PREPARATION, CHARACTERIZATION AND PROPERTIES OF POLYPROPYLENE/WASTE TIRE DUST (PP/WTD) BLENDS

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PREPARATION, CHARACTERIZATION AND PROPERTIES OF POLYPROPYLENE/WASTE TIRE DUST (PP/WTD) BLENDS

by

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DEDICATION

to my parents, wife, and kids….

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LIST OF ABBREVIATIONS

A-HDPE	acrylic-modified HDPE
ATR	attenuated total reflection
AU	polyester urethanes
BR	butadiene rubber
CBS	*N-cyclohexyl-2-benzothiazole-2-sulfenamide*
CR	chloroprene rubber
DCP	dicumyl peroxide
DCPD	dicyclopentadiene
DSC	differential scanning calorimetry
DTDM	dithiodimorpholine
DTG	derivative thermogravimetric
ECO	epichlorohydrin rubber
ENB	5-ethylidene norbornene
ENR	epoxidized NR
EPDM	ethylene-propylene-diene terpolymer
EU	polyether urethanes
EVA	ethylene-vinyl acetate
FTIR	Fourier-transform infrared (spectroscopy)
h	hour
HDPE	high density polyethylene
HVA-2	*N, N'-m-phenylenebismaleimide*
IIR	isobutene-isoprene rubber (butyl rubber)
IPN	interpenetrating polymer network
IR	infra red
LDPE	low density polyethylene

LLDPE	linear low density polyethylene
LNR	liquid natural rubber
MA	maleic-anhydride
MIDA	Malaysian Industrial Development Authority
min	minute
NBR	acrylonitrile-butadiene rubber
NMR	nuclear magnetic resonance
NR	isoprene rubber (natural)
PE	polyethylene
PET	poly(ethylene terephthalate)
phr	part(s) per hundred rubber
PMMA	poly(methyl methacrylate)
PP	polypropylene
PS	polystyrene
PU	polyurethane
PVC	polyvinyl chloride
rpm	revolution(s) per minute
SBR	styrene-butadiene rubber
SBS	styrene-butadiene-styrene triblock copolymer
SEBS	styrene-ethylene-butylene-styrene
SEBS-g-MA	maleic-anhydride grafted SEBS
SEM	scanning electron microscopy
TDF	tire derived fuel
TG	thermogravimetric
TGA	thermogravimetric analysis
TMTD	tetramethylthiuram disulfide
TOR	*trans*-polyoctylene rubber

TPE	thermoplastic elastomer
TPO	thermoplastic olefins
TPV	thermoplastic vulcanizates
UV	ultraviolet
UV/VIS	ultraviolet-visible-spectroscopy or ultraviolet-visible-spectrophotometry
WRHA	white rice husk ash
WTD	waste tire dust
$WTD_{EPDM\text{-}M}$	EPDM modified WTD
WTD_{ML}	NR latex modified WTD
$WTD_{NR\text{-}M}$	NR modified WTD
$WTD_{P\text{-}HVA2}$	modified WTD with HVA-2 and DCP dynamic vulcanization
$WTD_{T\text{-}SDV}$	modified WTD with TOR and sulfur dynamic vulcanization
YBPO	ether-ester block co-polymer (thermoplastic polyether-ester)

LIST OF SYMBOLS

C	carbon
E	energy (Joule)
E_b	elongation at break
H	Plank's constant
kg	kilogram
kJ/kg	kilojoule per kilogram
O_2	oxygen
O_3	ozone
S	sulfur
S_x	polysulfidic
T	temperature
T_m	melting temperature
v	frequency (Hertz)
W_1	weight of sample before immersion
W_2	weight of sample after immersion
wt%	weight percent
ZnO	zinc oxide
ΔG_m	Gibbs free energy change on mixing
ΔH_m	enthalpy change on mixing
ΔS_m	entropy change on mixing
λ	wavelength (m)

PENYEDIAAN, PENCIRIAN DAN SIFAT-SIFAT ADUNAN POLIPROPILENA/SERBUK SISA TAYAR (PP/WTD)

ABSTRAK

Termoplastik dan getah sisa daripada tayar terbuang telah dicampurkan bagi menyediakan adunan polipropilena/serbuk sisa tayar (PP/WTD). Semua adunan disediakan di dalam pencampur dalaman pada suhu 180ºC, putaran 50 rpm untuk suatu tempoh adunan di antara 9 dan 13 minit. Pencirian telah dilakukan untuk mengenalpasti sifat-sifat adunan dan menyelidik kesan-kesan saiz serbuk sisa tayar, penggunaan pemvulkanan dinamik dan ko-agen, penambahan bahan polimer lain dan pendedahan pencuacaan semulajadi selama 6 bulan terhadap sifat mekanik, morfologi, rintangan pembengkakan, dan sifat-sifat haba adunan tersebut. Tanpa mengira saiz, sisa getah yang tersambung silang dan mengandungi kandungan karbon yang tinggi telah didapati berfungsi seperti pengisi tanpa-menguat. Peningkatan penyebaran zarah WTD dan interaksi dengan matriks PP menyumbang kepada sifat yang lebih baik bagi adunan yang mengandungi WTD halus. Peningkatan interaksi antara muka di antara matriks PP dan WTD akibat daripada penambahan getah *trans*-polioktilena (TOR) bersama sulfur, dikumil peroksida (DCP) dan *N, N'-m-fenilenabismalemida* (HVA-2) kepada adunan adalah punca utama peningkatan keseluruhan morfologi, sifat-sifat mekanik, rintangan pembengkakan, dan sifat-sifat haba adunan. Penambahan WTD yang terubahsuai dengan lateks getah asli (NR) merintis kekusutan zarah getah tersambung-silang dengan matriks PP yang menggalakkan peningkatan rekatan dengan WTD dan menyebabkan peningkatan terhadap sifat-sifat mekanik, rintangan pembengkakan, dan sifat-sifat haba adunan. Sementara itu, penambahan WTD yang terubahsuai dengan

