

DEVELOPMENT OF LAYERED SILICATES MONTMORILLONITE FILLED  
RUBBER-TOUGHENED POLYPROPYLENE NANOCOMPOSITES (RTPPNC)

LIM JIAN WEI

UNIVERSITI TEKNOLOGI MALAYSIA

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RUBBER-TOUGHENED POLYPROPYLENE NANOCOMPOSITES (RTPPNC)

LIM JIAN WEI

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‘Specially for My Parents’

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## ABSTRACT

Polypropylene is an outstanding thermoplastic with respect to its attractive combination of low cost and extraordinary versatility in terms of properties and applications. However, the increasing demand of polypropylene for various applications requires greatly improved physical and mechanical properties. Recently, the addition of nanoscopic fillers of high anisotropy instead of conventional reinforcing agents renders the polymer/nanoclay nanocomposites to exhibit interesting structure-property relationships and promising application perspectives. However, the low temperature impact properties polypropylene nanocomposites limit some of its application. In order to achieve improved impact properties, impact modifiers polyethylene octene known as polyolefin elastomer have been added to toughen the polypropylene nanocomposites. Rubber toughened polypropylene nanocomposites containing different content of organoclay and polyethylene octene were compounded in a twin-screw extruder. The mechanical properties of the nanocomposites were determined on injection-molded specimens in tensile, flexural and impact tests. From the tensile and flexural tests, the optimum loading of organoclay in nanocomposites was found to be 6 wt%. Maleic anhydride modified polypropylene was used as compatibilizer to mediate the polarity between the clay surface and PP. The modulus and strength of polypropylene nanocomposites were improved in the presence of polypropylene grafted maleic anhydride and achieved optimum modulus and strength at a compatibilizer content of 6wt% for the blend. The morphology of the nanocomposites was studied by scanning electron microscopy and X-ray diffraction. X-ray diffraction results showed the formation of nanocomposites as the organoclay was intercalated by polypropylene macromolecules. Incorporation of polypropylene grafted maleic anhydride could improve the degree of intercalation and hence resulting in better dispersion in the polypropylene matrix. Izod impact tests indicated that the polyethylene octene and maleated polyethylene octene were very effective in converting brittle polypropylene nanocomposites into tough nanocomposites. Scanning electron microscopy study revealed a two-phase morphology which was clearly visible for all systems and the droplets of elastomer dispersed uniformly within the blends. Thermogravimetric analysis showed that thermal stability of nanocomposites significantly increased with the incorporation of small amounts of organoclay in a platelet form. The essential work of fracture was used to evaluate the fracture toughness of the rubber toughened polypropylene nanocomposites. Essential work of fracture measurements indicated that the specific essential work of fracture decreased with increasing organoclay content. However, additions of polyethylene octene and maleated polyethylene octene are beneficial in enhancing the specific essential work of fracture of the polypropylene nanocomposites.

