PREPARATION AND PROPERTIES OF POLYPROPYLENE / WASTE TYRE DUST / SHORT GLASS FIBRE (PP/WTD/SGF) COMPOSITES

By

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Thesis submitted in fulfillment of the requirements

for the degree of

Masters of Science

May 2014

ACKNOWLEDGEMENT

Bismillaahirrahmaanirrahiim,

In the name of Allah, most gracious & most merciful and for HIM who open to us the path of knowledge and guide us to the true ways of Islam. First and foremost, I am truly grateful and would like to express my deep gratitude to my supervisor, Prof. Dr. Hj. Hanafi Ismail, who has supported me throughout my study at Universiti Sains Malaysia (USM) with his inspirational encouragement, patience and endless guidance. It is his continuous, unwavering support in the past two years that provides a strong motivation that I will enjoy the great benefit of it forever.

I would like to extend my gratitude to USM Fellowship for the financial support throughout my research studies at School of Materials and Mineral Resources, USM. Special thanks to all technicians and staff for their helping hand, co-operations and kindness in helping me to carry out and complete my research studies with a pleasant experience.

I also wish to thank all of my friends that always support and believe in me through thick and thin. Last but not least, I would like to thank my parents Encik Hj. Zainal Omar & Puan Hjh. Halimah Mohd Hassan, my beloved husband Mohd Fatihah Mohd Othman and all of my family members for their unconditional love, encouragement and endless support for me to complete my study. Indeed, I would never achieve this without the support from all of them.

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LIST OF ABBREVIATIONS

ASTM	:	American standard testing and materials
ATR	:	Attenuated total reflection
CB	:	Carbon black
CBS	:	N-cyclohexyl-2-benzothiazole-2-sulfenamide
CFRP	:	Carbon fibre-reinforced polymer
CMC	:	Ceramic matrix composite
DCP	:	Dicumyl peroxide
DV	:	Dynamic vulcanization
EPDM	:	Ethylene propylene diene terpolymer
FRP	:	Fibre-reinforced plastic
FTIR	:	Fourier transform infrared (spectroscopy)
GFRP	:	Glass fibre-reinforced polymer
GRT	:	Ground rubber tyre
HVA-2	:	*N,N'-m*-phenylenebismaleimide
ksi	:	Kilopound per square inch
LLDPE	:	Linear low density polyethylene
min	:	Minute
MMC	:	Metal matrix composite
NBR	:	Acrylonitrile-butadiene rubber
NR	:	Natural rubber
PBT	:	Poly(butylene terephthalate)
php	:	Part(s) per hundred polymer

PMC	:	Polymer matrix composite
PP	:	Polypropylene
PVC	:	Polyvinyl chloride
rpm	:	Revolution(s) per minute
RR	:	Recycled rubber
RTR	:	Reclaimed tyre rubber
RTTP	:	Rubber-toughened thermoplastic
SEM	:	Scanning electron microscope
SFRP	:	Short fibre reinforced polymer
SGF	:	Short glass fibre
SiO_2	:	Silicon dioxide
TGA	:	Thermogravimetric analysis
TOR	:	*Trans*-polyoctylene rubber
TPE	:	Thermoplastic elastomer
TPV	:	Thermoplastic vulcanizates
WTD	:	Waste tyre dust
WTR	:	Whole tyre reclaimed rubber

LIST OF SYMBOLS

E_b	:	Elongation at break
°F	:	Degree fahrenheit
g/cm^3	:	Gram per cubic centimetre
h	:	Hour
kg/cm^2	:	Kilogram per square centimetre
mm	:	Millimetre
m^2/g	:	Square metre per gram
ml/min	:	Millilitre per minute
MPa	:	Megapascal
Nm	:	Newton metre
Si-69	:	Silane coupling agent
T_{300}	:	300 °C of decomposition temperature
T_{400}	:	400 °C of decomposition temperature
T_{500}	:	500 °C of decomposition temperature
W_1	:	Weight of sample before immersion
W_2	:	Weight of sample after immersion
wt%	:	Weight percent
γ-APS	:	γ-aminopropyltrimethoxysilane
μm	:	Micrometre
°C	:	Degree celsius
%	:	Percentage

PENYEDIAAN DAN SIFAT-SIFAT KOMPOSIT POLIPROPILENA/ SERBUK SISA TAYAR/ GENTIAN KACA PENDEK (PP/WTD/SGF)

ABSTRAK

Komposit polipropilena/ serbuk sisa tayar/ gentian kaca pendek (PP/WTD/SGF) telah diadunkan dengan menggunakan pencampur dalaman pada suhu 180 °C dan putaran 50 rpm. Empat siri adunan dengan komposisi berbeza telah disedia menggunakan WTD dengan ukuran 250-500 μm dan pada pembebanan SGF yang berbeza iaitu 5, 10, 15 dan 20 php. Pencirian telah dilakukan untuk mengenalpasti sifat-sifat adunan dan justeru mengkaji kesan seperti pembebanan SGF, penambahan agen gandingan silane, aminopropyltrimethoxysilane (γ-APS) dan pemvulkanan dinamik (DV), penghibridan SGF dengan karbon hitam (CB) dan silika (Si) terhadap ciri-ciri pemprosesan, sifat mekanik, morfologi, rintangan pembengkakan dan kestabilan termal bagi komposit tersebut. Penambahan SGF pada pelbagai pembebanan telah mempamerkan peningkatan keseimbangan tork pemprosesan, modulus Young, kekuatan tegangan dan kestabilan termal manakala pemanjangan pada patah dan rintangan pembengkakan telah menunjukkan penurunan apabila pembebanan SGF meningkat dalam komposit PP/WTD/SGF. Lekatan antara muka yang lemah di antara SGF dan matrik PP/WTD telah digambarkan dalam analisis SEM. Sementara itu, penambahan γ-APS dan DV telah menunjukkan peningkatan keseimbangan tork pemprosesan, sifat-sifat tegangan kecuali E_b, dan rintangan pembengkakan bagi komposit PP/WTD/SGF. Manakala, kestabilan termal telah meningkat dan analisis SEM telah menunjukkan lekatan yang lebih baik di antara matrik PP/WTD dan SGF serta penyebaran SGF yang lebih menyeluruh di dalam komposit. Penghibridan SGF dengan CB bagi komposit

