

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

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RUBBER-TOUGHENED POLYPROPYLENE NANOCOMPOSITES (RTPPNC)

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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 penginterkalarian 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

## REFERENCES

- Ahmadi, S.J., Huang, Y.D., Li, W. (2005). Fabrication and physical properties of EPDM–organoclay nanocomposites. *Composites Science and Technology*. 65: 1069–1076.
- Akkapeddi, M.K. (2000). Glass fiber reinforced polyamide-6 nanocomposites. *Polymer Composites*. 21: 576-585.
- Alexandre, M., and Dubois, P. (2000). Polymer-layered silicate nanocomposites : preparation, properties and uses of new class of materials. *Materials Science and Engineering*. 28: 1-63.
- Alexandra, M., Dubois, P., Sun, T., Garces, J.M., and Jerome, R. (2002). Polyethylene-layered silicate nanocomposites prepared by the polymerization-filling technique: synthesis and mechanical properties. *Polymer*. 43: 2123-2132.
- Apoorva, P.S., Gupta Rakesh, K., Jones, J., Clifford, and Carlos, H. (2002). Flammability and mechanical properties of vinyl ester/clay nanocomposites. *Annual Technical Conference Proceedings, Society of Plastics Engineers*. 48: 2270-2274.
- Ashter, A. (2002). Elastomeric Nanocomposites: Quantifying the Effect of Modified Montmorillonite Clays on Styrene-Ethylene-Butadiene-Styrene (SEBS). University of Massachusetts Lowell: Master of Science Thesis
- ASTM, ASTM E813-89: Standard Test Method for  $J_{IC}$ , A Measure of Fracture Toughness in 1989 Annual Book of ASTM Standards, p. 7000, American Society for Testing and Materials, Philadelphia (1989).
- Arostegui, A., and Nazabal, J. (2003). New Super-tough Poly(butylenes Terephthalate) Materials Based on Compatibilized Blends with Metallocenic Poly(ethylene-octene). *Polymer Advanced Technologies*. 14: 400-408.
- Azhari, C.H., Zulkifli, R., Fatt, L.K., and Sahari, J. (2002). Interlaminar fracture properties of fibre reinforced natural rubber/polypropylene composites. *Journal of Materials Processing Technology*. 128: 33-37.

- Azman Hassan, Ching, Y.C., and Sivaneswaran (2001). Rubber-Toughened Polymers: The Importance and Recent Development. *Seminar on specialty additives/polymers for new decades*, Shah Alam, Malaysia
- Azman Hassan, Wahit, M.U., and Ching, Y.C. (2003). Mechanical and morphological properties of PP/NR/LLDPE ternary blend—effect of HVA-2. *Polymer Testing* 22: 281–290.
- Bensason, S., Minick, J., Moet, A., Chum, S., Hiltner, A., and Baer, E. (1996). Classification of Homogeneous Ethylene-Octene Copolymers Based on Comonomer Content. *Journal of Polymer Science: Part B: Polymer Physics*. 34: 1301-1316.
- Bensason, S., Nazarenko, S., Chum, S., Hiltner, A., and Baer, E. (1997). Elastomeric blends of homogeneous ethylene-octene copolymers. *Polymer*. 38: 3913-3919.
- Biasci, L., Aglietto, M., Ruggeri, G., and Ciardelli, F. (1994). Functionalization of montmorillonite by methyl methacrylate polymers containing side-chain ammonium cations. *Polymer*. 35: 3296-3304.
- Bielefeld, Z.J., and Schwerzenbach, G.W. (1999). *Collected Applications Thermal Analysis: Thermoplastics*. Mettler Toledo. 10.
- Billmeyer, F.W. *Textbook of Polymer Science*. John Wiley & Sons: A Wiley-Interscience Publication, 1984, 241.
- Boivin, K.C. (2000). The Effects of Polypropylene Type, Ethylene-Butene Type, and Filler on the Properties of Thermoplastic Olefin Blends. University of Massachusetts Lowell: Master of Science Thesis.
- Boucard, S., Ducheet, J., Gerard, J.F., Prele, P., and Gonzalez, S. (2003). Processing of polypropylene/clay hybrids. *Macromolecules Symposiums*. 194: 241-246.
- Broberg, K.B. (1971). Crack-growth criteria and non-linear fracture mechanics. *J. Mech.Phys. Solids*. 19: 407-418.
- Broberg, K.B. (1975). On stable crack growth. *J. Mech. Phys. Solids*. 23: 215-237.
- Brown, R. (1999). *Handbook of Polymer Testing. Physical Methods*. Marcel Dekker, Inc, New York, 782.
- Bucknall, C. B. (1977). *Toughened Plastics*. London, Applied Science, 9-20; 137-177; 286-289.
- Bureau, M.N., Perrin-Sarazin, F., and Ton-That, M.T. (2004). Polyolefin

