

**PREPARATION AND PROPERTIES OF RUBBER SEED KERNEL
POWDER/RECYCLED POLYSTYRENE COMPOSITES**

by

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LIST OF ABBREVIATIONS

| | |
|-------|---|
| ABS | acrylonitrile butadiene styrene |
| ASTM | American Society for Testing and Materials |
| BR | butadiene rubber |
| CR | chloroprene rubber |
| DOP | dioctyl phthalate |
| DSC | differential scanning calorimetry |
| ENR | epoxidized natural rubber |
| EPDM | ethylene propylene diene rubber |
| FESEM | field emission scanning electron microscope |
| HA | high ammonia |
| HDPE | high-density polyethylene |
| IIR | butyl rubber |
| LCD | liquid crystal display |
| LDPE | low-density polyethylene |
| MAH | maleic anhydride |
| MST | modified starch paste |
| NBR | nitrile-butadiene rubber |
| NR | natural rubber |
| PC | polycarbonate |
| PE | polyethylene |
| PET | polyethylene terephthalate |
| PP | polypropylene |
| PS | polystyrene |

| | |
|------|-------------------------------------|
| PVC | polyvinyl chloride |
| RPS | recycled polystyrene |
| RSK | rubber seed kernel |
| RSKP | rubber seed kernel flour |
| SEM | scanning electron microscopy |
| SBR | styrene butadiene rubber |
| TEGO | thermally-exfoliated graphite oxide |
| TGA | thermogravimetric analysis |
| TPE | thermoplastic elastomer |
| TSC | total solid content |
| UTM | universal testing machine |
| VPS | virgin polystyrene |

LIST OF SYMBOLS

| | |
|---------------|-----------------------------------|
| °C | degree celcius |
| E_b | elongation at break |
| cm | centimetre |
| cm^3 | centimetre cube |
| Nm | Newton metre |
| MPa | megaPascal |
| J/m | joule per metre |
| g | gram |
| g/10 min | gram per ten minute |
| wt% | percentage by weight |
| % | percentage |
| g/100 | gram per one hundred |
| mm/min | millimetre per minute |
| min | minute |
| mm | millimetre |
| kV | kilovolts |
| W_t | total water absorbed by sample |
| W_1 | weight of sample before immersion |
| W_2 | weight of sample after immersion |

**PENYEDIAAN DAN SIFAT-SIFAT KOMPOSIT POLISTIRENA KITAR
SEMULA/SERBUK ISI BIJI GETAH**

ABSTRAK

Komposit polistirena kitar semula (RPS)/serbuk isi biji getah (RSKP) pada komposisi RSKP 0, 1, 3, 5, dan 10 wt% telah disediakan menggunakan pencampur dalaman pada suhu 180°C dengan kelajuan rotor 60 rpm selama 8 minit. Kestabilan tork, kekuatan tensil, pemanjangan pada takat putus, modulus Young dan kekuatan hentaman berkurang manakala, penyerapan air meningkat dengan peningkatan pembebanan RSKP. Jika dibandingkan dengan komposit polistirena baru (VPS)/RSKP, komposit RPS/RSKP mempunyai kestabilan tork, kekuatan tensil, pemanjangan pada takat putus, kekuatan hentaman, dan penyerapan air yang lebih rendah. Penambahan maleik anhidrida (MAH) kepada komposit RPS/RSKP menunjukkan peningkatan kekuatan tensil, pemanjangan pada takat putus, modulus Young, dan kekuatan hentaman berbanding komposit RPS/RSKP. Kehadiran MAH meningkatkan kekuatan hentaman pada kandungan RSKP 1, 3, dan 5 wt%. Pengubahsuaian pengisi RSKP menggunakan lateks getah asli (NR) menyebabkan kekuatan tensil, pemanjangan pada takat putus, dan kekuatan hentaman komposit RPS/RSKP bertambah baik.

**PREPARATION AND PROPERTIES OF RUBBER SEED KERNEL
POWDER/RECYCLED POLYSTYRENE COMPOSITES**

ABSTRACT

Recycled polystyrene (RPS)/rubber seed kernel powder (RSKP) composites at 0, 1, 3, 5, and 10 wt% of RSKP were prepared in an internal mixer at 180°C with 60 rpm of rotor speed for 8 minutes. Processing torque, tensile strength, elongation at break, Young's modulus and impact strength decreased with higher RSKP loadings, but water absorption increased. In comparison to virgin polystyrene (VPS)/RSKP, RPS/RSKP composites had lower processing torque, tensile strength, elongation at break, impact strength and water absorption. Maleic anhydride (MAH) incorporation into RPS/RSKP composites showed higher tensile strength, elongation at break, Young's modulus and impact strength as compared to RPS/RSKP composites. The presence of MAH increased the impact strength at 1, 3, and 5 wt% of RSKP loadings. Modifying of RSKP filler with natural rubber latex improved tensile strength, elongation at break and impact strength for RPS/RSKP composites.