PP/WTD/SGF_{CB} telah menunjukkan kekuatan tegangan dan modulus Young yang lebih tinggi pada pembebanan 15/5 dan 10/10 (php/php) nisbah SGF/CB berbanding komposit PP/WTD/SGF manakala E_b adalah lebih rendah berbanding dengan komposit PP/WTD/SGF pada setiap pembebanan. Mikrografi SEM permukaan tegangan patah bagi komposit PP/WTD/SGF_{CB} telah mempamerkan mikrografi yang lebih baik berbanding dengan komposit anti hibrid manakala peratus pembengkakan bagi komposit PP/WTD/SGF_{CB} pada pembebanan 15/5 dan 10/10 (php/php) nisbah SGF/CB adalah lebih rendah berbanding komposit PP/WTD/SGF dan peratus kehilangan berat bagi komposit PP/WTD/SGF_{CB} pada suhu penguraian 500 °C dan pembebanan 10/10 (php/php) nisbah SGF/CB adalah yang terendah berbanding dengan komposit PP/WTD/SGF. Di samping itu, penghibridan SGF dengan silika telah menyebabkan kekuatan tegangan dan modulus Young bagi komposit PP/WTD/SGF_{Silica} pada pembebanan 0/20 (php/php) nisbah SGF/silika meningkat dan lebih tinggi berbanding dengan komposit PP/WTD/SGF manakala E_b menurun dan lebih rendah berbanding dengan komposit anti hibrid pada setiap pembebanan. Analisis morfologi telah menunjukkan mikrografi yang lebih baik bagi komposit PP/WTD/SGF_{Silica} berbanding dengan komposit anti hybrid manakala rintangan pembengkakan dan kestabilan termal telah menunjukkan penurunan apabila silika dimasukkan ke dalam komposit PP/WTD/SGF_{Silica}.

PREPARATION AND PROPERTIES OF POLYPROPYLENE/ WASTE TYRE DUST/ SHORT GLASS FIBRE (PP/WTD/SGF) COMPOSITES

ABSTRACT

Polypropylene/ waste tyre dust/ short glass fibre (PP/WTD/SGF) composites were melt-mixed in an internal mixer at 180 °C and 50 rpm rotor speed. Four series of composites with various compositions were prepared using WTD of 250-500 μm and at different 5, 10, 15 and 20 php SGF loading. Characterization was done to determine the properties of the composites and thus to study the effects of SGF loading, the incorporation of silane coupling agent, γ-aminopropyltrimethoxysilane (γ-APS) and dynamic vulcanization (DV), the hybridization of SGF with carbon black (CB) and silica on processing characteristics, mechanical properties, morphology, swelling resistance and thermal properties of the composites. The incorporation of SGF at various loadings exhibited increased equilibrium processing torque, Young's modulus, tensile strength and thermal stability while elongation at break (E_b) and swelling resistance decreased as the SGF loading increased in PP/WTD/SGF composites. Poor interfacial adhesion between SGF and PP/WTD matrix was depicted in the SEM analysis. In the meantime, the addition of γ-APS, and DV revealed the increased of equilibrium torque, tensile properties except E_b and swelling resistance of PP/WTD/SGF composites. Whilst, the thermal stability was enhanced and SEM analysis showed improved adhesion between the PP/WTD matrix and SGF as well as better dispersion of SGF in the composites. Meanwhile, the hybridization of SGF with CB revealed that the tensile strength and Young's modulus of PP/WTD/SGF_{CB} composites at 15/5 and 10/10 (php/php) of SGF/CB ratios of loadings were higher than that of PP/WTD/SGF composites while E_b

of PP/WTD/SGF_{CB} composites were lower than that of PP/WTD/SGF composites at all loadings. The SEM micrographs of tensile fractured surfaces of PP/WTD/SGF_{CB} composites shows better micrographs than the non-hybrid composites while the swelling percentage of PP/WTD/SGF_{CB} composites at 15/5 and 10/10 (php/php) of SGF/CB ratios of loadings were lower than that of PP/WTD/SGF composites and the weight loss percentage at 500 °C decomposition temperature of PP/WTD/SGF_{CB} composites at 10/10 (php/php) SGF/CB ratios of loadings is the lowest in comparison with PP/WTD/SGF composites. On the other hand, the hybridization of SGF with silica had caused the tensile strength and Young's modulus of PP/WTD/SGF_{Silica} composites at 0/20 (php/php) of SGF/silica ratios of loadings to increase and were higher than that of PP/WTD/SGF composites while E_b to decrease and were lower than the non-hybrid composites at all loadings. The morphological analysis shows better micrographs of PP/WTD/SGF_{Silica} composites than the non-hybrid composites while the swelling resistance and thermal stability were decreased when silica was introduced into PP/WTD/SGF_{Silica} composites.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Polypropylene (PP) had appears to be one of the most employed materials in various application fields, either indoor or outdoor. Its blend or composite had become an interest for many researchers to explore the possibilities and advantages it has to offer (Ismail and Awang, 2008). Besides, PP has become a very competitive thermoplastic material due to the low cost of its monomer and has a good balance of attractive properties for producing many manufactured goods (Smith and Hashemi, 2006).