## ABSTRAK

Polipropilena merupakan salah satu termoplastik yang terunggul dari segi kos rendah, sifat-sifat cemerlang and penggunaan yang luas. Namun, peningkatan sifat-sifat fizikal and mekanikal amat diperlukan atas permintaan yang semakin meningkat. Kini, penggantian pengisi lazim oleh pengisi bersaiz nanometer menghasilkan polimer/clay nanokomposit. Nanokomposit ini memberikan hubungan struktur-sifat yang unik and menjamin penggunaan dalam pelbagai sektor. Walaubagaimanapun polipropilena nanokomposit mempunyai sifat hentaman pada suhu rendah yang lemah telah menghadkan aplikasinya. Oleh itu, pengubahsuaian hentaman polietilena oktana, juga dikenali sebagai elastomer poliolefin digunakan untuk meningkatkan sifat hentaman polipropilena nanokomposit. Polipropilena nanokomposit terubahsuaian hentaman mengandungi organoclay and polietilena oktana disediakan menggunakan pengadun skru kempar. Sifat-sifat mekanikal nanokomposit diuji melalui ujian tegangan, lenturan and hentaman Izod. Kajian tegangan and lenturan mendapati 6 wt% organoclay adalah pemuatan yang optimum. Selain itu, penambahan polipropilena cangkuk maleik anhydride dapat meningkatkan lagi modulus dan kekuatan polipropilena nanokomposit disebabkan polipropilena cangkuk maleic anhydride dapat mengantarai perbezaan kekutuban antara polipropilena dan permukaan clay. Modulus and kekuatan nanokomposit mencapai takat optimum dengan pemuatan polipropilena cangkuk maleic anhydride pada 6 wt%. Mikroskop imbasan elektron and pembelauan X-ray digunakan untuk mengkaji sifat morfologi nanokomposit. Pengujian pembelauan X-ray menunjukkan pembentukan nanokomposit dimana makromolekul polipropilena telah interkalari antara organoclay. Penambahan polipropilena cangkuk maleic anhydride dapat meningkatkan darjah penginterkalari bagi organoclay dalam matriks polipropilena. Ujian hentaman Izod menunjukkan penambahan polietilena oktana cangkuk maleik anhydride lebih efektif bagi menukarkan polipropilena nanokomposit rapuh kepada nanokomposit yang kuat. Manakala ujian mikroskop imbasan elektron menunjukkan morfologi dua fasa dan partikel elastomer terserak sama rata bagi semua sistem. Analisis termogravimetrik menunjukkan kestabilan terma nanokomposit nyata meningkat dengan penambahan sedikit amaun organoclay yang berbentuk platelet. Kekuatan retakan polipropilena nanokomposit terubahsuaian hentaman diuji dengan kaedah *Essential work of fracture*. Ujian *Essential work of fracture* menunjukkan nilai *Essential work of fracture* khusus menyusut dengan pertambahan kandungan organoclay dalam nanokomposit. Sebaliknya, penambahan polietilena oktana dan polietilena oktana cangkuk maleik anhydride bermanfaat dalam mempertingkatkan nilai nilai *Essential work of fracture* khusus bagi polipropilena nanokomposit.

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## LIST OF ABBREVIATIONS AND SYMBOLS

ABS	-	Poly(acrylonitrile-co-butadiene-co-styrene)
ASTM	-	American Society for Testing and Materials
CaCO <sub>3</sub>	-	Calcium carbonate
CBR	-	Chlorinated butyl rubber
CEC	-	Cation exchange capacity
CGCT	-	Constrained geometry catalyst technology
CPE	-	Chlorinated polyethylene
$D_i$	-	Diameter dispersed domains
DDENT	-	Deep double-edge-notched-tension
DEM	-	Dimethyl maleate
DGEBA	-	Diglycidyl ether of bisphenol A
DMA	-	Dynamic mechanical analysis
DSC	-	Differential scanning calorimeter
$E'$	-	Storage modulus
$E''$	-	Loss modulus
EBR	-	Ethylene-butene rubber
HER	-	Ethylene-hexene rubber
EPDM	-	Ethylene propylene diene monomer rubber
EPDMgMAH	-	Ethylene propylene diene monomer rubber grafted maleic anhydride
EPR	-	Ethylene propylene rubber
EPRgMAH	-	Ethylene propylene rubber grafted maleic anhydride
EVA	-	Ethylene Vinyl Acetate
EWf	-	Essential work of fracture
G	-	Strain-energy release rate
G <sub>c</sub>	-	Critical strain-energy release rate
HDPE	-	High density polyethylene

HIPS	-	High impact polystyrene
HVA-2	-	N, N-phenylenebismaleimide
IFR	-	Imbedded fiber retraction
iPP	-	Isotactic polypropylene
K	-	Stress-intensity factor
K <sub>c</sub>	-	Critical stress-intensity factor
<i>l</i>	-	Ligament length
LEFM	-	Linear elastic fracture mechanics
LLDPE	-	Linear low density polyethylene
MAH	-	Maleic anhydride
MFI	-	Melt flow index
MMT	-	Montmorillonite
$N_i$	-	Number of dispersed domains
NBR	-	Butadiene-acrylonitrile rubber
NCH	-	Nylon-clay hybrids
NR	-	Natural rubber
PA	-	Polyamide
PA6	-	Polyamide 6
PBT	-	Polybutylene terephthalate
PC	-	Polycarbonate
PDMS	-	Poly(dimethyl siloxane)
PET	-	Polyethylene terephthalate
POE	-	Polyethylene octene
POEgMAH	-	Polyethylene octene grafted maleic anhydride
PP	-	Polypropylene
PPgMAH	-	Polypropylene grafted maleic anhydride
PPO	-	Poly(phenylene oxide)
PS	-	Polystyrene
PVC	-	Polyvinylchloride
tan $\delta$	-	Tangent delta
TEM	-	Transmission electron microscopy
T <sub>g</sub>	-	Glass transition temperature
$T_m$	-	Melting temperatures
$T_c$	-	Crystallization temperature

