

Microstructural Characterisations and Mechanical Properties of Compatibilized Polyamide 6/Polypropylene/Organoclay Nanocomposites

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ABSTRACT

Polyamide 6/polypropylene (PA6/PP=70/30 parts) blends containing 4 phr (parts per hundred resin) of organophilic modified montmorillonite (organoclay) were compatibilized with two different compatibilizer, i.e. maleic anhydride grafted polypropylene (MAH-g-PP) and maleic anhydride-grafted ethylene-propylene rubber (EPR-g-MA), respectively. The blends were melt compounded in a twin screw extruder followed by injection molding. The mechanical properties of PA6/PP nanocomposites were studied through tensile and flexural tests. The microstructure of the nanocomposites were assessed by scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). The strength and stiffness of compatibilized PA6/PP nanocomposites were improved significantly, attributed to the synergistic effect of organoclay and compatibilizer. This was traced to the formation of an interphase between PA6 and PP (i.e. PA6-g-PP, or PA6-g-EPR). It was established that the organoclay is well dispersed and preferentially embedded in the PA6 phase (evidenced by TEM). The PA6/PP/organoclay nanocomposites containing compatibilizer (MAH-g-PP, EPR-g-MA) showed a more homogeneous morphology supporting the compatibility improvement between PA6, PP and organoclay. Adding either MAH-g-PP or EPR-g-MA to the PA6/PP/organoclay nanocomposites resulted in a finer dispersion of the PP phase (evidenced by SEM, TEM and AFM). Further, by utilization of the AFM technique, it was demonstrated that, the organoclay was dispersed in the PA6-rich phase. TEM and XRD results revealed the formation of nanocomposites as the organoclay was partially intercalated and exfoliated.

1. INTRODUCTION

Polymer nanocomposites have attracted great interest in both academic and industrial area, owing to their remarkable improvement in materials properties (i.e. high modulus and strength, better heat and gaseous resistance, and etc.) when compared to conventional composites [1]. Layered silicates dispersed as a reinforcement in a polymer matrix are one of the forms of hybrids organic-inorganic nanocomposites, or we can call it, polymer/layered silicate nanocomposites [2]. Direct polymer melt intercalation is the most attractive routes for nanocomposite preparation because of its low cost, high productivity and compatibility with current polymer processing techniques (i.e. extrusion and injection molding machine). For direct polymer melt intercalation process, the polymer chain spread from the molten mass into the silicate galleries to form either intercalated or exfoliated hybrids or both [3]. The degree of dispersion (e.g. exfoliation, intercalation) and the compatibility of the nano-reinforcements (e.g. layered silicates, nanotubes, nano-fibers, nano-fillers) with the polymer matrix are important factors which result in remarkable changes in properties (mechanical, rheological, barrier etc.) of a polymer. Numerous reports described polymer/clay nanocomposites produced, via incorporation of either pristine (unmodified) clays or organophilic layered silicates (organoclay/OMMT) in a single polymer matrix [4]. However, thermoplastic nanocomposites based on polymer blends seem to be a new approach in the nanocomposite studies. The work presented in the present paper focuses on the study of thermoplastic nanocomposites based on blends of polyamide 6 (PA6) and polypropylene (PP). PA6 and PP has been chosen to achieve a good balance of properties in the final product. While PA6 has good overall mechanical properties, PP will help to provide a good resistance against moisture and ensures good processability. In a previous study on the PA6/PP

nanocomposites [5], 4 phr OMMT has been observed to be the optimum loading for the blends. A significant improvement in the strength and stiffness of the composites was reported when maleated polypropylene (MAHgPP) was used as compatibilizer for the PA6/PP blend [6]. The MAHgPP compatibilized blend-based nanocomposites which showed a more homogeneous morphology and a better clay dispersion than the uncompatibilized counterparts. In order to get a better understanding on the compatibilization for PA6/PP/organoclay system, in the present study maleic anhydride-grafted ethylene-propylene-rubber (EPRgMA) was chosen as another compatibilizer. Thus, the present work was devoted to the study of the effect of compatibilizer on the microstructure of PA6/PP-based nanocomposites, through several sophisticated techniques, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and x-ray diffraction (XRD).