The utilization of PP was found in many applications such as housewares, appliance parts, packaging, laboratory ware and bottles of various types. On the other hand, high-impact PP copolymers have replaced the hard rubber for battery housings in the transportation field. Also, filled PP finds application for automobile fan shrouds and heater ducts, where high resistance to heat deflection is crucial. Due to its various applications, PP has become the third most important plastic from a sales tonnage stand point and one of the lowest in cost since it can be synthesized from low-cost petrochemical raw materials (Smith and Hashemi, 2006).

Nowadays, there are materials that can be formulated with PP and a possible one is waste tyre dust (WTD). Since WTD availability is abundance and increasing every year (Araki et al., 1979), its usage in polymer composites can at least help to conserve the environment through recycling of waste rubber which at the same time reducing it from being disposed in landfills. The blends or composites possess good material utilizations as scrap or rejects can still be recycled (Ismail and Awang, 2008). Moreover, in countries other than the United States, alternative approaches may need to be considered for handling waste tyres since the number of landfill site is strictly controlled (Chien et al., 2003).

In every industrialized country, the development of a satisfactory disposal method for waste car tyres had become a common problem, where motorized vehicles play an essential role in daily living. About millions of tyres were generated in 1970's and the amount has been increasing from year to year. However, only about 35% of these waste rubbers are recovered by reclaiming and splitting while the rest is buried in landfills. Eventhough landfill method is very simple, but the available area is limited especially in a small country where there is no recovery of waste rubbers been done before they were buried in landfill (Araki et al., 1979).

Possible applications of waste rubber in many forms and disciplines have been studied and reported. Attempts have been made to reuse rubber from scrap tyres through formulating new reusable materials as well as improving waste rubber. In addition, PP appeared to be one of the most investigated thermoplastics for the use of scrap tyre

rubber in polymer composites mainly due to its low cost, processability and good balance of properties (Awang and Ismail, 2008).

Furthermore, in the past few decades, the mechanical properties of amorphous and semicrystalline polymers reinforced with short glass fibres have also been the subject of various investigations. This interest may be explained by wide-range industrial applications of thermoplastics reinforced with short glass fibres particularly in automotive industry (Drozdov et al., 2005). Short fibre compounds are excellent for material replacement applications where economics are an issue, but extra performance is necessary.

The benefits of fibre reinforcement are more dramatic in semi-crystalline polymers, particularly toughness. Extrusion compounding and injection-molding techniques are frequently employed to make short-fibre-reinforced polymer (SFRP) composites. Fibre attrition and fracture during the extrusion compounding and injection molding processes are important phenomena that determine the final composite properties (Fu et al., 1999).

Previous work has focused mainly on single-short-fibre-reinforced polymers (Fu et al., 1999). There are numbers of applications which can benefit from using short glass fibre compounds include power and hand tools, sporting goods, automotive, computer and electronic devices such as brackets and housings, outdoor gardening equipment, and door handles and levers.

Although glass-fibre reinforced polymer composites have been successfully applied to provide the combination of high stiffness and strength with low density materials for the past decades, the potential use of these composites are sometimes hindered by poor out-of-plane properties which mainly attribute to weak fibre/matrix interfaces and brittle nature of the polymer matrices itself (Diez-Pascual et al., 2011). Thus, there are attempts to synthesis hybrid composite which composed of two types or more fibres in order to create a new material that brings out only the advantages of each constituent and to reach the synergistic effect from the usage of hybrid filler system that is larger than the effects gain from the single fillers (Socher et al., 2011). Hence, in this study, the carbon black (CB) and silica fillers were used to partially replace short glass fibre (SGF) in PP/WTD/SGF composites.

At the same time, since it is intended to obtain good adhesion between the fibres and matrix, the utilization of various coupling or crosslinking agents and pretreatment of the fibres with suitable chemicals should be taken into account (Awang et al., 2008, Smith and Hashemi, 2006, Chien et al., 2003). In this study, silane coupling agent and dynamic vulcanization has been introduced into PP/WTD/SGF composites in order to improve the properties of such composites.

This study is an investigation of development of a composite material based on PP, WTD and SGF with improved process characteristic, mechanical, thermal, morphology and swelling resistant properties. Whilst, the effects of CB and silica as well as the incorporation of silane coupling agent and dynamic vulcanization in

PP/WTD/SGF composites are also been investigated by hoping to reveal a new path for improvement of the final product that will find suitable application in the future.

1.2 Problem Statement

Among different types of polymer, thermoplastic elastomers (TPEs) from rubber-thermoplastic blends are experiencing vastly growing usage in variety of applications due to good mechanical properties it has to offer. Studies on TPEs find out that the presence of small amount of rubber in polyolefin matrix could improve the elongation at break and impact resistance but at the same time decrease the modulus and toughness of the materials.

According to Ismail et al. (2006), researches have also come out with the preparation of TPEs as one of the promising alternatives to utilize waste tyre rubber in order to make use of the abundant waste rubber. This is because the disposal of used tyres is a global environmental problem and a serious threat. For instance, in European Union alone, it is estimated around 2.5 million tons of waste tyres generated per year while around 2.5 million tons were generated in North America and 1 million tons in Japan, respectively (Mazloom et al., 2009).

Generally, waste rubber powder has been incorporated into thermoplastic polymers in many studies for instance the WTD of mechanically reclaimed scrap tyres (in various sizes) was blended with PP in different compositions to prepare PP/WTD

blends as reported by Ismail et al. (2006) in their study of effect of waste tyre dust size on the mechanical and properties of polypropylene/ waste tyre dust (PP/WTD) blends. Thus, the utilization of WTD in this study is purposely to make use of the waste rubber and to come out with more valuable composite material.