- Nanocomposites: Essential Work of Fracture Analysis. *Polymer Engineering and Science*. 44: 1142-1151.
- Brydson, J.A. (1989). *Plastic Materials*. 5<sup>th</sup> ed. London: Mid-County Press. Inc. 196-241.
- Carriere, C.J. and Silvis, H.C. (1997). The Effects of Short-Chain Branching and Comonomer Type on the Interfacial Tension of Polypropylene-Polyolefin Elastomer Blends. *Journal of Applied Polymer Science*. 66: 1175-1181.
- Chan, W.Y.F., and Williams, J.G. (1994). Determination of the fracture toughness of polymeric films by the essential work method. *Polymer*. 34: 1666-1672.
- Chen, H.B., Karger-Kocsis, J., Wu, J.S. (2004). Effects of molecular structure on the essential work of fracture of amorphous copolyesters at various deformation rates. *Polymer*. 45: 6375-6382.
- Chen, D.Z., Yang, H.Y., He, P.S., and Zhang, W. (2005). Rheological and extrusion behavior of intercalated high-impact polystyrene/organomontmorillonite nanocomposites. *Composites Science and Technology*. 65: 1593-1600.
- Cho, J.W., Logsdon, J., Omachinski, S., Qian, G., Lan, T., Womer, T.W. and Smith, W.S., Nanocomposites: A Single Screw Mixing Study of Nanoclay-filled Polypropylene. *ANTEC 2000 Conference Proceedings*, May 8-9, 2000. Orlando Florida, Society of Plastics Engineers (SPE). 2000. 58(1), 428.
- Chouhary, N.R. Chaki, T.K., Dutta, A. and Bhowmick, A.K. (1989). Thermal, X-ray and Dynamic Mechanical Properties of TPE NR/PE Blends. *Polymer*. 30: 2047-2053.
- Choudhary, N.R, Chaki, T.K. and Bhowmick, A.K. (1991). Thermal Characterization of Thermoplastic Elastomeric Natural-Rubber-Polypropylene Blends. *Thermochimica Acta*. 176: 149-161.
- Ching, Y.C. (2001). Mechanical and Morphology Properties of impact Modified PP. Universiti Teknologi Malaysia. Master of Science Thesis.
- Chow, W.S., Mohd Ishak, Z.A., Karger-Kocsis, J., Apostolov, A.A., and Ishiaku, U.S. (2003). Compatibilizing effect of maleated polypropylene on the mechanical properties and morphology of injection molded polyamide6/polypropylene/ organoclay nanocomposites. *Polymer*. 44: 7427-7440.
- Chow, W.S., Mohd Ishak, Z.A., Karger-Kocsis, J., Apostolov, A.A., 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.
- Chow, W.S., Mohd Ishak, Z.A., Karger-Kocsis, J., Apostolov, A.A., Ishiaku, U.S. (2005a). Morphological and rheological properties of polyamide 6/polypropylene/ organoclay nanocomposites. *Macromolecular Materials and Engineering*. 290: 122-127.
- Chow, W.S., Mohd Ishak, Z.A., Karger-Kocsis, J., Apostolov, A.A., Ishiaku, U.S. (2005b). Effect of maleic anhydride-grafted ethylene-propylene rubber on the mechanical, rheological and morphological properties of organoclay reinforced polyamide 6/polypropylene nanocomposites. *European Polymer Journal*. 41: 687-696.
- Cogswell F.N. *Polymer Melt Rheology A guide for Industrial Practice*, George Godwin, John Wiley, 1981.
- Crawford, R.J.(1987). *Plastics Engineering*. 2<sup>nd</sup>.ed.Oxford: Pergamon Press Ltd. 140-144.
- D'Orazio, L., Mancarella, C. , Martuscelli, E., Sticotti, G., and Massari, P. (1993). Melt rheology, phase structure and impact properties of injection-moulded samples of isotactic polypropylene/ethylene-propylene copolymer (iPP/EPR) blends: influence of molecular structure of EPR copolymers. *Polymer*. 34: 3671-3681.
- Da Silva, A.L.N., Tavares, M.I.B., Politano, D.P., Coutinho, F.M.B., and Rocha, M.C.G. (1997). Polymer Blends Based on Polyolefin Elastomer and Polypropylene. *Journal of Applied Polymer Science*. 66: 2005-2014.
- Da Silva, A.L.N., Rocha, M.C.G., Fernanda M.B., Bretas R.E.S., Scuracchio C. (2000). Rheological, Mechanical, Thermal, and Morphological Properties of Polypropylene/Ethylene-Octene Copolymer Blends. *Journal of Applied Polymer Science*. 75: 692-704.
- Da Silva, A.L.N., Rocha, M.C.G., Coutinho, F.M.B., Bretas, R.E.S. and Scuracchio, C. (2001). Rheological and Thermal Properties of Binary Blends Polypropylene and Poly(ethylene-co-1-octene). *Journal of Applied Polymer Science*. 79: 1634-1639.
- Da Silva, A.L.N., Rocha, M.C.G., Fernanda M.B. (2002a) Study of rheological behavior of elastomer/polypropylene blends. *Polymer Testing*. 21: 289-293.

- Da Silva, A.L.N., Rocha, M.C.G., Fernanda M.B., Bretas R.E.S., Farah M. (2002b) Evaluation of rheological and mechanical behavior of blends based on polypropylene and metallocene elastomers. *Polymer Testing*. 21: 647-652.
- Danesi, S. and Porter, R.S. (1978). Blends of Isotactic Polypropylene and Ethylene Propylene Rubbers: Rheology, Morphology and Mechanics. *Polymer*. 19: 448-457.
- Di, Y., Iannace, S. and Nicolais, L. (2002). Thermal Behavior and Morphological and Rheological Properties of Polypropylene and Novel Elastomeric Ethylene Copolymer Blends. *Journal of Applied Polymer Science*. 86: 3430-3439.
- Dijkstra, K., Wevers, H.H., and Gaymans, R.J. (1994). Nylon-6/rubber blends: 7. Temperature-time effects in the impact behaviour of nylon/rubber blends. *Polymer*. 35:323-331.
- Ding, C., Jia, D.M, He, H., Guo, B.C., and Hong, H.Q. (2005). How organo-montmorillonite truly affects the structure and properties of polypropylene. *Polymer Testing*. 24: 94-100.
- Donald, A.M. (1994). Failure Mechanism in Polymeric Materials. In: Collyer, A.A. *Rubber Toughened Engineering Plastics*, 1<sup>st</sup> Edition, Chapman and Hall, London.
- Doo, J.G., and Cho, I. (1998). Synthesis and properties of polystyrene-organ ammonium montmorillonite hybrid. *Polymer Bull.* 41: 511-518.
- Dubnikova, I.L., Berezina, S.M. and Antonov, A.V. (2002). The Effect of Morphology of Ternary-Phase Polypropylene/ Glass Bead/Ethylene-Propylene Rubber Composites on the Toughness and Brittle-Ductile Transition. *Journal of Applied Polymer Science*. 85: 1911-1928.
- Eckel, F., Balogh, M.P., Fasulo, P.D., Rodgers, W.R. (2004). Assessing Organo-Clay Dispersion in Polymer I Nanocomposites. *Journal of Applied Polymer Science*. 93: 1110-1117.
- Eisenberg, A., and Tsagaropoulos G. (1995). *Macromolecules*. 28: 6067-6074.
- Ellis, T.S., and D'Angelo J.S. (2003). Thermal and Mechanical Properties of a Polypropylene Nanocomposite. *Journal of Applied Polymer Science*. 90: 1639-1647.
- Fasulo, P.D., Rodgers, W.R., and Ottaviani, R.A. (2004). Polyolefin Extrusion Processing of TPO Nanocomposites. *Polymer Engineering and Science*. 44: 1036-1045.