CHAPTER 1

INTRODUCTION

1.1 Overview

Concerns over the environment, waste disposal, and recycling of plastic materials worldwide has sparked interests in the search of new raw materials, especially biomaterials. This gave rise to the vast researches on composites based on natural fillers, which is environmentally friendly, biodegradable, and cost-effective (Pickering, 2008).

Plastics originated from oil, natural gas, or coal, all of which are natural resources that are limited and must be preserved. The production and manufacturing of plastics products also liberate harmful chemicals to the environments and humans or workers dealing directly with the process. There is a wide range of plastic products in the market nowadays, from laptops and cell phones casings, tableware, containers, furniture, car internals, and a lot more. Therefore, plastics are consumed everyday worldwide in a huge scale, in which when they are not used or unneeded anymore, will contribute to the increasing of solid waste that later affects our environment (KiaEIFar *et al.*, 2011).

In order to overcome this situation at the same time prevail sustainability, recycling provides convincing solutions. Recycling of the plastic wastes proves to reduce consumption of virgin plastics, at the same time diminish considerable cost of production (KiaEIFar *et al.*, 2011). Numerous successful researches had been done either on recycled plastic materials alone, or to compare with their respective virgin materials to produce composites filled with natural or synthetic fillers (Homkhiew *et*

al., 2014; Adhikary *et al.*, 2008; Yeh *et al.*, 2009; Khanam and AlMaadeed, 2014; AlMaadeed *et al.*, 2012).

Natural resources are found in abundance worldwide. Extensive research had also been done on polymeric composites filled with natural fillers. This is to fill in the demand of more eco-friendly options. Natural fillers are abundantly available, environmentally friendly, non-abrasive towards processing equipment, have low density, good thermal properties, high toughness, able to yield lighter composites, cheaper, and biodegradable (Akil *et al.*, 2011; Shubhra *et al.*, 2011; Thomas *et al.*, 2012).

Hevea brasiliensis or rubber trees are grown in rubber plantations throughout Malaysia (Claramonte *et al.*, 2010) and are no stranger in its ability to produce natural rubber (NR) latex (Kush *et al.*, 1990; Mokhtar *et al.*, 2011) that highly contributed in numerous applications such as gloves, tires, and shoes (Okoma *et al.*, 2011). Rubber trees also disperse rubber seeds that consist of a hard outer shell and a soft kernel on the inside. Rubber seed kernel contains oil substances that have potential for the use as biodiesel lubricant (Kamalakar *et al.*, 2013; Gimbun *et al.*, 2013). The attributes of rubber trees brought upon the interest of incorporating some of its components into thermoplastic.

Thermoplastic is a class of plastic materials able to shape in melt form when heated. Once shaped into products, they can be reheated and reprocessed again into other shapes or applications (Pickering, 2008). Examples of thermoplastics are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polycarbonate (PC). The vast range of thermoplastic products, however, pose environmental threat due to increased amount of municipal solid waste (Bajracharya *et al.*, 2014). Using recycled thermoplastic is

one of the many alternatives to curb with this situation. Recycled or scrap plastics may have reduced mechanical properties due to processing history and degradation (Najafi, 2013). This can be overcome by incorporating fillers into plastic composites to further reinforce the final properties.

Fillers that are used in polymeric composites can be of mineral or natural fibres. Their functions vary, either as reinforcing agent or to reduce cost (Stuart, 2002). In terms of sustainability, natural fillers offer advantages by means of abundance, choice, non-abrasive, cost effective, and biodegradable (Akil *et al.*, 2011; Shubhra *et al.*, 2011; Thomas *et al.*, 2012). The major disadvantage of using natural fillers in polymeric materials is the fact that these two phases are incompatible with each other. Polymeric materials are hydrophobic whilst natural fillers, which contain cellulosic components, are polar and hydrophilic. This will later affect the final properties of composites since adhesion at the interface is poor (Akil *et al.*, 2011). An additional element in the composite system called coupling agent is therefore required to introduce and enhance filler-matrix interaction at the interface (Aji *et al.*, 2009).

