

**RUBBER TOUGHENED POLYAMIDE 6/  
POLYPROPYLENE NANOCOMPOSITES:  
MECHANICAL, THERMAL AND  
MORPHOLOGICAL PROPERTIES**

by

**MAT UZIR BIN WAHIT**

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Prof. Madya Dr. Azman Hassan (Penyelia lapangan, UTM)

Dr. Azhar Abu Bakar (Penyelia bersama, USM)

Penyelidik dan juruteknik di Pusat Teknologi Plastik, SIRIM Berhad

Penyelidik dan juruteknik di Bahagian Teknologi Polimer, Institut Penyelidikan Nuklear Malaysia (MINT)

Pensyarah dan juruteknik di Jabatan Kej. Polimer, Fakulti Kej. Kimia dan Kej. Sumber Asli dan Fakulti Kej. Mekanikal, UTM

Pensyarah dan juruteknik di Fakulti Kejuruteraan, UKM

*Lecturer and technician at Dept of Polymer Engineering, Budapest University of Technology and Economis, Budapest, Hungary.*

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## LIST OF SYMBOLS

$a$	Length of the crack
$B$	Specimen thickness
$\Delta H_o$	Melting enthalpy of 100% crystalline polymer
$F_{max}$	Maximum load
$G_c$	Critical strain energy release rate
$K_c$	Critical stress intensity factor
$T_c$	Crystallization temperatures
$T_m$	Melting temperatures
$\theta$	Energy calibration factor
$\sigma_c$	Critical applied stress
$W$	Specimen width
$X$	Degree of crystallinity
$Y$	Geometrical factor

## LIST OF ABBREVIATION

ABS	Acrylonitrile-butadiene-styrene
CEC	Cation exchange capacity
DSC	Differential scanning calorimetry
DMA	Dynamic mechanical analysis
EPDM	Ethylene propylene diene monomer rubber
EPR	Ethylene propylene elastomer
EPRgMAH	Ethylene propylene elastomer grafted maleic anhydride
FTIR	Fourier transform infrared
LEFM	Linear Elastic Fracture Mechanics
MMT	Montmorillonite
PA 6	Polyamide 6
POE	Ethylene octane elastomer
POEgMAH	Ethylene octane elastomer grafted maleic anhydride
PP	Polypropylene
PPgMAH	Polypropylene grafted maleic anhydride
PVC	Polyvinylchloride
RT	Room temperature
SAN	Styrene acrylonitrile
SEBSgMAH	Styrene ethylene/butylene block copolymer grafted maleic anhydride
SEM	Scanning Electron Microscope
SENB	Single edge notch three point bending
TGA	Thermogravimetric analysis
XRD	X-ray diffraction

## LIST OF PUBLICATIONS & SEMINARS

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A.1	M.U. Wahit, A. Hassan, Z.A. Mohd Ishak, A. Abu Bakar (2005) The effect of polyethylene-octene elastomer on the morphological and mechanical properties of polyamide 6 / polypropylene nanocomposites. <i>Polymer &amp; Polymer Composites</i> , 13(8), p.795-806	242
A.2	M.U. Wahit, A. Hassan, Z.A. Mohd Ishak, A.R. Rahmat, A. Abu Bakar (2006) Morphology, thermal and mechanical behavior of ethylene octene copolymer toughened polyamide 6/polypropylene nanocomposites. <i>Journal of Thermoplastics Composites Material</i> . <i>Accepted in Press</i>	243
A.3	Mat Uzir WAHIT, Azman HASSAN, Zainal Ariffin MOHD ISHAK, Abdul Razak RAHMAT, Norhayani OTHMAN (2006) The effect of rubber type and rubber functionality on the morphological and mechanical properties of rubber-toughened polyamide 6/polypropylene nanocomposites. <i>Polymer Journal</i> . <i>Accepted in Press</i>	244
A.4	M.U. Wahit, A. Hassan, A.R. Rahmat, Z.A. Mohd Ishak (2006) Morphological and Mechanical Properties of Rubber-Toughened Polyamide 6/Polypropylene Nanocomposites Prepared by Different Methods of Compounding. <i>Journal of Elastomers and Plastics</i> . <i>Accepted in Press</i>	245
A.5	M.U. Wahit, A. Hassan, Z.A. Mohd Ishak, A.R. Rahmat, J.W. Lim (2006) Effect of Organoclay and Ethylene-Octene Copolymer Inclusion on the Morphology and Mechanical Properties of Polyamide/Polypropylene Blends. <i>Journal of Reinforced Plastics &amp; Composites</i> . <i>Accepted in Press</i>	246
A.6	M.U. Wahit, Z.A. Mohd Ishak, A. Hassan, J.W. Lim, A. Abu Bakar (2004) The Effect of Polyethylene-Octene Elastomer Content on The Mechanical Properties and Morphological of Polyamide 6/Polypropylene Blends. 4 <sup>th</sup> International Materials Technology Conference & Exhibition, 23 <sup>th</sup> -25 <sup>th</sup> March 2004, Kuala Lumpur.	247
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A.8	M.U. Wahit, J.W. Lim, A. Hassan, Z.A. Mohd Ishak (2004) PA6/PP blends nanocomposites: The effect of blend ratio on the mechanical properties. National Post Graduate Colloquium (NAPCOL 2004), 8 <sup>th</sup> – 9 <sup>th</sup> December, 2004, Penang	249

- A.9 M.U. Wahit, A. Hassan, A.R. Rahmat, J.W. Lim (2004) Studies on the Effect of Polyethylene Octene Elastomer on Polypropylene Nanocomposites: Mechanical Properties and Phase Morphology. 13<sup>rd</sup>. Scientific Conference and 14<sup>th</sup>. Annual General Meeting of the Electron Microscopy Society of Malaysia, 13-15 December 2004, Bangi, Selangor. 250
- A.10 M.U. Wahit, A. Hassan, Z.A. Mohd Ishak, A.R. Rahmat, J.W. Lim, N. Othman (2005) Morphological and Mechanical Properties Rubber-Toughened Nanocomposites, International Conference Advances in Polymer Blends, Composites , IPNS and Gel: Macro to Nano Scales (ICBC-2005), 21<sup>st</sup> -23<sup>rd</sup> March, 2005, Kerala, India. 251

# NANOKOMPOSIT POLIAMIDA 6/POLIPROPILENA DIPERLIATAN GETAH: SIFAT-SIFAT MEKANIKAL, TERMAL DAN MORFOLOGI

## ABSTRAK

Nanokomposit diperliatan getah yang terdiri dari siri adunan serasi poliamida 6 / polipropilena (PA6/PP) dengan komposisi 100/0, 70/30, 50/50, 30/70 and 0/100, getah polietilena-oktena (POE) dan organofilik terubahsuai organo-tanah liat telah dihasilkan menggunakan kaedah adunan leburan diikuti proses acuan suntikan. Polipropilena *grafted* malik anhidrida (PPgMA) telah digunakan sebagai penyerasi. Seterusnya, untuk adunan PA6/PP (70/30), kandungan POE dan organo tanah liat masing-masing telah diubah antara 5 dan 20% dan 2 dan 6 % mengikut berat. Untuk formulasi yang optimum, empat jenis getah berlainan telah dimasukkan ke dalam adunan iaitu getah polietilena-oktena (POE), getah etilena-propilena (EPR), POE maleated (POEgMAH) dan EPR maleated (EPRgMAH). Untuk formulasi yang terpilih, nanokomposit telah juga disediakan menggunakan teknik percampuran interkalasi leburan yang berbeza iaitu kaedah terus, kaedah dua kali dan kaedah dua langkah.

Sifat-sifat mekanikal telah dikaji berdasarkan ujian tegangan, lenturan, hentaman dan keliatan rekahan. Morfologi yang melibatkan taburan PP dan POE telah kaji menggunakan Mikroskop Imbasan Elektron (SEM). Serakan Sinar-X (XRD) pula digunakan untuk mengkaji pembentukan nanokomposit. Sifat-sifat thermal telah diselidiki menggunakan kalorimeter imbasan pembezaan (DSC). Sifat mekanikal dinamik telah dianalisis menggunakan pengalisis termal mekanikal dinamik (DMTA).

