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PREPARATION OF INJECTION-MOLDED POLYPROPYLENE/ RECLAIMED

บดคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์และปีการศึกษา 2554 อยู่ในคลังปัญญาจุฬาฯ (CUIR)

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Thesis Title

PREPARATION OF INJECTION-MOLDED POLYPROPYLENE/

Miss Sunaree Sribunruang

A Thesis Submitted in Partial Fulfillment of the Requirements  
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Faculty of Science  
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RECLAIMED TIRE RUBBER/SAWDUST BLENDS

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 Field of Study Petrochemistry and Polymer Science  
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สุนารี ศรีบุญเรือง: การเตรียมเบลนด์ของพอลิโพรพิลีน/ยางรถยนต์รีไซเคิล/ขี้เลื่อยที่ขึ้นรูปแบบฉีด (PREPARATION OF INJECTION-MOLDED POLYPROPYLENE/RECLAIMED TIRE RUBBER/SAWDUST BLENDS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.ศุภวรรณ ตันตยานนท์, 81 หน้า.

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v

# # 5272593223 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: INJECTION-MOLDED/RECLAIMED TIRE RUBBER/BLENDS

SUNAREE SRIBUNRUANG: PREPARATION OF INJECTION-MOLDED  
POLYPROPYLENE/RECLAIMED TIRE RUBBER/SAWDUST BLENDS.

ADVISOR: ASST. PROF. SUPAWAN TANTAYANON, Ph.D., 81 pp.

The blends of polypropylene (PP) / reclaimed tire rubber (RTR) /sawdust were prepared by injection molding vulcanized using sulphur system or maleic anhydride polypropylene (MAPP) system. The RTR and sawdust content were varied from 0% to 30% by weight, while PP content was kept constant at 70% by weight. The effect of blend ratio, properties on impact strength, tensile strength, water absorption, thickness swelling, accelerator weathering, swelling ratio and morphology of polypropylene (PP) / reclaimed tire rubber /sawdust blends were investigated. The properties of blends with maleic anhydride polypropylene system show slightly higher tensile strength and impact strength than composites with sulfur system. It evidenced that a maleic anhydride polypropylene improved the mechanical behavior of the blend. This causes an increase in interfacial adhesion. It was formed that physical and mechanical properties of all the blends with the same vulcanized using sulphur system and maleic anhydride polypropylene (MAPP) system before and after accelerator weathering that was similar, except the impact strength. The phase structure and miscibility of polypropylene (PP) / reclaimed tire rubber (RTR) /sawdust were assessed by scanning electron microscopy (SEM).

Field of Study : Petrochemistry and Polymer Science

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Student's Signature .....

Advisor's Signature .....

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### LIST OF ABBREVIATIONS

PP	Polypropylene
HDPE	High density polyethylene
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
EPDM	Ethylene-propylene-diene monomer
RTR	Reclaimed tire rubber
GRT	Ground rubber tire
MAPP	Maleic anhydride graft polypropylene
TMTD	Tetramethylthiuramdisulphide

MBT	3-mercaptopbenzothiazole
ZnO	Zinc oxide
SEM	Scanning Electron Microscopy
Wl	Weight loss
Wg	Weight gain

## CHAPTER I

### INTRODUCTION

#### 1.1 Introduction

Global warming is a major environmental problem nowadays. The main concern for its cause is the use of the huge amount of synthetic plastics. One of the methods to reduce the amount of synthetic plastics is to add natural material into plastic. Natural fibers are one of natural materials which have been increasingly used as alternative fillers in polymer composites. The polymer–sawdust fibre composites utilize sawdust fibres as a reinforcing filler in the polymer matrix and are known to be advantageous

over the neat polymers in terms of the materials cost and some mechanical properties such as stiffness and strength. The advantages of polymer composites from natural fibers besides the environmental concern (environmental friendly and biodegradability) are low cost, less tool wear during processing and low density [1-6].

Nowadays, waste tire rubber is large scale discarding of rubber products. It has caused a severe environmental problem. Recycle of waste tire rubber represents a great challenge in both environmental and economic reasons. The oldest method of recycling used, i.e., reclaiming and retreating, has been employed for many years although it has recently become less common for passenger tires in developed countries. Another strategy is to use as energy source by heating. Both incineration and pyrolysis methods are possible for large volumes of recycling. Major problems exist, however, with the avoidance of air pollution and expensive initial investment cost being major factors. A further, potentially attractive method is the utilization of powdered rubber. The rubber part can be ground to small particles, known as ground rubber tire (GRT) and can further be devulcanized to become reclaimed tire rubber (RTR) which is in powder form. There are a number of reports on the use of GRT as filler in thermoplastics such as, LDPE, LLDPE, HDPE, PVC [7-17].

Among natural fibers used in polymer composite, sawdust rubber is one of the interesting candidates. Sawdust rubber is a waste bio-material obtained from sawmill and wood processing industries. The specific properties of this natural product, namely low cost, lightweight, renewable character, high specific strength and modulus, availability in a variety of forms throughout the world, reactive surface and the possibility to generate energy, without residue, after burning at the end of their life-cycle, motivate their association with organic polymers to elaborate composite materials [18].

Polypropylene (PP) has been used in various applications for human daily life owing to its low density, excellent thermal and mechanical properties and good process ability with its appropriate price. But its toughness, strength and stiffness are not sufficient for applications as an engineering plastic [19].

In previous studied, using RTR, having a non-cross-linked rubber structure, as filler should be a more effective choice to impart elastic property to the

thermoplastics. In previous studied the dynamic vulcanization of RTR and PP blends, and found that sulphur vulcanization blend of 30/70 RTR/PP had higher impact strength than that of GRT/PP blend and of PP alone [20]. Bledzki et al. [21]. studied the wood fibre reinforced polypropylene composites of different fibre content (40, 50 and 60% by weight) have been prepared and wood fibres (hard and long fibre) were treated with compatibiliser (MAH-PP) to increase the interfacial adhesion with the matrix to improve the dispersion of the particles and to decrease the water sorption properties of the final composite. Results indicated that impact properties were affected by moisture content. The Charpy impact strength decreased and maximum force was increased with increasing of moisture content. In polyolefin composites functionalized polymers, usually maleated polypropylene (MAPP) or polyethylene (MAPE), are added to the composite during homogenization in order to improve interfacial adhesion and prevent deboning under the loading of the product. Maleic anhydride groups react chemically with the (–OH) groups of the wood flour and improve interfacial adhesion.

Thus in this research, polypropylene (PP)/reclaimed tired rubber (RTR)/sawdust are an interesting abundant composite material. The purpose of this research work involves the preparation of polypropylene (PP)/reclaimed tired rubber (RTR)/sawdust blends at various ratios using a injection molding for mixing. The compatibilizer and dynamic vulcanizing agents by using sulphur system and maleic anhydride polypropylene (MAPP) system were used to improve physical properties and mechanical properties.

## 1.2 Objectives

The objectives of this research are as follows:

1. To prepare injection-molded polypropylene/reclaimed tire rubber/sawdust blends.
2. To improve impact strength and tensile strength of reclaimed tire rubber/polypropylene /reclaimed tire rubber/sawdust blends by using different type of vulcanizing agents.

### **1.3 Scope of work**

- Reviews related previously published research.
- Design and prepare experimental procedure.
- Prepare the injection-molded polypropylene/reclaimed tire rubber/sawdust blends by using sulphur system and maleic anhydride polypropylene (MAPP) system.
- Study the mechanical properties of injection-molded PP/RTR/Sawdust blends.
- Study other properties of injection-molded PP/RTR/Sawdust blends.
- Compare the properties of injection-molded PP/RTR/Sawdust blends by using sulphur system and maleic anhydride polypropylene (MAPP) system.
- Analyze data and summarize the results

## **CHAPTER II**

### **THEORY AND LITERATURE REVIEWS**

#### **2.1 Preparation of composites Blends by injection moulding**

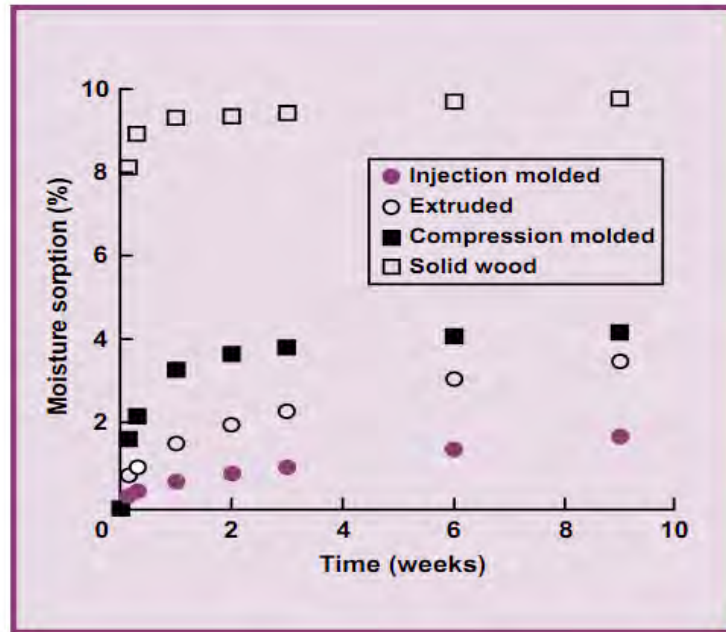
##### **2.1.1 Injection molding**

Composite materials are multiphase materials obtained from the artificial combination between different materials in order to achieve properties that the individual components by themselves. Composites were contain wood and thermosets or thermoplastics. Thermosets are plastics that, once cured, cannot be melted by reheating. These are include resins such as epoxies and phenolics. Thermoplastics are plastics that can be repeatedly melted such as polyethylene and polyvinyl chloride (PVC).

Other processing technologies such as injection molding and compression molding are also used to produce Wood Plastic Composites (WPCs), but the total pound



age is much less than what is produced with extrusion. These alternative processing methods have advantages when processing of a continuous piece is not desired or a more complicated shape is needed. Composite formulation must be adjusted to meet processing requirements (e.g., the low viscosity needed for injection moulding can limit wood content). The wide variety of WPCs makes it difficult to discuss the performance of these composites. Performance depends on the inherent properties of the constituent materials, interactions between these materials, processing, product design, and service environment. Moreover, new technologies are continuing to improve performance. General comments regarding performance can be made, but there are exceptions. Adding wood to unfilled plastic can greatly stiffen the plastic but often makes it more brittle. Most commercial WPC products are considerably less stiff than solid wood. Adding fibres rather than flour increases mechanical properties such as strength, elongation, and unnotched Izod impact energy. However, processing difficulties, such as feeding and metering low bulk density fibers, have limited the use of fibers in WPCs. Because WPCs absorb less moisture and do so more slowly than solid wood (Figure 2.1).



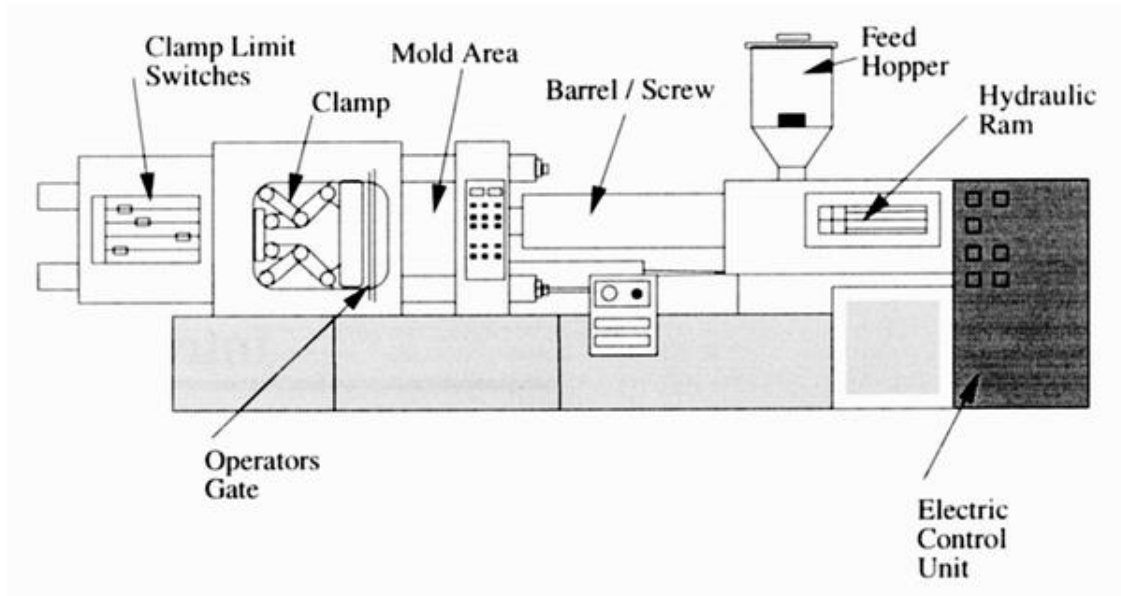
**Figure 2.1**  
Moisture sorption of solid high-density

polyethylene containing 50 percent wood flour processed by various methods. Conditions (80°F) and 65 percent relative humidity [22].

Thus in this research, an interested processing technologies injection moulding, Because WPCs absorb less moisture and do so more slowly than solid wood.

Injection moulding is one of the most common processes used to produce plastic parts. It is a cyclic process of rapid mould filling followed by cooling and ejection. A variety of materials both plastic and non-plastic can be used as feedstock. However, the machine must be configured for the type of material used. The material, which is generally available as grains or powder, is plasticised in an injection unit and injected into a clamped mould under high pressure (500-1500 bar). The main advantage of injection moulding is that it is a very economical method of mass production. Ready parts with tight tolerances can be produced in one step, often completely automatically. In general after-processing is not necessary. It is also possible to integrate different functions into one part to avoid the formation of different components that would be more expensive, e.g., the base of a typewriter with integrated guidance and fixing elements, the springy components of a printer element, a lens with integrated prisma to stop down a beam of light. To guarantee a high quality in the injection moulded parts the following points have to be considered. The material has to be plasticised and injected carefully to avoid negative effects on the material

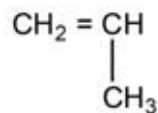
properties. The process settings (such as pressures and temperatures) concerning the machine and mould have to remain constant with regard to time and space. The basic parts that make up a machine are shown in Figure 2.2



**Figure 2.2** Basic components of an injection moulding machine [23].

## 2.2 Polypropylene (PP)

Polypropylene (PP) was first produced by G. Natta, following the work of K. Ziegler, by the polymerisation of propylene monomer in 1954 (Figure 2.8). The macromolecule of PP contains 10,000 to 20,000 monomer units. The steric arrangement of the methyl groups attached to every second carbon atom in the chain may vary. If all the methyl groups are on the same side of the winding spiral chain molecule, the product is referred to as isotactic PP. A PP structure where pendant methylene groups are attached to the polymer backbone chain in an alternating manner is known as syndiotactic PP. The structure where pendant groups are located in a random manner on the polymer backbone is the atactic form.



**Figure 2.3** Polypropylene monomer forms.

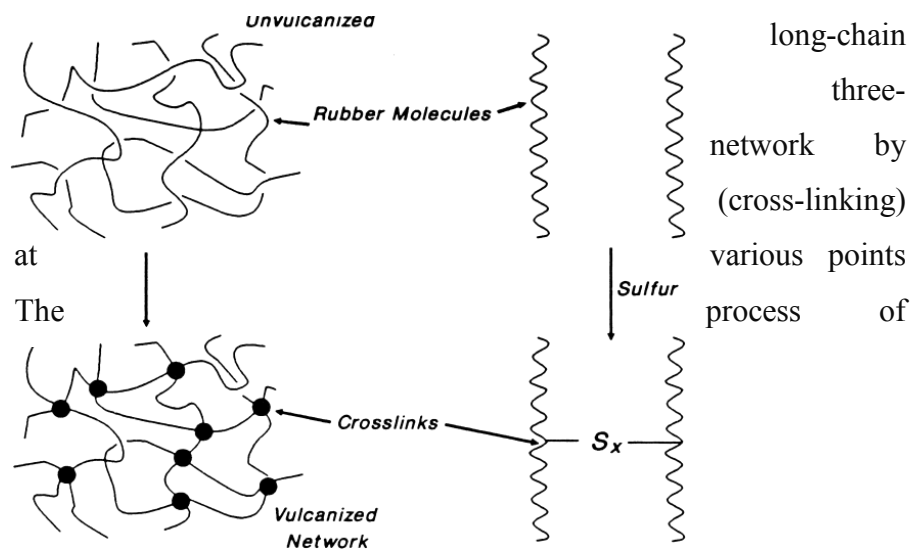
Polymers are generally accepted that crystalline polymers have superior impact properties to amorphous ones, The way the atoms are arranged in the polymer molecule has a great influence on the properties of a polymer component. This order is named the tacticity and with polypropylene there are two different arrangements commonly available isotactic and atactic. The degree of tacticity determines the level of crystallisation possible. Atactic polymers are those with side groups placed in a random order. Atactic PP with nonuniformly arranged methyl groups has a density of  $0.94 \text{ g/cm}^3$ . Isotactic polymers are those whose side groups are all on the same side. Isotactic polypropylene has a density of  $0.90 \text{ g/cm}^3$ . There are also copolymers with ethylene, to increase impact resistance below  $0^\circ\text{C}$ . [19]

### 2.3 Reclaimed Tired Rubber

The oldest method of recycling used, i.e., reclaiming and retreating, has been employed for many years although it has recently become less common for passenger tires in developed countries. Another strategy is to use as energy source by heating. Both incineration and pyrolysis methods are possible for large volumes of recycling. Major problems exist, however, with the avoidance of air pollution and expensive initial investment cost being major factors. A further, potentially attractive method is the utilization of powdered rubber. Rubber powder obtained from grinding tires can be classified as “crumb rubber”. The rubber part can be ground to small particles, known as ground rubber tire (GRT) and can further be devulcanized to become reclaimed tire rubber (RTR) which is in powder. The production of reclaim is a complicated physio-chemical process. Reclaimed tire rubber starts with bringing products to cut and grind to a powder with a grinder. Which is mainly used tires into how the blades rotating at high speed. Later, it will be additive to softeners and reclaiming chemicals and then into heat. Reclaimed after the procedure. Rubber will be depolymerization change from state to preserve vulcanized to restore the original state. Rubber (cross-linking) 3-D structure will be destroyed. Tires will have lower molecular weight. Change from state to preserve (vulcanized) to restore the original state [24].