1.2 Problem Statement

A by-product from rubber plantations that is often overlooked is the rubber seed that are dispersed throughout the rubber plantations. Rubber seeds are considered as agro-waste, meaning that they do not sit for a significant purpose; at the same time they also do not affect the environment negatively. Rubber seeds can be separated into rigid outer shell, enclosing a softer inner kernel. The oil from rubber seed kernel is useful in applications such as biodiesel lubricant, soap, coatings, and adhesives (Ebewele *et al.*, 2010; Asuquo *et al.*, 2012; Salimon and Abdullah, 2009; Yang *et al.*, 2011). However, to date, there are no researches implementing rubber seed as natural filler in polymer composites.

The incorporation of natural fillers into polymeric materials poses incompatibility between these two phases, which will commonly results in considerable reduction of mechanical properties, mainly contributed by poor filler dispersion, weak adhesion at the interface, and failure of the matrix to wet around the natural filler. Low filler-matrix adhesion also increases the opportunity of agglomerates formation due to higher filler-filler interaction, especially at higher filler loadings (Akil *et al.*, 2011). This phenomenon is the result from unifying incompatible polar hydrophilic natural fillers and hydrophobic polymer matrix, which also promotes high moisture absorption. The properties majorly attributed by cellulosic components containing free hydroxyl groups that permits hydrogen bonds formation between the natural fillers and water molecules.

To overcome these drawbacks, weak interfacial adhesion can be enhanced by surface treatment, which is incorporating coupling agent or compatibiliser, or modifying the natural filler to improve mechanical properties of the composites (Akil *et al.*, 2011; Aji *et al.*, 2009). This is essential as compatibiliser has the ability to

improve interfacial adhesion between incompatible hydrophilic natural filler with hydrophobic polymer matrix (Pickering, 2008; Aji *et al.*, 2009).

In this research work, the chosen recycled thermoplastic that will be used is polystyrene incorporated with rubber seed kernel powder (RSKP) natural filler; and compared with its virgin counterpart. The properties of the recycled polystyrene RPS/RSKP composites will be further enhanced by using maleic anhydride (MAH) and natural rubber latex as compatibilisers on the RPS/RSKP composites.

1.3 Research Objectives

- i) To study the potential use of RSKP as natural filler in polymer composites.
- ii) To compare the properties of RPS and (VPS) when using RSKP filler in terms of processing, mechanical, morphology and water absorption.
- iii) To study the effect of using MAH compatibiliser on processing, mechanical, morphology and water absorption properties of RPS/RSKP composites.
- iv) To study the effect of using NR latex as a filler modifier on processing, mechanical, morphology and water absorption properties of RPS/RSKP composites.

1.4 Thesis Outline

Chapter 1 begins by introducing general overview of the research, including the problem statement, which motivated this work. Research objectives are inserted next, followed by the flow and organisation of the thesis.

Chapter 2 describes literatures connected to this study, involving a number of previous publications and discoveries substantial to the research.

Chapter 3 outlines the materials involved in the research and methodologies in order to prepare and execute the research work.

Chapter 4 reports the findings and results of the research. After that, the findings are compared and discussed accordingly, covering from processing, tensile, impact, morphological, to water absorption properties.

Chapter 5 summarises the conclusions of the outcomes from previous chapters in this research with some recommendations for future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Thermoplastics

2.1.1 Polystyrene (PS)

Polystyrene is a type of clear thermoplastic with high modulus, extremely low water absorption, average glass transition temperature (T_g), and low density. However, polystyrene is well known for its rigidity and brittleness (Pickering, 2008) and sensitivity towards solvents. The brittle nature of polystyrene is caused by the alternating aromatic benzene ring on its backbone, resulting in steric hindrance. The brittleness of polystyrene can be suppressed by modification with rubber. Polystyrene is used to manufacture appliances for housings and packaging (Stuart, 2002).

Polystyrene that is used in the industry is mostly atactic, where it has random unordered structure to give its amorphous characteristics. Due to its brittle nature, polystyrene is commonly toughened by blending with an elastomer such as polybutadiene to form high-impact polystyrene (HIPS). The elastomeric regions in HIPS allow better stress transfer thus increasing its impact property, therefore opening opportunities for a wider range of applications (Harper, 1999).

Styrenic resins are also available for copolymerization to manufacture plastics of engineering grade where higher performance is desired. Such examples are acrylonitrile butadiene styrene (ABS) and styrene acrylonitrile (SAN). ABS, due to its three monomers existence, the ratios of the monomers can be altered to fit

specific applications. Acrylonitrile component gives heat resistance, strength and chemical resistance. Butadiene component, on the other hand, gives higher impact and toughness (Harper, 1999).