TGA	-	Thermogravimetric analysis
TPE	-	Thermoplastics elastomer
TPO	-	Thermoplastic olefins
R&D	-	Research and development
SBR	-	Styrene-butadiene rubber
SBS	-	Styrene-butadiene-styrene block copolymer
SEM	-	Scanning Electron Microscopy
SEP	-	Styrene-ethylene-propylene rubber
sPP	-	Syndiotactic PP
XRD	-	X-ray diffraction
$X_c$	-	Degree of crystallinity
$W_f$	-	Total fracture work
$W_e$	-	Essential work of fracture
$W_p$	-	Non-essential work of fracture
$w_f$	-	Specific total fracture work
$w_e$	-	Specific essential work of fracture
$w_p$	-	Specific nonessential work of fracture (or specific plastic work)
$w_{pp}$	-	Weight fraction of PP
$\beta$	-	Plastic zone shape factor
$\sigma_y$	-	Yield stress
$\Delta H_f^{obs}$	-	Measured enthalpy of melting
$\Delta H_f^0$	-	Ideal enthalpy of melting a perfect crystal

**LIST OF APPENDICIES**

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## **CHAPTER 1**

### **INTRODUCTION AND BACKGROUND**

#### **1.1 Current Perspectives and Future Prospects: An Overview**

Since the discovery of synthetic polymers during the early 1900's, compounding of polymers with inorganic fillers and fibers was developed as a versatile route leading to novel polymeric materials with improved thermal and mechanical properties with attractive cost/performance ratio. The field of materials science has lately begun to focus on the quest for composite materials that exhibit the positive characteristics of their initial components. Worldwide, there has been a new and intense desire to tailor the structure and composition of materials on the nanometer scale. Thus we are seeing the introduction of a new and improved class of composites, the nanocomposites.

##### **1.1.1 Nanocomposites**

Nanocomposites were first referenced as early as 1950, a synthetic polymer-clay nanocomposites were first reported as early as 1961, when Blumstein demonstrated polymerization of vinyl monomer intercalated into montmorillonite clay and polyamide nanocomposite were reported as early as 1976 (Ryan et al., 2001; Chetan, 2000). However, it was not until researchers from Toyota Central Research and Development Laboratories (CRDL) in Japan in the late 1980s began a detailed examination of polymer/layered silicate clay mineral composites that

nanocomposites became more widely studied in both academic and industrial laboratories.

In recent years polymer/clay nanocomposites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in materials properties when compared to virgin or conventional micro-composites. Today, more than 70 companies, government agencies and academic institutions have been identified as having research and development (R&D) activities (Agag et al, 2000, Chetan, 2000). These nanocomposites exhibit superior properties such as enhanced mechanical properties, reduced permeability, improved thermal stability and flame retardancy (Ray and Okamoto, 2003; Alexandre and Dubois, 2000; Ketan, 2002).

The total global market value for nanocomposites nears three million pounds; of which two million pounds are nanoclay-reinforced polyamides (nylon) produced by Unitika and Ube Industries in Japan for automotive and packaging application respectively. The remaining one million pounds are carbon nanotube-filled PPO/nylon alloy produced in North America for automotive body parts. Each of these developing product technologies is poised for strong growth over the next ten years. Market projections show that the demand in each region will grow at comparable rates from 2004 through 2009. The market will reach nearly 1.2 billion pounds in 2009, of which one billion pounds will be nanoclay reinforced compounds and 160 million pounds will be carbon nanotube-filled products (Nanocomposites, 1999).

Nanocomposites technology is applicable to a wide range of polymers, cutting across the materials classes of thermoplastics, thermosets, and elastomers. Over the next ten years, nanoclay composites of nearly 20 polymers are expected to be commercialized (Chetan, 2000). Therefore, nanocomposites technology is recognized as one of the promising avenues of technology development for the 21<sup>st</sup> century. Nanocomposites are currently used in two commercial applications: automotive under hood components and food packaging (Sherman, 1999). The goals are physical, mechanical and thermal properties enhancement and reduced permeability. Nylon-based nanocomposites were the first commercial materials to



emerge, and there is now a frenzy of activity aimed at nano-reinforcing commodity thermoplastics such as polypropylene (PP) and polyethylene terephthalate (PET) (Ketan, 2002). These end markets will continue to be the primary outlets for nanocomposites over the next ten years. Other markets, including non-food packaging and a range of other durables markets, will begin to adopt nanocomposites materials by 2004, and significant growth in demand will occur through 2009 (Chetan, 2000).