### 2.4 Vulcanization

Vulcanization is the process of treating an elastomer with a chemical to decrease its plasticity, tackiness, and sensitivity to heat and cold and to give it useful properties such as elasticity, strength and stability. Ultimately, this process chemically converts thermoplastic elastomer into three-dimensional elastic networks. This process converts a viscous entanglement of molecules into a dimensional elastic chemically joining these molecules at along the chain. The process of



vulcanization is depicted graphically in Figure 2.4 In this diagram, the polymer chains are represented by the lines and the cross-links by the black circles [25]

**Figure 2.4** The formation of a cross-linked network [25].

The vulcanization occurred by a free radical reaction initiated with accelerator. The accelerator has an-S-N-bond for which the dissociation energy is 35 kcal/mol, that can be easily dissociated by the heat of vulcanization process over 140 °C to produce-S and N-radicals. These radicals attack elemental sulfur with comparatively weak bonds rather than rubber chains to generate a sulfur radical, -Sx. The sulfur radicals attack allylic and benzylic hydrogens in the rubber to make crosslinks. This is simply explained by comparison of the related bond dissociation energies of sulfur, and allylic and benzylic hydrogens are 54, 77, and 77.5 kcal/mol, respectively. Hereafter, in referring to allylic hydrogen we mean allylic and benzylic hydrogen because they have nearly the same dissociation energy. Because it is easier to thermally split the lower energy bond, the accelerator first initiates sulfur radicals that react with rubber molecules successively. An accelerator can be activated by zinc stearate that is produced from stearic acid and zinc oxide by heat during the mixing process and forms a complex with the accelerator complex forms a higher active complex with sulfur that provides a polysulfide link to the rubber molecule. This polysulfide reacts further to form mono-,di-, and cyclic sulfide bonds during vulcanization via dissociation, recombination, and rearrangement of the sulfur linkages. These various types of the sulfur linkages affect the rubber properties and tire

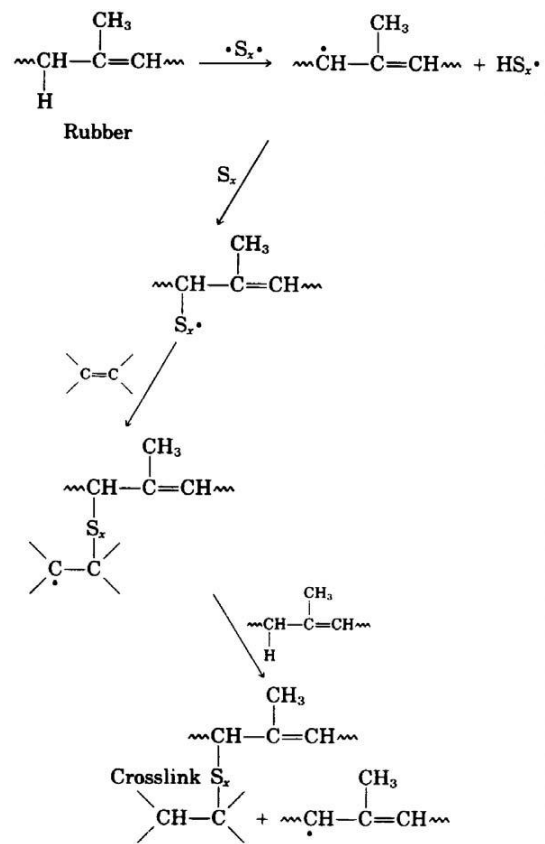
performance. In addition, the comparison between raw natural rubber and vulcanized natural rubber are summarized in Table 2.1

**Table 2.1** Comparison between raw natural rubber and vulcanized natural rubber [26].

<b>Raw Natural Rubber</b>	<b>Vulcanized Natural Rubber</b>
Soft and sticky	Comparatively hard and non-sticky
Low tensile strength and not very strong	High tensile strength and very strong
Low elasticity	High elasticity
Can be used over a narrow range of temperature from 10 to 60 degrees centigrade	Can be used over a wide range of temperature from -40 to 100 degrees centigrade
Low abrasion resistance	High abrasion resistance
Absorbs a large amount of water	Absorbs a small amount of water
Soluble in solvents like ether, carbon disulfide, carbon tetrachloride, and petrol	Insoluble in all the usual solvents

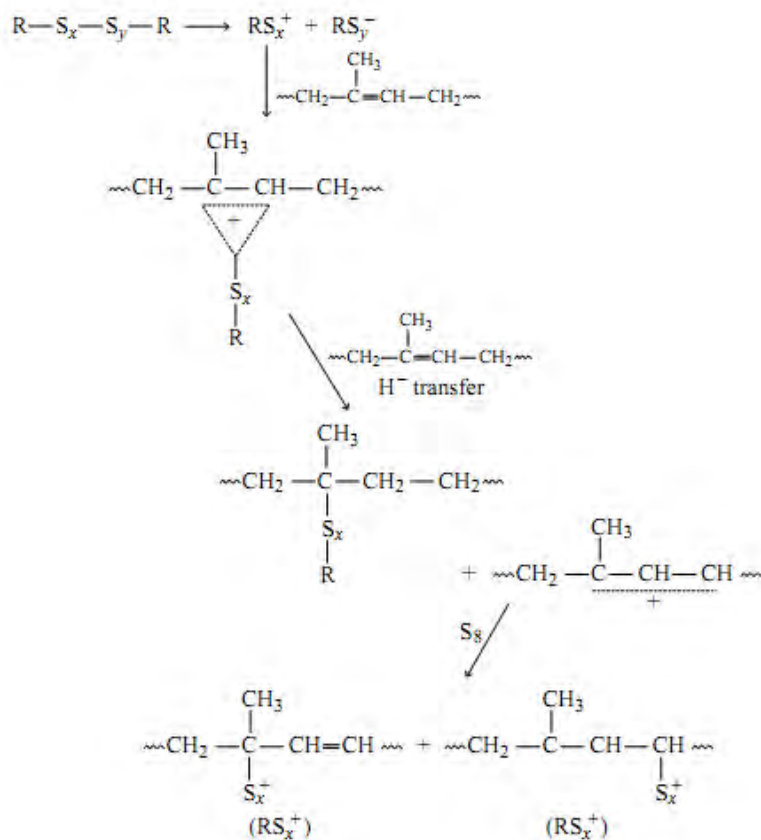
## 2.5 Sulfur Vulcanization and Acceleration

Initially, vulcanization was accomplished by using elemental sulfur at a concentration of 8 parts per 100 parts of rubber (phr). It required 5 hours at 140 °C. The addition of zinc oxide reduced the time to 3 hours. The use of accelerators in concentrations as low as 0.5 phr has since reduced the time to as short as 1 to 3 minutes. As a result, elastomer vulcanization by sulfur without accelerator is no longer of much commercial significance. (An exception to this is the use of about 30 or more phr of sulfur, with little or no accelerator, to produce molded products of hard rubber or “ebonite.”) Even though unaccelerated sulfur vulcanization is not of commercial significance, its chemistry has been the object of much research and study. The chemistry of unaccelerated vulcanization is controversial. Many slow reactions occur over the long period of vulcanization. Some investigators have felt that the mechanisms involved free radicals as illustrated in Scheme 2.1 [27]:



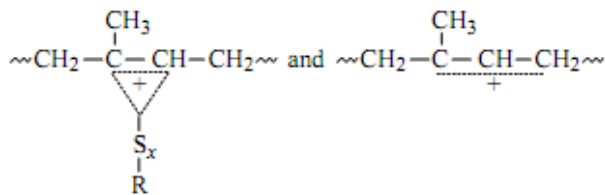
**Scheme 2.1** Mechanism of unaccelerated sulfur vulcanization of rubber.

Other investigators have promoted ionic mechanisms Scheme 2.2 [27].



**Scheme 2.2** Mechanism of unaccelerated sulfur vulcanization of rubber [27].

The intermediates,



were proposed in Scheme 2.2 to explain the fact that model compound reactions gave both unsaturated and saturated products, sulfur atoms being connected to both secondary and tertiary carbon atoms.

Although vulcanization takes place by heat and pressure in the presence of sulfur, the process is relatively slow, inefficient process. A faster process is normally achieved by the addition of small amounts of chemicals known as accelerators. For this reason over a century of research efforts have been directed toward the development of materials to improve the



efficiency of this process. The activators, accelerators, and retarders are associated with the sulfur vulcanization of polydienes, e.g. NR, as shown in Table 2.4

Zinc oxide is the most commonly used activator in both sulphur and sulphur donor vulcanisation. In addition to zinc oxide, magnesium oxide is often employed in the vulcanisation of CR. Lead oxide is an effective activator for sulphur vulcanisation but it is expensive and toxic, therefore seldom used. As an activator of vulcanisation, zinc oxide requires the presence of fatty acids, thereby converting the zinc into a rubber soluble form. Stearic acid is the most commonly used fatty acid but can be replaced by lauric acid. The latter, being more soluble in elastomers, provides more bloom resistance. Oleic acid is not recommended as it negatively affects the ageing properties of the vulcanisate. Fatty acids also provide enhanced compound processing characteristics together with improved dispersion of fillers and chemicals.

Vulcanisation retarders and inhibitors have been used in rubber compounds for many years as a means of increasing processing safety. A vulcanisation retarder increases scorch time, thereby improving processing safety, but also slows down the rate of vulcanisation. This reduced rate of vulcanisation, however, is often an undesirable effect. True vulcanisation inhibitors, on the other hand, increase scorch safety whilst having no adverse effect on the rate of vulcanization [27-29].

**Table 2.2** Classification of accelerators [28].

Class	Response speed
Mercapto-accelerators: 2-Mercaptobenzothiazole (MBT) Dibenzothiazyl disulfide (MBTS)	Semi-fast
Sulfenamide-accelerators: N-cyclohexyl-2-benzothiazylsulfenamide(CBS) N,N-dicyclohexyl-2-benzothiazylsulfenamide (DCBS)	Fast, delayed action
Thiuram-accelerators: Tetramethythyuram monosulfide (TMTM) Tetramehythyuram disulfide (TMTD)	Very fast
Dithiocabamate-accelerators: Zinc dimethyldithiocarbamate (ZDMC) Zinc dibutyldithiocarbamate (ZDBC)	Very fast
Guanidine-accelerators: Diphenylguanidine (DPG)	

Di-o-tolylguanidine (DOTG)	Medium
Sulfur donors: 2-Benzothiazole-N-morpholyldisulfide (MBSS)	-
Vulcanization retarders: Benzoic acid (BES) Salicylic acid (SCS) , Phtalic anhydride (PTA)	-

## 2.6 Sawdust rubber

Among natural fibers used in polymer composite, sawdust rubber is one of the interesting candidates. Sawdust rubber is a waste bio-material obtained from sawmill and wood processing industries. The specific properties of this natural product, namely low cost, lightweight, renewable character, high specific strength and modulus, availability in a variety of forms throughout the world, reactive surface and the possibility to generate energy, without residue, after burning at the end of their life-cycle, motivate their association with organic polymers to elaborate composite materials . Wood flour is a finely ground, dried wood product fibrous in structure, which acts as a reinforcing material polymer. Rubber wood flour is made from rubber sawdust, chips and shavings by grinding in a burrstone mill, and has the appearance of wheat flour. Particle sizes commonly used for polymer fillers are 40, 60 and 80 mesh, with sizes as fine as 140 mesh available [18].

The main components of wood are structural components. The structural components are cellulose, hemicelluloses and lignin, together with smaller amounts of pectic substances. For softwood and hardwood in general, the contents of the main components vary in the ranges shown in Table 2.3 Polysaccharides represent the major part of both wood types. In natural fillers, cellulose is the main component. The elementary unit of cellulose macromolecule is anhydro-d-glucose, which contains three hydroxyls (-OH). These hydroxyls form hydrogen bonds inside the macromolecule itself (intra-molecular) and also with hydroxyl groups from moist air which can be as high as 3-13% [30]. One of the common problems in using natural fillers in composites is the poor interface between the filler and the polymer matrix.

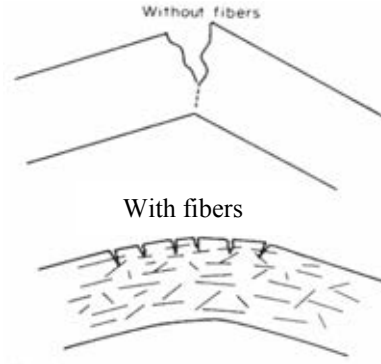
**Table 2.3** Contents of the main components, % of dry wood [31].

	Cellulose	Glucomannan	Xylan	Other polysaccharide	Lignin
Softwood	33-42	14-20	5-11	3-9	27-32
Hardwood	38-51	1-4	14-30	2-4	21-31

Cellulose fibers are derived from plant fibers by mechanical and chemical treatment to break up fiber bundles and remove some of the lignin or other compounds which may be present. All plant fibers are composed principally of cellulose, but the other materials present, and the structure and properties of the purified fibers, will depend upon the vegetable source used. Commonly used fibers are produced from wood, cotton or other plant sources. Cellulose fibers of high purity are readily made from cotton fiber by boiling with sodium hydroxide solution, neutralization with acetic acid, and prolonged washing with distilled water. Over the past decade there has been a growing interest in the use of lignocellulosic fibres as reinforcing elements in polymeric matrix. The specific properties of this natural product, namely low cost, lightweight, renewable character, high specific strength and modulus, availability in a variety of forms throughout the world, reactive surface and the possibility to generate energy, without residue, after burning at the end of their life-cycle, motivate their association with organic polymers to elaborate composite materials. Figure 2.5 shows a crack passing through a brittle material may not enter the fibers but leaves a crack straddled by fibers so that a material that would normally have broken with a single crack now has to be cracked in a large number of places before the fibers themselves fail or pull out. This is used in fiber-reinforced cement, which is based on the same principles as reinforced concrete, but since the fibers are very much finer than reinforcing bars and are often not visible to the naked eye, a homogeneous material is effectively produced that can show quasiplastic deformation.

Without fibers

Without fibers



**Figure 2.5** Demonstration of how cracks are prevented from running in a brittle material because of fibers in their path [31]

## 2.7 Maleic Anhydride Graft Polypropylene Process

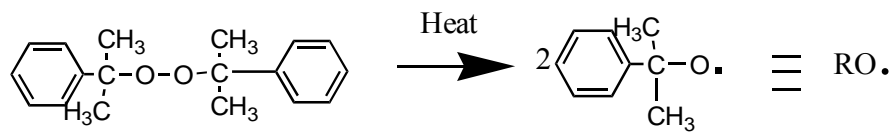
By reactive injection low-cost commercially available polymers such as PE, PP or PS can be converted into materials with tailor-made properties of increased value. They are upgraded by chemical reactions during processing. Injection act simultaneously as conventional polymer processing machinery and as pressure vessels for chemical synthesis in highly viscous media. Unlike organic chemistry, where the final product very often is obtained by multi-step synthesis, reactive injection requires high-yield one-step synthesis with very short reaction times. Only volatile unreacted monomers [e.g. maleic anhydride (MA)] and by-products can be removed in the venting section. Additional purification and separation processes are uneconomical.

The modification of conventional reactor polypropylene, usually having a relatively high molecular weight (MW) and broad molecular weight distribution (MWD), in an injection through the action of peroxides is a well-established method nowadays. In this so-called controlled rheology polypropylene, random chain scission reactions reduce MW and narrow MWD, thus reducing viscosity and elasticity. This type of PP shows improved processing characteristics for specialized applications (e.g. lower melt processing temperatures and higher speeds in melt spinning of very thin fibers). Controlled degradation at elevated temperatures leads to low-molecular waxes. By reactive injection

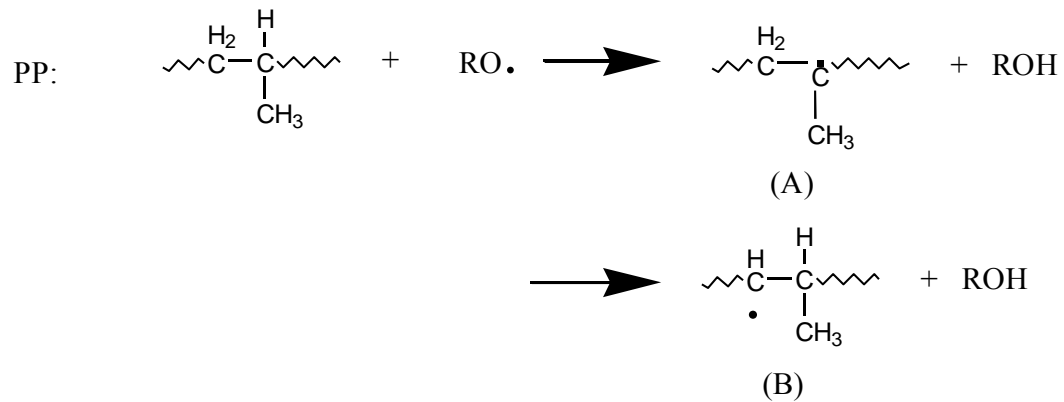
with monomers such as maleic anhydride (MA) polar functional groups are covalently bonded to the PP matrix.