The toughness improvement that associated with the addition of elastomers in a composite is achieved and translated by the expense of stiffness and strength characteristics (Tjong et al., 2002). However, it is highly known that a disadvantage of the reliance on an elastomeric phase for toughening is such inclusions usually reduce the modulus and strength which are obviously the benchmarks for acceptable material performance (Sui et al., 2001) and the addition of an elastomer to a rigid polymer matrix invariably reduces strength and stiffness relative to the unmodified material (Laura et al., 2000, Laura et al., 2002).

Indeed, polymer modifications had been implemented in many ways long ago which results in various properties that dependant on certain factors such as blend compositions, blending conditions and additives. But somehow or rather, there are still number of setbacks were reported in polymer modification due to several constraints for instance diminution of mechanical properties and lack of thermodynamic compatibility between polymers and one of the solution is to add in a suitable third polymeric component in order to minimize the constraints (Awang et al., 2007).

Therefore, it is a logical course to achieve strengthening and toughening by blending rubber-toughened polymers with short glass fibre for high strength and high toughness applications (Sui et al., 2001). This is also agreed by Laura et al. (2003) which stated that glass fibres are used in conjuction with rubber-toughening in order to produce materials with a balance of stiffness, strength and toughness. Short glass fibre (SGF) has emerged as a good reinforcing filler in composites since short fibre reinforced polymers (SFRPs) combine easier processability with low manufacturing cost compared to the continuous fibre composites (Jing et al., 2009). It is mentioned that the incorporation of inorganic fillers such as short glass fibres are able to restore the required stiffness and strength of rubber toughened polymer matrix which leads to the formation of ternary or hybrid composites (Tjong et al., 2002). In this work, SGF is loaded into WTD toughened polypropylene in order to study in more details about the possibility affect of SGF loading towards PP/WTD/SGF composites by hoping to impart improve properties.

On the other hand, although glass fibre reinforced polymer composites have been successfully applied to provide the combination of high stiffness and strength with low density materials for the past decades, the potential use of these composites are sometimes hindered by poor out-of-plane properties which mainly attribute to weak fibre/matrix interfaces (Diez-Pascual et al., 2011) and only few researches had focused on the relationship between fibre inherent properties and composite mechanical properties (Jing et al., 2009). In this work, the synthesization of hybrid composite is to create a new material that brings out only the advantages of each constituent. Hence, the carbon black (CB) and silica fillers were used to partially replace short glass fibre (SGF)

in PP/WTD/SGF composites by anticipation to result in enhancement of multi-scale reinforcement leading to increased stiffness, strength and toughness of the composites (Wood et al., 2012).

It is important to obtain a good adhesion between the fibres and matrix in a composite. Thus, attempts have been made to overcome this challenge by the utilization of various coupling or crosslinking agents and also through pretreatment of the fibres with suitable chemicals (Sarkhel and Choudhury, 2010, Ismail et al., 2002, Punnarak et al., 2006). In different study involving PP/WTD/*trans*-polyoctylene rubber (TOR) and dynamic vulcanization, it was observed that the chemical and oil resistance of PP/WTD blends was enhanced while micrographs analysis has proven a good adhesion between PP matrix and WTD with the presence on TOR and dynamic vulcanization in the blends (Awang et al., 2007). In this study, the silane coupling agent and dynamic vulcanization have been introduced into PP/WTD/SGF composites in order to improve the properties of such composites.

1.3 Research Objectives

The main aim in this study is to assess the potential of short glass fibre (SGF) as a reinforcement element in polypropylene/waste tyre dust/short glass fibre (PP/WTD/SGF) composites. The identified objectives for this research are as follows:

a) To investigate the effects of various SGF loading on the properties of polypropylene/ waste tyre dust/ short glass fibre (PP/WTD/SGF) composites.

b) To study the effects of silane coupling agent (γ-APS) and dynamic vulcanization on the properties of polypropylene/ waste tyre dust/ short glass fibre (PP/WTD/SGF) composites.

c) To examine the effects of short glass fibre/ carbon black (SGF/CB) hybrid fillers on the properties of polypropylene/ waste tyre dust/ short glass fibre (PP/WTD/SGF) composites.

d) To find out the effects of short glass fibre/ silica (SGF/silica) hybrid fillers on the properties of polypropylene/ waste tyre dust/ short glass fibre (PP/WTD/SGF) composites.

1.4 Scopes of Research

In order to achieve the above objectives, the following scopes of research have been drawn;

a) Preparing the PP/WTD/SGF composites by internal mixing in a Haake Rheomix Polydrive R 600/610 internal mixer at a temperature of 180 °C and a rotor speed of 50 rpm. Sieving the WTD to obtain rubber particle size of 250-500 μm to prepare the PP/WTD blends prior to the inclusion of SGF.

b) Fabricating the PP/WTD/SGF composites by dispersing the SGF particles into the continuous PP/WTD blends at different SGF loadings by using the internal

mixing method. The effects of SGF loadings were investigated by varying the SGF contents from 5 – 20 php.

c) Mixing the PP/WTD/SGF composites with silane coupling agent (γ-APS) and dynamic vulcanization. The effects of silane coupling agent (γ-APS) and dynamic vulcanization were investigated on the properties of PP/WTD/SGF composites.

d) Determining the effects of hybrid fillers in PP/WTD/SGF composites by partially replace the SGF with carbon black (CB) and silica by varying loadings of SGF/CB and SGF/Silica at 20/0, 15/5, 10/10, 5/15 and 0/20 (php/php).

e) Characterizing the fabricated PP/WTD/SGF composites by using tensile and swelling tests, Scanning Electron Microscope (SEM), Thermogravimetric Analysis (TGA) and Fourier Transform Infrared (FTIR) spectroscopy.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Thermoplastic elastomer is unique due to its combination properties of glassy or semicrystalline properties of thermoplastic and soft elastomers which at the same time make it easier for the rubbery material to be process as thermoplastics (Najib et al., 2009). In the last few decades, the short fibre reinforced thermoplastics and elastomers have gained their own importance (Roy et al., 1993). In this particular study, waste tyre dust (WTD) of a mechanically ground scrap tyre rubber product is used and as an extension to previous studies related to thermoplastic blends involving rubber waste (Ismail et al., 2006, Awang and Ismail, 2008, Satapathy et al., 2010).