General-purpose polystyrene (GPPS) is a rigid plastic as compared to foamed polystyrene. Bulky benzene side groups causes steric hindrance resulting in its brittle properties where elongations revolves around 3 % depending on molecular weight and levels of additive. The amorphous structure imparts transparency due to the lack of crystalline structure. This can be an advantage during processing since it does not crystallize; therefore GPPS has low shrinkage values and high dimensional stability. GPPS with lower molecular weight is easier to flow, increasing processing speed, at the same time reducing processing time (Harper, 1999).

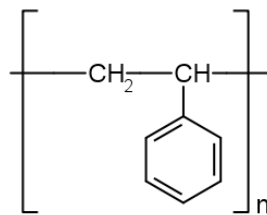


Figure 2.1: Chemical structure of polystyrene.

2.2 Recycled plastics

Plastic products from consumers that are no more used or scrap plastics from the industries can become a crisis and produce a considerable amount of solid waste if left unused, which later will give negative impacts on the environment. Annual consumption of plastic materials throughout the world has increased from approximately 5 million tons around the 1950s to almost 100 million tons in the year 2007. This is not a surprising figure since plastics are used effectively in packaging, food preservation and distribution, communication materials, housing, security

systems, healthcare applications, artificial implants, medical delivery systems, automotive, and industrial applications (Bajracharya *et al.*, 2014). This value will only increase to an estimation of 400 million tons by 2020 (Zare, 2013).

To manage this crisis, one of the best solutions is to recycle waste plastic materials in an effort to reduce volume of solid waste and preserve the environment (Najafi, 2013; Zare, 2013; Rajendran *et al.*, 2012). This seemed to be a relevant alternative since it can cut cost and reduce overflowing of landfills. Recycled plastics made into composites nowadays are mainly focused on applications that does not require high load such as park benches, picnic tables, floor carpets, flower vases, and plastic lumber (Najafi, 2013; Bajracharya *et al.*, 2014).

After the first life cycle of plastic products, these plastics can then be recycled into new products. The properties and performance of the new products will depend heavily on their level of degradation, or in other words, previous applications, storage conditions, and reprocessing methods (Najafi, 2013).

Many researches had been done to study and compare the properties of recycled against virgin polymers in the hope of producing polymer composites from recycled materials that can compete and replace the use of virgin materials. For example, Homkhiew *et al.* (2014) studied natural weathering of rubberwood flour-filled recycled and virgin PP composites on their physical and mechanical properties. Adhikary *et al.* (2008) also did a research on the mechanical properties, stability, and microstructure of wood plastic composites based on recycled and virgin HDPE incorporating wood flour as filler. The study presented composites from recycled HDPE composites has higher dimensional stability compared to HDPE composites. Also studying wood plastic composites were Yeh *et al.* (2009), formulating recycled and virgin acrylonitrile butadiene styrene (ABS).

An interesting analysis done recently by Khanam and AlMaadeed (2014) when they combined three types of recycled plastics, which were recycled LDPE, recycled HDPE, and recycled PP with date palm fibre as reinforcement in the composites. AlMaadeed *et al.* (2012) tried to reinforce and impart enhanced mechanical properties of recycled PP composites by incorporating palm wood flour/glass fibre. The study discovered increased tensile strength and Young's modulus of the hybrid composites.

In terms of researches that used polystyrene as a recycled matrix, Zizumbo *et al.* (2011) incorporated residue bagasse fibers of sugarcane modified with dichloromethylvinylsilane grafted with recycled polystyrene. Another study done by Hamad and Deri (2012) where they were studying the effects of recycling on rheological and mechanical properties of poly (lactic acid) and polystyrene blend. Joshi *et al.* (2006) did a selective physical characteristic of injection moulded polystyrene/high density polyethylene composites from virgin and recycled materials. Other than that, Lisperguer *et al.* (2013) studied the structure and thermal properties of recycled polystyrene with the incorporation of maleated lignin composites.

The extensive researches on recycled plastic materials discussed above only strengthen the fact that scholars worldwide are trying their best for the sustainability of the environment by reducing the amount of plastic waste.

2.3 Polymer Composites

2.3.1 Definition of Polymer Composites

Composite material is a mix and fusion of two or more materials (Stuart, 2002 and Pickering, 2008) by chemical and physical means, separated at the interface of the different phases. Incorporating fibres or particles into the polymer matrix can reinforce the system structurally and functionally (Thomas *et al.*, 2012). This is done to enhance the mechanical properties of the matrix (Shubhra *et al.*, 2011). The mechanical stress put upon the composite will be sustained by the reinforcement, whilst the matrix transfers the stress, thus interfacial adhesion between the two phases will determine the final properties of the composites (Pickering, 2008). Advantages of composites include low weight, resistant to corrosion, high fatigue resistance, and fast assembly. Polymer composites are used in various demanding applications such as structures for aircraft, medical apparatus, electronic packaging, space vehicles, and home building (Thomas *et al.*, 2012).