The crosslink between PP and RTR by the corporation reaction of MAPP as follows;

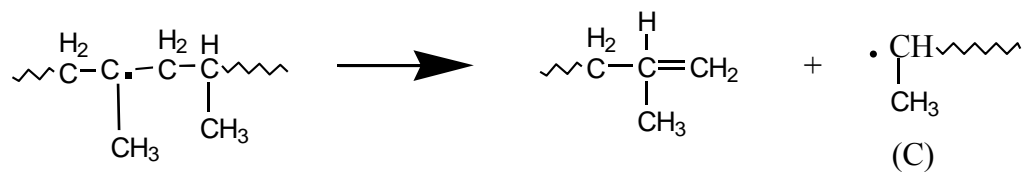
### Initial Decomposition of DCP



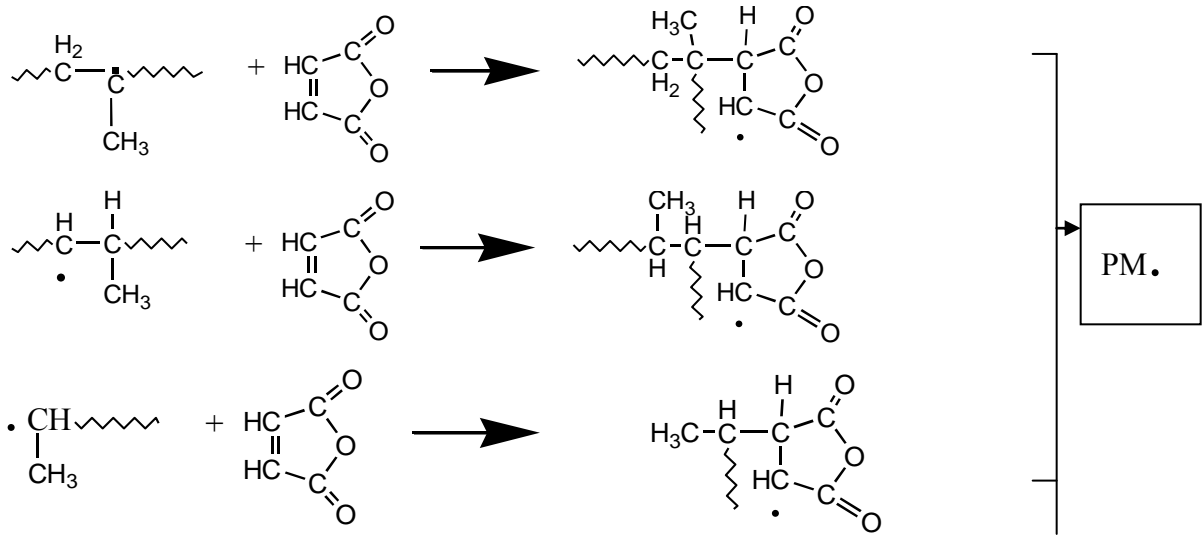
### H-abstraction



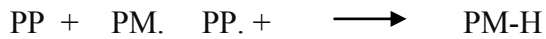
### Beta-scission of PP



### Anhydride grafting

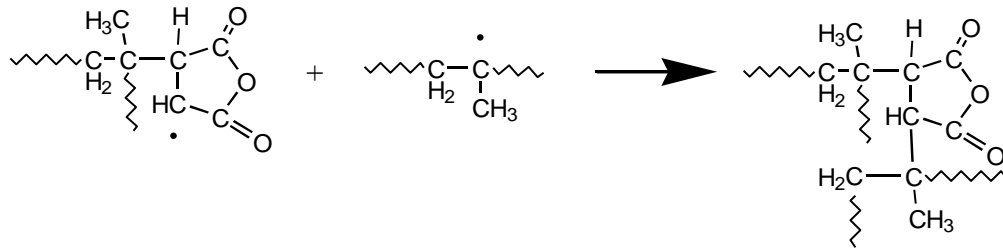


### Chain transfer

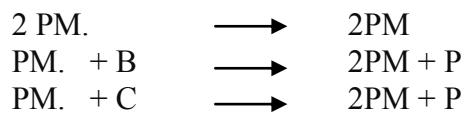


### Termination

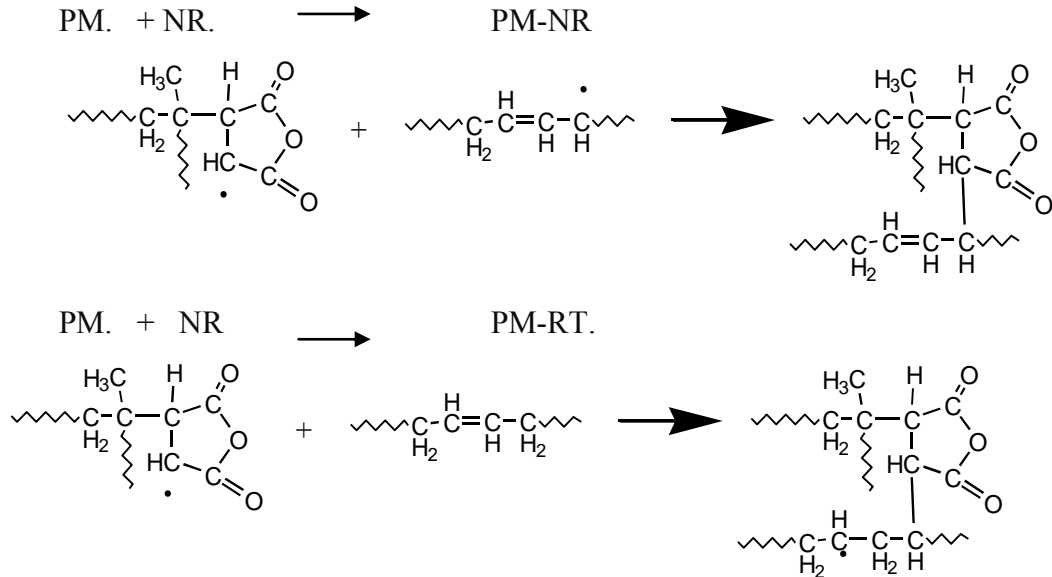
- Termination via combination of PP-PP



- Termination via disproportionation of PP-PP



- Termination via disproportionation of PP-Rubber



**Scheme 2.3** The crosslink between PP and RTR by the corporation reaction of MAPP.

## 2.8 Properties of Blends Prepared by Dynamic Vulcanization

Dynamic vulcanization is the process of vulcanizing elastomer during its intimate melt mixing with a nonvulcanizing thermoplastic polymer. Small elastomer droplets are vulcanized to give a particulate vulcanized elastomer phase of stable domain morphology during melt processing and subsequently. The effect of the dynamic vulcanization of elastomer-plastic blends is to produce compositions that have improvements in permanent set, ultimate mechanical properties, fatigue resistance, hot oil resistance, high temperature utility, melt strength and thermoplastic fabricability. Permanent set of these compositions can be improved by only slight or partial vulcanization of the elastomer before mixing with plastic or by dynamic vulcanization (during mixing with plastic). However, the other improvements can be obtained only by dynamic vulcanization in which the elastomer is technologically fully vulcanized. The term fully vulcanized refers to a state of cure such that the crosslink density is at least  $7 \times 10^{-5}$  mol per milliliter of elastomer (determined by swelling) or that the elastomer is less than about 3% extractable by cyclohexane at  $23^\circ\text{C}$  [44,56].

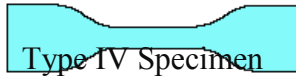
## 2.9 Characterization Techniques

### 2.9.1 Measuring Tensile Strength

Tensile strength measurement was performed on dumbbell specimens at ambient temperature according to ASTM D 638-96 Standard Test Method for Tensile Properties of plastic, Type I test specimens using universal testing machine (UTM)



Type I, II, III, and V Specimen



Type IV Specimen

**Figure 2.6** Specimen Tensile Tester [33].

**Table 2.4** Specimen Tensile Tester Summary [33].

Specimen	Rigidity Case	Note	Thickness
Type I	Rigid	Preferred specimen.	<7 mm (0.28 in)
Type II	Rigid	Use when Type I specimen does not break in the narrow section.	<7 mm (0.28 in)
Type III	Rigid/Nonrigid	-	>7 mm (0.28 in) <14 mm (0.55 in)
Type IV	Rigid/Nonrigid	Should be used for	<4 mm (0.16 in)



		comparison between materials in different rigidity cases. Essentially the same as Die C specimen from ASTM D412.	
Type V	Rigid	Used when limited material is available or laboratory space is a concern (for environmental testing)	<4 mm (0.16 in)

**Table 2.5** Specimen Tensile Tester Summary [34].

Property	Definition
Tensile Elongation at Break	Tensile elongation corresponding to the point of rupture.
Tensile Elongation at Yield	Tensile elongation corresponding to the yield (an increase in strain does not result in an increase in stress).
Tensile Strength at Break	Tensile stress corresponding to the point of rupture.
Tensile Strength at Yield	Tensile stress corresponding to the yield point (an increase in strain does not result in an increase in stress).
Tensile Strength	Tensile stress at a specified elongation.

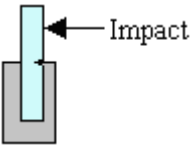
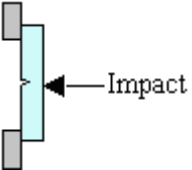
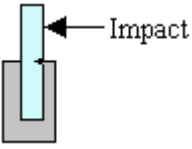
Tensile Strength, Ultimate	The highest tensile stress a material can support before failing.
Tensile Modulus	The ratio of tensile stress to tensile strain of a material in the elastic region of a stress-strain curve. A "Tangent" tensile modulus value is the slope of the elastic region of the stress-strain curve and is also known as Young's Modulus, or the Modulus of Elasticity. A "Secant" tensile modulus value is the slope of a line connecting the point of zero strain to a point on the stress-strain curve at a specified strain. This is used for materials that exhibit little or no linear behavior.

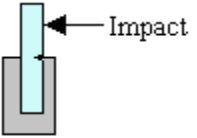
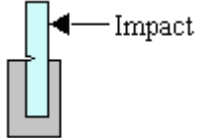
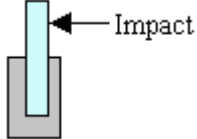
### 2.9.2 Measuring Impact Strength

Charpy Impact tester is a single point test that measures a materials resistance to impact from a swinging pendulum. Charpy impact is defined as the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. Charpy Impact specimens are notched to prevent deformation of the specimen upon impact. This test can be used as a quick and easy quality control check to determine if a material meets specific impact properties or to compare materials for general toughness.

The specimen is clamped into the pendulum impact test fixture with the notched side facing the striking edge of the pendulum. The pendulum is released and allowed to strike through the specimen. If breakage does not occur, a heavier hammer is used until failure occurs. Since many materials (especially thermoplastics) exhibit lower impact strength at reduced temperatures, it is sometimes appropriate to test materials at temperatures that simulate the intended end use environment [35].

**Table 2.6** Type Izod Impact Strength ASTM D256 [35].

	Name	Test Description	Diagram
A	Notched Izod Impact Strength	Specimen is held as a vertical cantilevered beam and is broken by a pendulum. Impact occurs on the notched side of the specimen.	
B	Charpy Impact Strength	Specimen is held as a simply supported beam and is impacted on the side opposite the notch. This method is no longer covered under ASTM D256 but is still reported as such.	
C	Estimated Net Izod Impact Strength	This method is the same as Method A except that the energy required to toss the broken portion of the specimen is included in the energy calculation. Preferred over Method A for materials with impact strength below 27 J/m (0.5 ft-lb/in)	

D	Notch Radius Sensitivity Test	<p>Provides an indication of notch sensitivity. Notch sensitivity is calculated using:</p> $b = (E_2 - E_1) / (R_2 - R_1)$ <p>where b is the notch sensitivity, E<sub>1</sub> and E<sub>2</sub> are the energy required to break a small and large radius notched specimen, and R<sub>1</sub> and R<sub>2</sub> are the radii of the small and large radius notches. Units are J/m/mm of notch radius.</p>	 <p>The diagram shows a light blue rectangular specimen with a notch on its top surface. It is held in a grey support. An arrow labeled 'Impact' points to the right, hitting the specimen on the side opposite to the notch.</p>
E	Reversed Notched Izod Impact Strength	<p>Same test as Method A except the specimen is impacted on the side opposite the notch.</p>	 <p>The diagram shows a light blue rectangular specimen with a notch on its top surface. It is held in a grey support. An arrow labeled 'Impact' points to the right, hitting the specimen on the side opposite to the notch.</p>
F	Unnotched Izod Impact Strength	<p>Unnotched specimen is held as a vertical cantilevered beam and is broken by a pendulum. This method is covered under ASTM D4812 but is commonly reported under ASTM D256.</p>	 <p>The diagram shows a light blue rectangular specimen held in a grey support. An arrow labeled 'Impact' points to the right, hitting the specimen on its side.</p>

## 2.10 Literature Reviews

Ruksakulpiwat et al. [6] In this research, vetiver grass was used as a filler in polypropylene (PP) composite. Chemical treatment was done to modify fiber surface. Natural rubber (NR) and Ethylene Propylene Diene Monomer (EPDM) rubber at various contents were used as an impact modifier for the composites. The composites were

prepared by using an injection molding. Rheological, morphological and mechanical properties of PP and PP composites with and without NR or EPDM were studied. Adding NR or EPDM to PP composites, a significant increase in the impact strength and elongation at break is observed in the PP composite with rubber content more than 20% by weight. However, the tensile strength and Young's modulus of the PP composites decrease with increasing rubber contents. Nevertheless, the tensile strength and Young's modulus of the composites with rubber contents up to 10% are still higher than those of PP. Moreover, comparisons between NR and EPDM rubber on the mechanical properties of the PP composites were elucidated. The PP composites with EPDM rubber show slightly higher tensile strength and impact strength than the PP composites with NR.

Punnarak and Tantayanon [36] studied the dynamic vulcanization of reclaimed tire rubber (RTR) and HDPE blends. The effect of blend ratio, methods of vulcanization, i.e. sulphur, peroxide, and mixed system and the addition of compatibilizer on mechanical, thermal, and rheological properties were investigated. The blend with highest impact strength was obtained from 50/50 RTR/HDPE vulcanized by sulphur. Increasing the RTR content to more than 50% resulted in a decrease in the impact strength of blend, most likely due to the increasing carbon black content. For tensile strength, the presence of rubber and carbon black, however, unavoidably caused a drop in this property. Comparing among three methods of vulcanization, sulphur system seems to be the most effective method. Results from solvent swelling ratio, glass transition temperatures and viscosity indicated that the sulphur vulcanization created the highest degree of cross-link and filler-matrix interaction in the RTR/HDPE blend. Morphology of the blends was also assessed by scanning electron microscopy (SEM).

Tantayanon and Juikham [37] studied the dynamic vulcanization of reclaimed tire rubber (RTR) and homopolypropylene (PP) by using a sulfur crosslinking agent, maleic anhydride (MA), dicumyl peroxide (DCP), or the combination of MA and DCP. They found that the RTR/PP blend with sulfur crosslink agent had the highest impact strength at the ratio of 30/70. This could be attributed to the limitation of carbon black in the blend.

When the combination of MA and DCP was applied, the result was higher impact strength of the blend at the same ratio. This could be attributed to not only the cohesion between the polymer chains in each phase, PP phase and rubber phase, but also the interfacial adhesion between PP and RTR chains in these two phase. For comparison, the GRT/PP blends with and without sulfur crosslinking agent were prepared as well. All these blends showed low impact strength, which was nearly the same as that of PP. It can be concluded that RTR plays an important role in toughening of PP by thorough dispersion into the PP matrix. Furthermore, during dynamic vulcanization by MA/DCP, the crosslinked rubber phase become finer and is uniformly distributed in the PP matrix thus attaining a stable morphology.

Rajalingam et al. [38] investigated the effect of GRT characteristics on toughness of LLDPE/ GRT composites. They found that the wet ambient ground GRT based composites show higher surface oxidation and gave better impact energy than cryo-ground and normal air ground GRT based composites. Smaller GRT particle size results in a small increase in the impact property of the composite and a greater influence on the melt processability of the composites. Of the different GRT surface modification techniques studies for improved composite interfacial adhesion and impact properties the composites from electron beam radiation treated GRT yield higher increases in impact energy in comparison to corona and plasma treated GRT based composites.