As far as mechanical properties are highly concerned, the aim would be to strike a balance between strength, stiffness and toughness properties. The presence of strong and stiff reinforcing fibre such as glass fibres inside the thermoplastics is subjected to enhancement in strength and stiffness. Approaches that have been identified as potential routes are the incorporation of short-fibre reinforcements and modifiers into thermoplastic matrices in order to form short-fibre-reinforced thermoplastics and also rubber-toughened thermoplastics (RTTPs), respectively (Mohd Ishak et al., 2000).

Therefore, in this study, short glass fibre (SGF) has been utilized as the reinforcing fibre in PP/WTD matrix blends by hoping to enhance the strength and stiffness of PP/WTD/SGF composites.

At present, the short fibre reinforced rubber has been successfully utilized in the hoses, V-belts, tyre thread and complex-shaped mechanical goods production (Ismail et al., 2002). On the other hand, the elastomers composites containing either natural or synthetic rubber are available for pneumatic tyres, flexible couplings and airsprings due to their flexibility, light weight and highly suitable for making air-tight components (Shonaike and Matsuo, 1995).

During the preparation of composites, it is important to obtain a good adhesion between the fibres and matrix. Therefore, attempts have been made to overcome this challenge by grafting onto the fibres, utilization of various coupling or crosslinking agents and also through pretreatment of the fibres with suitable chemicals (Sarkhel and Choudhury, 2010, Ismail et al., 2002, Punnarak et al., 2006). Coupling agents are widely used as they can improve the filler-matrix interaction and result in better reinforcement in composites. They also act as molecular bridges at the interface between two different substrates, for instance, organic polymer matrix and inorganic/organic filler, fibre or pigment (Alkadasi et al., 2005).

In this study, the silane coupling agent and dynamic vulcanization have been introduced into PP/WTD/SGF composites in order to improve the properties of such

composites. The silane coupling agent, known as bifunctional compound is utilized to improve reinforcing efficiency by improving the rubber-filler interaction via chemical linkages (Sae-oui et al., 2005). Silanes are a group of organo-fuctional compounds that are capable to bond inorganic materials for instance glass, mineral fillers, metals and metallic oxides to organic matrix (Nelson and Kutty, 2004). The readily hydrolyzable alkoxy group will react with silanols that present on the short glass fibre surface to form stable siloxane linkages while the other end group, namely the organo-functional group, can take part in sulfur vulcanization leading to chemical linkage with the rubber (Sae-oui et al., 2005).

Additionally, in order to improve the mechanical properties of PP/WTD/SGF composites, better control of phase morphology and good interfacial adhesion must be attained by using compatibilizing agents. The compatibilization can be achieved by in-situ formation of an interfacial agent and dynamic vulcanization (Supri and Ismail, 2006). Dynamic vulcanization is a process of vulcanizing the elastomer during melt mixing with molten plastics under dynamic conditions (Ismail et al., 2010, Huang et al., 2002, Nakason et al., 2008, Babu et al., 2009) and is carried out under high shear rate and above the melting point of thermoplastic (at sufficiently high temperature) to activate and complete the process (Halimatuddahliana and Ismail, 2009). This process was first described by Gessler and Haslett in 1962 (Huang et al., 2002, Nakason et al., 2008, Babu et al., 2009), is a route to new thermoplastic elastomers (TPEs) that possess many good properties in return and has lead to many new products commercialized since the era of the 1980s (Huang et al., 2002). Furthermore, dynamically vulcanized

thermoplastic elastomers are widely used due to their advantages in terms of processing and end use properties (Supri and Ismail, 2006).

This study is an attempt to develop PP/WTD/SGF composites with improved processing, tensile, morphological and thermal properties as well as swelling resistance. Whilst, it is intends to explore the possibility to impart and improve the chemical interactions between SGF and PP/WTD matrix by hoping to reveal a new path for improvement. In this work, the effects of SGF loading, the addition of γ-APS silane coupling agent and dynamic vulcanization together with the hybridization effect by partial replacement of SGF with carbon black and silica on process development, tensile properties and swelling resistance as well as thermal stability of PP/WTD/SGF composites were studied. Morphological studies and FTIR analysis were also carried out and investigated.

2.2 Composites

A composite material with respect to materials science and engineering is defined as a materials system which composed of a mixture or combination of two or more micro or macro constituents that can be distinguished in its form and chemical composition and generally insoluble with each other (Smith and Hashemi, 2006).

For the past 20 to 30 years, fibre-reinforced plastics (FRPs) composites have been used extensively in engineering design as it offers ease of processing, tailorable properties and weight saving compared to metal alloys. Although FRPs possess

excellent properties along the fibre direction, the weaknesses of these composites were highlighted in terms of failure in matrix-rich interlaminar regions whereby less effiency of stress transfer occur from the fibres to polymer (Wood et al., 2012).

Meanwhile, fibre-reinforced polymer composites are widely used in various engineering applications due to enhance factors they can offer such as high specific strength and stiffness, tailorability and corrosion resistance. Whilst, the consumption of both glass fibre-reinforced polymers (GFRPs) and carbon fibre-reinforced polymers (CFRPs) continues to expand in main structural applications (Ireland et al., 2011). Both GFRPs and CFRPs have been developed during the past decades providing wide range on materials with combined properties of high stiffness and strength with low density particularly for aerospace, automotive and energy sector applications (Diez-Pascual et al., 2011).

