PC8:

PRELIMINARY STUDIES ON THE EFFECT OF POLYETHYLENE OCTENE ELASTOMER ON POLYPROPYLENE NANOCOMPOSITE: - MECHANICAL PROPERTIES AND PHASE MORPHOLOGY

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The melt-direct intercalation method was employed to prepare rubber toughened polypropylene nanocomposites (RTPPNC). The blends composition was kept constant (PP + organoclay 6wt%) while the polyethylene octane (POE) content was varied between 0 and 20wt%. Maleated PP (PP-g-MAH) was used as compatibilizer in the blend system. The POE used had 25wt% 1-octene content. X-ray diffractometer (XRD) revealed that an intercalation MMT silicate layer structure was formed in rubber-toughened polypropylene nanocomposite (RTPPNC). Izod impact measurements indicated that the POE addition led to a significant improvement in the impact strength of the RTPPNC, from 6.2 kJ/m² in un-toughened PP/ Org-MMT nanocomposite to 17.8 kJ/m² in RTPPNC containing 20wt% POE. However, the flexural modulus and flexural strength of the blends decreased with respect to neat PP as the weight fraction of POE was increased to 20wt%. Scanning electron microscope (SEM) was used for the investigation of the phase morphology, rubber particles size and particle-size distribution. SEM study revealed a two-phase morphology where POE as droplets dispersed finely and uniformly in the PP matrix.

[Keywords]: Polypropylene (PP); polyethylene octane (POE); nanocomposite; rubber-toughened; mechanical properties

INTRODUCTION

Development of nanocomposites is one of the latest evolutionary steps of the polymer technology. Nowadays, more than 70 companies, government agencies and academic institutions have been identified as having research and development activities related to nanocomposites (1-3). It is hoped that nanotechnology can lead the way to better materials for many application, from nanowires and nanodots in electronics to nanoblends and nanocomposites in automotive applications. The current interest is the use of layered silicates as nanoscopic filler materials such as montmorillonite (MMT). By modifying the surface through the use of organic surfactant molecules, high aspect-ratio platelets can be incorporated in to a polymer matrix. The surface modified layered silicates increases their interlayer basal spacing, thereby increasing the ease of entry of polymer and serves as a compatibilizer between the hydrophilic clays and hydrophobic polymers. Using such modified silicates, various polymer nanocomposite have been produced including polypropylene/MMT (4-9), polystyrene/MMT (10-11), polyamide/MMT (12-15) and others (16-19).

Currently, the study on PP/organoclay nanocomposites (PPNC) has attracted the interest of many researchers, due to huge commercial opportunities in both automotive and packaging. However, PPNC is relatively difficult to produced because polypropylene does not contain any polar group in its backbone chain and not compatible with organoclay. Kawasumi wt al. (20) were the first to developed an approach to create PPNC by direct melt compounding of PP with inorganic MMT in the presence of maleic anhydride modified polypropylene (PP-g-MAH) oligomer as a compatibilizer. A good dispersion and mechanical properties such as stiffness, heat distortion temperature (HDT), dimensional stabilities and enhanced barrier to gas permeation, have been achieved (8, 21).

One of the major deficiency of PP and PPNC is its low impact resistance, particularly at low temperatures because of its relatively high glass transition temperature, Tg. Blending PP with an elastomeric modifier may provides the way to improve the impact resistance of the base resin. Articles published by Liang and Li (21) and Utracki (22) had reviewed the advances mechanisms in toughening PP-elastomer blends in the last 20 years. At present, ethylene-propylene rubbers (EPR) and ethylene-propylene diene rubbers (EPDM) are the most frequently used PP impact modifiers.

In this study, an attempt has been made to investigate the toughening of PPNC blends via an incorporation of a relatively new type of impact modifier known as polyethylene octene (POE) copolymer. It is a novel polyolefin elastomer which was developed using metallocene catalyst by Dow Chemical Co. These new ethylene octane (EO) copolymers offer a controlled level of chain branching along the polymer backbone. The narrow composition and molecular weight distribution result in improved rheological properties, such as better shear thinning behaviour, melt elasticity and melt processability. These enhanced rheological properties, which match that of the polypropylene, improve dispersion and faster mixing in rubber-modified polypropylene blends. This results in better stiffness and toughness balance than traditional EPDMs or EPRs (23-25). Little work has been done on combination of both polymer nanocomposites with rubber toughening. The aim of the research is to study the effect of POE content on mechanical, phase morphology and thermal properties of the rubber toughened polypropylene nanocomposites (RTPPNC).