2. EXPERIMENTAL

2.1 Materials and specimen preparation

The PA6 (Amilan CM 1017) used in this study was a commercial product from Toray Nylon Resin AMILAN, Japan. The melt flow index (MFI at 230 °C and 2.16 kg load) and density of PA6 were 35 g/10 min and 1.14 g/cm³, respectively. PP (Pro-Fax SM-240) was supplied by Titan Himont Polymer (M) Sdn. Bhd. MFI and density of PP is 25 g/10 min. (at 230 °C and 2.16 kg load) and 0.9 g/cm³, respectively. MAH-g-PP (Polybond 3200) with 1.2 wt% of maleic anhydride (MA) was supplied by Uniroyal Chemical, Middlebury. The MFI of MAH-g-PP is 105g/10min. at 190 °C and 2.16 kg load. EPR-g-MA (Exxelor VA 1801) containing 1 wt% MA was supplied by Exxon Mobil Chemical. The ethylene/propylene ratio of this material was 70/30 wt%. Organoclay (Nanomer 1.30TC) was a commercial product from Nanocor, Inc, USA. This organoclay is a white powder containing montmorillonite (70 wt%) intercalated by octadecylamine (30 wt%). Mean dry particle size of the organoclay is 16 – 22 microns. PA6/PP/organoclay (70/30/4 parts) blends were extrusion compounded and injection molded as described in our earlier papers [5,6]. The designation, composition and density value of the materials tested is given in Table 1.

Table 1. Designation of Materials

Material Designation	Composition	Parts
PA6/PP	Polyamide 6/Polypropylene	70/30
PA6/PP/4TC	Polyamide 6/Polypropylene/Organoclay	70/30/4
PA6/PP/5M/4TC	Polyamide 6/Polypropylene/MAHgPP/Organoclay	70/30/5/4
PA6/PP/5E/4TC	Polyamide 6/Polypropylene/EPRgMA/Organoclay	70/30/5/4

2.2 Mechanical properties

Tensile test was carried out with an Instron-5582 machine at 23 °C, according to ASTM D638, at a crosshead speed of 50 mm/min. E-modulus, tensile strength and elongation at break were

evaluated from the stress-strain data. Flexural measurements were carried out according to ASTM D790 using 3-point bending configuration at 3 mm/min. deformation rate.

2.3 Microscopic examination (SEM and TEM)

The fracture surface of selected PA6/PP based nanocomposites was inspected in a scanning electron microscope (SEM; Leica Cambridge Ltd. model S 360). The fracture surface were gold coated to avoid electrostatic charging during examination. Transmission electron microscopy (TEM) measurements were carried out with a LEO 912 Omega transmission electron microscope applying an acceleration voltage of 120 keV. The specimens were prepared using an Ultracut E (Reichert & Jung) ultramicrotome. Thin sections of about 100 nm thickness were cut with a Diatome diamond knife at room temperature.

2.4 X-ray diffraction (XRD)

Wide-angle X-ray spectra were recorded with a D 500 diffractometer (Siemens) in step scan mode using Ni-filtered Cu K α radiation (0.1542 nm wavelength). Powder samples were scanned in reflection, whereas the injection-molded compounds were scanned in transmission in the interval of $2\Theta = 2-10^\circ$. The interlayer spacing of the organoclay was derived from the peak position (d_{001} -reflection) in the XRD diffractograms according to the Bragg equation.

2.5 Atomic force microscopy (AFM)

Specimens were taken from the gauge section of the injection molded dumbbells. Their orientation was transverse to the mold flow direction. The surface profile was scanned by AFM (MultiModeTM Scanning Probe Microscope, Digital Instruments) in tapping mode and the related topography image captured.

3. RESULTS & DISCUSSION

The effect of compatibilizer (MAHgPP and EPRgMA) on the tensile and flexural properties is presented in Table 2. The incorporation of the organoclay increase the stiffness of the uncompatibilized PA6/PP blends significantly. Further enhancement of the modulus of the PA6/PP nanocomposite is observed with the incorporation of compatibilizer. This may be attributed to the improvement in the interfacial interaction of the organoclay with the PA6/PP in the presence of compatibilizer. Incorporation of the organoclay into PA6/PP mildly increased the ultimate strength. However, a remarkable improvement in the ultimate strength was observed by adding compatibilizer (MAHgPP and EPRgMA). This is believed to be associated with two factors: first, the degree of dispersion (i.e. degree of exfoliation/intercalation) of the silicate layers of organoclay in the PA6/PP matrix; second, the interfacial interaction of the organoclay and the PA6/PP matrix. MAHgPP and EPRgMA compatibilizer may favour the degree of dispersion of the organoclay via intercalation into the silicate layers of the organoclay and subsequent exfoliation during shear and elongational flows in extrusion and injection molding operations. Some maleic anhydride group of the compatibilizer may react and form H-bonds with the octadecylamine groups of the initial intercalant of the organoclay. The possible mechanism of interaction is reported elsewhere [6].