2.2.1 Classification

There are three main classes of composites which classified according to the nature of the composites that are polymer matrix composites (PMCs), metal matrix composites (MMCs) and ceramic matrix composites (CMCs). In industrial area, most composites used are of PMCs which are thermoplastics and thermosets. Yet, the MMCs and PMCs are still been utilized but their usage is relatively limited due to difficult to manufacture compared to the PMCs (Hull and Clyne, 1996). The composite classified by the matrix type is exhibited in Table 2.1. Meanwhile, the classification of composite

materials based on their reinforcing phase for instance fibre-reinforced, particle-reinforced and structural composites is demonstrated in Figure 2.1 below.

Table 2.1 Composites classified by matrix type (Hull and Clyne, 1996).

Matrix Type	Common Designation	Matrix Properties			Most Effective Reinforcement
		Stiffness	Strength	Ductility	
Polymer	PMC	Low ($1.4x10^6$ – $3.4x10^6$) MPa	Low (3.5 –34. 5) MPa	Low (< 2%)	Continuous fibre
Metal	MMC	Moderate ($41.4x10^6$ – $110.3x10^6$) MPa	High (69 – 1034) MPa	High (20%)	Continuous and discontinuous fibre
Ceramic	CMC	High ($137.9x10^6$ – $551.6x10^6$) MPa	High (137.9 – 551.6) MPa	Low (< 1%)	Discontinuous fibre or whisker and particulate

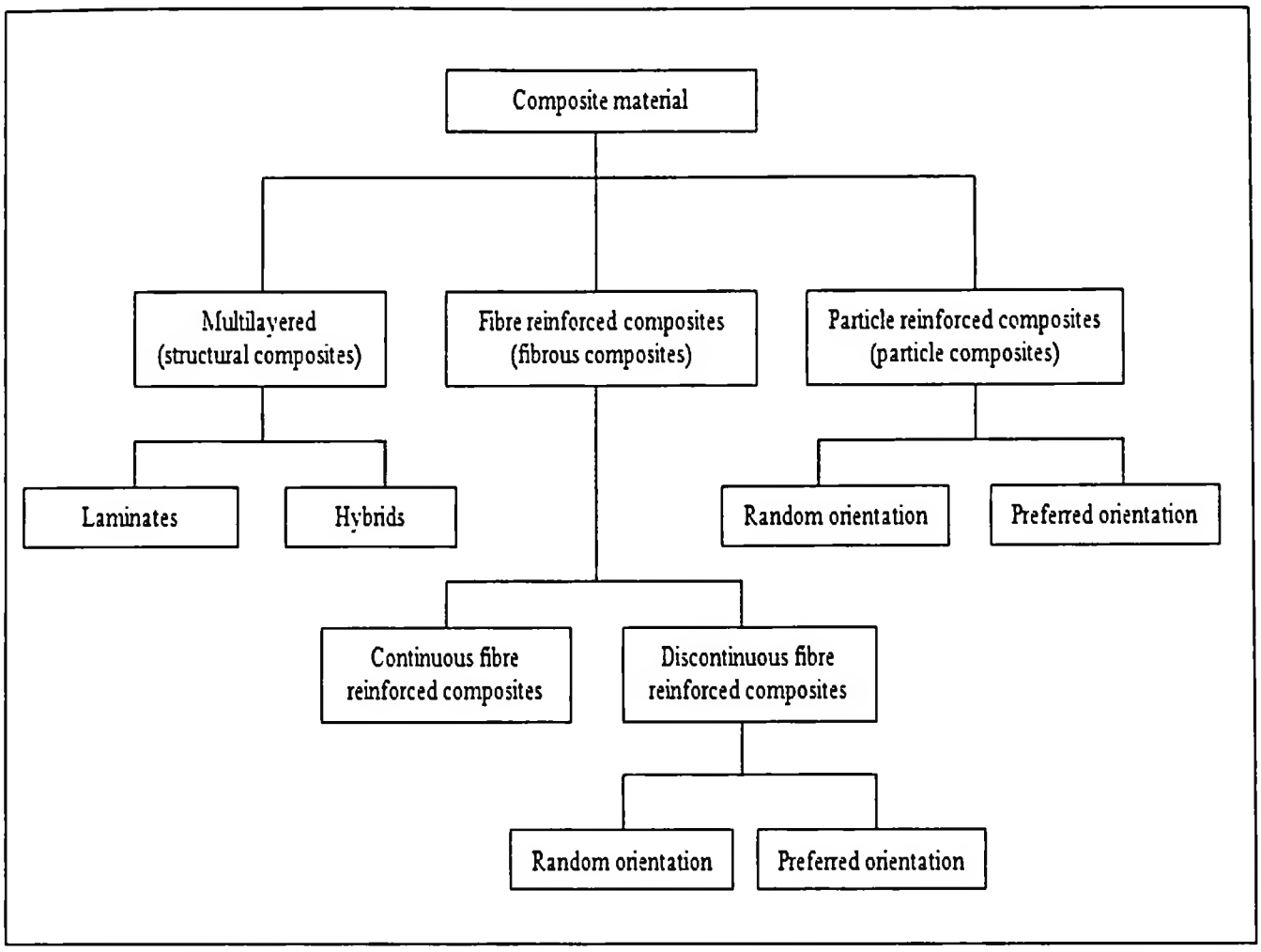

Figure 2.1 Classifications of composite materials by reinforcement type (Callister, 2000).

2.2.2 Matrix Phase

It is mentioned earlier that matrix phases are available in polymer, metal or ceramic forms. Matrix phase is the continuous phase that is tougher than other phases which support and binds the reinforcement together. The matrix carries the shear stresses of the composite and transmits the load from one piece of reinforcement to another. Besides, it provides environmental protection for the reinforcement such as from surface

damage resulting from mechanical abrasion or chemical reaction with the environment since those interactions might enhance flaws and crack initiation which may lead to failure at low tensile stress level (Hull and Clyne, 1996).