Ismail et al. [39] The effects of dynamic crosslinking on mechanical properties, water absorption and morphology of rubber wood filled polypropylene (PP)/natural rubber (NR) blends were studied. The blends were prepared at 180°C using a rotor speed of 50 rpm for 12 min. Sulfur concentration was steadily increased from 0 to 2.0 (wt%) in order to study the vulcanization effect. It was found that dynamic crosslinking has enhanced the tensile strength, stress-at-peak, Young's modulus, flexural modulus and stabilization torque (at the end of the mixing stage) of the rubberwood-filled PP/NR blends. This has been attributed to the increase in crosslink density which was indicated by a reduction of weight gain (water absorption) and weight loss of the blends with increasing sulfur concentration.

Ismail and Suryadiansyah. [40] Fine rubber powder obtained from the sanding process of polishing rubber balls and artificial eggs (recycled rubber, RR) was used to prepare polypropylene (PP)/RR blends, a thermoplastic elastomer using different RR content. A similar series of blends using natural rubber, SMR L (NR) was also prepared. The results indicated that at a similar rubber content, PP/RR blends have higher, tensile strength and Young's modulus but lower elongation at break and stabilization torque than PP/NR blends. Scanning electron microscopy (SEM) examination of the tensile fracture surface of PP/RR blends indicates that a higher energy is needed to cause catastrophic failure compared to PP/NR blends.

Xin et al. [41] Microcellular polypropylene/waste ground rubber tire powder blend processing was performed on an injection-molding machine with a chemical foaming agent. The molded samples produced based on the design of experiments (DOE) matrices were subjected to tensile testing and scanning electron microscope (SEM) analyses. Molding conditions and waste ground rubber tire (WGRT) powder have been found to have profound effects on the cell structures and mechanical properties of polypropylene (PP) and waste ground rubber tire powder composite samples. The result shows that microcellular PP/WGRT blend samples exhibit smaller cell size and higher cell density compare with polypropylene resin. Among the molding parameters studied, chemical foaming agent weight percentage has the most significant effect on cell size, cell density, and tensile strength. The results also suggest that tensile strength of microcellular PP/WGRT composites is sensitive to weight reduction, and skin thickness.

Kuo et al. [42] The objective of this study was to investigate the effects of material compositions on the mechanical properties of wood-plastic composites (WPCs) manufactured by injection molding. Using a ratio of wood flour/plastic matrix/MAPP (maleic anhydride polypropylene)/zinc stearate of 47:47:3:3, the tensile strength and modulus of rupture (MOR) of WPCs manufactured with LDPE (low-density polyethylene) and PP (polypropylene) were found to be larger than those of LDPE and PP themselves. However, contrasting findings were obtained when the polymer matrix was ABS

(acrylonitrile-butadiene-styrene). In comparison to the mechanical properties of RPP (recycled polypropylene) itself, the MOR increased and the tensile strength decreased for WPCs manufactured with RPP. The tensile strength, MOR, and storage modulus of WPCs made from PP mixed with 47% wood flours (<180  $\mu\text{m}$ ) and 3–4.5% MAPP were larger than those of the other WPCs manufactured in this study. However, the polymer damping peaks showed a contrary result.

Radheshkumar et al. [43] investigated the use of thermo mechanically reclaimed GRT composed of LDPE, fresh rubber (SBR or NR or EPDM). During blending dynamic curing was achieved using sulphuric, phenolic, and peroxide curing agents. They found sulphuric and phenolic curing agents proved to be most suitable for dynamic curing. Thermoplastic vulcanizates with the best mechanical performance contained SBR and EPDM rubber. The observed improvement in mechanical performance were attributed to chain entanglement and co-crosslinking in the interphase.

Bledzki et al. [21] studied the wood fibre reinforced polypropylene composites of different fibre content (40, 50 and 60% by weight) have been prepared and wood fibres (hard and long fibre) were treated with compatibiliser (MAH-PP) to increase the interfacial adhesion with the matrix to improve the dispersion of the particles and to decrease the water sorption properties of the final composite. Results indicated that impact properties were affected by moisture content. The Charpy impact strength decreased and maximum force was increased with increasing of moisture content. With the addition of MAH-PP (5% relative to the wood fibre content), damping index decreased around 145% for hard wood fibre–PP composites at 60 wt.% wood fibre content. Long wood fibre–PP composites showed more impact resistance than hard wood fibre–PP composites. Short term flexural creep tests were conducted to investigate the creep behaviour of wood fibre–PP composites. Three experimental parameters were selected: the addition of compatibiliser, temperature and wood fibre content. The addition of MAH-PP, increased creep modulus that means reduced the creep. The extent of creep resistance (creep modulus and creep strength)



decreased with increasing temperature. It was also found that wood fibre content has a great effect on creep resistance which is increased with increasing wood fibre content.

## **CHAPTER III EXPERIMENTAL**

### **3.1 Materials**

#### **3.1.1 Polypropylene (PP)**

Polypropylene homopolymer (1100NN) used in this study was of injection molding grade from IRPC Co., Ltd. It had melt flow rate of (2.16 kg/230 °C) and processing temperature 190-240 °C.

**Table 3.1** Specification of Polypropylene homopolymer (Polene 1100NN).

Typical Data	Unit	Value	Test Method
MFI (2.16 kg/230 °C)	g/10 min	11	ASTM D 1238
Tensile strength at yield	N/mm <sup>2</sup>	33	ASTM D 638
Elongation at yield	%	30	ASTM D 638
Charpy notched impact strength at 23 °C	mJ/mm <sup>2</sup>	3	DIN 53453
Flexural modulus (1% Secant)	MPa	1300	ASTM D790

Rockwell hardness	R-Scale	105	ASTM D785
Heat distortion temperature (Load 0.45 N/mm <sup>2</sup> )	°C	95	ASTM D 648

### 3.1.2 Reclaimed Tire Rubber (RTR)

Reclaimed tire rubber (RTR) with particle size distribution of 500-600  $\mu\text{m}$  was purchased from Union Commercial Development Co., Ltd. The RTR comprised of 67.57% rubber, 25.35 % carbon black and 7.08% residue.

**Table 3.2** Specification of Reclaimed Tire Rubber.

Typical Data	Unit	Value	Test Method
Mooney viscosity	ML 1'+4' at100 °C	60	ASTM D 1646
Specific gravity at 25 °C	-	1.14	-
Tensile strength	MPa	6.38	ASTM D 412
Ultimate elongation	%	250	ASTM D 638

### 3.1.3 Sawdust

Sawdust fillers with density of 1.4 g/cm<sup>3</sup> were obtained from rubber wood. Sawdust was prepared into 60 meshes. After that was dried in an oven at 100 °C for 24 hr. from Artowood Co., Ltd.

### 3.1.4 Crosslinking agents

Crosslinking agents and compatibilizer used in this work were obtained from various suppliers as shown in Table 3.3

**Table 3.3** Source of materials.

<b>Materials</b>	<b>Company</b>
Sulfur (S)	Merck
Maleic anhydride polypropylene (MZ203D)	Dupont
2-Mercaptobenzothiazole (MBT)	Fluka
Zinc oxide (ZnO)	Merck
Stearic acid	Fluka
Zinc stearate	Merck
Waxes	Merck
Toluene	Earth Cheme Lab Ltd., Part.

### 3.2 Instruments

- Injection Molding Machine.
- Impact Tester, Gotech.
- Tensile Tester, Universal Testing Machine.
- Scanning Electron Microscope.
- Thickness Swelling, Thickness Gauge.
- Weathering resistance, Weathering test chamber

### 3.3 Experimental Procedure

#### 3.3.1 Blend preparation

Sawdust was prepared into 60 meshes. After that was dried in an oven at 100 °C for 24 hr. The compositions of polypropylene (PP)/reclaimed tire rubber (RTR) /sawdust with sulphur system and additive systems are indicated in Tables 3.4-3.5. The RTR and sawdust content were varied from 0% to 30% by weight, while PP content was kept content at 70% by weight. The mixing temperature was 180 °C and rotor speed was 50 rpm with 15 min of mixing time.

**Table 3.4** Formulation of PP/ RTR/sawdust blends.

Entry	Material (%by weight)			Sulphur system (%by weight)				
	PP	RTR	Sawdust	ZnO <sup>1</sup>	Stearic acid	MBT <sup>2</sup>	TMTD <sup>3</sup>	Sulphur
1	70	0	30	0	0	0	0	0
2	70	5	25	0.25	0.1	0.25	0.075	0.25
3	70	10	20	0.5	0.2	0.5	0.1	0.5
4	70	15	15	0.75	0.3	0.75	0.125	0.75
5	70	20	10	1	0.4	1	0.3	1
6	70	25	5	1.25	0.5	1.25	0.375	1.25
7	70	30	0	1.5	0.6	1.5	0.45	1.5

<sup>1</sup>Zinc oxide (ZnO), <sup>2</sup>2-Mercaptobenzothiazole (MBT),

<sup>3</sup>Tetramethylthiuramdisulfide (TMTD)

**Table 3.5** Formulation of PP / RTR/sawdust blends.

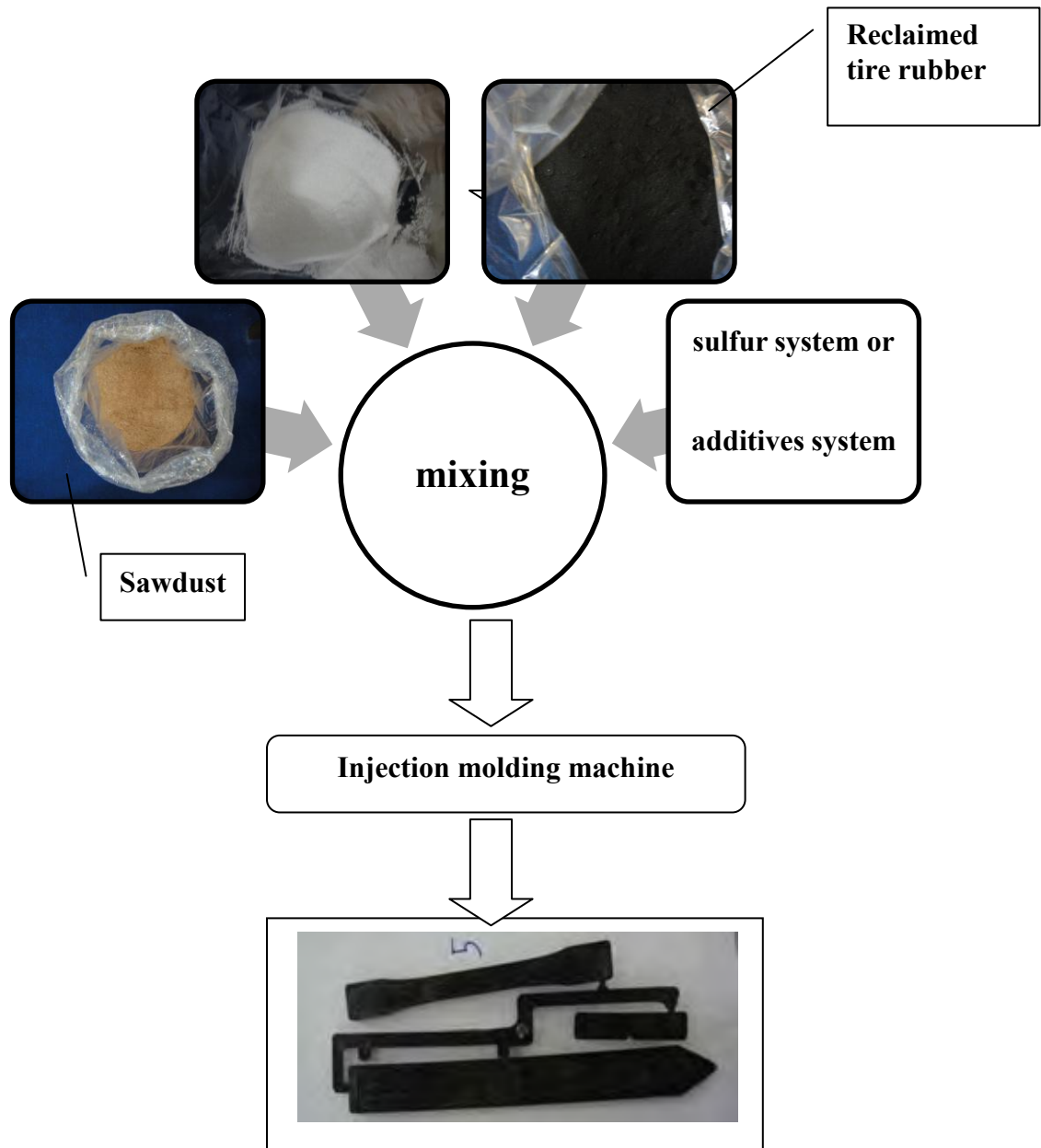
Entry	Material (%by weight)			Additive system (%by weight)		
	PP	RTR	Sawdust	MAPP <sup>1</sup>	Zinc stearate	waxes
8	70	0	30	4	5	1
9	70	5	25	4	5	1
10	70	10	20	4	5	1
11	70	15	15	4	5	1
12	70	20	10	4	5	1
13	70	25	5	4	5	1
14	70	30	0	4	5	1

<sup>11</sup> Maleic anhydride polypropylene

Prepare the injection-molded polypropylene/reclaimed tire rubber/sawdust blends using sulphur system or additive system

**Polypropylene**





### 3.3.2 Measuring Charpy Impact Strength

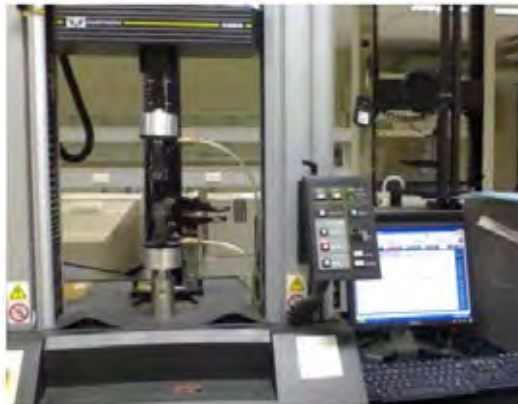
The impact properties were measured according to ASTM D256 or ISO 180. Impact specimens had dimensions of 63.5 mm. by 1.27 cm. by 3 mm. (weight 1.357 kg, maximum capacity 100 kg-cm). The results are reported in Kg-cm/cm<sup>2</sup> notch unit.



**Figure 3.1** Impact Tester, Gotech.

### **3.3.3 Measuring Tensile Strength**

Tensile strength measurement was performed on dumbbell specimens at ambient temperature according to ASTM D 638-96 Standard Test Method for Tensile Properties of plastic, Type I test specimens using universal testing machine (UTM).



**Figure 3.2** Universal testing machine (UTM)

### **3.3.4 Determination Water Absorption**

The PP/RTR/Sawdust blends sample of approximate dimension (2.40 x 22.00 x 0.38 cm<sup>3</sup>) were used for the measurement of water absorption and thickness swelling. The samples were air dried at 70 °C until a constant weight was reached prior to the immersion in static deionized water bath. The specimens were periodically taken out of the water, reweighed and dimensions measured and immediately put back into the water. At least three specimens for each sample were used.

Water absorption test, samples which were immersed in water were then dried for 24 h at room temperature under normal conditions. Weights of the samples were recorded at different times. Samples were wiped with tissue paper to remove surface water before weighing. Finally the weight gain and the weight loss were calculated [19]. Water absorption (i.e. weight gain and weight loss) was determined by the following equation.

#### **3.3.4.1 Weight gain**

Weight gain was determined by the following equation, where  $W_g$  is the percent of weight gain,  $W_e$  the equilibrium weight after water treatment, and  $W_o$  the oven dry weight before water treatment.

$$W_g (\%) = [(W_e - W_o)/W_o] \times 100 \quad (3.1)$$

#### **3.3.4.2 Weight loss**

Samples which were immersed in water were then dried at 70°C for 24 h, after which they were cooled at ambient temperature under normal conditions. Their final weights were taken to determine the weight loss according to the following equation.

$$W_l (\%) = [(W_i - W_o) / W_o] \times 100 \quad (3.2)$$

where  $W_i$  is the oven dry weight after immersion in water,  $W_o$  the oven dry weight before water treatment, and  $W_l$  the percent of weight loss.

#### **3.3.5 Determination Thickness Swelling**

Thickness Swelling (TS) was assessed by measuring the average thickness of each specimen during the immersion tests ( $h_t$ ) and after oven drying ( $h_o$ ), and then calculated using the following equation.

$$TS (\%) = [(h_t - h_o)/h_o] \times 100 \quad (3.3)$$

### 3.3.6 Swelling ratio

Samples were cut into disc approximately 6 cm diameter and 0.3 cm thickness, then weighed accurately before being immersed into toluene. The sample were kept in a dark place for 7 days at room temperature. The swollen sample was then removed from the toluene and the excess toluene was rapidly removed by absorption paper. The swollen weight of the samples had been recorded for the determination of swelling ratio. At least 5 samples for each vulcanizates were tested and the average values were reported. The degree of swelling (Q) was calculated by using the equation.

$$Q (\%) = [(W_2 - W_1) / W_1] \times 100 \quad (3.4)$$

where  $W_1$  is the weight of the dry sample  
 $W_2$  is the weight of the swollen sample.

