at 230°C and 2.16 kg load and the density was 1.14 g/cm³. POE grade Engage 8150 was supplied by DuPont Dow Elastomers. Its octane content and MFI were 25wt% and 0.5g/10min, respectively. Polyethylene octene random (11wt% octene) copolymer grafted with maleic anhydride of DuPont (Fusabond MN493D) with density of 0.87 g/cm³ was supplied by DuPont Dow Elastomers. The organoclay (Nanomer 1.30TC) used was a commercial product from Nanocor Inc. USA. This organoclay is a white powder containing montmorillonite (MMT) (70wt %) intercalated by octadecylamine (30wt %).

Table 1: Blends used in this work (wt%)

<i>Formulation</i>	<i>PA6</i> <i>(Amilan</i> <i>CM 1017)</i>	<i>Organoclay</i> <i>(Nanomer</i> <i>1.30TC)</i>	<i>POE</i> <i>(Engage 8150)</i>	<i>POE-g-MA</i> <i>(Fusabond</i> <i>MN493D)</i>
PA	100	-	-	-
PAFA4	96	4	-	-
PAFA4POE	86	4	10	-
PAFA4POE-g	86	4	-	10

Specimen preparation

PA6, MMT, and POE or POE-g were dry blended in a tumbler mixer according to the composition in Table 1. The polymers and additives were then melt blended by simultaneous addition for all components into a Berstoff co-rotating twin screw extruder. The barrel temperatures were gradually increased from hopper to die at 200, 220, 230 and 240°C and the rotating screw was 50 rpm. Prior to extrusion, PA6 pellets were dehumidified by using a dryer at 80°C for 8 hours. The pelletized materials were dried and injection molded into a standard specimen for mechanical tests.

Materials characterization

Mechanical Testing

Tensile test were carried out according to ASTM D638 method using an Instron 5567 Universal Testing Machine under ambient condition. The crosshead speed for tensile test was 50 mm/min. The Izod impact test was carried out on notched specimens using Toyoseiki impact tester at ambient condition according to ASTM D256. In all cases, five specimens of each were tested and the average values were reported.

Microscopy examination (SEM)

The morphology of the blends was examined using a Philips scanning electron microscope. Samples were cryogenically fractured in liquid nitrogen and etched in hot heptane for 5 hours to extract the elastomeric POE phase. Samples were coated with gold prior to examination under the electron beam. An operating voltage of 30kV and a magnification of 1000x were used.

X-ray diffraction (XRD)

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

RESULT AND DISCUSSION

Mechanical properties

The mechanical properties of PA6, PA6NC and toughened PA6NC are tabulated in Table 2. The addition of organoclay increased the Young's modulus and tensile strength of pure PA6, but with a sacrifice in impact strength. The blends stiffness was enhanced with the incorporation of organoclay due to the stiffness of the silicates layers which contributes to the presence of immobilized or partially immobilized polymer phase [18]. The incorporation of 10wt% POE and POE-g into PA6NC lead to an improvement of 17% and 37% in impact strength, respectively. The higher impact strength enhancement in POE-g was attributed to better interfacial adhesion between POE-g and PA6 as a result of formation PA6-g-POE copolymer, thus improving the distribution of POE-g particles in the matrix. According to Premphet et al. [12] the presences of POE-g in the blends lead not only in reduction in rubber particles sizes but also changes in fracture mechanisms, which enhanced the impact resistance of the blends.

Table 2: Mechanical properties of PA6, PA6NC and toughened PA6NC

<i>Materials</i>	<i>Tensile strength</i> <i>MPa</i>	<i>Young's modulus</i> <i>MPa</i>	<i>Impact strength</i> <i>kJ/m²</i>
PA	59	1890	4.6
PAFA4	66	2471	4.1
PAFA4POE	48	2391	4.8
PAFA4POE-g	59	2129	5.6

For ternary composites of PA/elastomer/filler, the arrangement of filler in the PA6 matrix gives rise to the formation of two dissimilar morphologies as mentioned earlier in introduction, which is core shell and separated morphologies. The presence of POE-g could encapsulate organoclay particles due to interaction of maleic anhydride group with octadecylamine group from organoclay forming core shell inclusion structure. As shown by previous studies on ternary composites [9-10,12], encapsulation was also achieved by using other functionalized elastomer. The encapsulation of the filler by elastomer resulted higher impact strength than unmodified

elastomer. According to Li et al. [9] the encapsulation structure increased apparent volume fraction of elastomer, which decreased the distance between elastomer particles resulted higher impact strength than separated structure.