The two separate constituents of polymer composites are the matrix and dispersed phases. The matrix phase is a continuous primary phase that is more ductile. This phase will share loads with and hold the other phase. The dispersed phase is a discontinuous phase embedded and incorporated into the matrix phase. This phase typically has higher strength than the matrix, therefore can sometimes be called the reinforcing element of the composites. After homogenous mixing, composites are expected to have superior properties compared to their constituents separated (Thomas *et al.*, 2012).

2.3.2 Polymer Composites Based on Thermoplastic Matrices

Thermoplastic is a type of polymer that softens and melted into viscous liquid when heated, therefore easy to shape upon heating, and solidified into amorphous, semi-crystalline, or crystalline solid upon cooling (Stuart, 2002 and Pickering, 2008). The degree of crystallinity plays an important role in determining the final properties of the matrix. It can also undergo reversible and multiple heating cycles that allow repeated process of heating and cooling (Pickering, 2008). Utilising synthetic or natural fillers and additives can improve various properties of thermoplastic. Some majorly consumed thermoplastics are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polycarbonate (PC).

Thermoplastics is commonly inferior compared to thermosets in terms of stability against high temperatures and chemical attack, however, they are excellent at resisting cracking and impact force. The advantages of thermoplastics are able to be processed repeatedly by heating and cooling, short processing time, production in high volume, reusable wastes or scrap materials, and considerably cheap. Some of its disadvantages are decreased in modulus at high temperatures, properties reduction at higher processing cycles and poor creep and relaxation behaviours compared to thermosets.

2.4 Types of Filler in Polymer Composites

Generally, fillers are solid substances in the form of particle or fibre that can be incorporated and embedded into polymers and functions to improve material performance such as compressive strength, thermal stability, abrasion resistance, and impact strength, as well as providing dimensional stability and reducing the cost

(Stuart, 2002). Properties of the fillers such as geometry in terms of size, shape, and aspect ratio and interactions between filler and matrix will determine the final implementation of composites. Fillers can either have irregular shapes or can be in the shapes of sphere, cube, platelet or regular geometry (Thomas *et al.*, 2012).

Filler shapes can be in sphere, cube, block, plate or flake, needle, or fiber. Different filler shapes give specific range of aspect ratios with cube, sphere and block shapes approximately from one to four, while plate, flake and fiber have aspect ratios ranging from 30 to 200. Aspect ratio of needle or fiber is the ratio of its mean length to mean diameter whereas for plate, its aspect ratio is the mean diameter to the mean thickness. Smaller sized filler as well as high aspect ratio will give greater contact surface area with the matrix, allowing better stress transfer throughout the composite system.

2.4.1 Particulate Fillers

Particulate fillers such as silica, alumina, titania, glass, clay, talc, wollastonite, graphite, and calcium carbonate (Bao *et al.*, 2008; Stuart, 2002; Mirmohseni and Zavareh, 2010) are reinforcing fillers that are resistant to biodegradation, which at some point can threaten the environment (Thomas *et al.*, 2012). Inorganic fillers have the ability to improve fracture toughness, tensile strength, wear resistance, and stiffness of composites with the reduction of cost (Claiden *et al.*, 2014; Mirmohseni and Zavareh, 2010; Bartczak *et al.*, 1999). However, incorporation of inorganic fillers into polymer composites will cause brittleness and rigidity that will affect impact strength negatively (Bartczak *et al.*, 1999).

2.4.2 Natural Fillers

Some of the examples of natural fillers are wood fiber, oil palm, bamboo, hemp, jute, silk, kenaf, and cotton. These fillers are popular for their high strength and are used in thermoplastics and thermosets to improve their mechanical properties for load-bearing applications (Thomas *et al.*, 2012). Natural fillers are environmentally friendly and can be found abundantly, non-abrasive, low density, good thermal properties, high toughness, produce lighter composites, reduce cost, and biodegradable (Akil *et al.*, 2011; Shubhra *et al.*, 2011; Thomas *et al.*, 2012). The non-abrasive characteristic of natural fillers allows minimal equipment maintenance, therefore cutting considerable cost. Processing of natural fillers is also safer and environmentally friendly, posing no health risk to human.