Polymer/layered silicate nanocomposites are currently prepared in four ways: in-situ polymerization, intercalation from a polymer solution, direct intercalation by molten polymer (melt compounding) and sol-gel technology. Direct polymer melt intercalation is the most attractive and most R&D works focused because of its low cost, high productivity and compatibility with current processing techniques (i.e. extrusion and injection molding) (Alexandre and Dubois, 2000). Besides that, direct polymer melt intercalation is an effective technology for polyolefin-based nanocomposites, especially for polypropylene based nanocomposites.

PP based nanocomposites constitute a major challenge for industry since they represent the route to substantially increase the mechanical and physical properties of one of the most widely thermoplastics. The dispersal of clay nanolayers into the nonpolar polyolefin PP systems proves to be a challenge since the polarity of organoclay does not match well with such polymers. Recently, Toyota research group (Kawasumi *et al.*, 1997; Kato *et al.*, 1997; Hasegawa *et al.*, 1998) melt-processed the mixture of stearylammmonium-exchanged montmorillonite, maleic anhydride modified polypropylene oligomer and homopolypropylene to obtain a successful polypropylene-clay hybrid wherein a larger fraction of the clay nanolayers were found to be exfoliated.

### **1.1.2 Rubber-Toughened Thermoplastics**

Recently introduced thermoplastic elastomers and engineering thermoplastics are example of the success of polymer blend technology has also become an

increasingly important technique for improving the cost performance ratio of commercial polymers (Azman Hassan *et al*, 2001, Ching, 2001). Blending of thermoplastics with elastomer has been commercialized as rubber-toughened plastics (RTTP) or as thermoplastics elastomer (TPE). Generally, if a relatively large portion of a the hard plastics is used, the composition can be used as an impact resistance plastics; whereas, if a relatively large amount of rubbery phase is used, the blend will be soft and have at least some of the properties of an elastomer (Ibrahim and Dahlan, 1998; Okada et al, 1999).

The first impact-modified polymer was polystyrene, patented by Ostromislenky in 1927 described the process for making toughened polystyrene by polymerizing a solution of rubber in styrene monomer. This material demonstrated high impact strength, but was a closer to a thermoset than a thermoplastic. Although the polymer was never commercially produced, the discovery provided the focus on rubber modified polystyrene. In 1948 the first commercial impact modified polystyrene was introduced by the Dow Chemical Company (Bucknall, 1977; Lynch, 2000). The polymer was produced by a batch polymerization of styrene monomer and styrene-butadiene rubber (SBR) to produce high impact polystyrene (HIPS). An improved continuous HIPS process was introduced in 1952. In 1957, impact modified polyvinylchloride was commercially produced into marketplace. Since then, RTTP blends have been the fastest growing segment of the plastics industry.

Recently, the blending of various rubbers with PP to provide an improvement in its properties, especially in impact resistance at low temperature and at any given stiffness, has been widely studied. Articles published by Liang and Li (1999) and Utracki (1999) had reviewed the advances in mechanisms toughening of PP/elastomer blends in the last 20 years. Blending PP with an elastomeric modifier provides a simple way to significantly improve the impact resistance of the base resin. Impact modified polypropylene is in the class of thermoplastic olefins (TPO). TPOs have been the fastest growing segment of the thermoplastic elastomers for the last ten years. The automotive industry is one of the major growth market for TPOs with new applications such as interior trim and exterior fascia. To date, many rubber or elastomers are compatible with PP has been developed and studied from the most frequently used ethylene propylene rubber (EPR) and ethylene propylene diene

monomer rubber (EPDM) to the relatively new type of impact modifier known as polyethylene octene (POE) copolymer.

## 1.2 Problem Background

One of the most important aspects in the materials development of engineering thermoplastics is to achieve a good combination of properties and processability at moderate cost. In the development of engineering thermoplastics as far as mechanical properties is concerned, the main target is to strike a balance of stiffness, strength and toughness. There are a few approaches that have been identified as potential routes to achieving this goal (Mohd Ishak *et al.*, 1999):

- i) Blending of thermoplastics with thermoplastic with elastomers as major components to form thermoplastic elastomers (TPE) or rubber-toughened thermoplastics (RTTP).
- ii) The inclusion of fillers or fiber reinforcement into thermoplastic matrices to form thermoplastics composites.