EXPERIMENTAL

Materials

The blends used in this work are described in Table 1. PP copolymer (SM-240) supplied by Titan, Malaysia. MFI and density of PP is 25.0g/10min (at 230°C and 2.16kg load) and 0.9 g/cm^3, respectively. POE (Engage 8150) a metallocene catalysed copolymer of ethylene and 1-octene with 25wt% of comonomer was supplied by DuPont Dow Elastomer. Maleated PP (PP-g-MA) used was Orevac CA 100 with ~ 1 wt% of maleic anhydride (MA) produced by ATOFINA, France. Organoclay (Nanomer 1.30P) was a commercial product from Nanocor Inc. USA, containing MMT (70-75 wt%) intercalated by octadecylamine (25-30 wt%).

Table 1: Blend Compositions

System	PP (wt%)	Org-MMT (wt%)	PP-g-MAH (wt%)	POE (wt%)
PP	100	0	0	0
PPFB6C6	88	6	6	0
PPFB6C6E5	83	6	6	5
PPFB6C6E10	78	6	6	10
PPFB6C6E15	73	6	6	15
PPFB6C6E20	68	6	6	20

Compounding and Test Specimen Preparation

Blends of PP, PP-g-MAH, MMT and POE according to Table 1 were compounded after tumbler mixing using a Berstoff co-rotating twin-screw extruder. The temperature profile adopted during compounding of all blends was 180°C at the feed section increasing to 230°C for the die head. Tensile, flexural, and impact test specimens were produced using injection molding machine with the temperature profile maintained from 170°C at feed zone to 220°C at nozzle section. All test specimens were allowed to condition under ambient conditions for at least 48 hours prior to testing.

Mechanical Analysis

Flexural tests were carried out according to ASTM D790 method respectively using an Instron 5567 Universal Testing Machine under ambient condition. Crosshead speed of 3mm/min respectively was used for flexural test. The Izod impact tests were carried out on notched impact specimens using impact tester at ambient conditions. Five specimens of each were tested and the average values were calculated.

X-Ray Diffraction (XRD)

X-ray diffraction analysis (XRD) was carried out in order to confirm whether the PP/PP-g-MAH/org-MMT nanocomposites were formed. The XRD patterns were scanned in 2θ ranges from 1.5° to 10° and at a step size of 0.02°. The interlayer distance of org-MMT in composite was calculated from the (001) peak by using Bragg equation.

Phase Morphology

The morphology of the blends was examined using a Philips ZL40 scanning electron microscope. Samples were cryogenically fractured in liquid nitrogen and etched in heptane at 50°C for 3 hours to extract the elastomeric POE phase. Samples were coated with gold prior to examination under the electron beam. An operating voltage of 10kV and a magnification of 500X and 1000X were used.

## RESULTS AND DISCUSSION

X-Ray Diffraction Analysis (XRD)

The X-ray diffraction patterns of org-MMT (1.30P) and PP/PP-g-MAH/Org-MMT nanocomposite with different content of PEO (0 wt% - 20 wt%) are shown in Figure 1 and Figure 2. X-ray parameters calculated from the (001) peaks are summarized in Table 2. As can be seen from Figure 1, in the PPFB6C6 composites, the (001) plane peaks of 1.30P (Org-MMT) around $2\theta= 3.401°$, as expected, were shifted to lower angles about $2\theta= 2.465°$ comparable to that of Org-MMT, implying that the interlayer distance was multitude from 2.596 nm to 3.581nm during direct melt process. This clearly indicates that macromolecule chains had intercalated into the galleries of Org-MMT. X-ray diffraction patterns of neat PP did not show any peak in the testing.