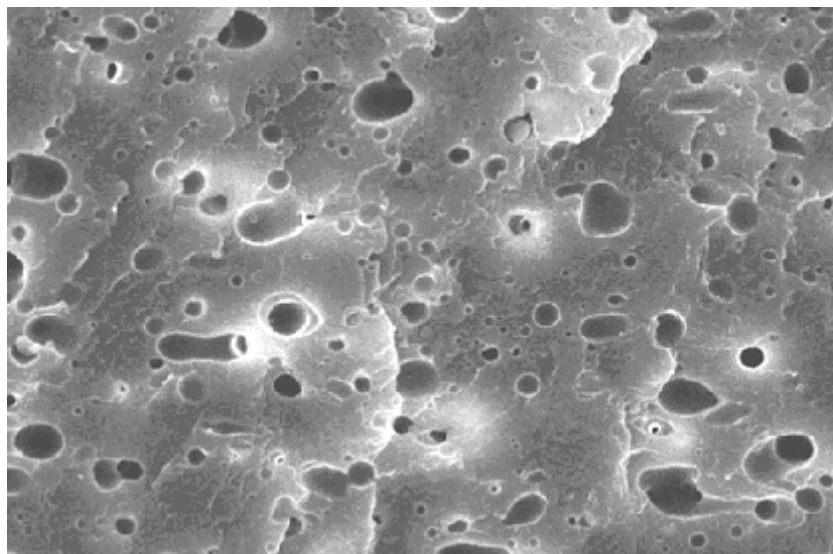
However addition of POE and POE-g decreased the tensile strength of PA6NC. It was observed that composites with POE decreased by 27% which is significantly greater than POE-g which decreased by only 10%. The plausible explanation for this is the improvement in interfacial adhesion between organoclay and PA6-g-POE. Some of maleic anhydride group of the POE-g may react and form hydrogen-bond with the octadecylamine group of the intercalate organoclay. Besides that, high similarity between the surface polarities of PA6-g-POE and organoclay leads to platelet exfoliated of clay among the matrix resulting in more efficient reinforcement effect [19]. An extra contribution arises from the specific interaction derived by hydrogen bonding between silicate layer and maleic anhydride group. Such interaction is no doubt beneficial to form randomized delamination of silicates layers [20].

The incorporation of POE or POE-g caused a reduction in modulus of PA6NC. This is expected as both POE and POE-g are low modulus materials. The results show that a composite with POE has a higher Young's modulus compared to POE-g. Theoretically, composites containing POE-g should have higher modulus than that containing POE as POE-g had higher modulus (2.7MPa at 100% strain) than POE (2.3MPa at same strain) [12]. A similar result was also reported by Premphet et al.[12], where lower modulus was found in PA6/POE-g compared to PA6/POE. Li et al.[9] reported that in ternary composites where core shell morphology exists (that is when elastomer encapsulates fillers particles), the modulus of the blends was decreased due to the soft layer of elastomer adhered to the surfaces of filler thus inhibiting the stiffening action of filler particles. For ternary composites of PA/elastomer/filler, higher modulus was obtained when the elastomer and filler dispersed separately compared to core shell structure.

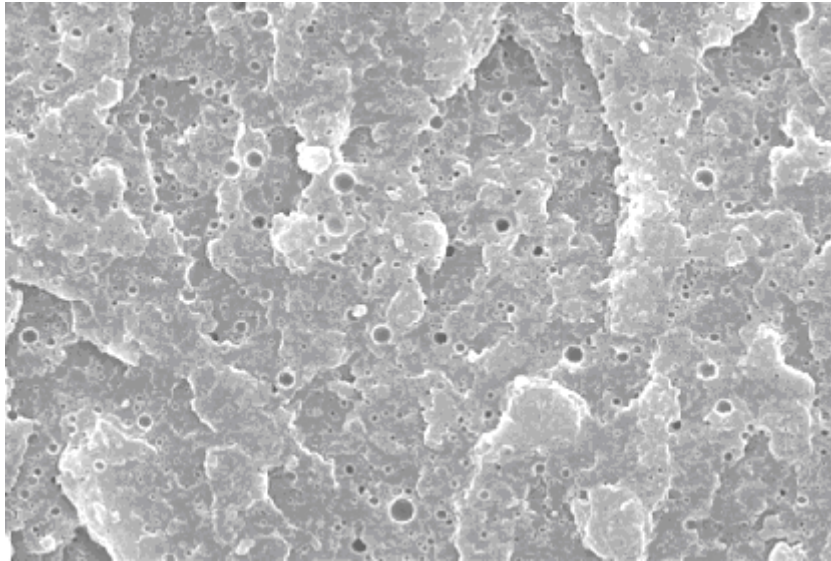
Phase morphology

Figure 1 shows SEM micrographs of freeze-fractured surfaces under liquid nitrogen. The cryo-fracture surfaces were extracted by heptane. The etched surfaces showed voids which represent

the POE particles as heptane dissolved only rubber phase but did not dissolve the PA6. From Figure 1(a) it can be seen that the sizes of elastomer particles of POE blends were relatively large with average diameter of POE particles approximately $6.9\mu\text{m}$. This revealed that low compatibility and weak interfacial adhesion between PA6 and POE. The influence of POE-g on the morphology of the PA6NC is shown in Figure 1(b). It showed significant change in phase morphology owing to 'in situ' compatibilizing effect resulting in better interfacial adhesion between PA6NC and POE-g. Blends containing of POE-g showed a very fine size of POE-g particles with average diameter of about $0.9\mu\text{m}$ and uniformly dispersed in PA6 matrix. The greater adherence in the POE-g blends is believed due to the chemical reaction during melt blending between terminal amine groups of PA6 and the anhydride functions of modified POE thus, forming POE-g-PA6 copolymer and reduced the rubber particles sizes. Similar findings have been reported when functionalized rubbers were used in replaced of unmodified rubber [10-11,13-15].