getah asli (NR) dan WTD yang terubahsuai dengan etilena-propilena diena terpolimer (EPDM) meningkatkan keanjalan rantaian adunan PP/WTD. Penambahan bahan-bahan berkenaan telah menggalak pembentukan kawasan antara muka dan seterusnya meningkatkan lagi interaksi di antara matriks PP dan WTD sebagaimana yang dibuktikan oleh sifat-sifat adunan yang lebih baik. Selepas 6 bulan pendedahan kepada pencuacaan semulajadi, keseluruhan adunan telah menunjukkan kemerosotan sifat. Sementara adunan yang mengandungi WTD halus telah menunjukkan sifat mekanik yang lebih baik daripada adunan yang mengandungi WTD kasar, kebanyakan adunan yang mengandungi WTD terubahsuai telah mempamerkan sifat mekanik yang lebih unggul dan penahanan sifat yang pelbagai beserta sifat haba yang lebih baik daripada adunan asal tanpa sebarang pengubahsuaian terhadap WTD. Ini menunjukkan kewujudan interaksi yang lebih baik di antara matriks PP dan WTD yang terubahsuai.

PREPARATION, CHARACTERIZATION AND PROPERTIES OF POLYPROPYLENE/WASTE TIRE DUST (PP/WTD) BLENDS

ABSTRACT

Thermoplastics and waste rubber from scrap tires were mixed to prepare polypropylene/waste tire dust (PP/WTD) blends. All blends were prepared in an internal mixer at a temperature of 180ºC, a rotor speed of 50 rpm and a mixing period between 9 and 13 min. Characterization was done to determine the properties of the blends and to investigate the effects of WTD size, application of dynamic vulcanization and co-agents, addition of other polymeric materials and a 6-month exposure to natural weathering on the mechanical properties, morphology, swelling resistance and thermal properties of the blends. Irrespective of size, the highly cross-linked waste rubber with a high content of carbon black behaved like non-reinforcing fillers. An improved distribution of WTD particles and hence interactions with the PP matrix rendered superior properties to the blends with fine WTD. Formations of enhanced interactions across the interface of the PP matrix and WTD as a result of addition of *trans*-polyoctylene rubber (TOR) together with sulfur, dicumyl peroxide (DCP) and *N, N'-m-phenylenebismaleimide* (HVA-2) to the blends were the pivotal ascriptions to the overall improvements in morphology, mechanical properties, swelling resistance and thermal properties of the blends. Addition of natural rubber (NR) latex modified WTD initiated the creation of entanglements of vulcanized rubber particles with the PP matrix promoting improved adhesion with WTD resulting in enhanced mechanical properties, swelling resistance, and thermal properties of the blends. Meanwhile, the addition of NR modified WTD and ethylene-propylene diene terpolymer (EPDM) modified WTD improved chain flexibility of the PP/WTD blends. Their addition to the blends favored formations of interfacial region and hence improved interaction between the PP matrix and WTD as evidenced by superior properties of the blends. After the 6-month exposure to natural weathering, all blends exhibited deteriorations in properties. Whilst, blends with fine WTD demonstrated higher mechanical properties after the exposure than those with coarse one, mostly all blends with WTD modification exhibited higher mechanical properties with variations of retention and unveiled better thermal properties than those without any modification alluding to the presence of improved interactions between the PP matrix and modified WTD.

CHAPTER 1

INTRODUCTION

1.1 Polymeric Materials and the Environment

Polymeric materials either natural or synthetic have been in use for years. Since their early exploitation, the materials have been ubiquitous in human daily life and continue to remain a nifty material. If our forebears availed themselves of mostly natural polymeric materials to make their clothing and other articles which they required, today we have become engulfed with even broader range of polymeric materials which are extensively modified from their natural state. Until now, these materials continue to gain trust and being relevant in knotty, advanced, and various applications such as construction and aerospace due to their expansive attributes and aptness in numerous environments. For instance, the annual world production of plastics for the year of 1992 reached 102 x 10^6 m^3 at a value of over USD 300 billion, while that of steel was 50 x 10^6 m^3 at a value of USD 125 billion (Utracki, 1998).