This may be the result of the strong interaction between polar PP-g-MAH molecule and the silicate layer. The driving forces of the intercalation originate from the strong hydrogen bonding between maleic anhydride group (COOH group generated from the hydrolysis of the maleic group) and the oxygen groups of the silicates. The interlayer spacing of the clay increases and the interaction of the layers should weaken. The intercalated clay with the oligomers contacts with PP under a strong shear field during extrusion process will lead macromolecule PP chains intercalated into the galleries of Org-MMT (26).

Kim et al (9) have presumed that when three components of PP, PP-g-MA and organoclay were put together and melt mixed, only PP-g-MAH would penetrate into the organoclay interlayer. Once the functionalized polymers are intercalated into the gallery, they constitute the long-chained surfactants. The matrix polymer can then readily penetrate into thick interlayer and form a broad interphase, which results in the formation of exfoliated structure.

Table 2: 2θ and d values for org-MMT and PPNC contained PEO from 0-20wt%

Sample	2θ (deg)	d (nm)
1.30 P	3.401	2.596
PP	-	-
PPFB6C6	2.465	3.581
PPFB6C6E5	2.777	3.178
PPFB6C6E10	2.668	3.309
PPFB6C6E15	2.668	3.308
PPFB6C6E20	2.647	3.334
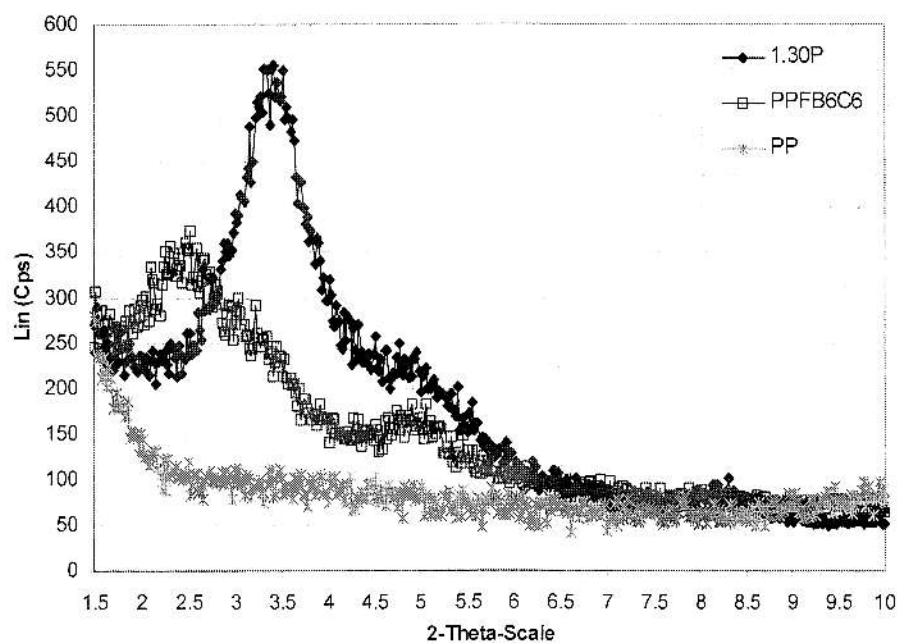
Figure 1: XRD pattern for org-MMT and PPNC.