- Ferry, J.D. (1980). *Viscoelastic Properties of Polymers*. New York: John Wiley.
- Fu, X. and Qutubuddin, S. (2001). Polymer-clay nanocomposites: exfoliation of organophilic montmorillonite nanolayers in polystyrene. *Polymer*. 42: 807-813.
- Garcia-Lopez, D., Picazo, O., Merino, J.C., and Pastor, J.M. (2003). Polypropylene-clay nanocomposites: effect of compatibilizing agents on clay dispersion. *European Polymer Journal*. 39: 945-950.
- Gaymans R.J. Toughening of Semicrystalline Thermoplastics In: Paul, D.R. and Bucknall, C.B. *Polymer Blends. Volume 2: Performance*, John Wiley & Sons, A Wiley-Interscience Publication, 2000, Ch. 25: 177.
- George, J. G., Reethamma, J., Sabu and Varughese, K.T. (1995). High Density Polyethylene/ Acrylonitrile Butadiene Rubber Blends: Morphology, Mechanical Properties, and Compatibilization. *Journal of Applied Polymer Science*. 57: 449-465.
- Gonzalez, J., Albano, C., Candal, M.V., Ichazo, M.N., Hernandez, M. (2005). Characterization of blends of PP and SBS vulcanized with gamma irradiation. *Nuclear Instruments and Methods in Physics Research B*. 57: 133.
- Gonzalez-Montiel, A.G. (1995a). Reactive Compatibilization and Toughening of Nylon 6/Polypropylene Blends. The University of Texas at Austin: Doctor of Philosophy Dissertation.
- Gonzalez-Montiel, A.G., Keskkula, H., and Paul, D.R. (1995b). Impact-modified Nylon 6/Polypropylene blends: 1. Morphology-property Relationships. *Polymer*, 36: 4857-4603.
- Gonzalez-Montiel, A.G., Keskkula, H., and Paul, D.R. (1995c). Impact-modified Nylon 6/Polypropylene blends: 2. Effect of Reactive Functionality on Morphology and Mechanical Properties. *Polymer*. 36: 4605-4620.
- Ha, M.H., Kim, B.K., and Kim E.Y. (2004a). Effects of the blending sequence in polyolefin ternary blends. *Journal of Applied Polymer Science*. 92: 804-811.
- Ha, M.H., Kim, B.K., and Kim E.Y. (2004b). Effects of dispersed phase composition on thermoplastic polyolefins. *Journal of Applied Polymer Science*. 93: 179-188.
- Hambir, S., Bulakh, N., Kodgire, P., Kalgaonkar, R. and Jog, J.P. (2001). PP/Clay Nanocomposites: A Study of Crystallization and Dynamic Mechanical

- Behavior. *Journal of Polymer Science: Part B: Polymer Physics*. 39: 446-450.
- Hambir, S., Bulkh, N., and Jog, J.P. (2002). Polypropylene/Clay Nanocomposites: Effect of Compatibilizer on the Thermal, Crystallization and Dynamic Mechanical Behavior. *Polymer Engineering and Science*. 42: 1800-1807.
- Hasegawa, N., Kawasumi, M., Kato, M., Usuki, A. and Okada, A. (1998). Preparation and Mechanical Properties of Polypropylene-Clay Hybrids Using a Maleic Anhydride-Modified Polypropylene Oligomer. *Journal of Applied Polymer Science*. 67: 87-92.
- Hasegawa N., Okamoto H., Kawasumi M., Usuki A. (1999), Preparation and mechanical properties of polystyrene-clay hybrids. *Journal of Applied Polymer Science*, 74: 3359-3364.
- Hashemi, S., and Williams, J.G, (1996). Fracture Characterization of Tough Polymers Using the J Method. *Polymer*. 27: 384.
- Hashemi, S. (1997). Work of Fracture of PBT/PC Blend: Effect of Specimen Size, Geometry, and Rate of Testing. *Polymer Engineering and Science*. 37: 912-922.
- Hashemi, S. (2003). Work of fracture of high impact polystyrene (HIPS) film under plane stress conditions. *Journal of Materials Science*. 38: 3055-3062.
- Ho, R.M., Wu, C.H. and Su, A.C. (1990). Morphology of Plastic/Rubber Blends.” *Journal of Applied Polymer Science*. 30: 511-518.
- Hornsby P.R. and Premphet K. (1997). Fracture toughness of multiphase polypropylene composites containing rubbery and particulate inclusions. *Journal of Materials Science*. 32: 4767-4775.
- Hornsby, P.R. and Premphet, K. (1998). Influence of Phase Microstructure on the Mechanical Properties of Ternary Phase Polypropylene Composites. *Journal of Applied Polymer Science*. 70: 587-597.
- Huang D.D. and Williams J.G. (1990). Comments on Fracture Toughness of Impact Modified Polymers Based on the J-Integral. *Polymer Engineering and Science*. 30: 1341.
- Ibrahim, A. and Dahlan, M. (1998), Thermoplastics Natural Rubber Blends, *Progress Polymer Science*, 23, 665-706.
- Jancar, J., DiAnselmo A., DiBenedetto, A.T., and Kucera, J. (1993). Failure mechanics in elastomer toughened polypropylene. *Polymer*. 34: 1684-1694.