The wide-ranging application and the usefulness of polymers portray the encouraging aspects of them but their chemically irreversible state imperils the environment. As majority of today's polymer modifications are carried out in chemically irreversible ways and the produced polymeric materials are not biodegradable, their disposal so far have caused damages to the environment. For instance, scrap tire stockpiles present the danger of self-sustaining fires which cause air and water pollution. As reported in an incident in Washington, USA approximately one million scrap tires caught fires in the early 1980's caused tremendous pollution besides costly clean up efforts after fire (Rosenberg, 1998). In 2005, for example, around 11.6 million tonnes of plastics waste in Europe went to disposal (Johansson and Vorspohl, 2007). In Malaysia, the total amount of collected solid waste was about 9664 tonnes daily or 3.5 million tonnes annually and the amount of plastics which could be recycled was nearly half a million tonnes annually (Nasir et al., 2000). If these wastes which include polymeric materials are not properly managed, they in a short or long run will disturb the environment as they do not degrade easily.

Not only they pollute the environment, the disposed polymers epitomize a palpable loss of natural resources which are non-renewable. As most of today's polymeric materials derived from gas or crude oil and their manufacturing requires energy, the disposed parts definitely represent the energy lost. For instance, ditching just a beverage can is comparable to throwing away approximately 500 ml of gasoline (Agamuthu, 2001). The use of recycled rubber replacing primary raw materials in rubber manufacture is reported to save approximately 45% energy (Porter and Roberts, 1985). Hence, utilizing any part of the discarded polymeric materials promotes natural resource conservations as well as energy saving.

Discarded polymeric materials should instead be dealt with a more sustainable way so that the usage of natural resource is maximized and the waste generation is minimized. Options which aim to turn discarded polymeric materials or waste back into resources and reduce the environmental damage should be regarded as the priority. For instance, the desirable option such as re-use and recycling of discarded polymeric materials should be chosen instead of other options i.e. incineration and landfill which are known to cause air pollution and other environmental damages. Re-use and recycling not only reduce the need for disposal capacity and litters but also decrease emission from incinerators or landfills.

1.2 Research Background

In the efforts to limit the magnitude of environmental problems and conserve the natural resources related to discarded polymeric materials, the focus on exploiting one of the complex and abundant polymeric materials, waste rubber, is indispensable. There have been ongoing tasks in reuse or recycling of waste rubber. Recently, a leap in the worldwide consumption in the form of reclaim rubber has been observed. For example, at the end of 1950s, only about one fifth of the rubber hydrocarbon used by the United States and Europe was reclaimed. By the middle of 1980s only less than 1% of the worldwide polymer consumption was in the form of reclaim. However, it is reported that at the beginning of the 20th century, 50% of the rubber consumed was in the form of reclaim (Adhikari et al., 2000). The total number of scrap tires in the United States going to a market from 1998 through the end of 2001 increased from 177.5 million tires (66% of the 270 generated) to 218 million tires (77.6% of the 281 million generated) (Rubber Manufacturer Association, 2002). In developed countries, the current trend is towards options that promote material and energy recovery. In Malaysia, a number of projects involving a huge investment in waste rubber recycling have been observed. For instance, in 2002 a project totaled RM4.74 billion was approved by Malaysian Industrial Development Authority (MIDA) to proceed with the recycling project of scrap tires to manufacture synthetic rubber powder and thermoplastic elastomer (TPE) (Miti, 2003).

One of the promising alternatives to utilize the recycled tires is the formation of blends with thermoplastics. The blends show elastomeric behavior and can be processed at elevated temperatures. They exhibit properties typical of rubbery materials but can be processed like thermoplastics. They can be easily processed by internal mixer or extrusion, and their productivity is high as no vulcanization is required. Besides, these types of blends provide better material utilization as scrap and rejects can be recycled (Lopez-Manchado and Arroyo, 2000). It not only contributes to the development of new materials but also for practical recycling purposes (Phinyocheep et al., 1999). So far, waste rubber has found its applications in athletic and recreational application, molded products such as soundproofing solutions, truck bed liner, and safety devices as well as automotive products. With a proper formulation, waste rubber/plastics blend is seen to have a great potential in other applications such as erosion control and oil spill recovery.

1.3 Problem Statement

A number of blends containing waste rubber powder have been reported. Research findings show promising results while some of them encountered a setback in formulation properties.

Generally, waste rubber powder has been incorporated into thermoplastic polymers with the objective to improve their properties. For instance, waste rubber powder has been incorporated with a view to obtain impact-resistant TPE (Pramanik and Baker, 1995). Another experimental finding shows that the TPE based on polypropylene (PP) with natural rubber (NR) and waste rubber powder has higher tensile strength, Young's Modulus and energy needed to cause catastrophic failure than that of NR blends (Ismail and Suryadiansyah, 2002b). Enhancement in PP toughness is possible while maintaining stiffness, strength and processability by additions of elastomers. It is reported that among the waste rubber powder/low-density polyethylene (LDPE) containing NR, styrene-butadiene rubber (SBR) and ethylene-propylene-diene terpolymer (EPDM), waste rubber powder/LDPE/EPDM composites have the best mechanical properties (Kumar et al., 2002). In a different study involving waste rubber powder/EPDM/acrylic-modified HDPE (A-HDPE) composites, it was observed that 50% of EPDM could be replaced by waste rubber powder without adverse effects on the processability and physical properties of the composites (Naskar et al., 2001). It is also reported that partial replacement of NR with waste rubber powder improves the processability of the polypropylene/NR/waste rubber powder (Ismail and Suryadiansyah, 2002a). Variation in composition blends produces materials with a wide range of properties (Norzalia et al., 1993).