(a)



(b)

Figure 1: SEM micrographs of cryogenic fractured and etched surfaces of toughened PA6NC (a) POE (b) POE-g

X-ray diffraction

Figure 2 shows the XRD patterns in the range of $2\theta = 2-10^\circ$ for toughened PA6NC and PA6NC. The XRD spectrum of the organoclay exhibited a broad intense peak at around $2\theta = 3.52$ corresponding to a basal spacing of 2.48 nm. The XRD spectra of PA6NC and toughened PA6NC did not show any obvious peak in any case either POE or POE-g added. It indicates that the organoclay structure has delaminated. Wu et al. [22] and Cho et al [6] reported similar observations in the cases of nylon 1012 nanocomposites and nylon 6 nanocomposite, respectively. The absence of the characteristic clay d_{001} peak indicates that delamination of organoclay structure, thus dispersed randomly in polymer matrix which is nylon 1012 and nylon 6 respectively. Note that the incorporation of POE or POE-g did not change the distribution of clay in the matrix.

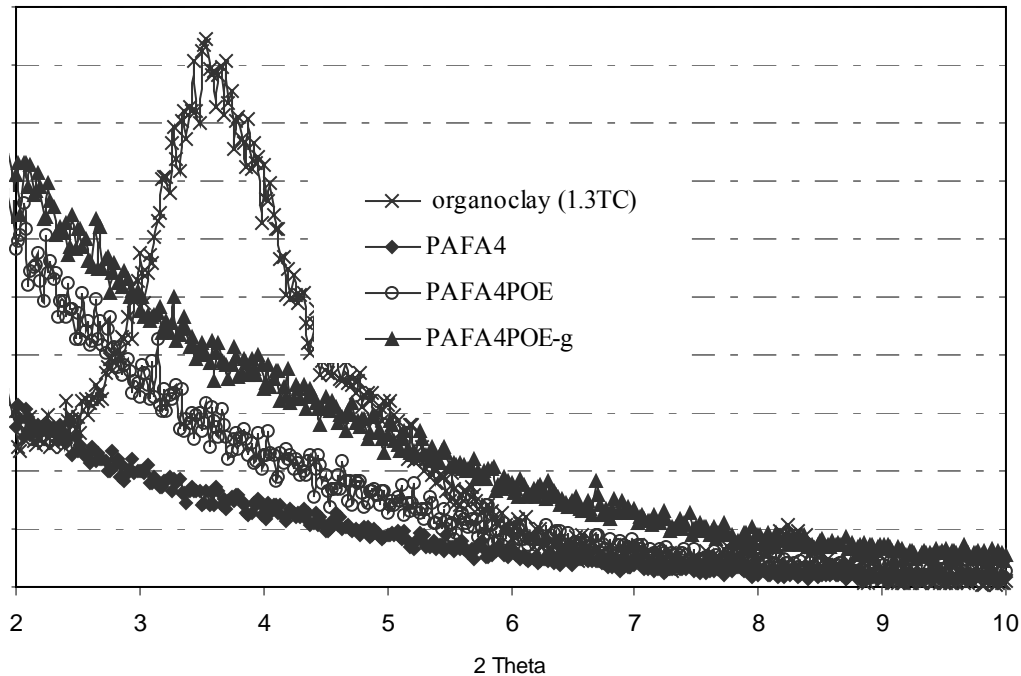


Figure 2: XRD pattern for organoclay, PA6NC and toughened PA6NC

CONCLUSION

The effect of POE and POE-g on the mechanical and morphology of toughened PA6NC have been investigated. The mechanical properties of the ternary composites were influenced by the interfacial adhesion and the morphology. The impact and tensile strength of POE-g toughened PA6NC were higher than POE. However Young's modulus of toughened PA6NC with POE-g was lower than POE. The higher impact strength and lower Young's modulus of POE-g toughened PA6NC is believed due to the presence of core shell structure. XRD evidenced that organoclay were delaminated in PA6 and toughened PA6 regardless of POE or POE-g added. SEM observations on the cryogenic surface indicate that the rubber particles sizes were decreased due to the formation of POE-g-PA6 copolymer. A reduction in dispersed particles size and an increase in adhesion between phases brought by the reaction between PA6 and anhydride group of POE-g, were also believed to be responsible for the toughness enhancement of the blends.

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