2.2.3 Reinforcing Phase

The main function of the reinforcing phase is to improve the mechanical and physical properties of the matrix. Reinforcing phase will act as load bearing material by supporting the stress that transferred from the matrix. Thus, this phase is usually stronger, harder and stiffer than the matrix. A composite will exhibit high mechanical performance if the reinforcement material carries a relatively high proportion of the external applied load that is transferred from the matrix to the reinforcement via the interface (Hull and Clyne, 1996).

Basically, fibre reinforcement materials are added to the resin system in order to provide high stiffness and strength to the finished part. Apparently, stiffness and strength are the most short term properties in application while the resistance to creep and fatigue failure is the long term properties. All of these properties can be upgraded in the composites by the fine selection of reinforcing fillers. Besides, it is also mentioned that the geometry of the reinforcing phase is the most crucial part in determining the effectiveness of the reinforcement meaning that the shape and dimensions of the reinforcement functionalized the mechanical properties of the composites (Callister, 2000).

2.2.4 Hybrid Composite

Generally, the hybrid composite is composed of more than two types of fibres. The main purpose of hybridization is to create a new material that highlights up only the advantages out of each constituent. Meanwhile, the hybrid effect is the positive effect of any properties risen up through the rule of mixture (You et al., 2007). In hybrid composites, the goal is to reach the synergistic effect solely from the usage of hybrid filler system which is larger than that of summarized effects gain from the single fillers (Socher et al., 2011).

Hybrid composites are differ from the customary FRPs by the incorporation of fillers in the matrix phase that results in enhancement of multi-scale reinforcement leading to increased stiffness, strength and toughness of the composites. Besides, the hybrid composites will promote multi functionality in terms of enhanced barrier properties or electrical and thermal conductivity based on the type of reinforcing fibres used in the composites (Wood et al., 2012). Meanwhile, it is also reported that hybrid filler systems have also been practiced into rubber based composites such as the usage of carbon black and carbon nanotubes together in styrene-butadiene rubber (Socher et al., 2011).

The multi-scale fibre reinforced composites can also be classified into two types of systems that are mixed inclusion system and hybrid fibre system as shown in Figure 2.2. Figure 2.2 (a) shows the independent dispersion of fillers throughout the polymer matrix creating the mixed inclusion system which might involve various types of fillers

such as rubber particles, elastomeric block copolymers or the combination of both. On the other hand, Figure 2.2 (b) depicts hybrid fibre composite system which involves chemically linked fibres to the fillers through chemical vapor deposition prior to infiltration by the polymer matrix (Wood et al., 2012).

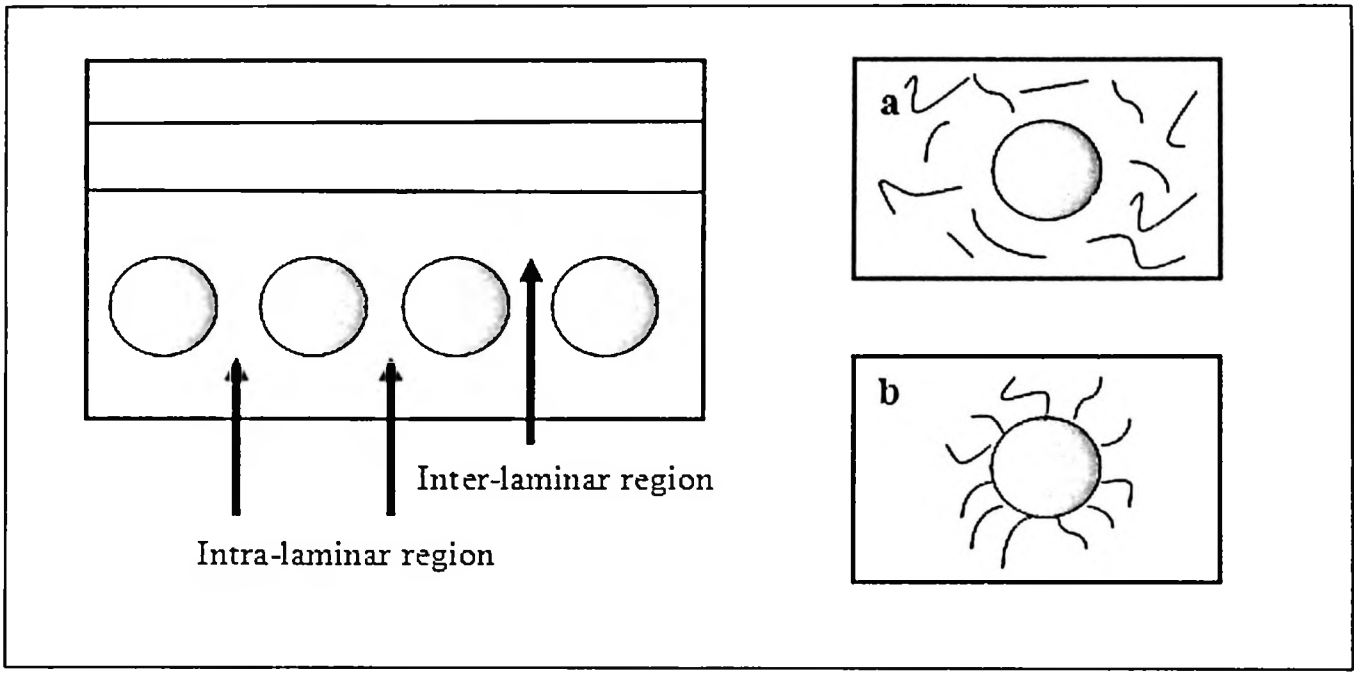

Figure 2.2 Schematic illustrations of two types of multi-scale fibre reinforced composites systems: (a) mixed inclusion system of micro and nano-scale fibres independently dispersed through the polymer matrix and (b) hybrid-fibre system with fibres and grafted nanoparticles embedded in the polymer matrix (Wood et al., 2012).