The addition of the organoclay caused a tremendous drop in the elongation at break of the PA6/PP blends. This is likely due to the co-existence of agglomerated layered silicates (un-exfoliated organoclay), and exfoliated/intercalated organoclay layers and particles in the matrix.

However, a slight increase in the ductility (as indicated by the increase of elongation at break) of PA6/PP/organoclay nanocomposite was observed with the incorporation of EPRgMA. This may be related to the formation of copolymer (PA6-g-PP or PA6-g-EPR), which improved the interfacial bonding between PA6 and PP.

Table 2. Mechanical Properties of PA6/PP blends and its nanocomposites

Mechanical Properties		Materials			
		PA6/PP	PA6/PP/4TC	PA6/PP/5M/4TC	PA6/PP/5E/4TC
Tensile	E-modulus (GPa)	1.9	2.1	2.4	2.3
	Tensile strength (MPa)	32.1	38.0	49.7	46.9
	Yield stress (MPa)	38.6	38.9	50.1	48.7
	Elongation at break (%)	22.8	4.2	4.8	6.7
Flexural	Modulus (GPa)	1.7	1.9	2.1	2.0
	Flexural strength (MPa)	76.2	78.7	97.9	95.9

Figure 1 shows the XRD patterns (in the range of $2\theta = 2-10^\circ$) for organoclay and uncompatibilized and compatibilized PA6/PP nanocomposites. The organoclay patterns reveals a broad intense peak at around $2\theta = 3.25^\circ$, corresponding to a basal spacing of 2.72 nm. The XRD pattern of uncompatibilized and compatibilized PA6/PP/organoclay composites do not show the characteristic basal reflection of the pristine organoclay. However, the XRD traces show a shoulder at $2\theta = 2.85^\circ$ superimposed to the declining part of the XRD spectrum. This is a clear indication that a portion of the organoclay is intercalated. XRD spectra of the organoclay filled PA6/PP nanocomposites display a prominent increase in the intensity at lower 2θ values when compared with those of the unfilled blends. This likely reflects that the organoclay used was partly exfoliated and partly intercalated (and the related XRD peak lays $2\theta < 2^\circ$).

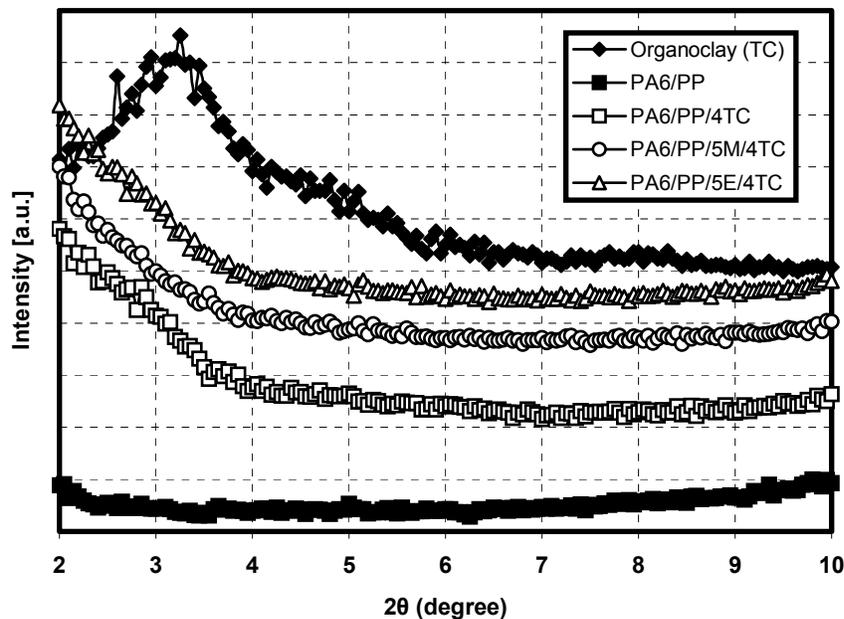


Fig. 1: XRD spectra of the PA6/PP/organoclay nanocomposites.