Among the setback, however, the addition of waste rubber powder into a thermoplastic polymer causes considerable deterioration of the mechanical properties of the polymers (Li et al., 2003). The deterioration is often attributed to poor compatibility between waste rubber powder and polymer (Phadke and De, 1986). Therefore, various compatibilizers were used for the modification of TPE from scrap rubber powder and thermoplastic polymer (Oliphant and Baker, 1993).

In this study, waste tire dust (WTD) will be used to prepare waste rubber powder/polypropylene (PP) blends with a variation of WTD contents. A series of tests will be conducted to investigate the respective formulation properties.

1.4 Objectives of the Research

The overall aim of this work was to assess the potential of waste tire dust (WTD) as an element in polypropylene (PP)-based blends. The principal objectives of this research were as follows:

i) to investigate the effects of WTD content and size variations on process characteristics, tensile properties, swelling resistance, and morphological properties of PP/WTD blends.

ii) to study the variations of tensile properties, swelling resistance, morphological and thermal properties of PP/WTD blends in the influence of sulfur dynamic vulcanization and *trans*-polyoctylene rubber (TOR) as well as dicumyl peroxide (DCP) dynamic vulcanization and *N, N'-m-phenylenebismaleimide* (HVA-2).

iii) to examine the effects of natural rubber (NR) latex modified WTD on tensile properties, swelling resistance, morphological and thermal properties of PP/WTD blends.

iv) to assess the variations of tensile properties, swelling resistance, morphological and thermal properties of PP/WTD blends in the presence of natural rubber (NR) modified WTD as well as ethylene-propylene diene terpolymer (EPDM) modified WTD.

v) to study the effects of natural weathering on tensile properties, morphological and thermal properties of PP/WTD blends.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Generally, polymer blend stands for a mixture of at least two substances. It has been defined accordingly by several authors to represent the general and specific reference to the mixture. According to Utracki (1995), polymer blend represents a mixture of at least two macromolecular substances, polymer or co-polymers with ingredient content of more than 2 wt%. The blend also represents physical mixture of two or more polymers prepared by mechanical mixing (Kumar and Gupta, 2003). Osswald (1998) defined polymer blend as a mixture of two or more polymers to enhance the physical properties. Polymer blends are also meant for a physical combining of two or more polymers without appreciable reaction (Progelhof and Throne, 1993). There are several other definitions whereby the common and central point of polymer blend has been the mixture of at least two substances.

In this section, the background and contributing factors to variations in polymer blend properties are initially elaborated and discussed. Subsequently, the discussion related to scrap tires and features of scrap tire-derived waste rubber, which is a constituent of the researched PP/WTD blends is included. Lastly, the overall effects and degradation mechanisms of natural weathering on the general polymer materials are discussed.

2.2 Polymer Blending

2.2.1. Background

The raison d'être of polymer blending has varied with time. For instance, the principal motivation to blend polymers during 1960’s was modification of a specific resin for exclusive properties especially for impact strength improvement. Then, the subsequent decade observed economy issues dominated the polymer blending activities by diluting pricey engineering resins with commodity ones. In the 1980’s, the improvement of processing for the high temperature resins became the theme issue. During the previous decade, the polymer blending aimed at securing sets of specific properties required for an envisaged application (Utracki, 1998). In the present time, the environmental issues have dominated many aspects of today’s life and this may become one of the drives to include discarded or biodegradable materials on the list of polymer blend constituents as portrayed by the emergence of various researches in both blends (Doan et al, 2006, Shanmugaraj et al., 2005, Ismail and Suryadiansyah, 2002a, Naskar et al., 2002, and Rozman et al., 2000a).

Principally, polymer blend could be categorically grouped into three main types namely rubber-rubber, plastics-rubber, and plastics-plastics blends. Each group epitomizes the exclusive combination of characteristics of the blend constituents. For example, the rubber-rubber blending between NR and EPDM which is known highly resistance to ozone and oxygen (School, 2001) resulted in a material with improved properties (Ghoneim and Ismail, 1999).

The mixture of plastics and rubber has produced a wide range of materials with preferred properties which are obtainable by varying blend composition, processing and additives. For instance the blending of PP and EPDM has imparted a TPO with an improved resistance to degradation by oxidation and ozone due to the absence of un-saturations in the polymer backbones. On the contrary, EPDM/PP TPOs have very poor resistance to hydrocarbon fluids such as the alkanes, alkenes, or alkyl-substituted benzenes, especially at elevated temperature (Arnold and Rader, 1992). Naira et al. (1995) discovered that the content of PP up to 30% did not affect EPDM thermal stability. With incorporation of vulcanization agent or co-agents, the plastics-rubber blends have emerged TPVs with variations of properties. For example, the addition of HVA-2 to PP/EPDM-NR blends was reported to bring about an increment in tensile strength, modulus and percentage of crystallinity but adversely affected E_b (Ismail et al., 2005). Furthermore, addition of preferred additive in PP/EPDM peroxide cured TPV contributed to stable blends against ageing and imparted no discoloration (Naskar et al., 2004). In PP/NR blends, dynamic vulcanization rendered viscosity increment and reduced crystallinity. In the same PP/NR blend statically vulcanized blends did not bring about any improvement and enhancement of properties was observed whenever the PP/NR blends were dynamically vulcanized (Hernandez et al., 2006).