Keputusan menunjukkan bahawa penggunaan organo-tanah liat telah meningkatkan kekakuan dan kekuatan bahan tetapi terdapat penurunan dalam keliatan. Di sebaliknya, penggunaan POE telah meningkatkan keliatan tetapi menyebabkan penurunan dalam kekuatan dan kekakuan. Nanokomposit PA6/PP yang

mengandung organo-tanah liat dan POE sebanyak 4 % dan 10 % mengikut berat adalah yang seimbang dari segi kekakuan, kekuatan dan keliatan. Keputusan juga menunjukkan modulus dan kekuatan nanokomposit tidak dipengaruhi oleh jenis getah serta kefungsiannya dan turutan adunan. Bagaimanapun, nanokomposit yang diperliat getah *maleated* didapati lebih liat berbanding getah tanpa *maleated*. Kaedah dua langkah menghasilkan nanokomposit dengan sifat-sifat mekanikal terbaik disebabkan oleh organo-tanah liat dan getah yang terserak dengan baik di dalam matriks. Keputusan ujian XRD mengesahkan bahawa organo-tanah liat terserak secara sempurna (*exfoliated*) di dalam fasa PA6. Jenis getah yang berlainan dan kefungsiannya tidak memberi kesan yang serius terhadap penyerakan organo-tanah liat di dalam sistem. Nisbah adunan dan kehadiran organo-tanah liat mempunyai pengaruh terhadap morfologi sistem (saiz partikel dan taburan POE). POE dengan saiz partikel yang halus serta taburan yang baik telah diperhatikan di dalam sistem adunan yang mempunyai kandungan PP yang tinggi. Pemerhatian keputusan SEM juga membuktikan bahawa kefungsi getah dan kaedah dua langkah dapat mengurangkan saiz partikel getah di dalam matriks PA6/PP.

# RUBBER TOUGHENED POLYAMIDE 6/POLYPROPYLENE NANOCOMPOSITES: MECHANICAL, THERMAL AND MORPHOLOGICAL PROPERTIES

## ABSTRACT

Rubber-toughened nanocomposites (RTNC) consisting of a series of compatibilized polyamide 6 / polypropylene (PA6/PP) blends, of composition 100/0, 70/30, 50/50, 30/70 and 0/100, polyethylene-octene elastomer (POE) and organophilic modified montmorillonite (organoclay) were produced by melt compounding followed by injection moulding. Polypropylene grafted maleic anhydride (PPgMA) was used as compatibilizer. Subsequently, for PA6/PP (70/30), the POE and organoclay loading was varied between 5 and 20 wt% and 2-6 wt%, respectively. For the optimum formulation, four different types of elastomer were incorporated into the blends i.e. ethylene-octene elastomer (POE), ethylene-propylene elastomer (EPR), maleated POE (POEgMAH) and maleated EPR (EPRgMAH). For the selected formulation, the nanocomposites were also prepared through different mixing sequence of melt intercalation i.e. direct, two times and two steps method.

The mechanical properties were studied through tensile, flexural, Izod impact and fracture toughness testing. The morphology, essentially comprised of PP and POE particles dispersed in the PA6 matrix, was characterized by scanning electron microscopy (SEM). Wide angle X-ray diffraction (XRD) was used to characterize the formation of the nanocomposites. The thermal properties were characterized by using differential scanning calorimeter (DSC) and thermogravimetry analysis (TGA). The dynamic mechanical were analyzed by using dynamic mechanical thermal analyzer (DMTA).



The results showed that, the incorporation of organoclay significantly increased the stiffness and strength but at the expense of the toughness. Conversely, the incorporation of the POE increased the toughness, while the strength and stiffness decreased. The PA6/PP nanocomposites containing 4 wt % of organoclay and 10 wt% of POE had the best balance of stiffness, strength and toughness. The results also showed that modulus and strength of the nanocomposites was not significantly affected by types of elastomer and their functionality and the blending sequence. However, the toughness of the nanocomposites toughened by maleated elastomer was higher than the unmaleated elastomer. Two steps method gave the best mechanical properties due to its good dispersion of the organoclays and elastomer in the matrix. XRD established that the organoclay was well dispersed (exfoliated) and preferentially embedded in the PA6 phase. The type of elastomer and functionality and method of processing did not significantly affect the dispersion of the organoclay in the system. Blend ratio and the presence of organoclay were found to influence the morphology (e.g. POE particle size and distribution) of the system. A finer particles size and better distribution of POE elastomer has been observed in higher PP concentration system. The SEM observation also revealed that rubber functionality and two steps method reduces the elastomer particle size in the PA6/PP matrix.

## CHAPTER 1. INTRODUCTION AND BACKGROUND

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

#### 1.1.1 Polymer Blend

The increasing demand of polymers for various applications requires polymeric materials with greatly improved physical and mechanical properties. There are a myriad of homopolymer available in the marketplace. However, simple homopolymer often do not possess all requisite physical, mechanical, thermal, and chemical properties for specific application. Considering that the polymer industry is fairly mature and the discovery of a new class of homopolymer does not occur often, so new polymers are often obtained by blending existing polymers (Wei, 1999).

Furthermore, the homopolymer development cost an average of US\$10 million (1990) with additional US\$100 million for pilot plant cost in the development and commercialization step. By contrast, polymer blend development cost less than a few million dollars. As a result, around 4500 blend patents and 50,000 articles published annually (Tucker *et al.*, 2000).

Blending of polymers provides attractive opportunities for achieving unique property combinations such as the enhancements in the impact strength, processibility, tensile strength, chemical resistance, barrier properties and etc. The production of new materials designed through blending implies lower costs together with a shorter time scale with respect to the search for new monomers and new copolymer synthesis. More recently, polymer blending also has enabled the reuse of recycling industrial and municipal plastics scrap. The mentioned technological, economical, and ecological advantages resulting from polymer-mixing processes led over the last decade to a 9%

annual increase in the production of polymer blends, which recently has reach about 30% of overall plastics production (Donald, 1994; Tang, 2000).

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

Blending of thermoplastics specifically with elastomer has been commercialized as rubber-toughened plastics or as thermoplastics elastomer (Chung and Coran, 1997; Ibrahim and Dahlan, 1998). Generally, if a relatively large portion of hard plastics is used, the composition can be used as an impact resistance plastic; 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 (Okada *et al.*, 1999).

The history of rubber-toughened plastics can be traced back as far as 1927. In that year, Ostromislenky patented a process for making toughened polystyrene by polymerizing a solution of rubber in styrene monomer (Bucknall and Lazerri, 2000). 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 (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 1952, the US Rubber Company introduced a melt blended material which was a blend of styrene acrylonitrile (SAN) and acrylonitrile-butadiene rubber (NBR) to produce acrylonitrile-butadiene-styrene (ABS). In 1957, impact modified polyvinylchloride was commercially produced into marketplace. Since then, rubber-toughened plastics have been the fastest growing segment of the plastics industry.

### 1.1.3 Nanocomposites

Nanotechnology is recognized as one of the promising avenues of technology development for 21<sup>st</sup> century. Although research has been done for a couple of, only now have polymers producers taken the major proactive steps towards evaluating the technology for commercial pursuits (Ashter, 2002). More than 70 companies, government agencies, and academic institutions in US have been identified as having R&D activities in nanocomposites (Agag *et al.*, 2001; Makadia, 2000). However, relatively few have commercial activities.

The global market for nanocomposites merely three million pounds; of which two million pounds were nanoclay-reinforced polyamide (nylon) produced by Unitika and Ube Industries in Japan for automotive and packaging application respectively. The remaining one million pounds was carbon nanotube-filled PPO/nylon alloy produced in North America for automotive body part. However, each of these developing product technologies is poised for strong growth over the next ten years. Market projections show 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 compound and 160 million pounds will be carbon nanotube-filled products (Makadia, 2000).

Nanocomposites technology is applicable to 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.

Nanocomposites are currently used in two commercial applications: automotive under hood components and food packaging. For example, Nylon M2350 has been used by Mitsubishi Motors for engine cover and Toyota Motor Corporation for Toyota

Camry timing belt cover. Bayer AG is currently marketing nylon 6 nanocomposites for a transparent barrier film packaging (Sherman, 1999). 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, have begun to adopt nanocomposites materials since 2004, and significant growth in demand will occur through 2009.