Figure 2(a) display a SEM picture taken from of the fractured surface of the uncompatibilized PA6/PP/organoclay nanocomposite. Large and irregular PP particles, dispersed in the PA6 matrix, can be resolved on the fractured plane. These particles seems to be easily debonded and detached from the PA6 matrix due to the poor interfacial adhesion between them. Incorporation of the organoclay alone does not produce a finer morphology in the PA6/PP blends. The lack of plastic deformation on the fracture plane explains the sharp drop in the ductility of the PA6/PP blend in the presence of organoclay [5].

Figure 2(b) and (c) shows the transformation from brittle to ductile failure mode due to the compatibilization effect of MAHgPP and EPRgMA, respectively. A more homogeneous, fibrillated morphology characterizes the fracture surface of compatibilized PA6/PP/organoclay nanocomposites. The compatibilizer, located in the interphase, may act as a “bridge” between the PA6 and PP phases and thus enhances the loadability of the blend. It is believed that there are also interfacial interactions between the compatibilizer (MA groups) and the organoclay (octadecylamine groups).

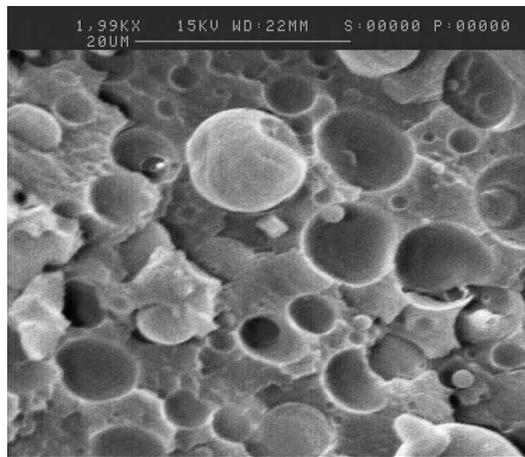


Fig. 2a: SEM micrograph of the tensile fractured surface of uncompatibilized PA6/PP/organoclay nanocomposites.

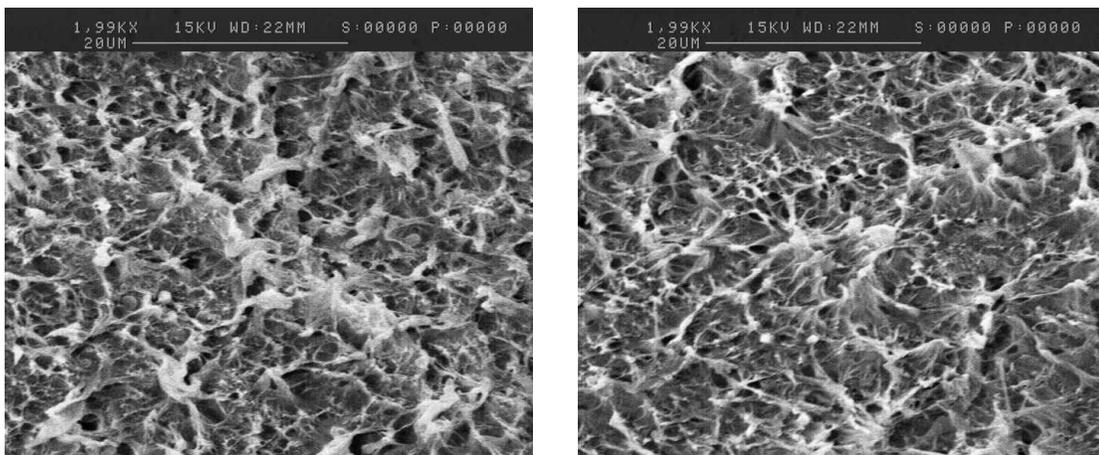


Fig. 2b & c: SEM micrograph of the tensile fractured surface of compatibilized PA6/PP/organoclay nanocomposites. (note: b = MAHgPP compatibilized; c = EPRgMA compatibilized)

Figure 3(a), (b) and (c) show characteristic TEM micrographs taken from the uncompatibilized, MAHgPP and EPRgMA compatibilized PA6/PP/organoclay nanocomposites,

respectively. The dark lines represent the thickness of individual clay layers or clay agglomerates. Thick darker lines display stacked silicate layers (tactoids). In uncompatibilized PA6/PP nanocomposites the organoclay was partly intercalated and partly exfoliated, as shown by TEM (cf. Figure 3(a)). This indicates that a mixture of delaminated, intercalated silicate layers and aggregated tactoids may co-exist in the PA6/PP matrix. However, a more pronounced exfoliation can be noticed with the incorporation of MAHgPP and EPRgMA compatibilizer (cf. Figure 3(b) and 3(c)). Our earlier investigations revealed that the clay layers and particles are preferentially located in the PA6 phase [5,6].