Meanwhile, plastics-plastics blend exhibits better properties than that of its single constituent. The mixture of PP and PVC produces a high impact strength pipes or electrical insulation (Utracki, 1998). A third constituent may also be included to enhance the properties of plastics-plastics blends (Feng et al., 1998).

There are so many other encouraging encounters and attention-grabbing variations of properties relating to the blend of various polymers by different blending processes and diverse blend constituents. Thus, polymer blend has still remained a key component of the present polymer research and technology (Shonaike and Simon, 1999).

2.2.2. Variations of Polymer Blend Properties

The properties of polymer blends may vary depending on several contributing factors which are interdependent. Alger and Dyson (1990) list and summarize the factors as follow:

i) type of polymers;
ii) composition;
iii) compatibility;
iv) phase morphology;
v) method of blend preparation.

2.2.2 (a) Type of Polymers

This is an obvious contributing factor to variations in polymer blend properties as there are three general types of polymers that may be blended together namely thermoplastics either amorphous or semi-crystalline thermoplastics, thermo-set and elastomers (Hall, 1989).

Thermoplastics

Thermoplastics are polymers which soften and liquefy when heated and harden when cooled whereby the processes are reversible. This is associated with the absence of chemical cross-links in thermoplastics. Most thermoplastics are relatively soft and ductile. Most linear and branched polymers with flexible chains are thermoplastics. Thermoplastics may be fabricated a number of times by the simultaneous application of heat and pressure without changes in their properties. As the temperature increases, secondary bonding forces are diminished by increased molecular motion so that the relative movement of adjacent chain is facilitated when the stress is applied. However, irreversible degradation occurs whenever the temperature of melting thermoplastics is raised to a point at which molecular vibrations become violent enough to break the primary covalent bonds (Callister, 2000, Crawford, 1998, and Challa, 1993).

Amorphous thermoplastics solidify in such a way that their molecular chains are randomly arranged. Visually, this type of polymer could be identified as they are transparent if filler or color pigment is not present. This is due to the characteristic size of the largest ordered region is much smaller than the wavelength of visible light (Richardson and Lokensgard, 1997, Menges and Osswald, 1996, and Grulke, 1994).

Molecules of semi-crystalline thermoplastics align in an ordered crystalline structure. The crystalline structure is part of a amellar crystal which forms spherulites. Linearity and less bulkiness in the chain are associated with the factors attributed to crystallization tendency. T_m is considered as the highest temperature at which crystallinity could be detected in semi-crystalline materials.

As crystallinity represents orderly aligned molecules, semis-crystalline materials are higher in density than amorphous polymers. The tight packing favors better inter-chain interaction irrespective of bonding types. Visually, the semi-crystalline thermoplastics are translucent due to the size of spherulite structure which is larger than the wavelength of visible light. LDPE, HDPE and PP which is one of thermoplastics used in this research are examples of semi-crystalline polmers (Osswald and Menges, 1996, Xanthos and Dagli, 1991, Hall, 1989, Cowie, 1986, Milby, 1973, and Nielsen, 1962).

Polypropylene (PP)

PP is a linear polymer with regular steric or spatial features prepared by the Ziegler/Natta coordination catalyst system. The presence of the methyl group as shown in Figure 2.2.1 restricts the rotation of PP chain and produces a less flexible but stronger polymer. The relative position of methyl group determines tacticity or stereochemistry namely atactic, isotactic, and syndiotactic forms of PP. Atactic PP which contains methyl groups at random site is rubbery and transparent polymer and of little commercial value. While isotactic PP shows a high degree of order with all methyl groups along one side, methyl groups are positioned alternately from side to side in syndiotactic PP. PP exhibits high impact strength, excellent retention of its electrical properties over a wide temperature range and an excellent electrical insulator. The fairly high T_m gives rise to the fact that it retains its mechanical strength up to a temperature of 140°C.

PP shows several attractive properties such as resistant to environmental stress cracking and very low moisture-absorption characteristics. It is also highly resistant to chemicals such as acids, alkaline media, and inorganic salt solution at elevated temperatures. PP is soluble only at elevated temperatures associated with its crystalline character. These characteristics make PP suitable for a wide range of applications such as electrical appliances, chemical piping, pumps, valves, blowers, bottles, carpets, casings and packaging. However, PP is susceptible to oxidation at elevated temperatures and also UV degradation in strong sunlight (Stuart, 2002, Fenner, 1992, and Nicholson, 1991).

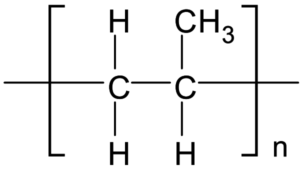

Figure 2.2.1. Structure of polypropylene (Moore and Kline, 1984).

Thermosets

Thermosets possess a networked structure which could be prepared by heating or via chemical reaction. Thermosets are substances which cannot be melted and remelted but set irreversibly as their molecules are chemically linked to each other. They are normally non-melting, insoluble solids and tend to possess excellent thermal stability and rigidity. One of the oldest thermosetting polymers is phenol-formaldehyde or phenolic. Other examples of thermosetting polymers are silicone, polyester, epoxy, urea-formaldehyde and melamine-formaldehyde (Stuart, 2002, Osswald and Menges, 1996, and Hall, 1989).