#### **1.1.4 Current Research**

At present, despite the concept of polymer nanocomposites being existence for almost two decades, there are still considerable efforts need to be carried out, including effective toughening of polymer nanocomposites. So far, little work has been done on combination of both polymer nanocomposites technology with polymer blend and rubber-toughening technology. It is interesting to look at the system where rubber-toughened thermoplastics blends combined with nanofillers. Therefore, the current research deals with the combination of nanocomposites, polymer blends and rubber-toughened thermoplastics. The nanofillers and impact modifier distribution, concentration, morphology of the system and their effect on mechanical properties were investigated. The effects of compatibilization systems were studied as well.

#### **1.2 Problem Statements**

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 balance of stiffness, strength and toughness. Two approaches have been identified as potential route to achieving this goal. This involves:

- i) The inclusion of fillers or nanofillers into thermoplastic matrix or blends to form thermoplastics composites or nanocomposites
- ii) Blending of thermoplastic or blends with elastomer to form rubber-toughened thermoplastics.

However, several studies have indicated that the above mentioned 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 stiffness and strength. On the contrary, the presence of fillers or reinforcement such as organoclay into polymers leads to an increase in stiffness/strength and decrease in toughness. Thus, the next logical approach to follow is to combine both filler and impact modifier into thermoplastic matrix or blends. However, the literature on combined reinforcement and rubber toughening is quite sparse. Therefore, this research is initiated to explore the limits of possibilities for making engineering thermoplastics simultaneously stiffer/stronger and tougher by combining these two approaches.

Beside that, to date most of the scientific research in polymer nanocomposites have been focus on single matrix system. Thermoplastics nanocomposites or rubber-toughened thermoplastics based on blends of two or more polymeric materials have not yet been explored in open literature. However, this could be a new approach in rubber-toughened and nanocomposites studies, in the sense that it will produce the materials with good balance of properties such as mechanical, thermal as well as good processability.

### 1.3 Objectives

The present proposal work aims to develop new advanced polymeric composite materials namely rubber-toughened polyamide 6 (PA6) / polypropylene (PP) blends nanocomposites. In this research, rubber-toughened PA6/PP blends nanocomposites were produced via polymer melt intercalation method (extrusion and injection moulding) by blending of thermoplastics blends (PA6/PP) with elastomer such as ethylene-octene copolymers (POE) or ethylene-propylene elastomer (EPR) with the incorporation of nanofillers (organoclay) in the presence of compatibilizer such as polypropylene grafted maleic anhydride (PPgMAH). The target application of these new materials is for engineering application such as automotive component.

The objectives of this works are:

- i) To examine the effect of the incorporation of the organoclay and the elastomer into the PA6/PP blend with different ratio.
- ii) To investigate the effect of organoclay and elastomer concentration on the mechanical properties and determine the optimum formulation for the PA6/PP blends in order to achieve a good balance of mechanical properties
- iii) To characterize the formation and morphology of RT[PA6/PP]NC i.e. exfoliated/intercalated structure of the organoclay and elastomer particle size and distribution by several technique such as X-ray diffraction (XRD) and scanning electron microscope (SEM) and relate the mechanical properties of the RT[PA6/PP]NC with the morphology (structure-property relationship).
- iv) To study how the melt intercalation method affect the microstructure of the nanocomposites
- v) To study the effect rubber type and functionality on the morphological and mechanical properties of the nanocomposites.

## CHAPTER 2. LITERATURE REVIEW

### 2.1 Thermoplastics

Thermoplastics have become part of the fabric of modern life. The production of thermoplastics is estimated to be over 200 billion pound per year world wide (Lynch, 2000). This number is expected to increase as plastics are substituted into applications traditionally held by glass, metal and wood.

#### 2.1.1 Nylon (Polyamide)

Nylon was one of the early polymers developed by W.H. Carothers and co-workers who first synthesized nylon 6,6 in 1935 (Nelson, 1976). Du Pont Company commenced commercial production of this polymer for subsequent conversion into fibres in 1939. Nylon, are also called polyamide (PA), because of the characteristic amide groups (-CONH-) in the backbone chain as can be seen in Figure 2.1 (Nelson, 1976; Baker and Mead, 2002). These amide groups are polar in nature and significantly affect the polymer properties. The polarity of these amide groups allows for hydrogen bonding between chains, improving the interchain attraction, and this gives nylon polymers good mechanical properties (Vroom, 1997).

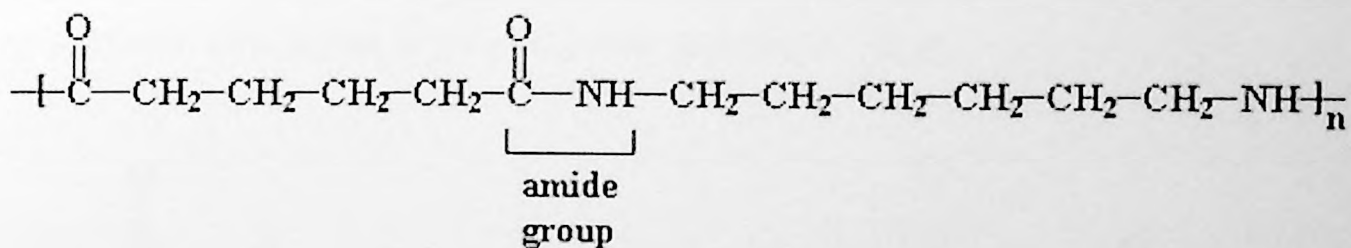


Figure 2.1. The basic structure of PA

The nylon in Figure 2.1 is called nylon 6,6, because each repeat unit of the polymer chain has two stretches of carbon atoms, each being six carbon atoms long.



Other nylons can have different numbers of carbon atoms in these stretches. Nylons can be made from diacid chlorides and diamines. Nylon 6,6 is made from the monomers adipoyl chloride and hexamethylene diamine (see Figure 2.2)

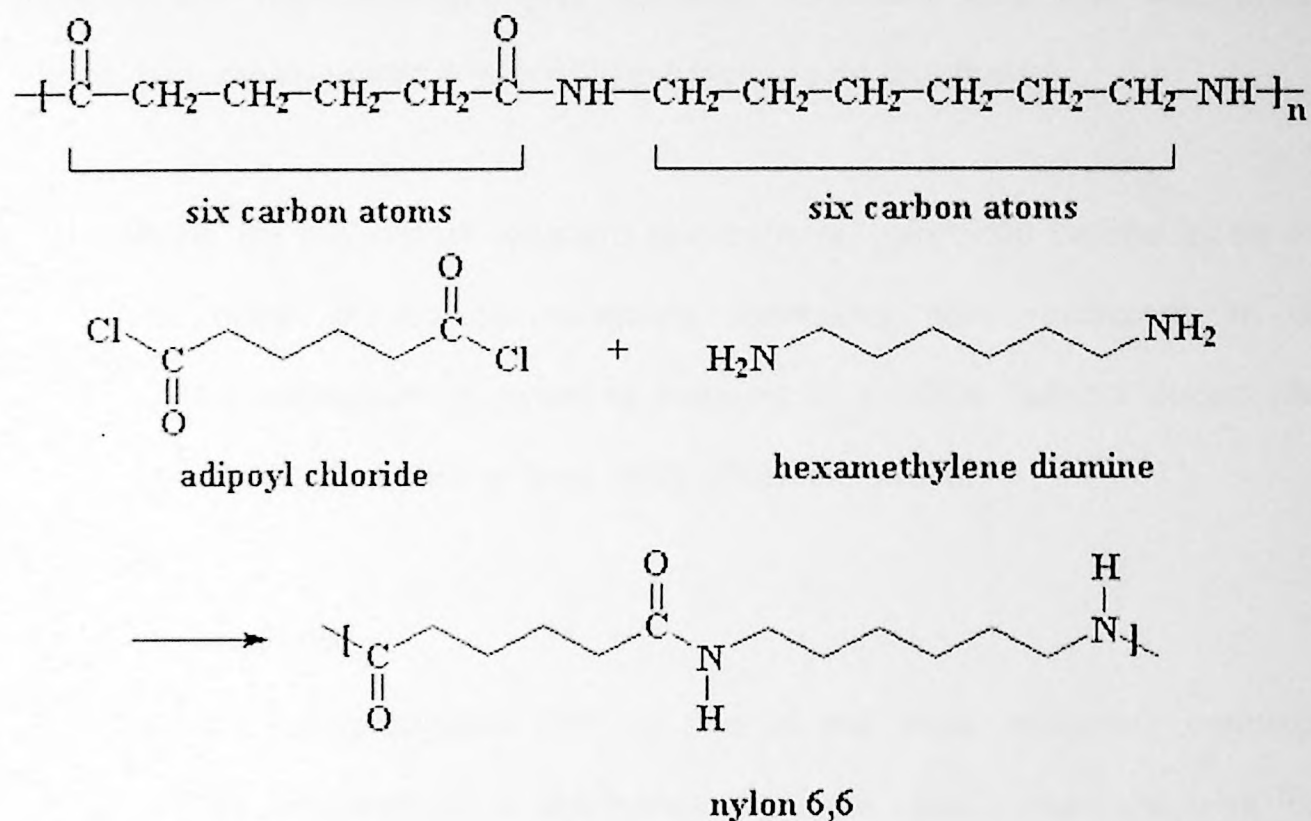


Figure 2.2. Synthesis of nylon 6,6 (Painter and Coleman, 1994).