Meanwhile, Ireland et al. (2012) stated that in any engineering application, one or more hybrid joint structure maybe be experienced various complex failure modes depending on the joint construction itself. The common failure modes occur in hybrid joints are shear-out, cleavage, tensile failure, microcrack propagation, delamination and

debonding. Besides, adhesive joints are more prone to failure modes such as moisture absorption and fracture toughness which enhanced more study on failure behaviour of adhesive hybrid joints nowadays.

2.3 Thermoplastic Elastomers (TPE)

The polymer modifications have been carried out in various ways by means to increase their performance. Depending on many factors for instance the nature of individual components, processing parameters, blend composition and additives which results in various properties of a polymer blend eventually (Awang et al., 2007, Johns and Rao, 2009). TPEs from rubber-thermoplastic blends rise among different types of polymer blends due to their importance in various application sectors as they offer good mechanical properties (Sarkhel and Choudhury, 2010).

TPEs are material that is processed in the same way as rigid thermoplastic whether by means of injection moulding or extrusion and possess the same properties and performance as the conventional thermoset rubber. The TPEs can be classified into two groups that are block copolymers and rubber-plastic blends (Nakason et al., 2008). Meanwhile, Nakason et al. (2006) also explained that TPEs reveal the functional properties of conventional elastomeric materials and ready to be processed by using a thermoplastic processing machine to be produced as block copolymers or as blends. At elevated temperature, the hard domains of TPEs undergo dissociation which allows the material to flow while at lower temperature, the domains will solidify. Therefore, the strength properties of TPEs were improved at service temperatures.

Among different types of polymer, TPEs from rubber-thermoplastic blends are experiencing vastly growing usage in variety of applications due to good mechanical properties it has to offer. Few studies on TPEs suggested that the presence of small amount of rubber in polyolefin matrix could improves the elongation at break and impact resistance whilst, decrease the modulus and toughness of the materials. Nevertheless, the usage of curing agent at optimum level can lead to controlled crosslinking degree in rubber phase thus improved the toughness properties of the TPE blends (Sarkhel and Choudhury, 2010).

On the other hand, Ismail et al. (2006) mentioned that researches have also come out with the preparation of TPEs as one of the promising alternatives to utilize waste tyre rubber in order to make use of the abundant waste rubber. Infact, TPEs provides better utilization as scrap while the waste can be recycled. The most commonly used thermoplastics to form the TPEs are polypropylene (PP) mainly due to its low in cost and density. Previous works have shown that blending the PP with recycled rubber (PP/ RR) enhanced the tensile strength and Young's modulus but lower the elongation at break than that of PP/ natural rubber blends. Thus, in this study, with the abundance of waste tyres and the advantages of PP, the formulation of TPEs blends was formulated base on the PP/ waste tyre dust (WTD) blends as the matrix in PP/WTD/SGF composites by hoping that the rubber is finely dispersed in the thermoplastic matrix and thus, results in fully or partially crosslinked rubber phase.

In addition, there are many methods that can be used to combine the desired features of each component presence in TPEs blends and one of it is by preparing the blend in an intensive internal mixer. Meanwhile, dynamically vulcanized TPEs were also used due to their technical advantages in processing as well as their enhanced end use properties. Technically, the blends possess the processing advantages because of the thermoplastic nature of the melt although they contain a vulcanized rubber in their components (Ismail et al., 2001). Besides, Soares et al. (2007) also mentioned that TPEs must present a suitable morphology whereby the rubber phase is finely dispersed in a relatively small amount of plastic and this features are more likely to be achieved by promoting the crosslinking of the rubber phase during melt-mixing process of the TPEs.

The most crucial part in considering material developments of engineering thermoplastics is to have both good properties and processability at a moderate cost. Since good mechanical properties are desired, the balance between stiffness, strength and toughness of a material must be attained. Thus, there are two approaches that can be applied that are by incorporation of short fibre reinforcements and impact modifiers into thermoplastics matrices in order to form short-fibre-reinforced-thermoplastics and rubber-toughened thermoplastics (RTTPs), respectively (Mohd Ishak et al., 2000). Besides, Gupta et al, (2004) also mentioned that the investigations of melting and crystallization behavior of PP had become a subject of interest since thermoplastics polymers are used as matrices in the development of fibre-reinforced composite materials.

2.4 Scrap Tyres

The ongoing accumulation of scrap tyres had become a major threat to public health as well as to the environment worldwide. Besides, the increasing demand of automobiles had caused the unremittingly abundant scrap tyres that exist for a very long time. Thus, more extensive researches and broader applications of scrap tyres are required aiming to reduce their volume (Awang and Ismail, 2008).

Basically, the reclaim rubber usually consists of 65 % rubber, 28 % carbon black and 7 % residue, respectively (Satapathy et al., 2010). The properties of reclaimed rubber are shown in Table 2.2.

Table 2.2 Properties of reclaimed rubber (Satapathy et al., 2010).

Typical data	Unit	Value	Test Method
Mooney Viscosity	ML (1 + 4) at 100 °C	53	ASTM D 1646
Density	g/cm^3	1.2	ASTM D 792
Tensile Strength	MPa	5.5 ± 0.3	ASTM D 638

2.4.1 Recycling of Scrap Tyre Rubber

The whole tyre reclaim derived from scrap tyres and butyl reclaim derived from scrap tubes are the major streams of reclaimed rubber produced worldwide. Disposal of