However these approaches have their own potential and limitation. Generally, the inclusion of elastomer as an impact modifier will result in a significant improvement in toughness but at the expense of strength and stiffness. On the contrary the presence of fillers or reinforcement such as glass fiber and carbon fiber in polymer leads to increase in stiffness and strength, but decrease in toughness. Thus the next logical approach to follow is to combine both filler or short fiber reinforcement and impact modifier into thermoplastic matrix (Mohd Ishak *et al.*, 1999). The strategy behind this approach is to develop a material which posses a significant improvement in toughness without sacrificing the desirable stiffness and strength properties.

However, studies on the blending of thermoplastic (PP) with elastomers (POE) with the incorporation of nanofillers (org-montmorillonite) in the presence of compatibilizer (PPgMAH) has not yet been explored. Therefore, it is interesting to look at the system where rubber-toughened thermoplastics blends are combined with nanofillers.

### 1.3 Objectives

The present work aims to develop new advanced polymeric composite materials namely rubber-toughened PP nanocomposites (RTPPNC). In this research, nanocomposites will be first prepared by adding nanoclay (MMT) to the PP with the presence of compatibilizer (PPgMAH) to form PP nanocomposites (PPNC). Then this material as a major component will be melt-mixed with elastomer.

The main objective can further be divided into:

- i) To study the effect of organoclay concentration on the physical and mechanical properties of RTPPNC.
- ii) To study the effect of incorporating compatibilizer into RTPPNC on the physical and mechanical properties.
- iii) To investigate the effect of elastomer concentration and functionality on the physical and mechanical properties of RTPPNC.
- iv) To determine the effect of organoclay and elastomer on the fracture toughness of the RTPPNC.

### 1.4 Scopes

In order to achieve the objectives of the research, the following activities have been carried out:

#### 1. Literature review

Literature search on the latest development in the area of rubber-toughened thermoplastic composites and nanocomposites to ensure relevancy of the research

2. Sample preparation

Sample preparation will be conducted via melt intercalation method. This involves:

- a) Twin-screw extrusion process to blend PP, elastomer, nanofiller and compatibilizer.
- b) Injection molding to prepare test specimen according standard.

3. Physical and Mechanical properties study

- a) Density
- b) Tensile test
- c) Flexural Test
- d) Izod impact test
- e) Fracture Mechanics

4. Sample characterization and morphological study. To characterize the RTPPNC, the following apparatus will be used:

- a) X-ray diffraction (XRD)
- b) Scanning electron microscopy (SEM)
- c) Differential scanning calorimeter (DSC)
- d) Dynamic mechanical analysis (DMA)
- e) Thermogravimetric analysis (TGA)

5. Rheological properties of the blends study by:

- a) Melt flow index
- b) Capillary rheometer

6. Data analysis

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By the example of polypropylene-organic montmorillonite composite (PP-OMMT), the abilities of the method of equal channel multiangular extrusion have been studied with respect to the modification of the structure and the properties of polymeric nanocomposites. With using X-ray structure analysis, TEM, DSC, and dilatometry, it has been demonstrated that this kind of processing provides an additional intercalation of the polymer into OMMT tactoids with the succeeding exfoliation and facilitates an increase in the aspect ratio, the degree of platelet orientation, the crystalline lamellar thickness. The synthetic routes and materials properties of polypropylene/montmorillonite nanocomposites are reviewed. The nanocomposite formation is achieved in two ways: either by using functionalized polypropylenes and common organo-montmorillonites, or by using neat/unmodified polypropylene and a semi-fluorinated organic modification for the silicates. All the hybrids can be formed by solventless melt-intercalation or extrusion, and the resulting polymer/inorganic structures are characterized by a coexistence of intercalated and exfoliated montmorillonite layers. Small additions - typically less than Polypropylene/organo montmorillonite nanocomposites modified with 0.001-0.1 wt% calcium pimelate, a  $\beta$ -nucleating agent, were prepared using twin screw extruder. The effects of calcium pimelate content on crystallization behavior were investigated using differential scanning calorimeter (DSC). The crystallization kinetics were studied using both nonisothermal and isothermal methods. The development of relative crystallinity with the crystallization time was analyzed by the Avrami equation. For nonisothermal studies, the Kissinger's theory was employed and the crystallization activation energy wa