Another type of nylon is PA6. It is made by a ring opening polymerization from the monomer caprolactam as can be seen in Figure 2.3. Ring opening polymerization of caprolactam is a commercially important process, more than the analogous polymerization of lactones to give polyester (Billmeyer, 1974).

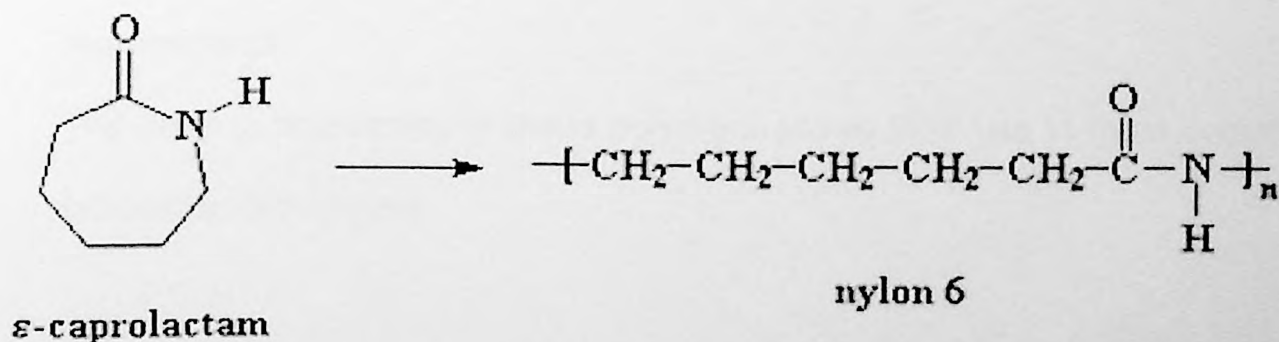


Figure 2.3. Typical ring-opening polymerization of caprolactam (Billmeyer, 1971)

Nylon has been used in numerous engineering applications since they became available as moulding and extrusion materials (Kohan, 1973). Nylons are one of the most common polymers used as a fiber. Some of their desirable properties for demanding applications are high strength and stiffness, excellent chemical and abrasion resistance, high melting point, low coefficient friction and toughness.

However, for the impact resistant applications, nylon has proved to be notch sensitive and brittle at low temperatures, indicating poor resistance to crack propagation. This inclination of nylon to fracture in a brittle fashion under certain conditions was a major limitation of their utility (Poznick, 1998).

### **2.1.2 Polypropylene**

At present, polypropylene (PP) is one of the most important commercial thermoplastics; its consumption is still increasing more rapidly than the total for all thermoplastics. This situation is likely to continue into the future for the following reasons (Brydson, 1989; Lynch, 2000):

- i. The relatively low cost of the product is due to low monomer cost and ancient polymerization technology, compared with other thermoplastics.
- ii. The polymer can be modified for a variety of applications. Through copolymerization, orientation, and other techniques the physical properties of the product can be varied to meet a wide range of thermal and mechanical requirements.
- iii. The ease in processing of these polymers allows their use in most commercial fabrication techniques.

PP is a linear hydrocarbon polymer containing little or no unsaturation. The presence of a methyl group attached to alternate carbon atoms on the chain backbone

can alter the properties of the polymer in number of ways (Brydson, 1989). The most significant influence of the methyl group is that it can lead to products of different tacticity, ranging from completely isotactic and syndiotactic structures to atactic molecules. The isotactic form is the most regular since the methyl groups are all disposed on one side of the molecule. The isotactic polymer is stiff, highly crystalline and with a high melting point. The melting point of isotactic is 165°C. Within the range of commercial polymers the greater the amount of isotactic material the greater the crystallinity and hence the greater the softening point, stiffness, tensile strength, modulus and hardness, all other structural features being equal.

The influence of molecular weight on the bulk properties of PP is often opposite to that experienced with most other well-known polymers. Although an increase in molecular weight leads to an increase in melt viscosity and impact strength, in accordance with most other polymers, it also leads to a lower yield strength, lower hardness, lower stiffness and softening point. This effect is believed to be due to the fact that high molecular weight polymer does not crystallize so easily as lower molecular weight material and it is the differences in the degree of crystallization which affect the bulk properties (Lieberman and Barbe, 1990). It may also be mentioned that an increase in molecular weight leads to a reduction in brittle point.

One unfortunate characteristic property of PP is the dominating transition point at about 0 °C with the result that the polymer becomes brittle as this temperature is approached. Even at room temperature the impact strength of some grades is not satisfactory. Products of improved strength and lower brittle points may be obtained by block copolymerization of propylene with small amounts (4 - 15%) of ethylene copolymers and are often preferred to the homopolymer in injection molding and bottle blowing applications (Brydson, 1989).

## 2.2 Multiphase Polymers

### 2.2.1 Introduction

A multiphase polymer is one that has two or more distinct phases. The phases may differ in chemical composition and/or texture (Utracki *et al.*, 1989). Ueda (2001) stated that the term multiphase as a generic name for macromolecular multicomponent system of strong interaction containing two more kinds of macromolecular. Thus, in its broadest sense, the term includes copolymers, such as block copolymers and graft copolymers, and interpenetrating polymer networks (encircled by dotted line in Figure 2.4). Polymer blends are mixtures of at least two macromolecular species; they are either miscible or immiscible, where these terms are understood in purely thermodynamic sense (that is, in miscible blends the level of miscibility extends to the molecular level).