### 3.3.7 Weathering tests

The composites were the xenon arc test chamber according to ASTM G 155 or ISO 17025 test for 100, 200 minutes. The spectrum emitted by xenon arcs is not a direct match to sunlight. The procedure that calls for a spectrum very close to natural sunlight. The test protocol also uses periodic water sprays to simulate the synergistic effects of sun and rain. Specifically, we normally use a spectral irradiance of 0.35 watts/meter<sup>2</sup>, a black panel temperature of 63°C ( $\pm 2.5^\circ$ ), and an exposure cycle of 102 minutes of light exposure followed by light and water spray for 18 minutes [45-46].





**Figure 3.3** Weathering test chamber

### **3.3.8 Scanning Electron Microscopy (SEM)**

SEM photomicrographs of fractured surface were taken in a scanning electron microscope (SEM) in order to investigate the morphology of various blend systems. The fracture surfaced samples were immersed in liquid nitrogen and gold-coated prior to SEM study.



**Figure 3.4** Scanning Electron Microscopy (SEM)

## **CHAPTER IV RESULTS AND DISCUSSION**

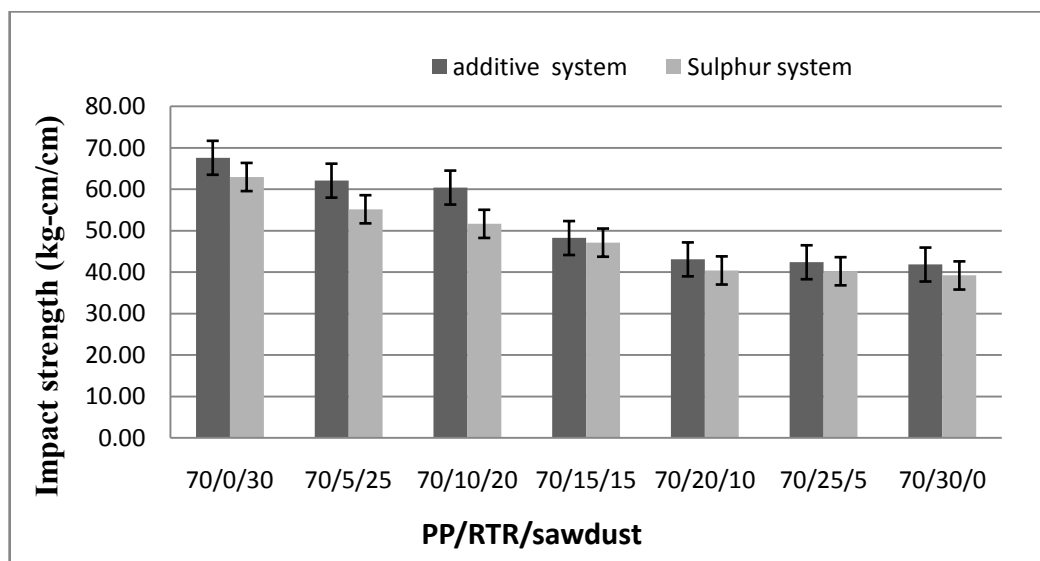
In this research, the blends of polypropylene (PP) / reclaimed tire rubber (RTR) /sawdust were prepared by injection molding vulcanized using sulphur system or additive system. The RTR and sawdust content were varied from 0% to 30% by weight, while PP content was kept constant at 70% by weight. The constituent materials were combined in a mixer according to Tables 3.4-3.5. The mixing speed, temperature, and time were 50 rpm 180 °C and 5 min., respectively. After mixing at given plate condition each blend was injection molded. The measurements mechanical properties of tensile strength and Charpy impact strength were performed in accordance with ASTM D 638-96 (type I) and ASTM D 256. The measurements physical properties of weathering resistant in accordance with ASTM G 155. Solvent swelling study indicates filler-matrix interaction makes the physical bonds at the interface to withstand the shear force. The phase structure and miscibility of polypropylene (PP) / reclaimed tire rubber (RTR) /sawdust were assessed by scanning electron microscopy (SEM).

#### **4.1 Mechanical properties of polypropylene/reclaimed tire rubber/sawdust blends**

##### **4.1.1 Impact strength of polypropylene/reclaimed tire rubber/sawdust blends**

Figure 4.1 shows the PP/RTR/sawdust blends on the impact strength. It is observed that the impact strength of all blends increases with increasing sawdust, the impact strength of all blends decreases with increasing RTR. The component ratio of PP/sawdust (70/30) show slightly higher impact strength than the component ratio of PP/RTR (70/30). The blends of PP/RTR/sawdust (70/30/0) and (70/0/30) samples showed the minimum (41.83) and the maximum (67.6) impact strength with additive system, respectively. The PP/RTR/sawdust (70/30/0) and (70/0/30) samples showed the minimum (39.19) and the maximum (62.96) impact strength vulcanized using sulfur system, respectively. Stark N. [57] studies the properties of composites made from wood-flour-filled PP using ponderosa pine, loblolly pine, oak, and maple at 20,30,40,50, or 60% by weight wood flour. while PP content was kept constant at 60% by weight. Results of tests for notched impact energy increased with increasing wood flour content. However, at around 50% wood flour content,

the notched impact energy for all the species experienced a leveling off or a decline. The blends of PP/RTR/Sawdust with additive exhibits high impact strength than sulphur system, this can be explained that MAPP is a suitable compatibilizer for this blend. Compatibilizer helps reduce the interfacial energy of both phases. This results improved interfacial adhesion and leads to the immiscible blend. Maleic anhydride polypropylene was used as a compativilizer to improve the adhesion between the reinforcements and the matrix material. Punnarak et al. [36] shows that the RTR/HDPE blend with the compatibilizer exhibits the higher impact strength all blends (i.e. sulphur system, Mixed system, peroxide system, and unvulcanization) suggesting that MB226D (maleic anhydride grafted polyethylene) is a suitable compatibilizer for impact strength improvement. The compatibilizer helps to reduce the interfacial energy of RTR and HDPE, resulting in an improvement of the interfacial adhesion between the two phases. Because of Blending MAPP with RTR results in the generation of a compatibilizing agent containing segments of PP and segments of RTR, which can enhance the compatibilization of PP/RTR, two normally incompatible polymers. In the blending process in an injection in the melt the compatibilizing agent becomes located at the interface of the incompatible polymers and a multiphase system is established in which particles of the polymer present in the lower concentration are dispersed through the matrix of the polymer which is present in the higher concentration.

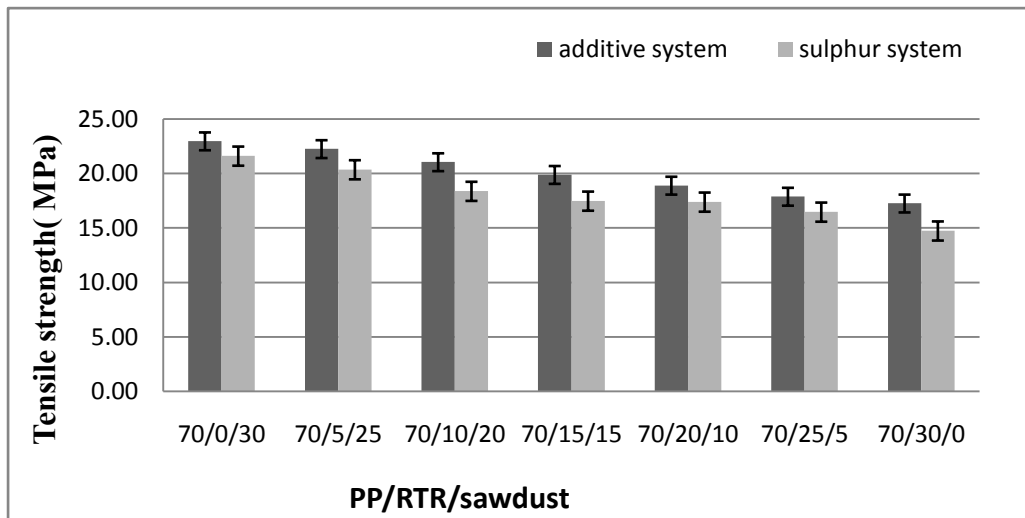


**Figure 4.1** Impact strength of injection-molded polypropylene/reclaimed tire rubber/sawdust blends vulcanized using sulphur system and additive system.

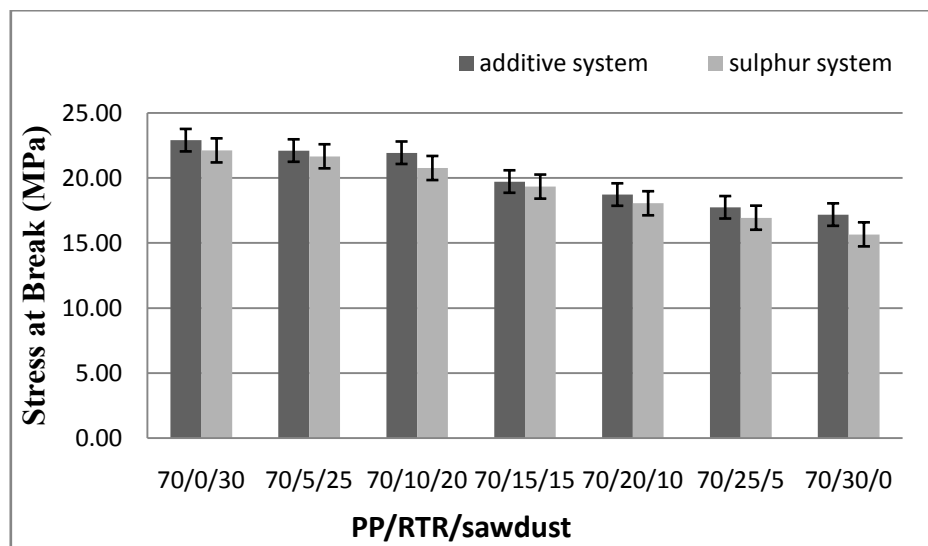
#### **4.1.2 Tensile strength of polypropylene/reclaimed tire rubber/sawdust blends**

Figure 4.2 shows the PP/RTR/sawdust blends on the tensile strength. It is observed that the tensile strength of all blends decreases with increasing RTR. Such a decrease due to the fact that RTR acts as flaws in PP matrix causes an early failure. In addition, this low level of homogeneity, coupled with the presence of carbon black, results in rapid decrease in tensile strength. Carbon black in RTR can basically inhibit the molecular orientations and mobility of both PP and rubber molecule in the blend. This can be explained that the component ratio of PP/sawdust (70/30) show slightly higher tensile strength than the component ratio of PP/RTR (70/30). The blends of PP/RTR/sawdust (70/30/0) and (70/0/30) samples showed the minimum (17.23) and the maximum (22.97) tensile strength with additive system, respectively. The PP/RTR/sawdust (70/30/0) and (70/0/30) samples showed the minimum (14.74) and the maximum (22.96) tensile strength vulcanized using sulfur system, respectively. The tensile strength that additive blend exhibits the higher sulphur system blends. It evidenced that additive system compatibilizer significantly improved the mechanical behavior of the blend. This causes an increase in interfacial adhesion, which increases the impact and tensile strength of the composite. Result for stress-at-break in Figure 4.3 and Young's modulus Figure 4.4 also exhibit a similar trend. Punnarak et al. [36] shows the tensile strength of all the blends. The tensile strength of each blend, either with each of the vulcanization system or with the addition of compatibilizer, decreases with increasing RTR loading and the tensile strength of all the blends well below pure HDPE. Such a decrease due to the fact that RTR acts as flaws in HDPE matrix causes an early failure. In addition, this low level of homogeneity, coupled with the presence of carbon black, results in rapid decrease in tensile strength. Carbon black in RTR can basically inhibit the molecular orientations and mobility of both HDPE and rubber molecule in the blend. Yang H. S. et al. [49] using rice-husk flour as the reinforcing filler and polypropylene as the thermoplastic matrix polymer, shows the tensile strength

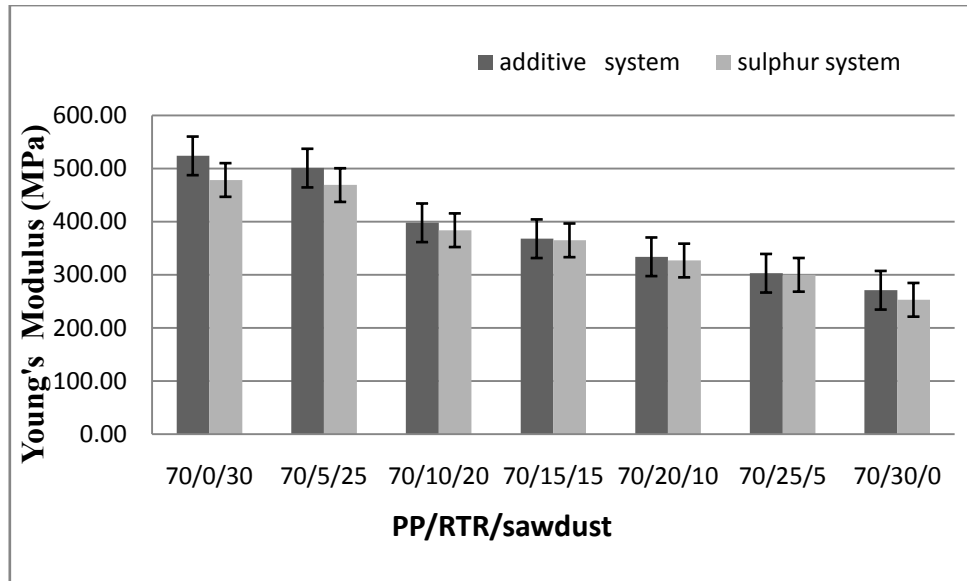
decreased with increasing filler loading due to the poor interfacial bonding between hydrophilic filler and hydrophobic matrix polymer as shown bonding between the hydrophilic filler and the hydrophobic matrix polymer causes decreased tensile strength. To improve the bonding strength between the filler and the matrix polymer, compatibilizing agents were used. With the addition of the compatibilizing agent, tensile strength of the composite significantly improved up to the same level of pure PP.



**Figure 4.2**  
Tensile strength of injection-molded polypropylene/reclaimed tire rubber/ sawdust blends vulcanized using sulphur system and additive system.



**Figure 4.3** Stress at Break of injection-molded polypropylene/reclaimed tire rubber/sawdust blends vulcanized using sulphur system and additive system.



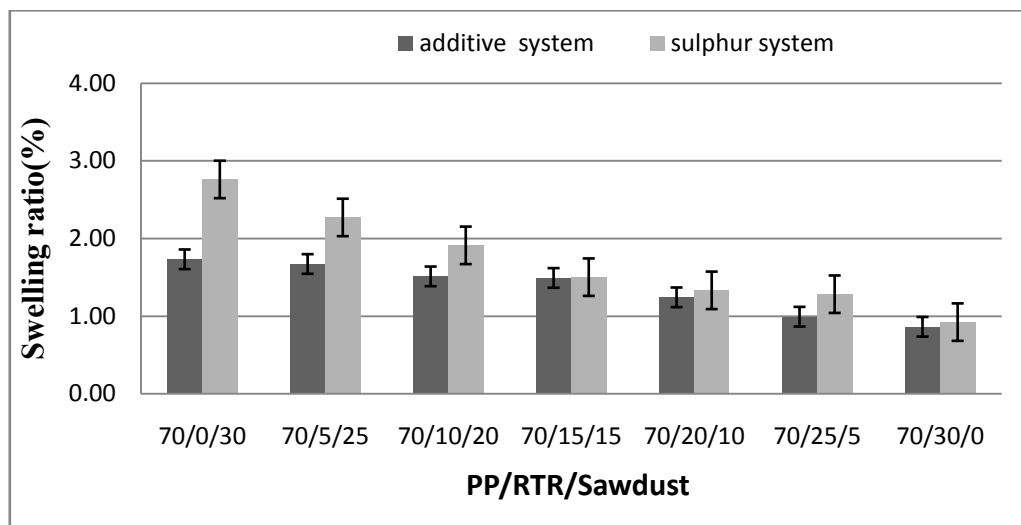
**Figure 4.4** Young's modulus of injection-molded polypropylene/reclaimed tire rubber/sawdust blends vulcanized using sulphur system and additive system.

## 4.2 Physical properties of polypropylene/reclaimed tire rubber/sawdust blends

### 4.2.1 Swelling ratio of polypropylene/reclaimed tire rubber/sawdust blends

The influence of RTR and sawdust addition to the solvent swelling values of the PP in toluene is plotted against the filler contents at room temperature as presented. The results exhibited that the weight of toluene absorbed per gram composite of, The degree of swelling (Q) was calculated by using the equation Q (equation 3.4) for all the vulcanization systems decreased with increasing loading of both type of RTR. As the Q is inversely proportional to the degree of crosslinking, this is the evidence of increment in crosslink density with increasing RTR contents in PP. Moreover, the higher reinforcement of RTR in the PP matrix restricts the extensibility of the composite chains induced by swelling. This

makes difficult for solvent to penetrate into the gaps between rubber molecules and hence decreases the Q value. Generally, the swelling ratio is influenced by various factors, such as crosslink type, amount, type of filler and polymer type [58-60].