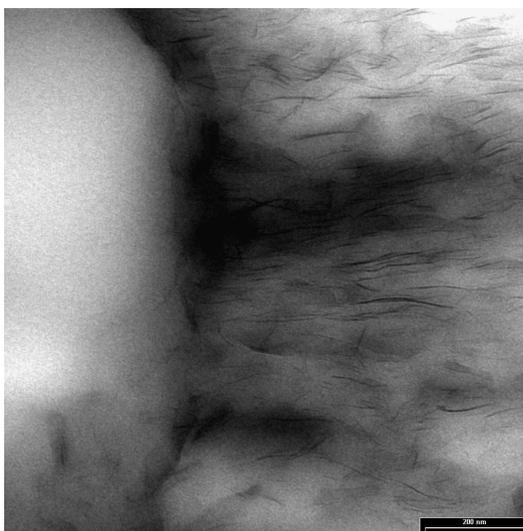


Fig. 3a: TEM pictures showing the dispersion of the organoclay in the uncompatibilized PA6/PP nanocomposites.

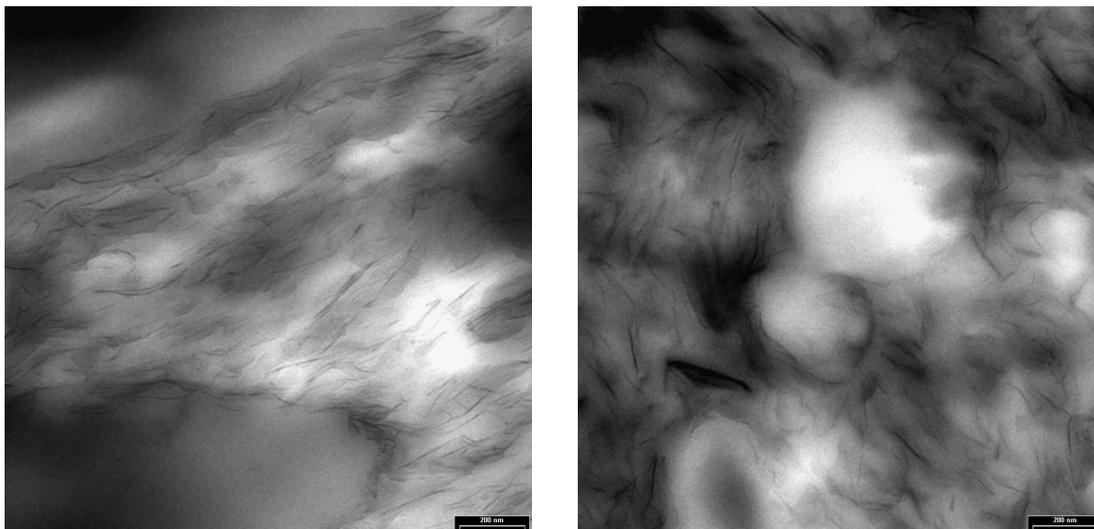


Fig. 3b & c: TEM pictures showing the dispersion of the organoclay in the compatibilized PA6/PP nanocomposites. (note: 3b = MAHgPP compatibilized; 3c = EPRgMA compatibilized)

Figure 4a demonstrates the AFM topography showing the dispersion of the organoclay particle in the uncompatibilized PA6/PP nanocomposites. Large PP particles could well be

resolved. As expected their size agrees well with the dimension derived from SEM, which is approximately 10 μm . Even the poor adhesion between PA6 and PP in the uncompatibilized blend can be deduced by considering the 3D scan in Figure 4a. Adding MAHgPP compatibilizer into PA6/PP/organoclay alters the blend morphology significantly. First, the PP dispersion becomes finer in the PA6 matrix. One can easily resolve the PP particles are in the range of 1-2 μm . A high resolution 3D AFM picture shown in Figure 4b displays the complex morphology of the compatibilized PA6/PP/organoclay composites. It is interesting to note that, for both uncompatibilized and compatibilized PA6/PP nanocomposites, the organoclay particle was presented by a “hump” (shown by arrows). Further information and discussion was reported elsewhere [7].