However, natural fillers give poor interfacial adhesion due to incompatibility between hydrophilic filler and hydrophobic matrix. Hydrophilic polar nature of natural filler also makes the composites absorb water moisture. This is mainly due to the presence of cellulosic components, which is a natural homopolymer, or in biological term, polysaccharides. Cellulose has free hydroxyl groups along its chains, allowing hydrogen bonds to form between the filler and water molecules (Akil *et al.*, 2011). Surface treatment is one of the methods to overcome this drawback, improving the interfacial adhesion. The problem of incompatibility also causes the formation of agglomerates due to higher filler-filler interactions compared to filler-matrix interactions that affected uniform filler distribution.

2.5 Rubber Tree (*Hevea brasiliensis*)

Hevea brasiliensis or rubber tree is a type of tropical plant originated from the Amazon, Brazil (Corpuz, 2013) and extensively cultivated in Southeast Asia such as in Malaysia, Indonesia, India, Philippines, China, Myanmar, Vietnam, Cambodia, Bangladesh, and Thailand (Claramonte *et al.*, 2010) mostly due to its ability to produce NR, which is the most popular product of rubber plantations (Kush *et al.*, 1990; Mokhtar *et al.*, 2011). Malaysia has approximately 1, 021, 540 hectares of rubber plantations reported in 2009 that is capable of producing more than 120, 000 tons of rubber seeds annually (Gimbun *et al.*, 2013).

Rubber trees can grow up to 20-30 meters in plantations (Corpuz, 2013). The wood from rubber trees can be used to make furniture (Mokhtar *et al.*, 2011). Rubber trees reproduce by bursting of the ripened fruits, scattering the seeds to the surrounding area.

2.5.1 Natural Rubber (NR) Latex

Natural rubber (NR) is obtained from the *Hevea brasiliensis* or rubber trees. Latex is the cytoplasm of lactifiers or specialised cells in the rubber tree. Lactifiers are damaged during tapping or removing of the bark, causing the latex to flow out. When the latex is exposed to air, it will coagulate and can be processed into NR. Coagulation of latex is the aggregation of rubber particles, which is a defence mechanism in rubber trees against pathogens (Gidrol *et al.*, 1994).

Rubber suspension in latex are polyisoprene that can vary from 20-60 % of the total wet weight of latex (Martin, 1991), which needs to be coagulated to obtain the rubber. NR is involved in industries such as biomedical, tire, shoes, mattress, and adhesives (Okoma *et al.*, 2011). NR latex has several properties that make it useful

such as elasticity, high mechanical strength, impermeable to liquid, high flexibility, low heat build up, and resilience (Mantello *et al.*, 2012; Riyajan and Sukhlaaied, 2013). On the other hand, the downsides of NR cannot be ignored, such as sensitive to chemicals and solvents, low flame resistance, and difficult to degrade (Riyajan and Sukhlaaied, 2013).

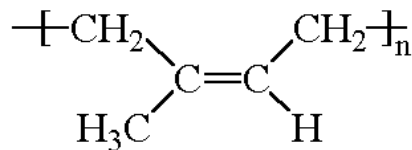


Figure 2.2: Chemical structure of polyisoprene in natural rubber latex.

2.5.2 Rubber Seed Kernel (RSK)

RSK comes from the seed released from the rubber trees. They are generally unneeded in the rubber plantations that they can be considered as agro-waste. RSK can be found by cracking open inside the hard and rigid shell of rubber seeds. The composition of RSK is shown in Table 2.1, whilst Table 2.2 tabulates the cellulosic components present in RSK.

Table 2.1. Composition of rubber seed kernel (Eka *et al.*, 2010).

| Component | Value |
|--------------------------------------|--------------|
| Moisture (%) | 3.99 ± 0.01 |
| Protein (g/100g) | 17.41 ± 0.01 |
| Fat (g/100g) | 68.53 ± 0.04 |
| Ash (g/100g) | 3.08 ± 0.01 |
| Total carbohydrate (% by difference) | 6.99 |

Table 2.2. Cellulose contents of rubber seed kernel (Hassan *et al.*, 2013).

| Biomass (%) | Value |
|---------------|-------|
| Extractives | 3.6 |
| Hemicellulose | 26.9 |
| Cellulose | 69.5 |

RSK is mostly chased for its oil that is mainly researched for biodiesel lubricant. This is a concern regarding the environment, where mineral resources for petroleum fuels are depleting, which shifted interest to find bio lubricants from natural resources (Kamalakar *et al.*, 2013; Gimbun *et al.*, 2013). This is because vegetable oil possesses higher viscosity, lubricant characteristics such as antiwear, antifriction, load carrying capacity, low temperature properties, and high flash points (Kamalakar *et al.*, 2013). Dried RSK contains 35-45 % of oil or fatty acids, which is nearly half of its total composition, in which, when extracted, reflects to around 20 million litres of oil annually that can be used as lubricants or potential biodiesel (Fadeyibi and Osunde, 2012; Asuquo *et al.*, 2012; Setapar *et al.*, 2013; Gimbun *et al.*, 2013). However, the oil content in rubber seed varies with origins or countries (Ikwuagwu *et al.*, 2000).