- Jancar, J., and Dibenedetto, A.T. (1994). Effect of interfacial interaction on morphology and mechanical properties of ternary composites. *Journal of Materials Science*. 29: 4651-4659.
- Jang, B.Z., Uhlmann, D.R., and Vander Sande J.B. (1985). Rubber-toughening in polypropylene. *Journal of Applied Polymer Science*. 30: 2485-2504.
- Jeon, H. S., Nakatani, A. I., Han, C. C., and Colby, R. H. (2000). Melt Rheology of Lower Critical Solution Temperature Polybutadiene/Polyisoprene Blends. *Macromolecules*. 33: 9732-9739.
- Jiang, T., Wang, Y.H., Yeh, J.T., Fan, Z.Q. (2005). Study on solvent permeation resistance properties of nylon6/clay nanocomposite. *European Polymer Journal*. 41: 459-466.
- Kaempfer, D., Thomann, R., and Mulhaupt, R. (2002). Melt compounding of syndiotactic polypropylene nanocomposites containing organophilic layered silicates and in situ formed core/shell nanoparticles. *Polymer*. 43: 2909-2916.
- Kale, L.T., Plumley, T.A., Patel, R.M. and Jain, P. (1995) Structure-property relationship of ethylene/1-octene and ethylene/1-butene copolymers made using INSITE Technology. ANTEC'95: 2249.
- Kato, M., Usuki, A., Okada, A., Kurauchi, T., (1997a). Synthesis of polypropylene-clay hybrid. *J Appl. Polym. Sci.* 63, 137-139.
- Kato, M., Usuki, A. and Okada, A. (1997b). Synthesis of Polypropylene Oligomer-Clay Intercalation Compounds. *Journal of Applied Polymer Science*. 66: 1781-1785.
- Kato M., Matsushita M., and Fukumori K. (2004). Development of a New Production Method for a Polypropylene-Clay Nanocomposite. *Polymer Engineering and Science*. 44: 1205-1211.
- Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. (1997). Preparation and Mechanical Properties of Polypropylene-Clay Hybrids. *Macromolecules*. 30: 6333-6338.
- Keawwattana W. (2002), Phase Behavior, Crystallization, and Morphological Development in Blends of Polypropylene Isomers and Poly(ethylene-Octene) Copolymer. University of Akron: Master of Science Thesis.
- Karger-Kocsis, J. and Czigány, T. (1996). On the essential and non-essential work of fracture of biaxial-oriented filled PET film. *Polymer*. 37: 2433-2438 .
- Karger-Kocsis, J., Czigany, T. and Moskala, E.J. (1998). Deformation rate

dependence of the essential and non-essential work of fracture parameters in an amorphous copolyester. *Polymer*. 39: 3939-3944.

- Karger-Kocsis, J. and Mouzakis, D.E. (1999). Effects of Injection Molding-Induced Morphology on the Work of Fracture Parameters in Rubber-Toughened Polypropylenes. *Polymer Engineering and Science*. 39: 1365-1374.
- Karian, H.G. (1999). *Handbook of Polypropylene and Polypropylene Composites*, 2<sup>nd</sup>. New York, Marcel Dekker,
- Kawasumi, M., Hasegawa, N., Kato, M., Usuki, A., and Okada, A. (1997). Preparation and Mechanical Properties of Polypropylene-Clay Hybrids. *Macromolecules*. 30: 6333-6338.
- Ke, Y.C., Long, C.F., and Qi, Z.N. (1999). Crystallization, properties, and crystal and nanoscale morphology of PET-clay nanocomposites *Journal of Applied Polymer Science*. 71: 1139-1146
- Keawwattana, W. (2002). Phase Behavior, Crystallization and Morphological Development in Blends of Polypropylene (PP) Isomers and Poly(Ethylene-Octene) Copolymer. University of Akron: Doctor of Philosophy Thesis.
- Ketan, K. Maniar (2002), A Literature Survey On Nanocomposites, University of Massachusetts Lowell: Master of Science Thesis.
- Khatua, B. B., Lee, D.J., Kim, H.Y., and Kim, J.K. (2004). Effect of Organoclay Platelets on Morphology of Nylon-6 and Poly(ethylene-ran-propylene) Rubber Blends. *Macromolecules*. 37: 2454-2459.
- Kim, K.N., Kim, H. and Lee, J.W. (2001). Effect of Interlayer Structure, Matrix Viscosity and Composition of a Functionalized Polymer on the Phase Structure of Polypropylene-Montmorillonite Nanocomposites. *Polymer of Engineering and Science*. 41: 1963-1969.
- Kim, J.K., Hu, C.G., Woo, R.S.C., Sham, M.L. (2005). Moisture barrier characteristics of organoclay-epoxy nanocomposites. *Composites Science and Technology*. 65: 805-813.
- Kodgire, P., Kalgaonkar, R., Hambir, S., Bulakh, N., and Jog, J.P. (2001). PP/Clay Nanocomposites: Effect of Clay Treatment on Morphology and Dynamic Mechanical Properties. *Journal of Applied Polymer Science*. 81: 1786-1792.
- Kojima, Y. (1993). Mechanical properties of nylon-6 clay hybrid. *Journal of Materials Research*. 8: 1185-1189.

- Kolarik, J. (1992). Ternary composites of polypropylene/elastomer/calcium carbonate: effect of functionalized components on phase structure and mechanical properties. *Polymer*. 33: 4961-4967
- Kornmann, X, Berglund, L.A., Sterte, J. and Giannelis, E.P. (1998), Nanocomposites Based on MMT and Unsaturated Polyester, *Polymer Engineering and Science*, 38, 1351-1358.
- Kornmann, X, Lindberg, H., and Berglund, L.A. (2000). Stiffness Improvement and Molecular Mobility in Epoxy-Clay nanocomposites, *Mat. Res. Soc. Symp. Proc.*, 628
- Kornmann, X. (2001), Synthesis and Characterization of Thermoset-Layered Silicate Nanocomposites. Lulea University of Technology: Doctoral Thesis.
- Kornmann, X, Lindberg, H., and Berglund, L.A. (2001a). Synthesis of Epoxy-Clay Nanocomposites: Influence of the nature of the Clay on Structure. *Polymer*, 42: 1303-1310.
- Kornmann, X, Lindberg, H., and Berglund, L.A. (2001b). Synthesis of Epoxy-Clay Nanocomposites: Influence of the nature of the Curing Agent on Structure. *Polymer*, 42: 4493-4499.
- Kurokawa, Y., Yasuda, H., Kashiwagi, M., and Oya, A. (1997). Structure and properties of a montmorillonite/polypropylene nanocomposite *Journal of Materials Science Letters*. 16: 1670-1676.
- Laura, D.M., Keskkula, H., Barlow, J.W., and Paul, D.R. (2003). Impact Strength and Dynamic Mechanical Properties Correlation in Elastomer-Modified Polypropylene. *Polymer*. 44: 3347-3361.
- LeBaron, P.C., Wang, Z. and Pinnavaia, T.J. (1999). Polymer-layered silicate nanocomposites: an overview. *Applied Clay Science*. 15: 11-29.
- Lee, D.C. and Jang, L.W. (1996). Preparation and characterization of PMMA-clay hybrid composite by emulsion polymerization. *Journal of Applied Polymer Science*. 61: 1117-1122.
- Lertwimolnun W., and Vergnes B. (2005). Influence of compatibilizer and processing conditions on the dispersion of nanoclay in a polypropylene matrix. *Polymer*. 46: 3462-3471.
- Lew, C.Y., Murphy, W.R., and McNally, G.M. (2004). Preparation and Properties of Polyolefin-Clay Nanocomposites. *Polymer Engineering Science*. 44: 1027-1035.