**Figure 4.5** Swelling ratio of injection-molded polypropylene/reclaimed tire rubber/sawdust blends vulcanized using sulphur system and additive system.

Figure 4.5 shows results of equilibrium swelling studies of all blends in toluene provide information about the filler-matrix interaction. Swelling ratio increases with increasing sawdust, the swelling ratio of all blends decreases with increasing RTR. This can be explained that the particles RTR (60 mesh) smaller than particles sawdust (40 mesh), the mixing of particles RTR are better than particles. The properties of RTR with vulcanized using sulfur are better than sawdust with sulfur, these results provide a clear indication of the increase in the crosslink density in the PP/RTR blends. As the crosslink density increases within the RTR phases, the blends became more stiff and less penetrable by the solvent molecules. The PP/RTR/sawdust (70/30/0) and (70/0/30) samples showed the minimum (0.86) and the maximum (1.73) swelling ratio vulcanized using additive system, respectively. The PP/RTR/sawdust (70/30/0) and (70/0/30) samples showed the minimum (0.92) and the maximum (2.76) swelling ratio vulcanized using sulfur system, respectively. Swelling ratio of PP/RTR/Sawdust blends with additive system is lower than the blends with sulphur vulcanizing agent. This indicates the properties of MAPP are better than vulcanized rubber with sulfur due to the sawdust enhancing mix ability of PP and RTR.

The hydrophilic nature of sawdust causes the swelling ratio in PP/RTR/sawdust blends. Because of varies sawdust content (0-30 % by weight) in all formulations, the different swelling ratio among all blends can be attributed to the role of MAPP. Figure 4.5 also shows that swelling ratio decreases by adding MAPP. This means that it is the interface region which influences swell ratio of blends. As uncompatibilize sawdust composite has a weak fiber–matrix adhesion by nature, the interface is enhanced in the presence of the compatibilizer. Generally, it is necessary to use compatibilizers in order to improve the polymer–fiber bonding and in turn enhance solvent resistance. The MAPP chemically bonds with the OH groups in the lignocellulosic filler and limits the swelling ratio and thickness swelling of the blends. As a result, it is important to use to improve the quality of adhesion between plastics and fibers, to reduce the gaps in the interfacial region, and to block the hydrophilic groups[48].

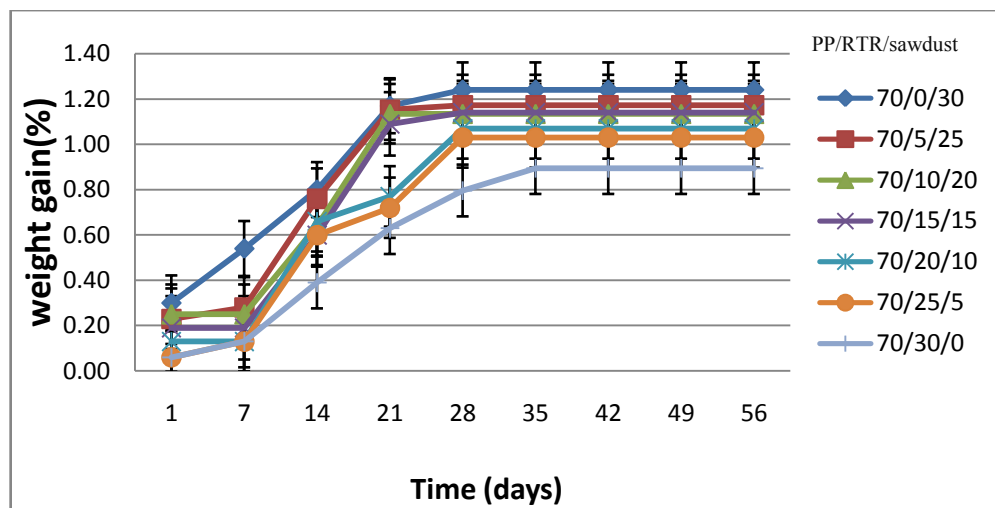
#### **4.2.2 Water Absorption of polypropylene/reclaimed tire rubber/sawdust blends**

Figure 4.6, 4.7 and 4.8 show the effect of PP/RTR/sawdust on the percentage of weight gain (Wg) and weight loss (Wl) vulcanized using sulphur system and additives system blends, results of water absorption studies of all blends in water provide information about the filler-matrix interaction. It can be seen that the percentage of Wg and Wl increase with increasing time, increases with increasing sawdust, the swelling ratio of all blends decreases with increasing RTR. This can be explained that the particles RTR (60 mesh) smaller than particles sawdust (40 mesh), the mixing of particles RTR are better than particles. The properties of RTR with vulcanized using sulfur are better than sawdust with sulfur, these results provide a clear indication of the increase in the crosslink density in the PP/RTR blends. As the crosslink density increases within the RTR phases, the blends became more stiff and less penetrable by the water molecules.

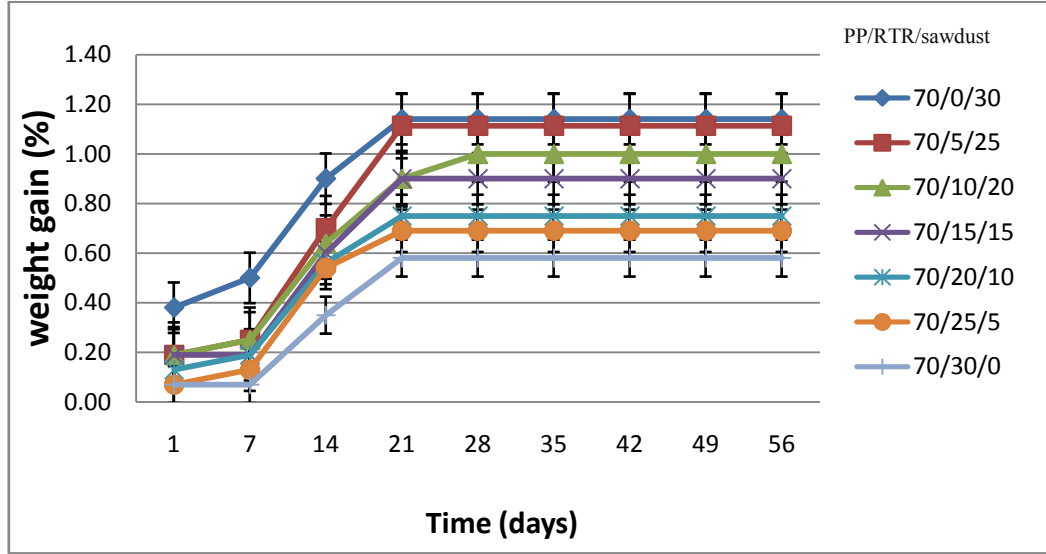
The PP/RTR/sawdust blends (70/30/0) and (70/0/30) samples showed the minimum (0.93) and the maximum (1.24) weight gain vulcanized using sulphur system, respectively. The PP/RTR/sawdust (70/30/0) and (70/0/30) samples showed the minimum (0.58) and the maximum (1.14) weight gain vulcanized using additive system, respectively. The ratio of



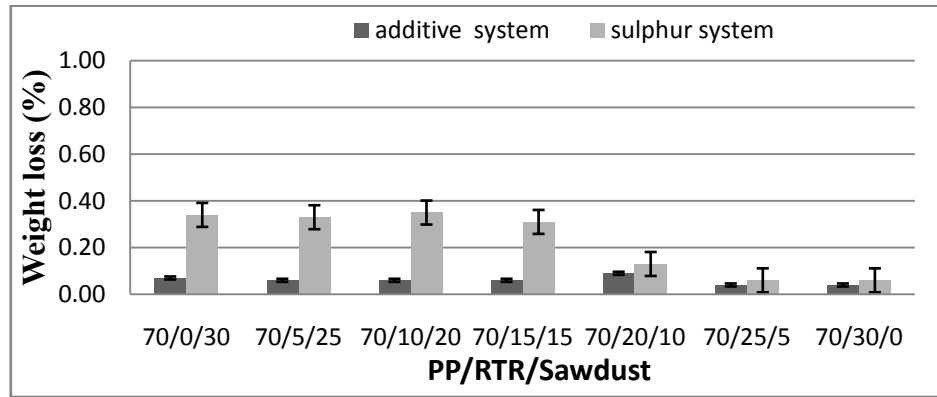
PP/RTR/Sawdust blends with additive system is lower than the blends with sulphur vulcanizing agent. This indicates the properties of MAPP are better than vulcanized rubber with sulfur due to the sawdust enhancing mix ability of PP and RTR. In their work, the effect of sulfur concentration on the weight loss of rubberwood-filled PP/RTR blends. These results provide a clear indication of the increase in the crosslink density in the rubberwood-filled PP/NR blends. As the crosslink density increases within the NR phases, the blends became more stiff and less penetrable by the water molecules. [39] The percentage of water absorption for composites. It can be seen that increasing the sawdust content leads to higher water absorption. However, this value considerably decreases with surface modification of RTR by using additive system.



**Figure 4.6** Weight gain of injection-molded polypropylene/reclaimed tire rubber/ sawdust blends vulcanized using sulphur system.



**Figure 4.7** Weight gain of injection-molded polypropylene/reclaimed tire rubber/ sawdust blends vulcanized using additives system.



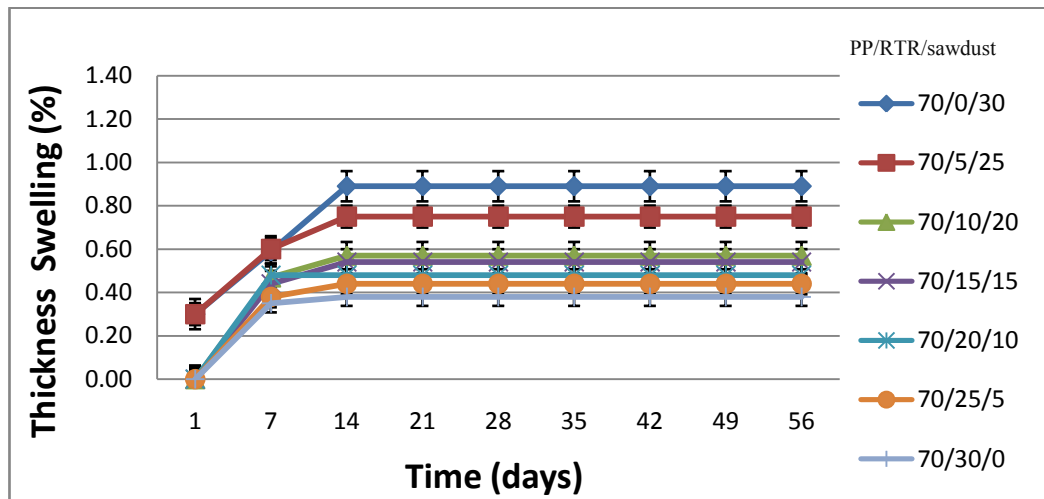
**Figure 4.8** Weight loss of injection-molded polypropylene/reclaimed tire rubber/ sawdust blends vulcanized using sulphur system and additive system.

#### 4.2.3 Thickness Swelling of polypropylene/reclaimed tire rubber/sawdust blends

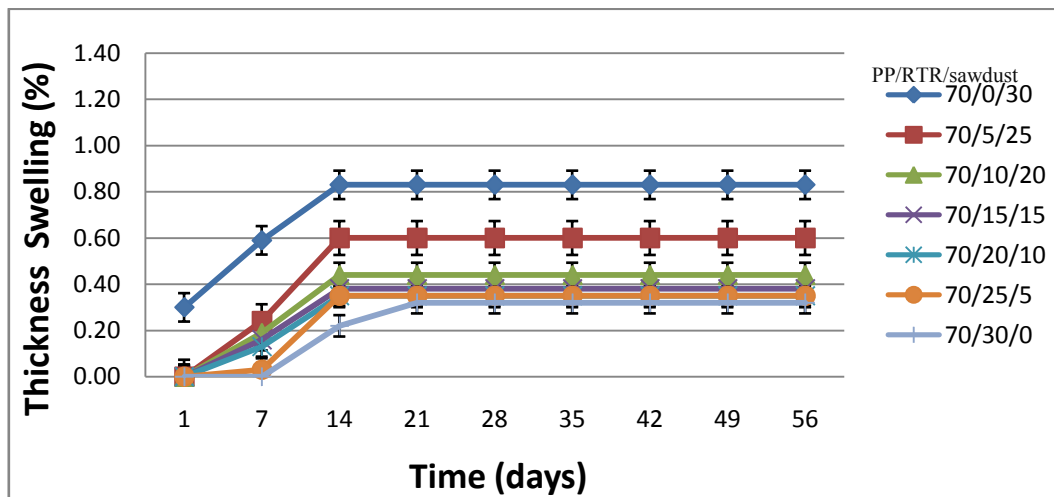
The wood-based composites are often subjected to the environment where the moisture conditions change rapidly. Wood is a hygroscopic and hydrophilic material that can absorb moisture from its surroundings. Wood composites swell at a rate defined by temperature, moisture, etc. Thickness swelling of wood composites is a serious and complex phenomenon because it can have a deleterious effect on other mechanical and physical properties of the composite. It has been shown that the water absorption of wood fiber/polymer composites obtained from the 24-h water immersion test may not be comparable to composites made with 100% wood fiber because of the different swelling rates of the composites manufactured with different polymer contents. In comparing the thickness swelling of different wood composites, the different test durations of water immersion or water vapor exposure will provide different results because of swelling rate differences. The wood-based composites are often subjected to the environment where the moisture conditions change rapidly. In addition to the total amount of thickness swelling rate of composites is also an important parameter that can influence the durability of the composites. For example, composites with a higher swelling rate are likely to be subjected to fatigue when the relative humidity fluctuates because of the more rapid rate of change in the induced internal stress of the composites. In comparing the thickness swelling of different wood composites, the different test durations of water immersion or water vapor exposure will provide different results because of swelling rate differences [47,48].

Thickness swelling curve is illustrated in Figure 4.9-4.10, where the percentage of thickness swelling is plotted against time for all samples. As it is clearly seen, generally, thickness swelling increases with immersion time, reaching a certain value beyond which such swelling is not observed. The time to reach the saturation point was not the same for all formulations. The PP/RTR/sawdust blends of ratio (70/30/0) and (70/20/10) samples showed the minimum (0.38%) and the maximum (0.89%) thickness swelling using sulfur system, respectively. The PP/RTR/sawdust blends of ratio (70/30/0) and (70/20/10) samples showed the minimum (0.32%) and the maximum (0.83%) thickness swelling using additive system, respectively. The thickness swelling that additive blend exhibits the higher sulphur system blends. It evidenced that additive system dynamic vulcanization significantly improved the physical behavior of the blend. This causes an increase in

interfacial adhesion, the hydrophilic nature of sawdust causes the thickness swelling in composite (the plastics have negligible water absorption). Because PP/RTR/sawdust of constant varies content in all formulations, the different thickness swelling among all composites can be attributed to the role of sulphur system and additives system. Figure 4.11 also shows that thickness swelling decreases by adding additives system. This means that it is the interface region which influences water absorption of the composite. As uncompatibilized composite has a weak fiber–matrix adhesion by nature, the interface is enhanced in the presence of the compatibilizer. Generally, it is necessary to use compatibilizers or coupling agents in order to improve the polymer–fiber bonding and in turn enhance water resistance. The MAPP chemically bonds with the OH groups in the lignocellulosic filler and limits the water absorption and thickness swelling of the composites. As a result, it is important to use coupling agents to improve the quality of adhesion between plastics and fibers, to reduce the gaps in the interfacial region, and to block the hydrophilic groups. The another reason for less water absorption could be the change in crystallinity of composite coupled by coupling agent (MAPP) as a nucleating agent. It was reported that crystallinity of the composite is much greater than that of the corresponding composite without the MAPP modification. On the other hand, the nucleation efficiency and the crystallinity of the hybrid composite can be improved in the presence of nanofiller as a nucleating agent. As the crystalline regions are impermeable, the thickness swelling is less in the composites [47-48].



**Figure 4.9** Thickness swelling of injection-molded polypropylene/reclaimed tire rubber/sawdust blends vulcanized using sulphur system.



**Figure 4.10** Thickness swelling of injection-molded polypropylene/reclaimed tire rubber/sawdust blends vulcanized using additive system.