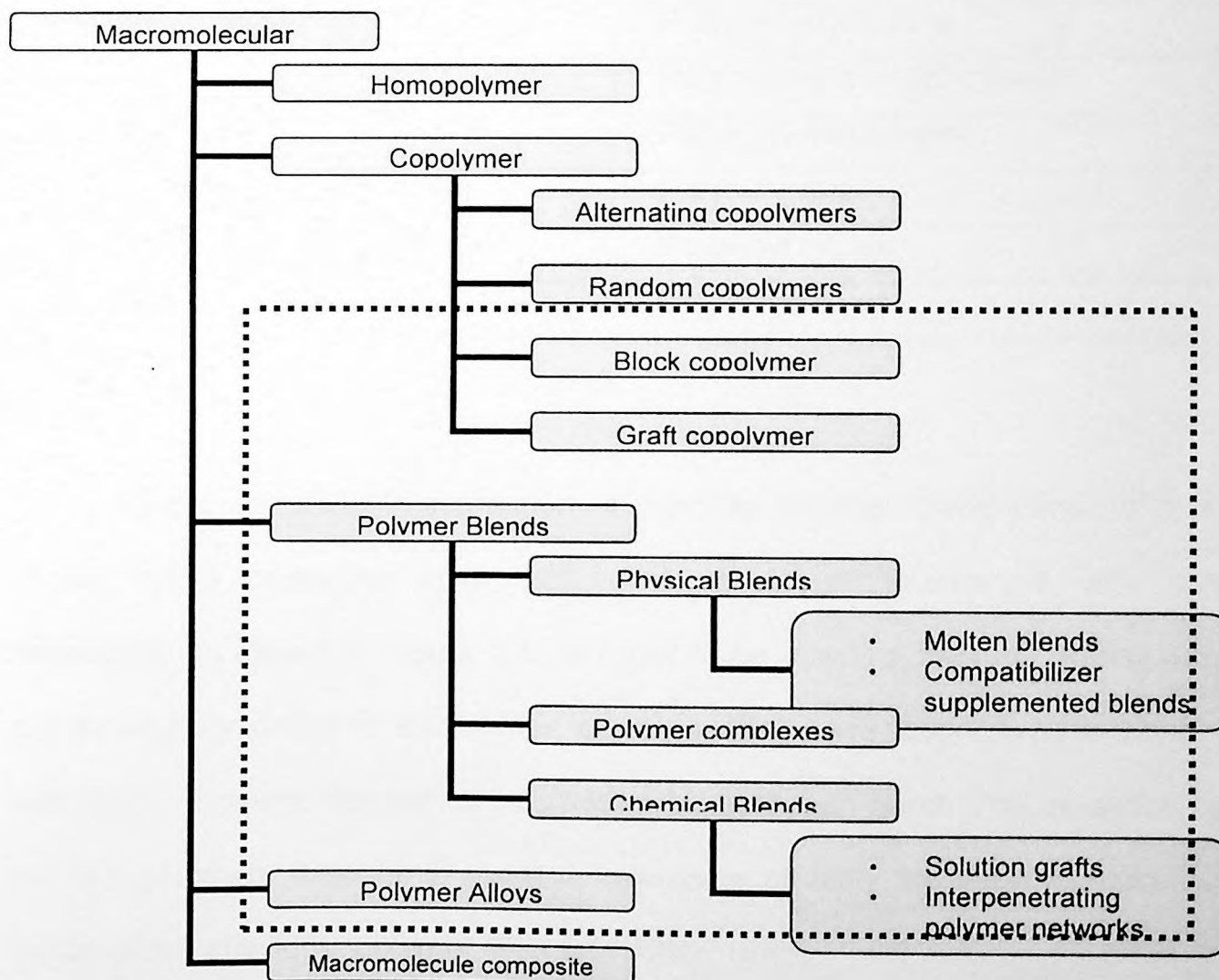


Figure 2.4. Macromolecular material classification (Ueda, 2001)

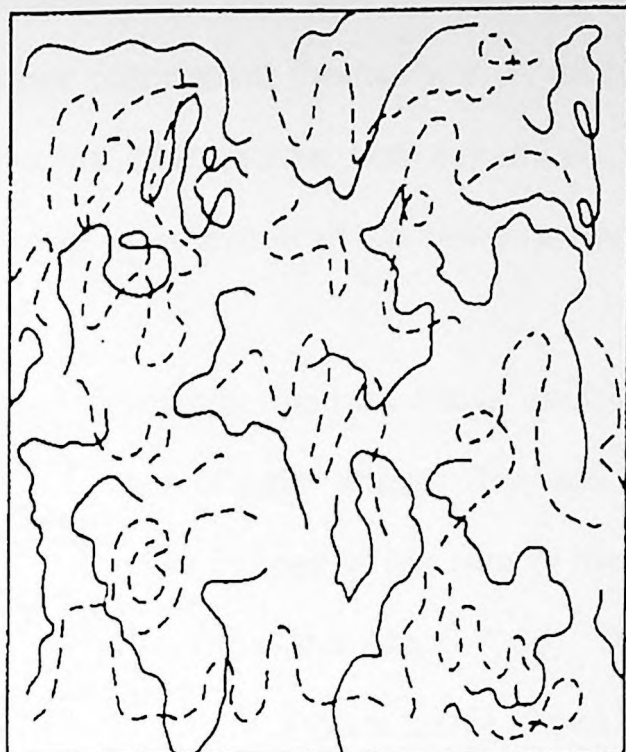
## 2.2.2 Miscibility and Compatibility of Polymer Blends

Polymer blends can be categorized into two broad categories, miscible and immiscible. Utracki (1998) defines “miscible blends” as a polymer blend homogeneous to the molecular level, associated with a negative value of free energy. Miscible blends or homogeneous have a single thermal transition intermediate between the components, molecular scale mixing and light transparency (Olabisi *et al.*, 1979). They only have one phase and behave like a single phase material (Fox and Allen, 1985). Table 2.1 shows the currently known polymer combinations that form miscible systems, including commercially available polymer blends products.

Table 2.1. Example of miscible polymer pairs (Ueda, 2001)

Polymer A	Polymer B
Polyvinyl chloride	Polymethyl acrylate
Polyvinyl chloride	Polybutyrene terephthalate
Polystyrene	Polyvinyl methyl ether
Polypropylene	Polybutyrene
Polymethyl acrylate	Polyvinyl nitrate
Polyvinyl acetate	Polyvinyl nitrate

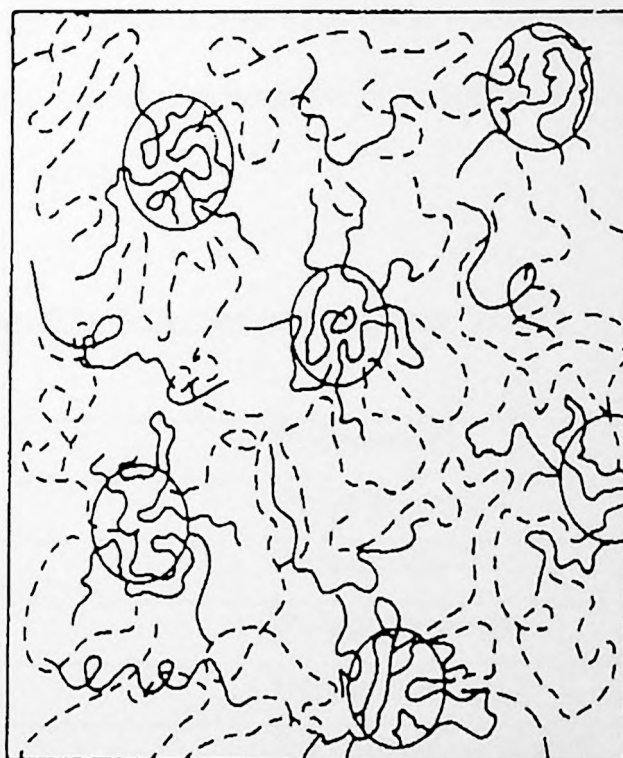
Under microscopic inspection, a miscible polymer blend consists of a single phase; on a molecular level, polymer-A molecules intermingle with polymer-B molecules, as shown in Figure 2.5. In order to be miscible Polymer A and Polymer B are structurally similar to each other, or unless they have respective functional groups with dipole moment that attract each other by hydrogen bond. The attraction between the two polymers must be present to overcome partially the intramolecular cohesive forces of the individual polymer (Fox and Allen, 1985).



(a)



(b)



(c)

Figure 2.5. Morphologies of a blend of polymer A (solid lines) and polymer B (dashed lines) (a) miscible (b) immiscible (c) partially miscible (Fox and Allen, 1985)

Since a miscible polymer blend has only one phase, it is much like a random copolymer in properties and processing. Miscible materials are homogeneous on a

molecular level and their characteristics are similar to those of normal individual polymer component themselves. A mixture of two completely miscible polymers has properties intermediate between those of its constituents, and is in many respects similar to a copolymer of the same composition.

Immiscible blends show multiple phases and exhibit thermal transition characteristics of each phase. They are usually opaque, unless the components have equal refractive indices or the size of the dispersed phase is less than the wavelength of visible light (Fox and Allen, 1985). The examples of immiscible polymer pairs are given in Tables 2.2. Figure 2.5(b) shows the morphology of an immiscible blend where polymer A forms a separate phase from polymer B. The polymer present in the lower concentration usually forms a discontinuous or discrete phase (domain), whereas the polymer present in the higher concentration forms a continuous phase. Other factors, such as relative viscosity and blend preparation procedure, could also determine blend morphology (Paul and Kale, 1978).

Table 2.2. Example of immiscible polymer pairs (Ueda, 2001)

<b>Polymer A</b>	<b>Polymer B</b>
Polystyrene	Polyethylene
Polystyrene	Polyamide
Polystyrene	Polypropylene
Polypropylene	Polyamide
Polyamide	Polyethylene glycol
Polyvinyl chloride	Polystyrene

Often, a blend of two polymers is neither totally miscible nor totally immiscible, but falls somewhat in between. A blend of this type is termed partially miscible. Partially miscible polymers may form completely miscible blends when either polymer is present in small amounts (Fox and Allen, 1985). However, as the ratios progress

toward equality, the phases separate. At compositions where a partially miscible polymer blend is in two phases, the phases may not have a clear boundary, since polymer A molecules can significantly penetrate into the polymer-B phase, and vice versa, as depicted in Figure 2.5(c). The molecular mixing that occurs at the interface of a partially miscible two-phase blend can stabilize the domains and improve interfacial adhesion.