- Li, W.D., Li, R.K.Y., Tjong, S.C. (1997). Fracture Toughness of Elastomer-Modified Polypropylene. *Polymer Testing*. 16: 563-574.
- Li, J.X., Wu, J.S., Chan, C.M. (2000). Thermoplastic Nanocomposites. *Polymer*. 41: 6935-6937.
- Li, Y.M. (2001). *Mechanical Behavior of Multi-Phase Clay-Modified Polypropylene Blend Systems*. Texas A&M University: Doctor of Philosophy.
- Li, Y.M., Wei, G.X., Sue, H.J. (2002). Morphology and toughening mechanisms in clay-modified styrene-butadiene-styrene rubber-toughened polypropylene. *Journal of Materials Science*. 37: 2447-2459.
- Li, J., Zhou, C.X., Wang, G., Yu, W., Tao, Y., Liu Q. (2003). Preparation and linear rheological behavior of polypropylene/MMT nanocomposites. *Polymer Composites*. 24: 323-331.
- Li, Z., Guo, S.Y., Song, W.T. and Hou, B. (2003a). Effect of interfacial interaction on morphology and mechanical properties of PP/POE/BaSO<sub>4</sub> ternary composites. *Journal of Materials Science*. 38: 1793-1802.
- Li, Y.J., Shimizu, H. (2004). Novel morphologies of poly(phenylene oxide) (PPO) / polyamide 6 (PA6) blend nanocomposites. *Polymer*. 45: 7381-7388.
- Li, Y., Zhang, Y., Zhang, Y.X. (2004). Morphology and mechanical properties of HDPE/SRP/elastomer composites: effect of elastomer polarity. *Polymer Testing* 23: 83-90.
- Liang, J.Z. and Li, R.K.Y. (2000). Rubber Toughening in Polypropylene: A Review. *Journal of Applied Polymer Science*. 77: 409-417.
- Lieberman, R.B. and Barbe, P.C. (1990). Polypropylene. In: Corish, P.J. *Concise Encyclopedia of Polymer Processing & Application*. Oxford: Pergamon Press. 533-537.
- Lind, E.V. (1992). Polymers: Tests for Mechanical Properties. In: Corish, P.J. *Concise Encyclopedia of Polymer Processing & Application*. Oxford: Pergamon Press. 533-537.
- Liu, Y. and Truss, R. W. (1996). Study of Dispersion Morphologies of Isotactic Polypropylene and Linear Low Density Polyethylene Blends by Scanning Electron Microscopy. *Journal of Applied Polymer Science*. 60: 1461-1473.
- Liu, X., and Wu, Q. (2001). PP/clay nanocomposites prepared by grafting-melt Intercalation. *Polymer*. 42: 10013-10019.
- Liu X., Wu Q., Berglund L.A. (2002). Polymorphism in Polyamide 66/clay



- Nanocomposites. *Polymer* 43: pp 4967-4972.
- Liu, T., Lim, K.P., Tjiu, W.C., Pramoda, K.P., and Chen, Z.K. (2003). Preparation and Characterization of Nylon 11/Organoclay Nanocomposites. *Polymer*. 44: 3529-3535.
- Liu, W.P., Hoa, S.V., Pugh, M. (2005). Organoclay-modified high performance epoxy nanocomposites. *Composites Science and Technology*. 65: 307–316.
- Long, Y., and Shanks, R.A. (1996). PP-elastomer-filler hybrids. I. Processing, microstructure, and mechanical properties. *Journal of Applied Polymer Science*. 61: 1877-1885
- Lotti, C., Correa, C.A., Canevarolo, S.V. (2000). Mechanical and Morphological Characterization of Polypropylene Toughened with Olefinic Elastomer. *Materials Research*. 3: 37-44.
- Lynch, J.C.(2000). Impact Modification of Polypropylene as a Function of Rubber Toughening Parameters. Rensselaer Polytechnic Institute Troy, New York, PhD Thesis
- Ma, J.S., Qi, Z.N., and Hu, Y.L. (2001). Synthesis and Characterization of Polypropylene/Clay Nanocomposites. *Journal of Applied Polymer Science*. 82: 3611-3617.
- Ma, J., Zhang S., Qi, Z. and Hu, Y. (2002). Crystallization Behaviors of Polypropylene/Montmorillonite Nanocomposites. *Journal of Applied Polymer Science*. 83: 1978-1985.
- Ma, K.X., Liu, T.X., Liu, Z.H., Shen, L., Zeng, K.Y., and He, C.B. (2003). Morphology, Thermal and Mechanical Behavior of Polyamide 6/Layered-Silicate Nanocomposites, *Composites Science and Technology*. 63: 331-337.
- McGrath, G.C. Fracture and Toughening in Fibre Reinforced Polymer Composites. In: Coller, A.A. "Rubber Toughened Engineering Plastics". Chapman & Hall, London, 1994, 57-89.
- Mai, Y.W., Wong, S.C., and Chen, X.H. *Polymer Blends, Volume 2: Performance* (ed. D.R. Paul and C.B. Bucknall), 17-57, 2000, John Wiley & Sons, Inc.
- Maiti, P., Nam, P.H., Okamoto, M., Kotaka, T., Hasegawa, N., Usuki, A. (2002a). Influence of Crystallization on Intercalation. Morphology, and Mechanical Properties of Polypropylene/Clay Nanocomposites. *Macromolecules*, 35: 2042-2048.
- Maiti, P., Nam, P.H., Okamoto, M., Kotaka, T., Hasegawa, N., Usuki, A. (2002b).

The Effect of Crystallization on the Structure polypropylene/Clay Nanocomposites. *Polym Engng Sci.* 42:1864-1871.