In the other hand, with addition of PEO elastomer into PPFB6C6, the peak position moves to ward a higher angel about 2.647 compared to PPFB6C6 at 2.465, as shown in Figure 2. However, the interlayer distance PPFB6C6 with different concentration PEO are in the same range about 3.3 nm. This result was quite different from the study of Li (24), where her study found that addition of SEP rubber would increase the clay's interlayer spacing. This implies that polar SEP rubber has good interaction with clay particles and this interaction helps to reduce clay particle size and disperse clay uniformly, but non-polar PEO had no such interaction.
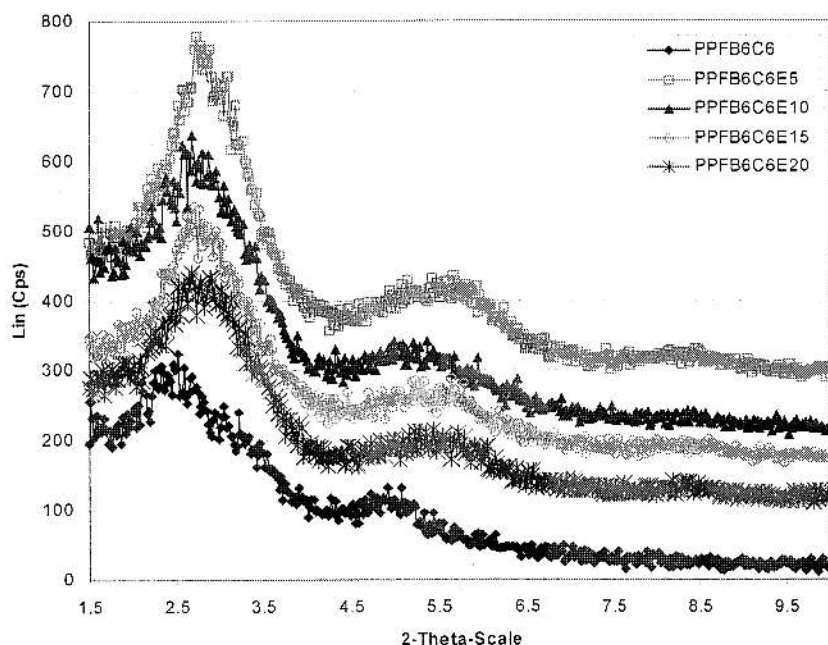
**Figure 2:** XRD pattern for PPNC contained PEO elastomer from 0-20wt%

Mechanical Properties

The flexural properties of rubber toughened polypropylene nanocomposites are measured and summarized in Figure 3. As expected, the flexural modulus and flexural strength decrease almost linearly with increasing rubber content. This observation 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 to the matrix. Therefore, the subsequent steps of our research have been directed towards improving the toughness-to-stiffness balance in PP nanocomposites by incorporation of POE as impact modifier and organoclay as filler reinforcement.
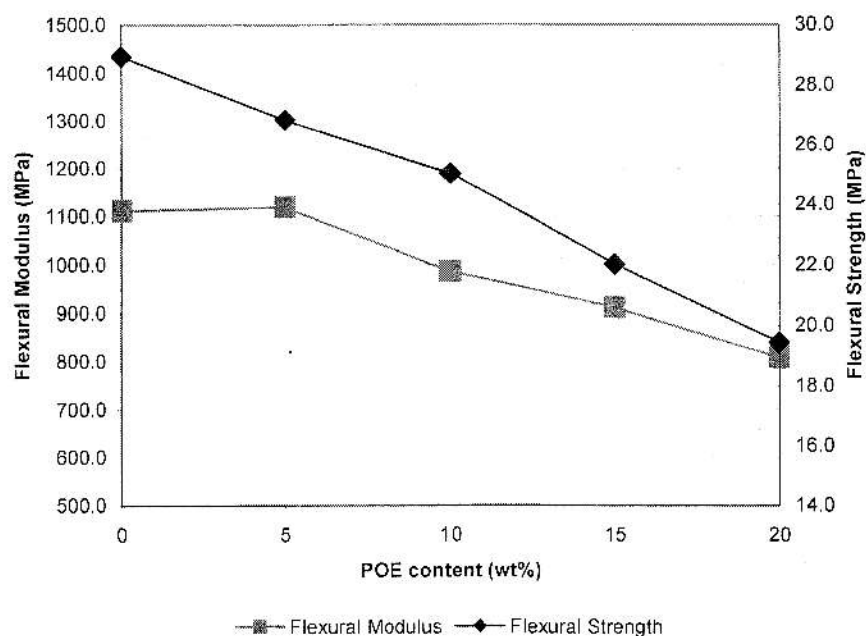
Figure 3: Effect of PEO content on flexural strength and flexural modulus PPNC.