Plate 2.1: Rubber seed kernel.

Rubber seed oil has also been used mostly in laundry soap, foaming agent in latex foam, production of fat liquor for leather tanning and grease preparation; and alkyd resin synthesis for paints and anticorrosive coatings and adhesives (Ebewele *et al.*, 2010; Asuquo *et al.*, 2012; Salimon and Abdullah, 2009; Yang *et al.*, 2011). The oil in rubber seed is also capable as plasticiser and activator in NR and SBR (Salimon and Abdullah, 2009). The potential use of rubber seed oil as plasticiser is

emphasized by Joseph *et al.* (2003) in a study for acrylonitrile butadiene rubber, which resulted in comparable properties with dioctyl phthalate (DOP) plasticiser.

To date, there are no researches or literature regarding the use of RSK as natural filler in polymer composites.

2.6 Filler-Matrix Interfaces

The behaviour of composites can be predicted and depends on the types of reinforcement, the polymer matrix itself, and the interaction between filler and matrix at the interface. Excellent and optimum mechanical properties can be attained with strong filler-matrix interfacial adhesion (Pickering, 2008). Interfacial adhesion can be enhanced by chemical reaction between the two phases (Thomas *et al.*, 2012). Strength the interface is highly dependable on the formation of bonds between the filler and matrix phases (Simonsen *et al.*, 1997). Enhancing the interfacial adhesion is mostly important and useful when it comes to polymer composites intending to incorporate natural fillers. This is due to the fact that hydrophilic and polar natural filler is incompatible with hydrophobic polymer matrix. The difference in polarities between polymer matrix and natural fillers (Simonsen *et al.*, 1997) causes incompatibility between these two phases that can lead to catastrophic mechanical properties due to poor stress transfer (Akil *et al.*, 2011; Aji *et al.*, 2009; Simonsen *et al.*, 1997).

2.6.1 Compatibiliser

Compatibiliser is used essentially to increase interfacial adhesion effectiveness between hydrophilic fillers containing cellulosic components and hydrophobic matrix (Pickering, 2008; Aji *et al.*, 2009). The technique requires

compatibiliser to be grafted with polymers, reducing the hydrophilic characteristic of natural filler, allowing the filler to be wetted by the polymer matrix, thus promoting interfacial bonding. Another method is by using coupling agents having two reactive functional groups to form covalent bond, one used to interact with the natural filler, while the other with the polymer (Aji *et al.*, 2009).

2.6.1(a) Maleic Anhydride (MAH)

Maleic anhydride (MAH) is a type of compatibiliser that has the ability to form ester linkage between the anhydride group and the hydroxyl group present in the cellulosic components of natural filler, consequently reducing the hydrophilicity of the natural filler (Sobczak *et al.*, 2012). Grafting the polymer matrix with MAH in polymer composites incorporated with natural fillers is able to increase the tensile strength and Young's modulus of the composites. The formation of ester linkages seemed to reduce polarity of cellulosic components in the natural fillers and improve wetting of natural fillers by the polymer matrix. In addition, using MAH also improves the processing properties of composites by reacting with the natural filler's hydroxyl groups, interfering with intermolecular hydrogen bonds between the natural filler, resulting in better filler dispersion among the polymer matrix (Pickering, 2008).

Maldas and Kokta (1991) did a study on the influence of peroxide on high impact polystyrene composites filled with hardwood aspen wood flour utilising MAH as the coupling agent. They discovered that surface modification by MAH gave positive impact on mechanical properties of the composites. A study by Mishra and Patil (2003) summarized that MAH reacted with free hydroxyl groups in cane

bagasse pith to form ester linkages, contributing to improved tensile strength of melamine-formaldehyde-resin composites.

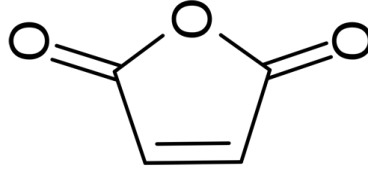


Figure 2.3: Chemical structure of maleic anhydride (MAH).