- Makadia, C.M. (2000). Nanocomposites of Polypropylene by Polymer Melt Compounding Approach. University of Massachusetts Lowell: Master of Science Thesis
- Manias, E., Touny, A., Wu, L., Strawhecker, K., Lu, B., and Chung, T.C. (2001). Polypropylene/Montmorillonite Nanocomposites. Review of the Synthetic Routes and Materials Properties. *Chem. Mater.* 13: 3516-3523.
- Marchant, D. and Jayaraman, K. (2002). Strategies for Optimizing Polypropylene-Clay Nanocomposite Structure. *Ind. Eng. Chem. Res.* 41: 6402-6408
- Masenelli-Varlot, K., Reynaud, E., Vigier G., and Varlet J., (2002), Mechanical Properties of Clay-Reinforced Polyamide. *Journal of Polymer Science: Part B: Polymer Physics*, 40, 272-283.
- McNally, T., McShane, P., Nally, G.M., Murphy, W.R., Cook, M., Miller, A. (2002). Rheology, phase morphology, mechanical, impact and thermal properties of polypropylene/metallocene catalysed ethylene 1-octene copolymer blends. *Polymer.* 43: 3785-3793.
- McNally, T., Murphy, W.R., Lew, C.Y. Turner, R.J., and Brennan, G. (2003). Polyamide-12 Layered Silicate Nanocomposites by Melt Blending. *Polymer.* 43: 2761-2772.
- Mehrabzadeh, M., Hossein, Nia K. (1999). Impact Modification of Polypropylene by Ethylene Propylene Copolymer-Grafted Maleic Anhydride. *Journal of Applied Polymer Science.* 72: 1257-1265.
- Mehta, S., Mirabella, F.M., Rufener, K. Bafna, A. (2005). Thermoplastic olefin/clay nanocomposites: Morphology and mechanical properties. *Journal of Applied Polymer Science.* 92: 928 – 936.
- Messermith, P.B. and Giannelis, E.P. (1994). Synthesis and characterization of layered silicate-epoxy nanocomposites. *Chemistry of Materials.* 6: 1719-1725.
- Messermith, P.B. and Giannelis, E.P. (1995). Synthesis and barrier properties of poly( $\epsilon$ -caprolactone)-layered silicates nanocomposites. *Journal of Applied Polymer Science. Part A.* 33: 1047-1057.
- Mishra, J.K., Hwang, K.J., Ha, C.S. (2005). Preparation, mechanical and rheological

properties of a thermoplastic polyolefin (TPO)/organoclay nanocomposite with reference to the effect of maleic anhydride modified polypropylene as a compatibilizer. *Polymer*. 46: 1995–2002.

- Mishra, J.K., Ryou, J.H., Kim, G.H., Hwang, K.J. Kim, I., and Ha, C.S. (2005). Preparation and properties of a new thermoplastic vulcanizate (TPV)/organoclay nanocomposite using maleic anhydride functionalized polypropylene as a compatibilizer. *Materials Letters*. 58: 3481–3485.
- Mohd Ishak Z.A., Ishiaku U.S., Karger-Kocsis J. (2000). Hydrothermal aging and fracture behaviour of short-glass-fiber-reinforced rubber-toughened poly(butylene terephthalate) composites. *Composites Science and Technology*. 60, 803-815.
- Montoya, M., Tomba, J.P., Carella, J.M., and Gobernado-Mitre M.I. (2004). Physical characterization of commercial polyolefinic thermoplastic elastomers. *European Polymer Journal*. 40: 2757–2766.
- Morgan, A.B. and Gilman, J.W. (2003). Characterization of Polymer-Layered Silicate (Clay) Nanocomposites by Transmission Electron Microscopy and X-Ray Diffraction: A Comparative Study. *Journal of Applied Polymer Science*. 87: 1329-1338.
- Mouzakis D.E., Mader D., Mulhaupt R., Karger-Kocsis J. (2000). Relationship between morphology and mechanical properties of polypropylene/ethane-co-butene binary blends with various butane contents. *Journal of Materials Science*. 35: 1219-1230.
- Nam, P.H., Maiti, P., Okamoto, M., Kotaka, T., Hasegawa, N. and Usuki, A. (2001). A hierarchical structure and properties of intercalated polypropylene/clay nanocomposites. *Polymer*. 42: 9633-9640.
- Nanocomposite 1999: *Polymer Technology for the Next Century*, Company Press Release, Principia Partners.
- Narisawa, I. and Takemori, M.T. (1989). Fracture Toughness of Impact-Modified Polymers Based on the J-Integral. *Polymer Engineering and Science*. 29: 671.
- Nielsen, L.E. and Landel, R.F. (1994). *Mechanical Properties of Polymers and Composites*. 2<sup>nd</sup> ed. New York: Marcel Dekker. In. 268-282.
- Nitta, K.H., Shin, Y.W., Hashiguchi, H., Tanimoto, S., and Terano, M. (2005). Morphology and mechanical properties in the binary blends of isotactic

polypropylene and novel propylene-co-olefin random copolymers with isotactic propylene sequence 1. Ethylene-propylene copolymers. *Polymer*. 46: 965-975.

- Nowacki, R., Monasse, B., piorkowska, E., Galeski, A., Haudin, J.M. (2004). Spherulite nucleation in isotactic polypropylene based nanocomposites with montmorillonite under shear. *Polymer*, 45: 4877-4892.
- Okada, A., Fukumori, K., Usuki, A., Kojima, Y., Kurauchi, T., Kamigaito, O. (1991). Rubber-clay hybrid- synthesis and properties. *Polym. Prep.* 32: 540-541.
- Okada, A., Usuki, A. (1995). The chemistry of polymer-clay hybrids. *Mater. Sci. Eng. C3*: 109-115.
- Okamoto, M., Kubo, H., and Kotaka, T. (1999). Elongational Flow-Induced Higher-Order Structure Development in a Supercooled Liquid of a Metallocene-Catalyzed Syndiotactic Polystyrene. *Macromolecules*. 32: 6206-6214
- Ostromislenky, I.I., US Patent. 1,613,673 (Jan. 1927)
- Ou, Y.C., Guo, T.T., Fang, X.P., Yu, Z.Z. (1999). Toughening and reinforcing polypropylene with core-shell structured fillers. *Journal of Applied Polymer Science*. 74: 2397-2403.
- Paul, S., and Kale, D.D. (2000). Impact Modification of Polypropylene Copolymer with a Polyolefinic Elastomer. *Journal of Applied Polymer Science*. 76: 1480-1484.
- Perera, R., Albano, C., Gonzalez, J., Silva, P., Ichazo M., (2004). The effect of gamma radiation on the properties of polypropylene blends with styrene-butadiene-styrene copolymers. *Polymer Degradation and Stability*. 85: 741-750.
- Perkin W.G. (1999). Polymer toughness and impact resistance. *Polymer Engineering and Science*. 39: 12.
- Petrovic, Z.S., Budinski-Simendi, J., Divjakovi, V., and Skrbic, Z.J. (1996). Effect of addition of polyethylene on properties of polypropylene/ethylene-propylene rubber blends. *Journal of Applied Polymer Science*. 59: 301-310.
- Plumley, T.A., Patel, R.M. and Jain, P. (1995). Structure-property relationship of ethylene/1-octene and ethylene/1-butene copolymers made using INSITE Technology. ANTEC'95, 2249.
- Premphet K., and Hornsby P. (1998). Influence of Phase Microstructure on the