This, explain why these two-phase blends generally have good bulk properties. The large number of blends in this category and their good properties has made them become the most common of the commercial blends. Partial miscible blends of technological importance are usually termed compatible blends. In such blends, satisfactory physical and mechanical properties are related to the presence of a finely dispersed phase and resistance to gross phase segregation (Xanthos and Gagli, 1991). From a practical point of view, it is useful to refer to a polymer as compatible when it does not show gross signs of polymer segregation. The simple observation that a blend is compatible is sufficient to establish the material as potentially useful. However, from a theoretical perspective, much can be learned about the nature of the compatibility and the expected properties of the blend by probing its morphology.

A blend that is heterogeneous on a macroscopic level would thus be considered incompatible (Krause, 1978). Incompatible system arises from a variety of reasons such as the absence of any specific interaction between their blend components, dissimilarity in structures and large differences in their viscosities, surface energy or activation energy of flow and polarity (White and Min, 1985). An incompatible rubber in a plastics matrix will not form a fine dispersion of the type required for good optical, mechanical and rheological properties. Nor will it produce a strong mechanical bond at the rubber-matrix interface. Therefore, the ideal rubber for purpose of plastics matrix



toughening is neither completely miscible nor completely immiscible, but is finely disperse in matrix with good interfacial adhesion.

Figure 2.6(a) shows compatible blend, with an interfacial region (interface) (Krause, 1978). The compatible blend has a large interface volume in which the two different polymer chains mix. Because the polymers are compatible, there is significant mixing of chains in this region. The intermixing of chains can help transfer mechanical stresses between the phases.

While, Figure 2.6(b) exhibits the interface for an incompatible blend. The incompatible blend has a thin interface with few chains extended into the opposite phase. This thinner region shows fewer interactions between the chains of the two different polymers, and the blend should have lower tensile strength than the compatible blend because the force is carried primarily by the continuous phases.

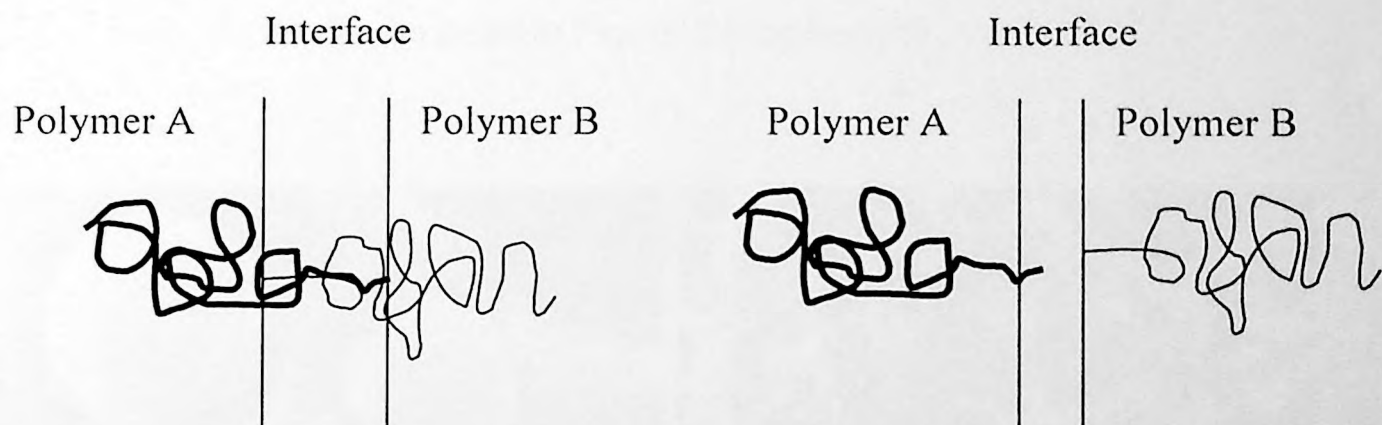


Figure 2.6. Sketches of polymer blends (a) compatible, (b) incompatible

## 2.3 Compatibilizing Agents

### 2.3.1 Introduction

When mixing polymers with other components, such as filler or other polymers, these two or more components will not necessarily like each other. In most of the cases

there will be a repelling force and there will be very poor or even no adhesion. The incompatibility between polymeric components is responsible for very poor mechanical properties of most polymer blends (Halimatudahliana *et al.*, 2002). In order to improve adhesion, compatibilizers or coupling agents can be added.

The purpose of compatibilizers is to act at the interface to increase the adhesion between two substrates through the reduction of the interfacial tension. Compatibilizers can be reactive or non reactive. In the case that they are reactive they will essentially chemically interact with the components of the mixture, form a covalent bond and this way reduce or entirely eliminate the repelling effect of the components of the mixture (Thwe and Liao, 2002).

The general principle of compatibilization is to reduce interfacial energy between two polymers in order to increase adhesion and also help dispersion. Generally, the addition of compatibilizers also allows finer dispersion, more regular and stable morphologies as can be seen in Figure 2.7(a) and (b).

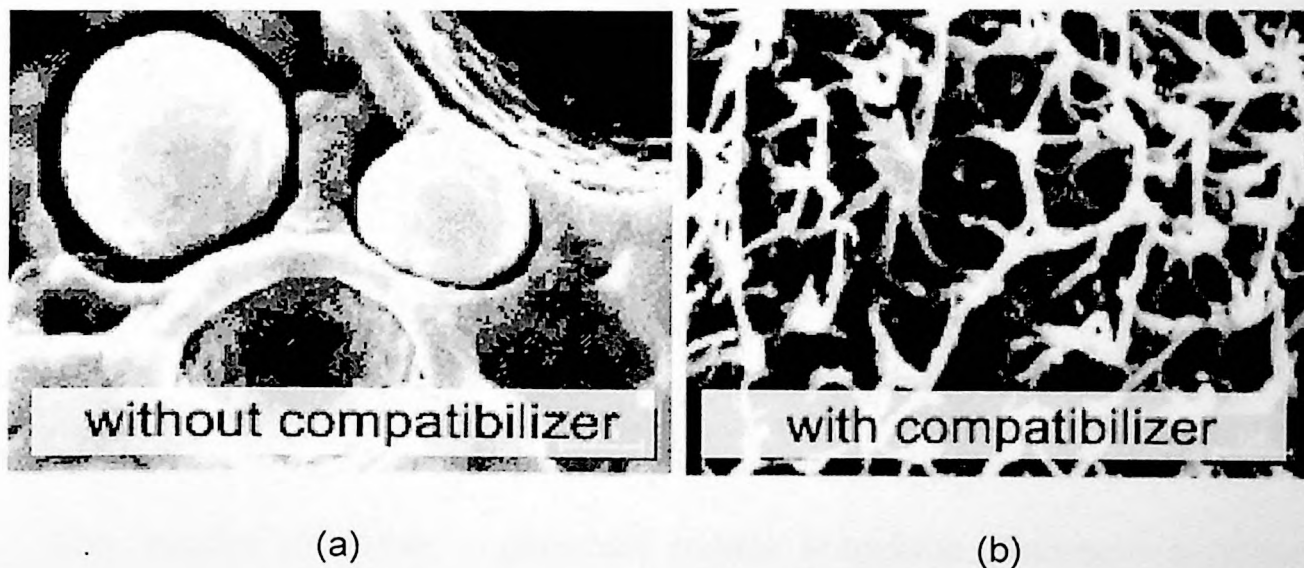


Figure 2.7. 30% PA6 / 70% LLDPE (a) without compatibilizer (b) with the addition of 10% polymeric compatibilizer (Thwe and Liao, 2002)

### 2.3.2 Compatibilizer Classification

Many compatibilizer comprise block copolymers or graft copolymers, typically exemplified by block copolymers and graft copolymer consisting of segments of the same structures as those of the respective polymer pair components to blended. Another type compatibilizer consist of block copolymers or graft copolymers of the same structure as that of one of the polymer pair components such as polypropylene grafted maleic anhydride (PPgMAH) for PA6/PP blends (Utracki, 1998).