Elastomers

Elastomers or rubbers are polymers that may be deformed to quite large deformations and return to their original dimension once the stress is removed. In the absence of stress, elastomers are amorphous and contain molecular chains that are highly twisted, kinked, and coiled. Elastic deformation in elastomers represents partial uncoiling, untwisting and straightening of chains in the stress direction and the chains return to their original position once the stress is removed. Generally, elastomers posses the following characteristics:

i) not easily crystallize;
ii) their chain bond rotations are relatively free in order for the coiled chains to readily respond to an applied force;
iii) and the onset of plastic deformation is delayed in order to experience a large elastic deformation.

Vulcanization of elastomers may be carried out in order to restrict the motion of chains past one another leading to a large elastic deformation. The cross-links formed as a result of vulcanization act as anchors between the chains and prevent chain slippage. Examples of elastomers are SBR, CR, IIR and NBR (Stuart, 2002, Callister, 2000, and Hall, 1989). Two other examples of elastomers used in this research work are NR and EPDM.

Natural Rubber (NR)

NR is the first recognized elastomer and is extracted from the latex of the tropical *Hevea brasiliensis* tree. The elastomer consists mainly of poly(*cis*-isoprene) mixed with a certain amount of non-rubber substances including fatty acids, proteins and lipids. The structure of repeat unit of poly(*cis*-1,4 isoprene) is illustrated in Figure 2.2.2. The raw gum rubber is mechanically weak and does not retain its shape after molding and is subject to swelling in liquids. Like other unsaturated polymers, NR shows poor resistance to ozone, high temperature, weathering, oxidation, oils, and concentrated acids and bases.

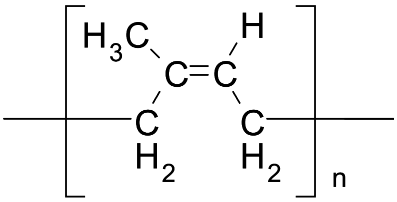

Figure 2.2.2. Structure of poly(*cis*-1,4 isoprene) (Nagdi, 1993).

In order to reduce plasticity and develop elasticity, NR could be vulcanized with sulfur. Three dimensional structures restrict mobility of molecules leading to a reduced tendency to crystallize, improved elasticity and constant modulus and hardness characteristics. Excessive cross-linking turns the elastic NR to a hard and brittle polymer (Kumar and Gupta, 2003, Stuart, 2002, Ciesielski, 1999, Nagdi, 1993, and Blow, 1971)

Ethylene-Propylene Diene Terpolymer (EPDM)

EPDM is a random, non-crystalline co-polymer which is chemically inert and rubbery produced by polymerization of ethylene and propylene with a small amount of a non-conjugated diene which provides un-saturation in side chain pendent from the fully saturated backbone. The diene is either 1,4 hexadiene (1,4 HD), dicyclopentadiene (DCPD) or 5-ethylidene norbornene (ENB) (Nagdi, 1993 and Synnott et al., 1990).

As un-saturations lie outside chain backbone, EPDM shows ozone resistance and good ageing characteristics. It also portrays resistance to chemicals but not to oil and other hydrocarbon. EPDM can be vulcanized with peroxides, sulfur or radiation. Figure 2.2.3 illustrates structure of EPDM grade containing ENB as a diene component which has high reactivity toward sulfur vulcanization. The reactivity increases with increasing ENB content. Vulcanized EPDM shows good strength, good low temperature flexibility, weather and ozone resistance (Nagdi, 1993 and Gary, 1986).

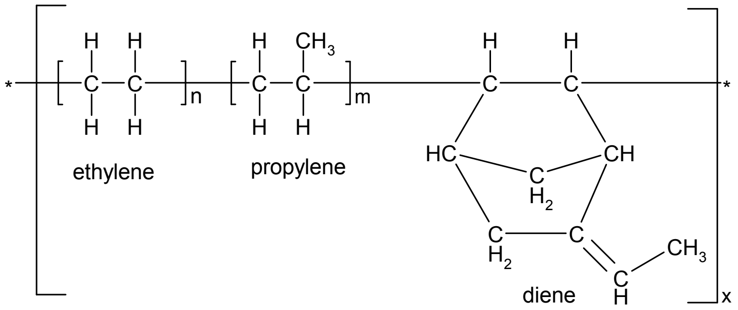

Figure 2.2.3. Structure of EPDM and ENB (Nagdi, 1993).

Hence, the application of polymers which possess different molecular structures and hence other related properties in the preparation of polymers blends definitely has a great influence in the final characteristics of polymer blends.

2.2.2 (b) Composition

The properties of polymer blends may vary depending on their compositions. The variations of properties are due to the changes in phase structure related to the composition. Variation in composition may affect phase morphology of polymer blends. For example, the polymer with higher concentration forms a continuous phase. In order to prevent phase separation and hence negatively affects the blend properties, the discontinuous phase of the other polymer blend constituent must have a small particle size. The PP/EPDM blends with higher concentration of EPDM for instance are soft and rubbery at room temperature. This type of polymer blend is found useful only in a range of temperature below 80°C and its characteristics quickly diminish at elevated temperature.