### 4.3 Weather resistance of polypropylene/reclaimed tire rubber/sawdust blends

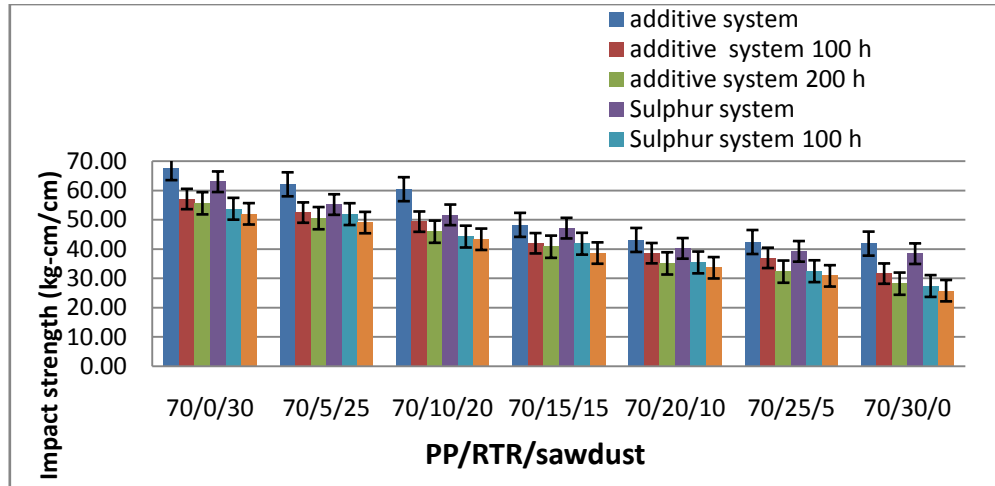
Weathering and light exposure are important causes of damage to coatings, plastics, inks and other organic materials. This damage includes loss of gloss, fading, yellowing,

cracking, peeling, tensile strength and mechanical properties. Generally, the accelerator weathering damage is caused by three factors: light, high temperature and moisture. Any one of these factors may cause deterioration. Together, they often work synergistically to cause more damage than any one factor alone. Weather usually causes the degradation of polymers under conditions that may be considered as normal, when other oxidative aging processes are very slow and the polymer retains its properties for a rather long time. Nowadays the weathering tests of polymer products is of paramount importance, because the problem has worsened as atmospheric ozone concentrations have gradually increased, especially in industrialized areas. [50-55].

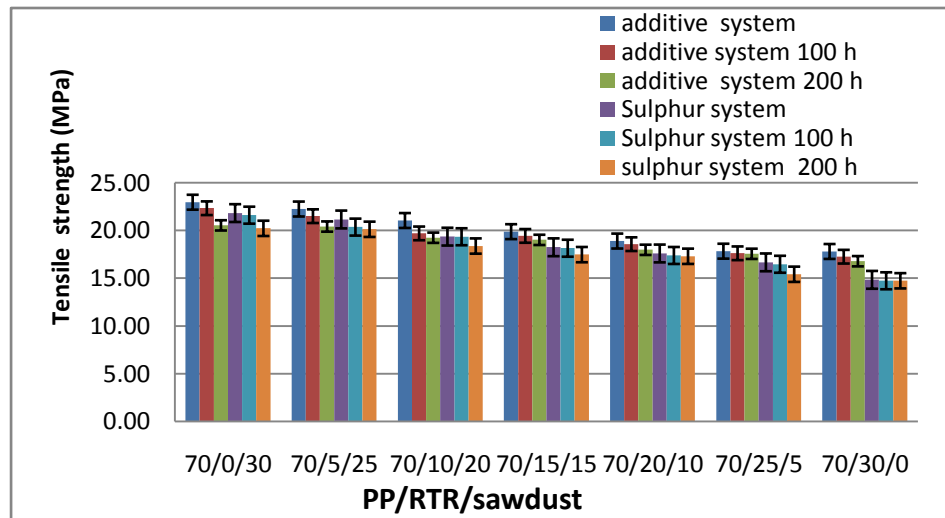
#### **4.3.1 Mechanical properties of polypropylene/reclaimed tire rubber/sawdust blends.**

The weathering test characteristics of the PP/RTR/sawdust blends for 100 and 200 h are presented in Figure 4.11. It can be observed that the impact strength and tensile strength changes are limited during the first 100 h of irradiation, while it starts to decrease significantly for longer exposure times. However, thanks to the stiffening effect of the filler, it stays higher in the filled samples. The impact strength and tensile strength decreases significantly in the polypropylene/reclaimed tire rubber/sawdust blends, because of the chain scission reaction induced by the irradiation, while the changes are less pronounced in the filled samples. The explanation can be easily found considering that filled samples have a lower amount of polymer subjected to the photo oxidative degradation; in fact, the decrease of impact strength upon increasing the irradiation time, light, high temperature and moisture. The effect of wood particles is even more pronounced for the impact strength. The decrease of the deformability upon increasing the UV exposure time is dramatic in the neat polypropylene, while is much less significant in the filled samples, where it stays almost constant. However, it is worth noting that the filled materials are very fragile even in the virgin conditions. These results show, on average, an advantage of the blends in comparison to the polypropylene/ reclaimed tire rubber/sawdust with sulphur and additives system when subjected to accelerated weathering. However, it has been pointed out that this is probably due to the lower amount of polymer used and to the fact that the photo oxidation mainly affects the polymer itself. More precisely,

mechanical tests alone could not be sufficient to assess the real influence of the wood flour on the photo oxidation mechanisms.



**Figure 4.11** Impact strength of injection-molded polypropylene/reclaimed tire rubber/sawdust blends vulcanized using sulphur system and additives system.



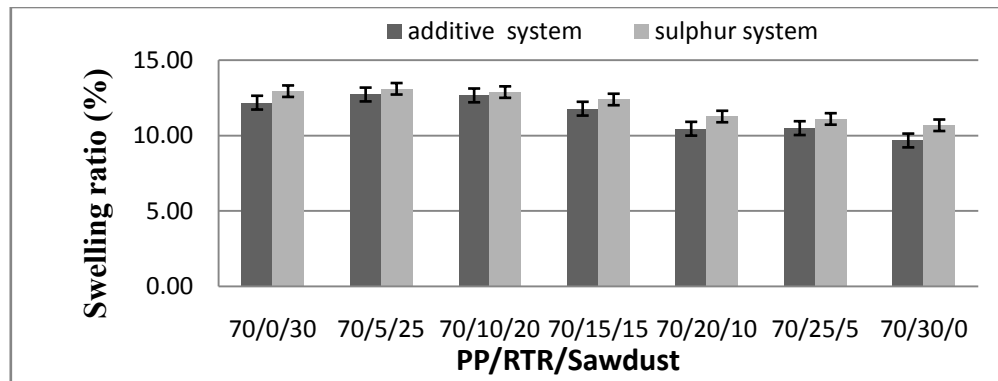
**4.12**

**Figure**  
Tensile

strength of injection-molded polypropylene/reclaimed tire rubber/sawdust blends vulcanized using sulphur system and additives system.

### 4.3.2 Physical properties of polypropylene/reclaimed tire rubber/sawdust Blends.

The weathering test characteristics of the PP/RTR/sawdust blends for 300 h are presented in Figure 4.13. It can be observed that the physical properties that the swell ratio, water absorption, and thickness swelling changes are limited during the first 100 h of irradiation, while it starts to increase significantly for longer exposure times. However, thanks to the stiffening effect of the filler, it stays higher in the filled samples. The physical properties increase significantly in the polypropylene/reclaimed tire rubber/sawdust blends, because of the chain scission reaction induced by the irradiation, while the changes are less pronounced in the filled samples. The explanation can be easily found considering that filled samples have a lower amount of polymer subjected to the photo oxidative degradation; in fact, the increase of physical properties upon increasing the irradiation time, light, high temperature and moisture.



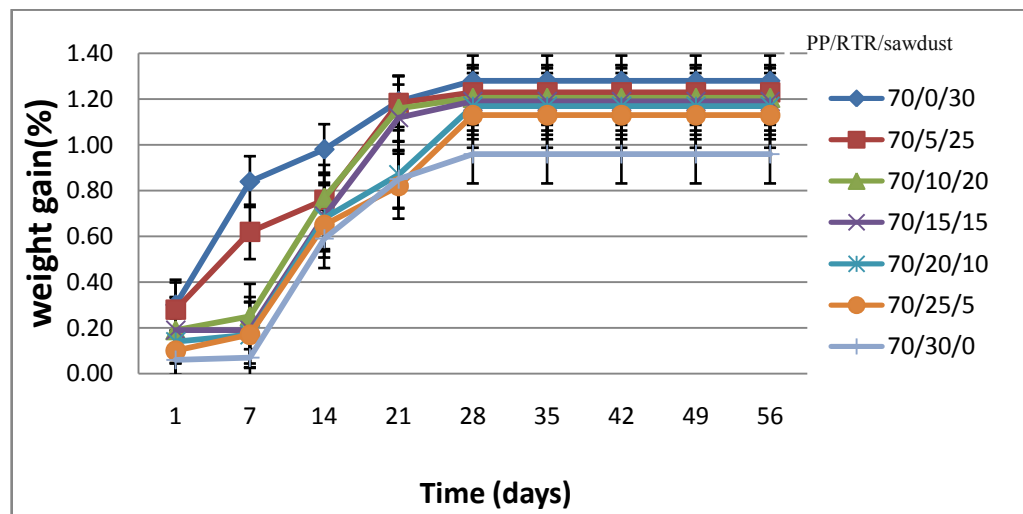
**Figure 4.13** Swell ratio of injection-molded polypropylene/reclaimed tire rubber/ sawdust blends vulcanized using sulphur system and additive system with weather resistance for 300 h.

Figure 4.13 shows results of equilibrium swelling studies of all blends in toluene with weather resistance provide provide information about the filler-matrix interaction, physical properties increase significantly in the polypropylene/reclaimed tire rubber/sawdust blends, because of the chain scission reaction induced by the irradiation, while the changes are less pronounced in the filled samples. The explanation can be easily found considering that filled samples have a lower amount of polymer subjected to the

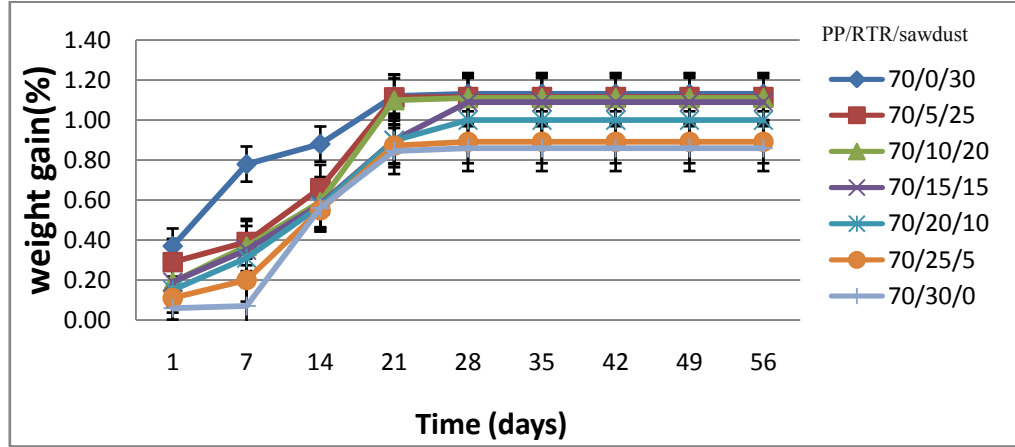


photo oxidative degradation; in fact, the increase of swelling studies upon increasing the irradiation time, light, high temperature and moisture.

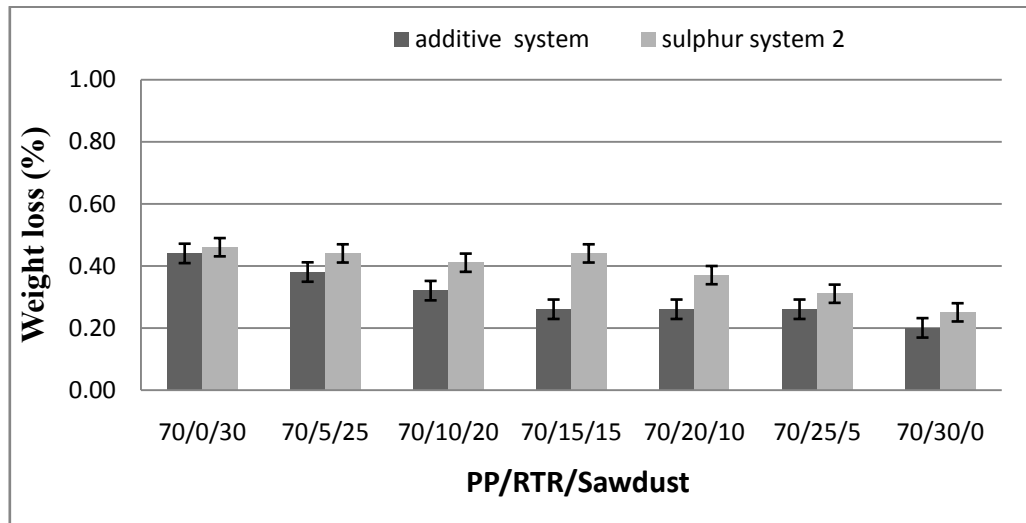
Swelling ratio increases with increasing sawdust, the swelling ratio of all blends decreases with increasing RTR. This can be explained that the particles RTR (60 mesh) smaller than particles sawdust (40 mesh), the mixing of particles RTR are better than particles. The properties of RTR with vulcanized using sulfur are better than sawdust with sulfur, these results provide a clear indication of the increase in the crosslink density in the PP/RTR blends. As the crosslink density increases within the RTR phases, the blends became more stiff and less penetrable by the solvent molecules. The PP/RTR/sawdust (70/30/0) and (70/0/30) samples showed the minimum (9.68) and the maximum (12.19) swelling ratio vulcanized using additive system with weather resistance, respectively. The PP/RTR/sawdust (70/30/0) and (70/0/30) samples showed the minimum (10.69) and the maximum (12.95) swelling ratio vulcanized using sulfur system with weather resistance, respectively.



**Figure 4.14** Weight gain (%) of injection-molded polypropylene/reclaimed tire rubber/sawdust blends vulcanized using sulphur system with weather resistance for 300 h.



**Figure 4.15** Weight gain of injection-molded polypropylene/reclaimed tire rubber/ sawdust blends vulcanized using additive system with weather resistance for 300 h.



**Figure 4.16** Weight loss of injection-molded polypropylene/reclaimed tire rubber/ sawdust blends vulcanized using sulphur system and additive system.

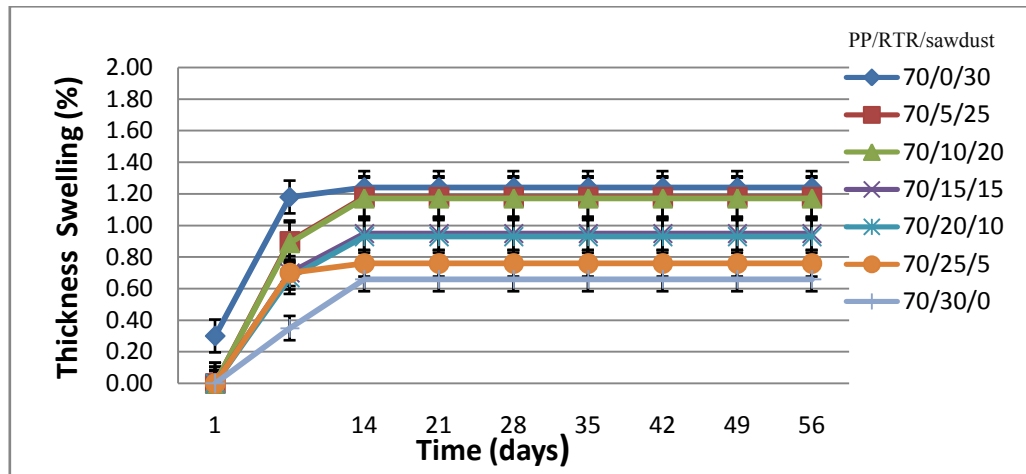
Figure 4.14 and 4.15 show the effect of the PP/RTR/sawdust blends (70/30/0) and (70/0/30) samples showed the minimum (0.96) and the maximum (1.28) weight gain vulcanized using sulphur system, respectively. The PP/RTR/sawdust (70/30/0) and

(70/0/30) samples showed the minimum (0.86) and the maximum (1.13) weight gain vulcanized using additive system, respectively.

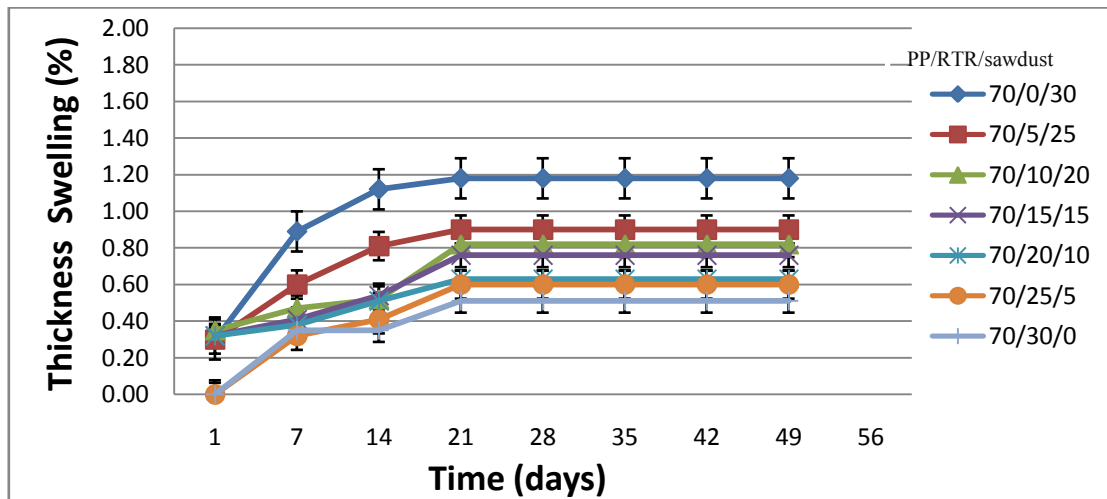
Figure 4.16 shows the effect of the PP/RTR/sawdust blends (70/30/0) and (70/0/30) samples showed the minimum (0.46) and the maximum (0.25) weight loss vulcanized using sulphur system, respectively. The PP/RTR/sawdust (70/30/0) and (70/0/30) samples showed the minimum (0.2) and the maximum (0.44) weight gain vulcanized using additive system, respectively.