The influences of adding the POE on impact strength of PPNC are shown in Figure 4. The result from our study revealed that in RTPPNC, the impact properties were significantly improved (187%) for RTPPNC contained 20wt% POE. This was similar with the report of Premphet and Chalearmthitipa (29) which showed that the incorporation 10% POE to neat PP matrix led to significant improvement in impact strength. High effectiveness of POE elastomer in toughening of PP was due to the high compatibility of PP/POE blend. According to the studies of Carriere and Silvis (30), increase in the length of side chain from ethylene-propylene to ethylene-octene causes a statistically significant drop in the measured interfacial tension. This result indicates that blends of PP with ethylene-octene are more compatible than those made with either ethylene-butene or ethylene-propylene.
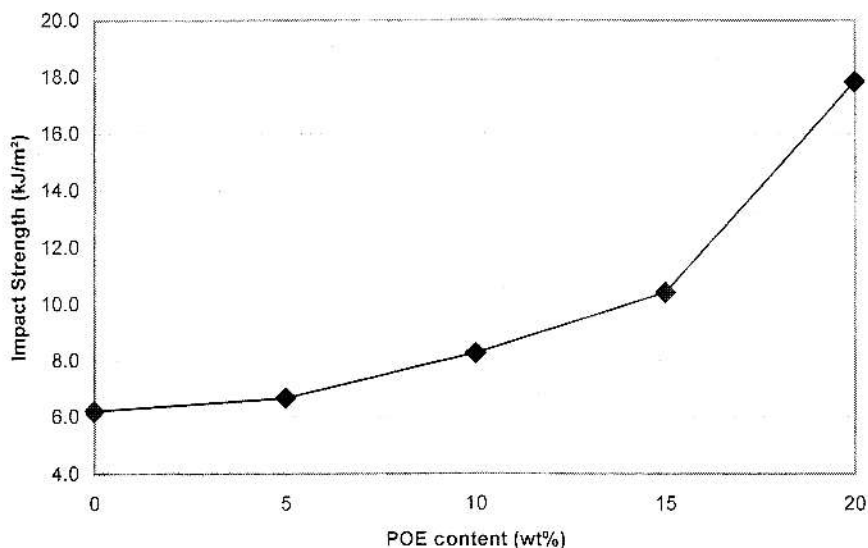
Figure 5:   **Effect of POE content on impact strength PP nanocomposites.**

Scanning Electron Microscope (SEM)

SEM was used to examine the morphology of the blends in order to investigate the particle size and the dispersion of POE phase in the blends system. Figures 5-7 displayed the phase morphology RTPPNC blends contained 5wt%, 10wt% and 20wt% POE, respectively. The voids observed on the fracture surface are believed to be due to the removal of POE domains. SEM photomicrographs showing that the two-phase morphology is clearly visible for all systems and the droplets of POE dispersed randomly and uniformly within the blends. The dispersed POE plays a crucial role in improving the impact strength.

The amount of discrete rubber particles evidently increases with increasing rubber concentration. Visual inspection of SEM micrographs suggested that the size and shape of the dispersed particles are similar in the blends contained 5wt% and 10wt% POE. A further increase in rubber content to 20wt% contributes to an increase in average particle sizes and the dispersed phase had transformed from a spherical like domain to more elongated feature caused by the presence of populations of larger sizes in the system (Figure 8(b)). This result are similar with the studies of McNally et al. (31) and Premphet et al. (32) where the distribution of rubber particles size seems to became broader and elongated as the concentration of POE in the blends more than 20wt%.
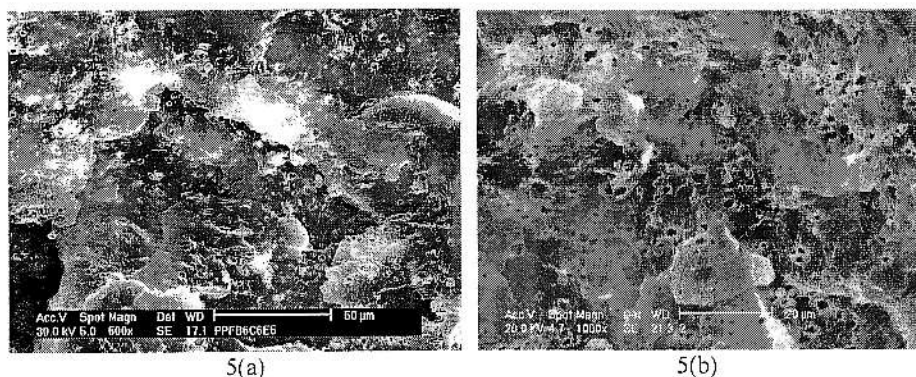
5(a)

5(b)

Figure 5: SEM micrograph of the cyro-fractured PPFB6C6E5 extracted by heptane.(a) 500X magnification, (b) 1000X magnification.