At the extreme case, variations in polymer blend composition may lead to phase inversion whereby a blend structure changes from that of a matrix of polymer A containing dispersed phase polymer B to that of A dispersed in B. (Arnold and Rader, 1992 and Alger and Dyson, 1990).

2.2.2 (c) Compatibility

Compatibility of polymer blends may refer to the ability of two or more polymers to exist in close and permanent association resulting in useful properties regardless of whether they are theoretically miscible or immiscible. Miscibility by itself is not the paramount criteria for utility. For instance, immiscibility is useful in the impact modification of relatively brittle polystyrene by rubber whereby energy absorption results from crazing of the polystyrene matrix in the region between the rubber particles. On the other hand, miscibility is important in applications where segregations of the constituents could lead to deleterious mechanical properties (Kumar and Gupta, 2003). Natural compatibility in polymer blends encompasses bonding, partial miscibility, interfacial tension as well as adhesion (Deanin and Manion, 1999).

Covalent Bonding

The presence of covalent bonds across the interface of polymer blends gives the greatest interfacial stability and ability to transfer stress and resist failure. The covalent bond across the interface may materialize by crystallization or formation of block and graft copolymers. Whenever a polymer crystallizes, it forms two phases, crystalline and amorphous with many molecules tying the two phases together strongly even though the crystalline polymer is not considered as polymer blends. Furthermore, two structures of polymer blends may join together in a block or graft co-polymer leading to a formation of a great number of covalent bonds across interface. The absence of good bonding at the polymer-polymer interface results in poor mechanical integrity due to poor stress transfer between two phases.

Miscibility

Although single-phase or miscible polymer blends are possible, majority of them are two-phase systems or sometimes referred to as immiscible polymer blends (Stuart, 2002 and Deanin and Manion, 1999). If they are very immiscible, the domain size is coarse, irregular and unstable with sharp and weak interface leading to poor properties. If the properties of the blends are naturally good, this relates to partial miscibility of the polymer blends. Generally, separation of two phase in polymer blends does not produce pure A and pure B but rather a solution of B in A and a solution of A in B leading to the formation of inter-phase which represents a broader gradual change in concentration from the high-A phase to the high-B phase. Such inter-phase would resist stress better than a very thin interface representing only few chain interactions between polymer blend constituents (Grulke, 1994 and Noorlandi, 1984).

Miscibility or immiscibility of polymer blends are governed by the Gibbs free energy change which occurs on their mixing (ΔG_m) based on the following equation:

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{2.1}$$

where T is the temperature, and ΔH_m and ΔS_m are the enthalpy and entropy of mixing respectively. If ΔG_m is negative, mixing is favorable and a polymer blend or solution is produced. For the case of low-molecular-weight polymer blend constituent, ΔS_m will be highly positive and hence $-T\Delta S_m$ will be negative and the mixing will be favored. Usually, ΔH_m, which depends upon energetic interactions between the molecules, is positive and therefore not favorable for mixing. In order to form miscible polymer blends, the positive ΔH_m has to be outweighed by negative entropy. For this reason, the more similar the chemical structure of the two polymer blend constituents, the lower is the value of ΔH_m value and the more likely to form miscible polymer blends. In many polymer blends, ΔS_m is much positive as randomization is quite restricted because of the large size of the molecules involved. Although the value of $-T\Delta S_m$ is still favorable, in most cases it is unable to overcome an unfavorable ΔH_m term resulting in mostly immiscible polymer blends. When these polymers are mixed, they form a two-phase rather than a single phase system with one polymer dispersed as particles or domains in a matrix of the other polymer (Stuart, 2002).

In this regard, miscibility may be associated with several contributing factors (Deanin and Manion, 1999). The factors include:

i) Polarity

Polymer blend constituents with similar structure or polarity are less likely to repel each other and more likely to become miscible. Diverging polarity associates with immiscibility.

ii) Specific group attraction

Polymer blend constituent drawn to each other by hydrogen bonding, acid-base, charge-transfer, ion-dipole, donor-acceptor adducts or transmission metal complexes are likely to produce miscibility although they are less common.

iii) Molecular weight

Miscibility is favorable in polymer blend constituents with lower molecular weight which allows greater randomization on mixing and hence greater gain of entropy. It is discovered that even at the same composition, polymer blend constituents with similar molecular weights show miscibility and polymer blend constituents with different weight may produce immiscibility.

iv) Ratio

Although two polymer blend constituents may appear immiscible at a fairly equal ratio, it is quite possible that a small amount of a polymer blend constituent may be soluble in a large amount of the other polymer blend constituent.

v) *Crystallinity*

When polymer blend constituent crystallizes, it adds another phase to the system and if both constituents crystallize usually two separate systems are formed with a rare case of a single crystalline phase. This promotes immiscibility in polymer blends.

Interfacial Tension and Adhesion

When two polymers repel each other and form a two-phase blend, the interfacial tension is high giving a coarse and unstable structure as well as adhesion between the two phases is low leading to poor stress transfer across the interface.