2.6.2 Filler Modification

Filler modification is also a type of compatibilisation that acts to increase interfacial adhesion between immiscible or incompatible filler and matrix. Filler modification can tremendously change the physical interaction between incompatible filler and matrix, thus altering the final properties of composites positively (Syzdek *et al.*, 2010).

A study by Popov *et al.* (1984) demonstrated essential changes of the physicomechanical properties of PVC composites when the mineral fillers is modified with polymers by grafting through polymerizing monomers on the surface of the fillers. In quite a different research by Riyajan and Sukhlaied (2013), epoxidized natural rubber (ENR) was modified with chitosan in latex form, which revealed good thermal resistance. Another investigation by Potts *et al.* (2013) by modifying thermally-exfoliated graphite oxide (TEGO) with NR latex gave better TEGO dispersion and showed impressive improvement in the mechanical properties of TEGO/NR nanocomposites. Liu *et al.* (2008) modified starch paste (MST) with polybutylacrylate to be used as reinforcing filler in NR latex as the polymer matrix. The MST proved to reinforce mechanical properties, namely tensile strength, elongation at break, tear strength, modulus, and hardness compared to unmodified

paste. This is mostly achieved due to uniform starch dispersion and strong interaction at the interface in the NR/MST composites.

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Materials

All materials used for this research is listed in Table 3.1. Apart from RSK and RSS, which were further processed from rubber seeds prior to mixing, all other materials were used as received.

Table 3.1: List of materials used.

| Materials | Purpose | Grade/Trade name | Supplier |
|----------------------------|----------------|----------------------------------|-------------------------|
| Recycled Polystyrene (RPS) | Matrix | rePS-5 | Total Petrochemicals |
| Virgin Polystyrene (VPS) | Matrix | PS 536 | Total Petrochemicals |
| Rubber Seed | Filler | - | - |
| Maleic Anhydride (MAH) | Compatibiliser | - | Sigma Aldrich |
| Natural Rubber Latex | Modifier | High ammonia (HA) natural rubber | Lee Latex (Pte) Limited |

3.1.1 Recycled Polystyrene (RPS)

RPS resin used in this research was obtained from Total Petrochemicals Malaysia Sdn. Bhd. As a recycled material, the standard properties of RPS vary due to thermal and mechanical shearing history. The melt flow index of RPS is 6.29 g/10 min (200°C/5kg) and measured according do ASTM D1238.

3.1.2 Virgin Polystyrene (VPS)

VPS resin was acquired from Total Petrochemicals Malaysia Sdn. Bhd. The melt flow index of VPS is 2.77 g/10 min (200°C/5kg) and measured according to ASTM D1238.

3.1.3 Rubber Seeds

Rubber seeds were collected in rubber plantations in Pasir Puteh, Kelantan state in Malaysia. They are considered as waste in this region.

3.1.4 Maleic Anhydride (MAH)

MAH was used in this study as a compatibiliser and supplied by Aldrich Chemicals Company Inc., in the form of white flakes. MAH is capable of reducing the polarity of natural filler, hence increase filler-matrix interaction.

3.1.5 Natural Rubber Latex

Natural rubber (NR) high ammonia (HA) latex used in this study was supplied by Lee Latex (Pte) Limited, Malaysia as a filler modifier. The Total Solid Content (TSC) of the latex was determined and confirmed to be at the value of 61%. The NR latex was used directly as received without any modification and additives other than the presence of ammonia.

3.2 Preparation of Fillers

3.2.1 Rubber Seed Kernel Powder (RSKP)

Rubber seed kernels were separated manually by using a rubberised hammer. The kernels were mechanically ground into flour using a mini grinder from Rong Tsong Precision Technology Co. The resulting RSKP was dried in an oven at 100°C for 24 hours prior to use to rid off moisture.

3.3 Preparation of Composites

3.3.1 RPS/RSKP Composites

The composition in weight percent (wt%), and mixing sequence used to study the effect of RSKP loading on the properties of RPS/RSKP composites is shown in Table 3.2.

Table 3.2: Composition and mixing sequence of RPS/RSKP composites with different RSKP loading

| Time (minutes) | Sequence of Mixing | Composition (wt%) |
|----------------|--------------------|---------------------|
| 0 | RPS | 100, 99, 97, 95, 90 |
| 4 | RSKP | 0, 1, 3, 5, 10 |
| 8 | Discharge | - |

3.3.2 VPS/RSKP Composites

The composition in weight percent (wt%), and mixing sequence used to study the effect of RSKP loading on the properties of VPS/RSKP composites is shown in Table 3.3.