Mechanical Properties of Ternary Phase Polypropylene Composites. *J. Appl. Polym. Sci.* 70, 587-597.

- Premphet, K. and Horanont, P. (1999). Influence of Stearic Acid Treatment of Filler Particles on the Structure and Properties of Ternary-Phase Polypropylene Composites. *Journal of Applied Polymer Science.* 74: 3445-3454.
- Premphet, K. and Horanont, P. (2000a). Phase structure of ternary polypropylene/elastomer/filler composites: effect of elastomer polarity. *Polymer.* 41: 9283-9290.
- Premphet, K. and Horanont, P. (2000b). Phase Structure and Property Relationships in Ternary Polypropylene/Elastomer/Filler Composites: Effect of Elastomer Polarity. *Journal of Applied Polymer Science.* 76: 1929-1939.
- Premphet, K. and Paecharoenchai, W. (2001). Quantitative Characterization of Dispersed Particle Size, Size Distribution, and Matrix Ligament Thickness in Polypropylene Blended with Metallocene Ethylene-Octene Copolymers. *Journal of Applied Polymer Science.* 82: 2140-2149.
- Ray, S.S., and Okamoto, M. (2003). Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in Polymer Science.* 28: 1539-1641.
- Pukansky B., Belina K., Rockenbauer A. and Maurer F.H.J. (1994). Effect of Nucleation, Filler Anisotropy and Orientation on the Properties of PP Composites. *Composites* 25: 205-209.
- Reichert, P., Nitz, H., Klinke, S., Brandsch, R., Thomann, R., and Mulhaupt, R. (2000). Poly(propylene)/organoclay nanocomposite formation: Influence of compatibilizer functionality and organoclay modification. *Macromol. Mater. Eng.* 275, 8-17.
- Scobbo, Jr., J.J. (1991). Dynamic Mechanical Analysis of Compatibilized Polym Blends. *Polymer Testing.* 10: 279-290.
- Scott C.E. and Macosko C.W. (1995). Morphology development during the initial stages of polymer-polymer blending. *Polymer.* 36: 461-470.
- Sengers, W.G.F., Sengupta, P., Noordermeer, J.W.M., Picken, S.J., Gotsis, A.D. (2004). Linear viscoelastic properties of olefinic thermoplastic elastomer blends: melt state properties. *Polymer.* 45: 8881-8891.
- Seo, Y.S., Kim, J.H., Kim, K.U., and Kim, Y.C. (2000). Study of the crystallization

- behaviors of polypropylene and maleic anhydride grafted polypropylene. *Polymer*. 41: 2639-2646.
- Sharif, J., Wan Yunus, W.M.Z., Mohd Dahlanb, K.Z.Hj., and Ahmad, M.Hj. (2005). Preparation and properties of radiation crosslinked natural rubber/clay nanocomposites. *Polymer Testing*. 24: 211–217.
- Shih, C.K. (1995). Mixing and morphological transformations in the compounding process for polymer blends: The phase inversion mechanism. *Polymer Engineering and Science*. 35: 1688-1694.
- Sichina, W.J. and Gill, P.S. (1986). Characterization of Composites by Thermal Analysis. *31<sup>st</sup> International SAMPE Symposium*. Wilmington: Concord Plaza. April. 7-10.
- Sichina, W.J. (1994). *Prediction of End-use characteristics of Polyethylene Materials Using Differential Scanning Calorimetry*. USA: Application Briff DSC-11.
- Su, S.P., Jiang, D.D., and Wilkie, C.A. (2004). Poly(methyl methacrylate), polypropylene and polyethylene nanocomposites formation by melt blending using novel polymerically-modified clays. *Polymer Degradation and Stability*. 83: 321-331.
- Sunil, D. Jain (1999), Maleated EPDM Polyblends, University of Massachusetts Lowell, Master of Science Thesis.
- Swei, H., Crist, B. and Carr, S.H. (1991). The *J* integral fracture toughness and damage zone morphology in polyethylenes. *Polymer*. 32: 1440-1446.
- Tam, W.Y., Cheung, T., and Li, R.K.Y. (1996). An Investigation on the Impact Fracture Characteristics of EPR Toughened Polypropylene. *Polymer Testing*. 15: 363-379.
- Tang H. (2000). Novel Polyolefin Elastomer-Based Blends and Their Applications, University of Florida. Doctor of Philosophy Dissertation.
- Thompson, E.V. (1990). Thermal Properties. In Kroschwitz, J.I. *Concise Encyclopedia of Polymer Science and Engineering*. New York: John Wiley & Sons. 1185-1187.
- Tidjani, A., Oliver Wald, Martina-M. Pohl, Manfred P. Hentschel, Bernhard Schartel (2003) Polypropylene-graft-maleic anhydride-nanocomposites: I - Characterization and thermal stability of nanocomposites produced under nitrogen and in air. *Polymer Degradation and Stability* 82 (2003) 133–140
- Tjong, S.C., Xu, S.A., Li, R.K.Y. and Mai, Y.W. (2002). Mechanical behavior and

fracture toughness evaluation of maleic anhydride compatibilized short glass fiber/SEBS/polypropylene hybrid composites. *Composites Science and Technology*. 62: 831-840.