Therefore, in the case of incompatible polymer blends or the requirement for a balance of polymer blend properties, compatibilization by human intervention is essential to produce the required level of phase separation, morphology and interfacial attraction. Compatibilization involves the process of modification of the interfacial properties to improve the adhesion and blend properties (Stuart, 2002). Compatibilizer may locate across the interface causing the reduction in interfacial tension leading to reduction of dispersed phase, improvement in interfacial adhesion and stabilizes the polymer blend morphology (Utracki, 1990). A low concentration of compatibilizers may reduce the particle size of dispersed phase due to the reduction in interfacial tension (Chiang and

Huang, 1999 and Brown, 1989). Such a control of polymer blend compatibility may be carried out by known physical processes, physical additives and reactive processes (Deanin and Manion, 1999).

2.2.2 (d) Phase Morphology

Morphology is the order or arrangement of the polymer structure. The possible range of order between a molecule or molecule segment and its neighbors can vary from a very ordered highly crystalline polymer structure to the highly disordered amorphous structure as shown on the left side of Figure 2.2.4. The semi-crystalline polymer blends is formed by a combination of amorphous and crystalline structures as shown in the middle of the figure. It can be captured with an electron microscope. A coarser macro-morphological structure such as spherulites in semi-crystalline polymer blends as shown in the right hand side of the figure can be observed with an optical microscope (Osswald and Menges, 1996).

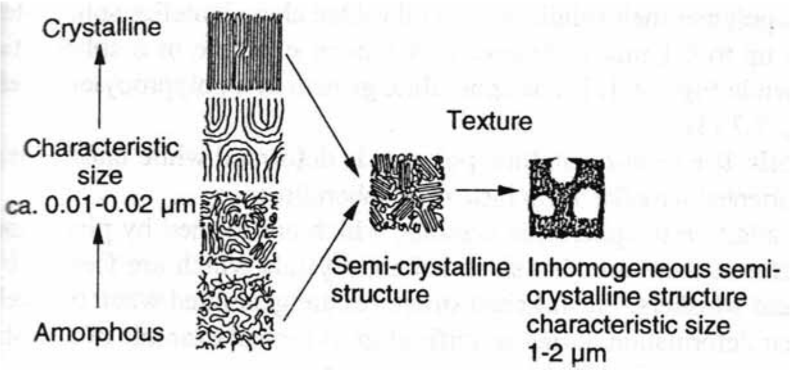

Figure 2.2.4. Schematic diagram of possible molecular structure which normally occurs in thermoplastics (Osswald and Menges, 1996).

There are a number of phase morphologies exhibited by polymer blends. The different types of dispersions of polymers in the matrix of immiscible polymers are illustrated in Figure 2.2.5. Blends may consist of one phased dispersed as simple spheres, platelets or fibrils in a matrix of the other polymers. A morphology consisting of an interpenetrating network of phases is also feasible. An interpenetrating polymer network (IPN) consists of an assembly of at least two polymers in network form, one of which is prepared or cross-linked in the presence of the other (Stuart, 2002).

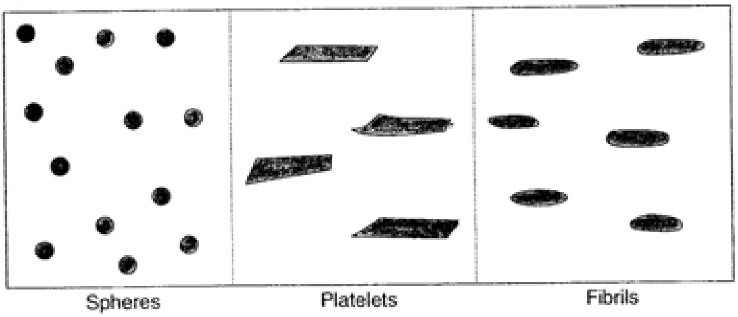

Figure 2.2.5. Different morphologies exhibited by immiscible blends of polymers (Stuart, 2002)

During mixing process, polymer blend constituents may become deformable solid or viscoelastic liquid which eventually burst into fibers or droplets. The domain size of polymer blends decreases as mixing energy was increased and the constituent with lower viscosity will be the continuous phase (Plochocki et al., 1990 and Boudreaux and Cuculo, 1977).

In incompatible polymer blends, domain size increases with increasing dispersed phase concentration due to increased coalescence with broader particle size distribution (Han and Yu, 1971). Coalescence may be curbed by addition of compatibilizers which results in smaller particle size and narrower particle size distribution (Sundararaj and Macosko, 1995).

2.2.2 (e) Method of Blend Preparation

Considering it as one of the flexibility of polymer blends, the blending process could be accomplished by several means whereby each may have a certain level of influence in the overall properties of the polymer blends. The selection of blending method is crucial as blending process involves transfers of polymer chains at polymer-polymer interfaces which determine homogeneity of polymer blends. The level of homogeneity of polymer blends is also influenced by techniques of blending as well as several other factors such as types of blend constituent and employed conditions during blending process (Lee, 1993). According to Utracki (1990), polymer blends may be prepared by the following methods:

i) mechanical blending;
ii) dissolution in co-solvent then film casting, freeze or spray drying;
iii) latex blending;
iv) fine powders mixing;
v) inter-penetrating polymer network technology.

Due to economic reasons, the mechanical mixing predominates. The mechanical blending of polymers can be performed using a two-roll mill, internal mixer or extruder. In this research work, the blending process of PP/WTD involves the use of a two roll mill and an internal mixer.