6(a)

6(b)

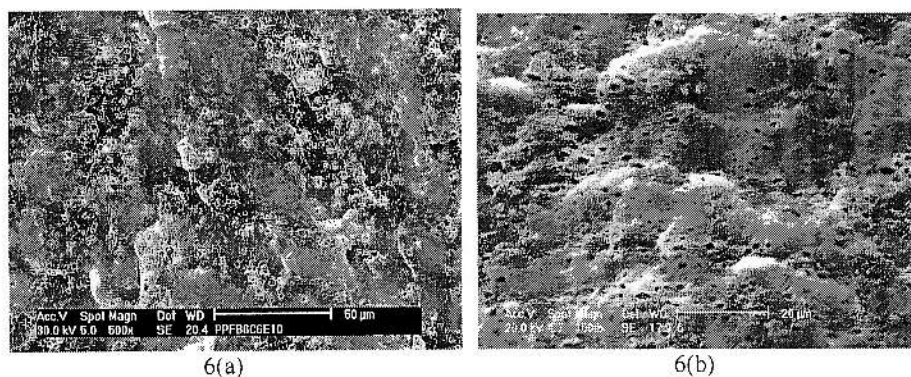**Figure 6:** SEM micrograph of the cyro-fractured PPFB6C6E10 extracted by heptane. (a) 500X magnification, (b) 1000X magnification.
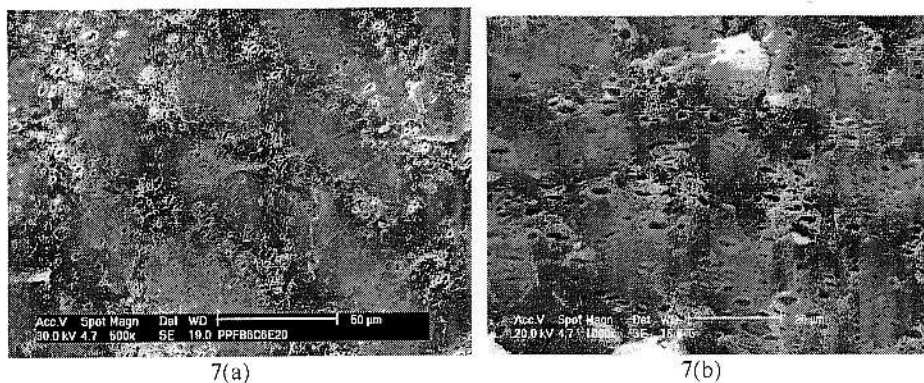

7(a)

7(b)

Figure 7: SEM micrograph of the cyro-fractured PPFB6C6E20 extracted by heptane. (a) 500X magnification, (b) 1000X magnification.

CONCLUSION

Blends of PP, organoclay and POE with incorporated of PP-g-MAH as compatibilizer were successfully prepared using a twin-screw extruder. XRD analysis shows that intercalated rubber toughened polypropylene nanocomposites have successfully been produced by direct-melt intercalation method. The particles of silicate layers were dispersed at the nanometer level in rubber toughened PP matrix. The Young's modulus and flexural modulus of the blends significantly improved with incorporating of 6wt% org-MMT. Conversely, Young's modulus, tensile strength, flexural modulus and flexural strength decreased with respect to pure PP as the concentration of POE in the blends was increased to 20wt%. This may compensate the loss of stiffness due to the adding of POE elastomer. However, the notched Izod impact strength drastically improved initially from 6.2kJ/m² for PPNC to 17.8kJ/m² for the RTPPNC with 20wt% POE, suggesting that POE copolymer efficient as impact modifier for PPNC blends. SEM study revealed a two-phase morphology where POE as droplets dispersed finely and uniformly in the PP matrix. A further increase in rubber content contributes to an increase in average particle sizes and transformed from a spherical like domain to more elongated feature.

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