- Ton-That, M.T., Perrin-Sarazin, F., Colek, K.C., Bureau, M.N., and Denault J. (2004). Polyolefin Nanocomposites: Formulation and Development. *Polymer Engineering and Science*. 44: 1212-1219.
- Ueda (2001). Polymer Alloy Compendium, *Lecture Note: High Performance Polymer Technology Courses*, Osaka Municipal Technical Research Institute, Japan.
- Utracki, L.A. Polypropylene Blends with Elastomers. In: Karger-Kocsis, K. *Polypropylene: A-Z Reference*. Dordrecht: Kluwer Publishers, 1999; 621.
- Van der Wal, A., Nijhof, R., and Gaymans, R.J. (1999). Polypropylene-rubber blends: 2. The effect of the rubber content on the deformation and impact behaviour. *Polymer*. 40: 6031-6044.
- Wan Abdul Rahman, W.A. (1996). SMR/ENR50/PVC Ternary Blends: Preparation, Blending Characteristics and Compatibilization Studies. Universiti Teknologi Malaysia: Ph.D. Thesis.
- Wang, Z. (1996). Toughening and Reinforcing of Polypropylene. *J. Appl. Polym. Sci.* 60, 2239-2243.
- Wang, S.J., Long, C.F., Wang, X.Y., Li, Q., Qi, Z.N. (1998). Synthesis and properties of silicone rubber organomontmorillonite hybrid nanocomposites, *J. Appl. Polym. Sci.* 69: 1557-1561.
- Wang, Z., Massam, J., and Pinnavaia, T.J. Epoxy-Clay Nanocomposites. In: Pinnavaia T.J. and Beall G.W. *Polymer-Clay Nanocomposites*. John Wiley & Son, Ltd, 2002; 127-150.
- Wang, S.F., Hu, Y., You, F., Song, L., Chen, Z.Y., and W.C. Fan (2003). Self-assembly of polycarbonate/acrylonitrile-butadiene-styrene/montmorillonite nanocomposites. *J. Appl. Polym. Sci.* 90, 1445-1446.
- Wang, Y., Chen, F.B., Li, Y.C., Wu K.C. (2004a). Melt processing of polypropylene/clay nanocomposites modified with maleated polypropylene compatibilizers. *Composites: Part B*. 35: 111-124.
- Wang, Y., Chen, F.B., Wu, K.C. (2004b). Twin-Screw Extrusion Compounding of Polypropylene/ Organoclay Nanocomposites Modified by Maleated Polypropylenes. *Journal of Applied Polymer Science*. 93: 100-112.

- Wang Y., Chen F.B., and Wu K.C. (2005). Effect of the molecular weight of maleated polypropylenes on the melt compounding of polypropylene/organoclay nanocomposites. *Journal of Applied Polymer Science*. 97: 1667-1680.
- Wetton, R.E. and Corish, P.J. (1989). DMTA Studies of Polymer Blends and Compatibility. *Polymer Testing*. 8: 303-312.
- Williams, J.G. *Fracture Mechanics of Polymers*. Ellis Horwood Limited, Chichester, England (1984).
- Wu, J.S and Mai, Y.W. (1996). The Essential Fracture Work Concept for Toughness Measurement of Ductile Polymers. *Polymer Engineering and Science* 36: 2275-2288.
- Wu, Z., Zhou, C., and Zhu, N. (2002). The nucleating effect of montmorillonite on crystallization of nylon 1212/ montmorillonite nanocomposite. *Polymer Testing*. 21: 479-483.
- Xiao, J.F., Hu, Y., Wang, Z.Z., Tang, Y., Chen, Z.Y., and Fan, W.C. (2005). Preparation and characterization of poly(butylene terephthalate) nanocomposites from thermally stable organic-modified montmorillonite. *European Polymer Journal*. 41: 1030–1035.
- Xu, W.B., Liang, G., Wang, W., Tang, S., He, P., and Pan, W.P. (2003a). PP-PP-g-MAH-Org-MMT Nanocomposites. I. Intercalation Behavior and Microstructure. *Journal of Applied Polymer Science*. 88: 3225-3231.
- Xu, W., Liang, G., Zhai, H., Tang, S., Hang, G. and Pan, W.P. (2003b). Preparation and crystallization behaviour of PP/PP-g-MAH/Org-MMT nanocomposite. *European Polymer Journal*. 39: 1467-1474.
- Yamaguchi, M., Miyata, H., and Nitta, K.H. (1996). Compatibility of binary blends of polypropylene with ethylene- $\alpha$ -olefin copolymer. *Journal of Applied Polymer Science*. 62: 87-97.
- Yasue, K, Katahira, S, Yoshikawa, M, Fujimoto, K. In: Pinnavaia, T.J. and Beall, G.W. *Polymer-Clay Nanocomposites*. New York: John Wiley & Sons, 2001; 111.
- Yu, J., and He, J. (2000). Crystallization kinetics of maleic anhydride grafted polypropylene ionomers. *Polymer*. 41:891-898.
- Zerda, A.S. and Lesser A.J. (2001). Intercalated Clay Nanocomposite: Morphology,



Mechanics and Fracture Behavior. *Journal of Polymer Science: Part B: Polymer Physics*, 39: 1137-1146.

- Zhang, Q., Fu, Q., Jiang, L., and Lei, Y. (2000). Preparation and properties of polypropylene/ montmorillonite layered nanocomposites. *Polymer International*. 49: 1561-1564.
- Zhang, H., Wang, J., Cao, S. and Shan, A. (2001). Toughened Polypropylene with Balanced Rigidity (III): Compositions and Mechanical Properties. *Journal of Applied Polymer Science*. 79: 1345-1350.
- Zhao, R.F. and Dai, G. (2002). Mechanical Property and Morphology Comparison between the Two Blends Poly(propylene)/Ethylene Propylene-Diene Monomer Elastomer and Poly(propylene)/ Maleic Anhydride-g-Ethylene-Propylene-Diene Monomer. *Journal of Applied Polymer Science*. 86: 2486-2491.
- Zhong, Y., Zhu, Z.Y., Wang, S.Q. (2005). Synthesis and rheological properties of polystyrene/layered silicate nanocomposite. *Polymer*. 46: 3006–3013.
- Zhu, L.J. and Xanthos, M. (2004). Effects of Process Conditions and Mixing Protocols on Structure of Extruded Polypropylene nanocomposites. *Journal of Applied Polymer Science*. 93: 1891-1899.