### 2.3.3 Reactive Functional Copolymers

The principle of action is to react at the interface to create "in-situ" a grafted block copolymer by reaction between functional groups of the different polymers as schematically shown in Figure 2.8. The functionalized copolymer is miscible with the matrix and can react with functional groups of the dispersed phase. The advantages are adjustable reactivity, high efficiency and generally cheaper than block copolymers.

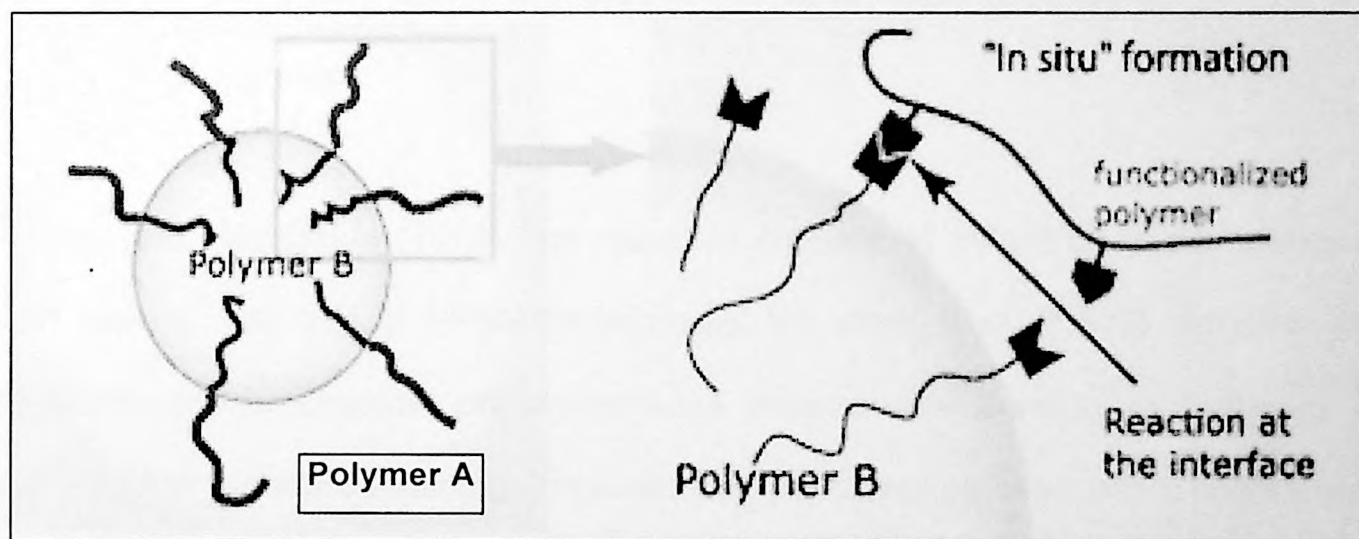


Figure 2.8. Compatibilization by reactive functional copolymers.

The reactive monomer is generally maleic anhydride. Maleated polymers are among the widest known family of functionalized polymers used as compatibilizer and coupling agents. They can be prepared directly by polymerization or by modification during compounding and this process is called reactive extrusion.

Among the maleated polymers, polypropylene grafted maleic anhydride (PPgMAH) was widely used as compatibilizer in polymer blends. This is due to fact that polymer blends based on polyolefins constitute materials of great interest owing to their broad spectrum of properties and practical application. However, in such polymer blends, due to the poor compatibility of the components, most of these systems are generally characterized by high interfacial tension, low degree of dispersion and poor mechanical properties. Blend of PP and PA6 is an example of blend with poor compatibility.

It is generally accepted that blends of PP and PA6 are immiscible throughout the whole range of compositions. In the absence of compatibilizer such as PPgMAH, such blends lack of interfacial adhesion and generally suffer from poor mechanical properties. The PPgMAH has anhydride and carboxyl group that interact with functional groups such as the amine group of PA6, which are capable of forming covalent or hydrogen bond therewith. Anhydride groups can also react with epoxy groups and eventually alcohol groups.

Ide and Hasegawa (1974) first reported the use of PPgMAH to compatibilize PA6/PP blends. The use of PPgMAH improved the dispersion of PA6 domains and consequently the mechanical properties were improved. According to Sathe *et al.* (1996), PA6/PP blends containing PPgMAH compatibilizer showed more regular and finer dispersion, different dynamic properties, and improved mechanical properties owing to the better adhesion between two phases. Similar compatibilization effect by adding PPgMAH was also reported for the PP/PA6 blends by Park *et al.* (1990) and Marco *et al.* (1997).

Besides that, maleated rubbers such as ethylene-propylene copolymer grafted maleic anhydride (EPRgMAH) and styrene ethylene/butylene block copolymer grafted

maleic anhydride (SEBSgMAH) are also known as compatibilizers for PA6/PP blends (Gonzalez-Montiel *et al.*, 1995a,b,c; Okada *et al.*, 1999; Oshinki *et al.*, 1996). More recently, ethylene-octene copolymer grafted maleic anhydride (POEgMAH) is used as compatibilizer for the same blends (Chen *et al.*, 1999; Premphet and Chalearmthitipa, 2003). The other benefit of using these reactive rubbers is the affinity of the olefinic for the PP such as POE. In the case of EPR elastomer, even though PP and EPR rubber are not miscible, there is a certain affinity that leads to good adhesion between the phases. Furthermore, high level of toughness for the blends can be achieved as they also act as impact modifier. The maleic anhydride group grafted to the rubber react with amine end-groups of the PA6, forming a graft copolymer that help to disperse the rubber in the PA6 and to strengthen the PA6/PP interface (Gonzalez-Montiel *et al.*, 1995a,b,c).

## **2.4 Polyamide 6/Polypropylene Blend**

PA6 and PP are two important classes of polymers used in the market. PP is widely employed because of its low cost, high barrier properties to moisture, and its ease of processing, but its high permeability to oxygen and many organic solvents limits its potential use. On the other hand, PA6 is a good barrier material for oxygen and organic compounds but it is relatively expensive, hygroscopic and thus poor barrier for water. Therefore, blending of PA6 and PP is a challenging task since combination of properties of both polymers might be a promising route to generate materials with new characteristic. The reason for blending PA6 with PP is to bridge the property gap between the two resins. Thus, the often cited advantages of PA6/PP blends are: low moisture absorption, improved processability, good impact resistance, and flexural modulus (Utracki and Dumoulin, 1995; Machado *et al.*, 2001).

Many reports on blending of PA6/PP have been published and the compatibilization of the blends has been their focus (Bohn *et al.*, 2001; Jafari *et al.*,

1999; Piglowski *et al.*, 2000). We can broadly differentiate two approaches for the compatibilization of these blends. One approach involving grafting a functional group on the polyolefin chain (either during synthesis or processing) followed by the reaction of this group with the amine group of the PA6 phase. The reaction forms a graft copolymer of PA6/PP that acts as a compatibilizer for the system. The second approach consists of adding a copolymer that will either react with polyamide (copolymer of ethylene and acrylic acid or maleic anhydride) or promote interactions between polyolefin and PA6 phase (ionomers). More than 50 publications related to PA6/PP blends were summarized by Gonzalez-Montiel (1995a) and Tang (2000) with different type of compatibilizer. However, the most popular compatibilizer used in the PA6/PP blends is PPgMAH (La Mantia and Capizzi, 2001; Tucker *et al.*, 2000; Bohn *et al.*, 2001; Tedesco *et al.*, 2001; Afshari *et al.*, 2002).

Gonzalez-Montiel and co-workers (1995a,b,c) published a series of papers focuses on the use of three types of maleated polymers as compatibilizer and/or impact modifier for PA6/PP blends, viz PPgMAH, EPRgMAH and SEBSgMAH. The morphology of the blends was found to depend on the content of maleic anhydride of PPgMAH, the miscibility of PP and PPgMAH and the relative ratio of PP to PPgMAH. However, all binary (PA/PPgMAH) and ternary (PA/PP/PPgMAH) blends showed low levels of toughness. Therefore, other attempts concentrated mainly on how to increase the impact toughness by adding an elastomer element into blends.

## **2.5 Rubber-Toughened Polymers**

### **2.5.1 Background**

Toughness is the ability of materials to absorb strain energy under applied force, without fracture (Walker and Collyer, 1994; Michler and Bucknall, 2001). A tough material is one that absorbs a large amount of energy before failure (Donald, 1994).