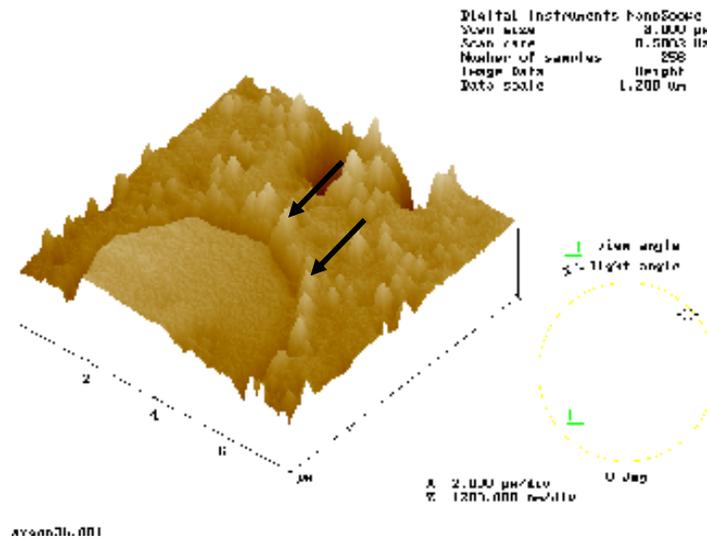


Fig. 4a: AFM 3D topography showing the dispersion of the organoclay in the uncompatibilized PA6/PP nanocomposites. Note: organoclay was shown by arrows.

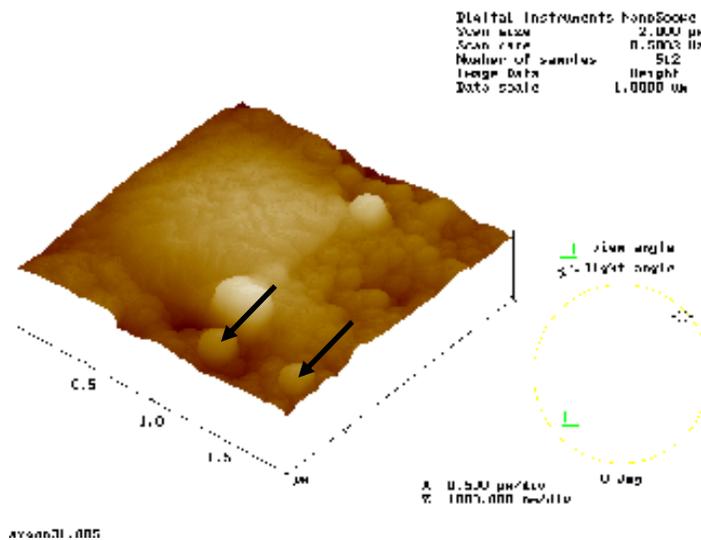


Fig. 4b: AFM 3D topography showing the dispersion of the organoclay in the MAHgPP compatibilized PA6/PP nanocomposites. Note: organoclay was shown by arrows.

4. CONCLUSIONS

Based on this work devoted to study the effect of compatibiliser (i.e. MAHgPP and EPRgMA) on the properties of PA6/PP (70/30 wt.%) blends containing 4 phr OMMT, the following conclusions can be drawn:

1. Incorporation of organoclay improved the stiffness and reduced the ductility as expected owing to its exfoliation/intercalation. This was attributed to the generation of a grafted co-polymer (i.e. PA6-g-PP and PA6gEPR) which formed an interphase between PA6 and PP.
2. The coarse dispersion of PP became markedly finer owing to the presence of compatibilizer (MAHgPP and EPRgMA). The organoclay was present in delaminated/exfoliated and intercalated forms simultaneously as evidenced by TEM, AFM and XRD studies. The incorporation of compatibilizer facilitated the dispersion of the organoclay in the PA6/PP matrix, and more exactly in the PA6 rich phase.

ACKNOWLEDGEMENTS

The authors would like to thank Ministry of Science, Technology and Environment (MOSTE), Malaysia for the IRPA grant (grant no: 063171/IRPA). Special scholarship granted by Universiti Sains Malaysia and German Academic Exchange Service (DAAD) scholarship to one of us (Mr. W.S. Chow) is gratefully acknowledged. We also thank to Dr. R. Thomann (Freiburg, Germany) Dr. A.A. Apostolov (Sofia University, Bulgaria) for performing the TEM and X-ray measurements, respectively.

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