While polymer toughness, in the form of impact resistance is a measure of the ability of a material to withstand the application of sudden load without failure (Perkins, 1999). Impact strength is a measure of toughness: the higher impact strength of a material, the higher the toughness and vice versa.

As mentioned earlier, most thermoplastics such as PA6, PP and PA6/PP blends have relatively poor impact resistance, especially at room and low temperatures. For many applications, the requirement is for the polymer materials to exhibit adequate stiffness and toughness over a wide range of temperatures. Impact behaviour can be generally improved by incorporating a discrete rubbery phase via blending or copolymerization (Karger-Kocsis and Kuleznev, 1982; Perkin, 1999; Ibrahim and Dahlan, 1998; Liang and Li, 2000;).

To improve the impact toughness of the polymer and extend its application range, a number of extensive and thorough studies on toughening the polymeric materials with rubber have been made in the last 20 years (Liang and Li, 2000; Lynch, 2000). Rubber toughening should impart greater ductility, improved crack resistance, and higher impact strength to the material, accompanied by only a small loss in stiffness and without detrimental effect on thermal stability (Perkins, 1999).

### **2.5.2 Impact Modification Techniques**

Polymerization is one of the techniques, which prove to be effective in producing impact modified polymers through the incorporation of rubber (Keskkula and Paul; 1994; Lynch, 2000; Okada *et al.*, 1999). For example, HIPS was produced by bulk/suspension polymerization while the ABS copolymer was produced by emulsion polymerization. The block copolymer materials will be formed, where soft and hard segments are appropriately arranged to obtain desirable mechanical behaviour. The other method for generating impact modified polymer is melt blending or compounding.

For example, impact modification of polyvinylchloride (PVC), polyphenylene oxide (PPO)/HIPS, and polycarbonate/ABS. To produce blends by conventional melt compounding, devices such as twin-screw extruders are used. Twin-screw extrusion is a continuous process in which the premixed feed material enters the extruder, usually in the form of a solid. The material is subjected to high shear by the co-rotating screws. This high shear aids in melting the material and provides excellent mixing.

### **2.5.3 Mechanism of Rubber Toughening**

The technology of rubber-toughening has been used commercially since late 1940s and has played a major part in the growth of polymer industry. However, the mechanism and the controlling parameters have been subject of much debate (Bucknall and Lazerri, 2000; Premphet and Chalearmthitipa, 2003). Deformation mechanisms of rubber-toughened polymers have received considerable attention during the last two decades (Gonzalez-Montiel *et al.*, 1995c).

The first theory explaining the mechanism of rubber toughening of glassy polymers is the rubber bridge theory or microcrack theory was published by Merz, Claver and Baer in 1956 (Walker and Collyer, 1994; Jain, 1999; Liang and Li, 2000). This theory is illustrated in Figure 2.9.

According to this theory, when blends of rigid plastics and rubbers are stressed to an extent to cause crack initiation, the propagating crack reaches the rubber particle and passes through it. While the fractured surfaces tend to separate, the rubber particles become extended in tension. These extended rubber particles absorb energy and resist further crack propagation. Failure occurs when a sufficient number of microcracks formed and the rubber particles holding them together were broken. The amount of energy absorbed in impact was attributed to the sum of energy to fracture the glassy matrix and the work to break the rubber particles. The theory was reinforced



by the observation of stress whitening which was explained as the formation of microcracks. For this mechanism to be effective there should be a good bond between the rubber particles and the polymer matrix. They believed that the polymer-rubber adhesion would have to be greater than the rubber tensile strength to achieve maximum toughness. The main shortcoming of this theory was that the deformation of the rubber phase could not possibly account for the large increase in toughness due to the low shear modulus of the rubber. In addition, the theory did not account for the toughness of other rubber modified polymers which did not exhibit microcracking in the form of stress whitening.

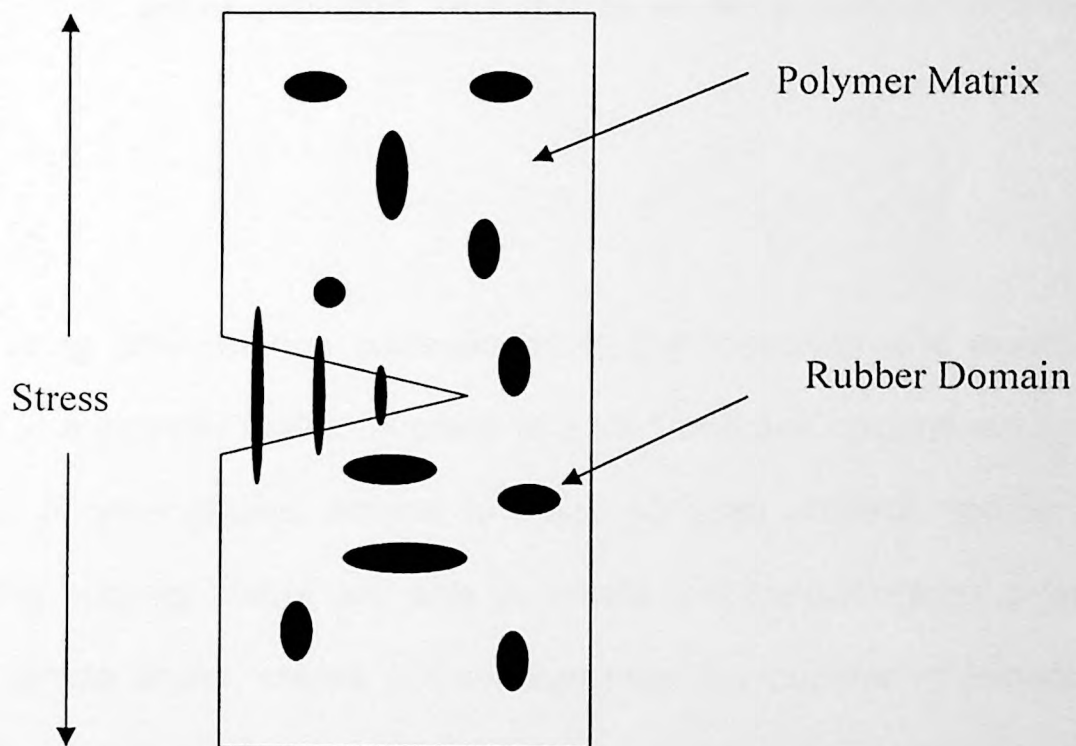


Figure 2.9. Rubber bridge theory of Merz, Claver and Baer in 1956 (Jain,2000).

#### 2.5.4 Yielding Mechanism

To further understand the toughening mechanism of rubber toughened polymers, the understanding of large strain behaviour of the homogenous plastics is necessary, the reason being that the deformation mechanisms responsible for large strains in toughened polymers are essentially the same as those observed in the

homogenous glassy polymers from which they are derived (Perkin, 1999). The rubber is present as a discrete dispersed phase within the glassy matrix, and can not itself contribute directly to a large deformation: the matrix must first yield, or fracture around the particles.

There are essentially two major theories interpreting the toughening mechanisms (Donald, 1994; Liang and Li, 2000). They are:

- Crazeing of the polymer matrix
- Shear yielding of the polymer matrix

Depending on the polymer system, either a single mechanism or a combination of different mechanisms will be activated. This section we will provide an overview of the different mechanism.

#### **2.5.4.1 Crazeing**

The crazeing phenomenon corresponds to the formation and extension of a craze network in a polymer matrix. A craze is a kind of crack but bridged by fibrils of oriented matrix polymer chains, normal to craze surfaces. Impact modifier particles dispersed in this polymer matrix, are able to initiate and control crazes growth (Jain, 1999). Under tensile stress, crazes are initiated near the equator of impact modifier particles due to high stress concentration, propagate almost normal to tensile stress direction and stop their growth when a neighbouring particles is encountered preventing the growth of very large crazes. The result is a large number of small crazes in contrast to a small number of larges crazes formed in the same polymer in the absence of rubber particles (Walker and Collyer, 1994).

The resulting multi-crazeing phenomenon is able to dissipate large amount of impact energy. Assuming that almost 50% of craze volume is void, crazeing is always accompanied by a pronounced stress whitening effect and a significant increase of