Figure 4.14, 4.15 and 4.16 show the effect of PP/RTR/sawdust blends on the percentage of weight gain (Wl) and weight loss (Wg) vulcanized using sulphur system and additives system blends, respectively. Results of water absorption studies of all blends in water provide information about the filler-matrix interaction. It can be seen that the percentage of Wg and Wl increase with weather resistance, the increase of swelling studies upon increasing the irradiation time, light, high temperature and moisture. Because of the chain scission reaction induced by the irradiation, while the changes are less pronounced in the filled samples. The explanation can be easily found considering that filled samples have a lower amount of polymer subjected to the photo oxidative degradation. The percentage of weight gain (Wl) and weight loss (Wg) increases, when increases time, increasing sawdust, the swelling ratio of all blends decreases with increasing RTR. This can be explained that the particles RTR (60 mesh) smaller than particles sawdust (40 mesh), the mixing of particles RTR are better than particles. The properties of RTR with vulcanized using sulfur are better than sawdust with sulfur, these results provide a clear indication of the increase in the crosslink density in the PP/RTR blends. As the crosslink density increases within the RTR phases, the blends became more stiff and less penetrable by the water molecules. The ratio of PP/RTR/Sawdust blends with additive system is lower than the blends with sulphur vulcanizing agent. This indicates the properties of MAPP are better than vulcanized rubber with sulfur due to the sawdust enhancing mix ability of PP and RTR. In their work, the effect of sulfur concentration on the weight loss of rubberwood-filled PP/RTR blends. These results provide a clear indication of the increase in the crosslink density in the rubberwood-filled PP/NR blends. As the crosslink density increases within the NR phases, the blends became more stiff and less penetrable by the water molecules. [39] The

percentage of water absorption for composites. It can be seen that increasing the sawdust content leads to higher water absorption. However, this value considerably decreases with surface modification of RTR by using additives system.



**Figure 4.17** Thickness swelling of injection-molded polypropylene/reclaimed tire rubber/sawdust blends vulcanized using sulphur system.



**Figure 4.18** Thickness swelling of injection-molded polypropylene/reclaimed tire rubber/sawdust blends vulcanized using additive system.

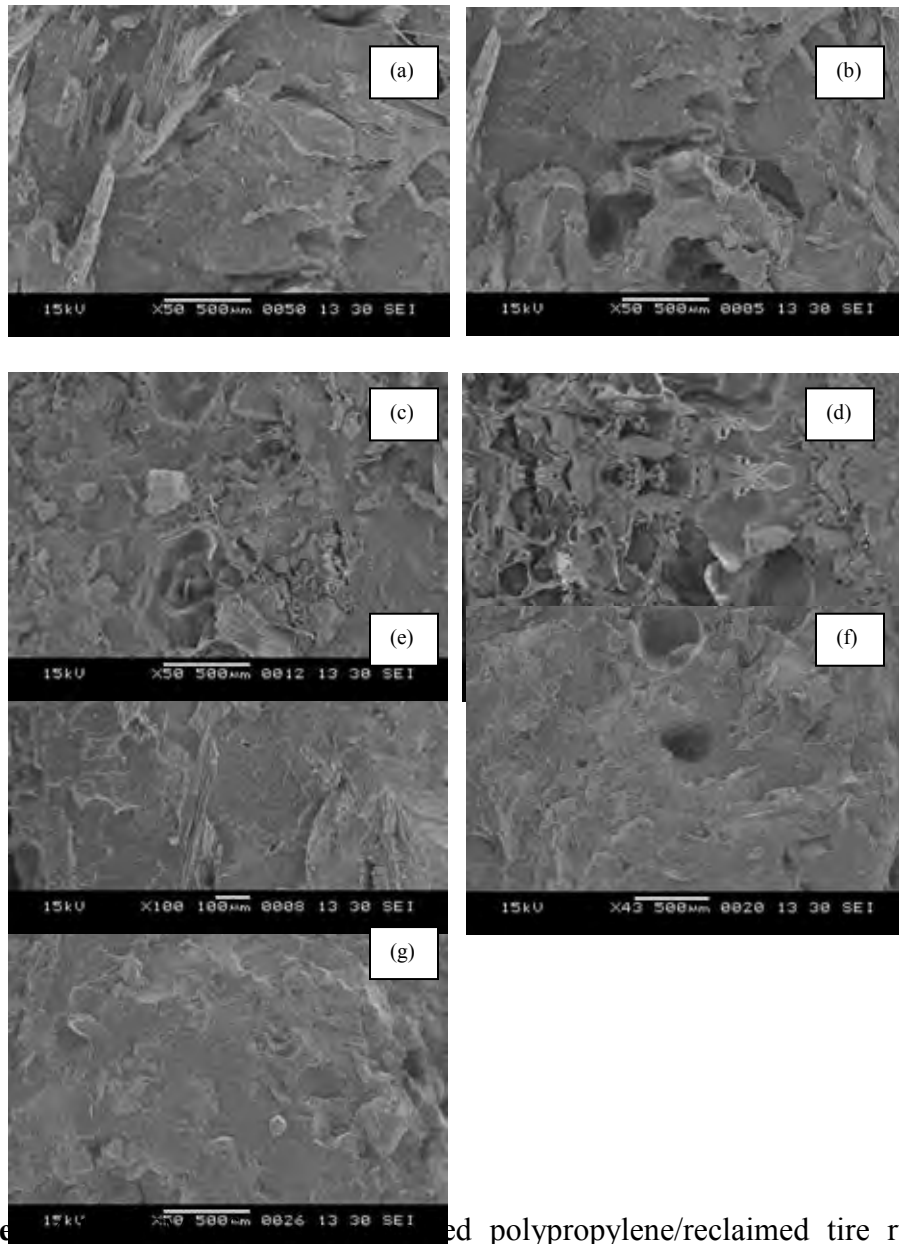
Thickness swelling curve is illustrated in Figure 4.17-4.18, where the percentage of thickness swelling is plotted against time for all samples. As it is clearly seen, generally,

thickness swelling increases with immersion time, reaching a certain value beyond which such swelling is not observed. The time to reach the saturation point was not the same for all formulations. The PP/RTR/sawdust blends of ratio (70/30/0) and (70/20/10) samples showed the minimum (0.38%) and the maximum (0.89%) thickness swelling using sulfur system, respectively. The PP/RTR/sawdust blends of ratio (70/30/0) and (70/20/10) samples showed the minimum (0.32%) and the maximum (0.83%) thickness swelling using additive system, respectively. It can be seen that the percentage of thickness swelling increase with weather resistance, the increase of thickness swelling studies upon increasing the irradiation time, light, high temperature and moisture. Because of the chain scission reaction induced by the irradiation, while the changes are less pronounced in the filled samples. The explanation can be easily found considering that filled samples have a lower amount of polymer subjected to the photo oxidative degradation. The thickness swelling with weather resistance that additive blend exhibits the higher sulphur system blends. It evidenced that additive system dynamic vulcanization significantly improved the physical behavior of the blend. This causes an increase in interfacial adhesion.

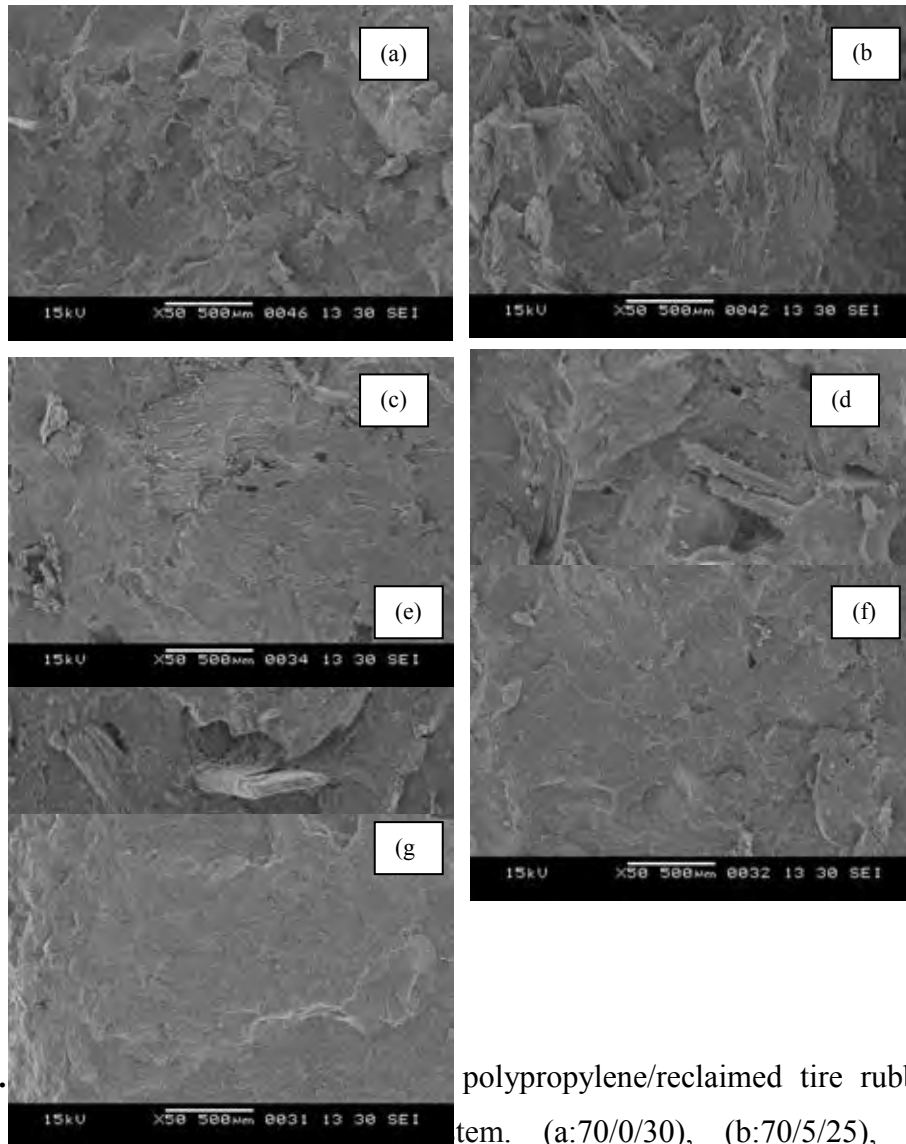
#### **4.4 Phase Morphology of Blends**

The RTR and sawdust can disperse well in PP matrix when the blend was vulcanized with additives system. This indicates that re-cross-linking is more effective in blending with additive systems leading to the improvement of physical properties. The phase morphology of with additives system blends were studied (Figure 4.20) and sulphur system (Figure 4.19) appears to have larger RTR aggregates particle size than the blend with additives system (Figure 4.20). This result can be explained that better dispersion apparently occurs from the effective role of crosslink in resisting rubber reagglomeration. This probably due to the limitation of the amount of carbon black/sawdust in the blend since carbon black/sawdust can produce a partial immobilization of the chain segment of polypropylene. This explains that RTR/sawdust particles of the blend with additive system can better disperse and finer distribution in PP matrix than sulphur vulcanizing agent. It is

seen that the distribution is fine and hence, the compatilizer is the most effective in these system causing improvement in physical properties



**Figure** vulcanized polypropylene/reclaimed tire rubber/ sawdust blends vulcanized using sulphur system. (a:70/0/30), (b:70/5/25), (c:75/10/20), (d:70/15/15), (e:70/20/10), (f:70/25/5), (g:70/30/0).



**Figures.** SEM images of polypropylene/reclaimed tire rubber blends with different compositions. (a:70/0/30), (b:70/5/25), (c:70/10/20), (d:70/15/15), (e:70/20/10), (f:70/25/5), (g:70/30/0).

## CHAPTER V CONCLUSION AND SUGGESTIONS

### 1.1 Conclusion

The polypropylene (PP)/reclaimed tire rubber (RTR) /sawdust blends were prepared by injection molding dynamic vulcanization. The blends of PP/RTR/Sawdust with additive exhibits high impact strength than sulphur system, this can be explained that MAPP is a suitable compatibilizer for this blend. Compatibilizer helps reduce the interfacial energy of both phases. This results improved interfacial adhesion and leads to the immiscible blend. Maleic anhydride polypropylene was used as a compatibilizer to improve the adhesion between the reinforcements and the matrix material. To characterize physical properties of solvent swelling ratio, water absorption and thickness swelling. The effect of physical properties of PP/RTR/sawdust blended with MAPP system is lower than with sulphur. Physical properties increases with increasing sawdust, the swelling ratio of all blend decreases with increasing RTR. This can be explained that the particles RTR (60 mesh) smaller than particles sawdust (40 mesh), the mixing of particles RTR are better than particles. The properties of RTR with vulcanized using sulfur are better than sawdust with sulfur, these results provide a clear indication of the increase in the crosslink density in the PP/RTR blends. As the crosslink density increases within the RTR phases, the blends became more stiff and less penetrable by the solvent molecules. This indicates higher degree of crosslinking density and the filler-matrix interaction makes the physical bonds at the interface to withstand the shear force caused by swelling of polymer. The phase structure of the composite blends was assessed by scanning electron microscopy (SEM). This explains that RTR/sawdust particles of the blend with MAPP/Zinc stearate/waxes system can better disperse and finer distribution in PP matrix than sulphur vulcanizing agent. It is seen that the distribution is fine and hence, the compatibilizer is the most effective in these system causing improvement in physical properties. The measurements accelerator weathering proved the physical and mechanical properties both declined. Because the blends damage is caused by light, high temperature, moisture and weather.

### **1.2 Suggestion for Further Work.**

1. The polypropylene (PP)/reclaimed tire rubber (RTR) /sawdust blends was used to make the floor tiles by using injection molding.



2. The polypropylene (PP)/reclaimed tire rubber (RTR) /sawdust blends vulcanized using peroxide and maleic anhydride polypropylene (MAPP).
3. The polypropylene (PP)/reclaimed tire rubber (RTR) /sawdust blends vulcanized using peroxide and sulphur.

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## APPENDICES

### APPENDIX A

**Table A 1** Charpy Impact Strength of injection-molded polypropylene/reclaimed tire rubber/sawdust blends without weather resistance..

Entry	Charpy Impact Strength(Kg-cm/cm)						X
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>	Data	
	62.21	62.78	63.78	63.89	62.12	5	62.96



1							
2	54.55	54.48	55.15	54.97	56.7	5	55.17
3	51.45	52.15	51.21	50.22	53.23	5	51.65
4	47.15	46.7	46.8	47.59	47.8	5	47.21
5	40.34	40.25	40.23	40.90	40.3	5	40.40
6	40.56	39.15	39.89	41.34	40.12	5	40.21
7	39.45	39.23	39.15	39.6	39.5	5	39.19
8	68.15	70.1	67.25	65.23	67.27	5	67.60
9	62.67	61.23	63.09	62.35	61.05	5	62.08
10	60.23	60.45	60.3	59.19	61.90	5	60.41
11	48.78	48.15	48.35	48.59	47.30	5	48.23
12	43.11	43.5	41.39	43.6	43.78	5	43.08
13	42.54	42.34	42.45	42.67	41.9	5	42.38
14	41.60	41.67	41.56	41.89	41.45	5	41.83

**Table A 2** Charpy Impact Strength of injection-molded polypropylene/reclaimed tire rubber/sawdust blends with weather resistance for 100 h.

Entry	Charpy Impact Strength(Kg-cm/cm)						X
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>	Data	
1	54.06	52.77	53.5	53.6	54.72	5	53.73
2	51.34	52.27	52.85	51.5	51.56	5	51.90
3	42.6	47.51	45.17	43.19	42.7	5	44.23
4	43.9	42.53	43.23	39.12	40.23	5	41.80
5	35.74	33.82	35.09	36.65	35.78	5	35.41
6	34.98	33.26	31.36	31.26	31.26	5	32.44
7	26.54	24.51	29.14	27.51	29.14	5	27.36
8	55.33	56.9	60.25	55.23	57.57	5	57.05
9	52.51	53.25	52.98	52.35	51.05	5	52.43
10	49.76	49.05	49.25	49.08	49.5	5	49.33
11	40.52	42.14	42.51	42.16	42.5	5	41.96
12	38.89	38.18	39.27	38.18	38.34	5	38.57
13	36.43	36.94	37.11	37.94	36.41	5	36.96
14	33.67	26.63	32.83	32.63	32.27	5	31.60

**Table A 3** Charpy Impact Strength of injection-molded polypropylene/reclaimed tire rubber/sawdust blends with weather resistance for 200 h.

Entry	Charpy Impact Strength(Kg-cm/cm)						X
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>	Data	
1	51.88	52.63	52.24	51.32	51.96	5	52.00
2	49	49.76	49.05	49.87	47.42	5	49.02
3	42.88	43.9	42.53	44.87	42.42	5	43.32
4	39.52	38.14	38.51	39.1	37.78	5	38.61
5	33.27	33.81	33.34	33.74	33.82	5	33.59
6	28.98	31.26	31.36	31.26	31.26	5	30.82
7	26.54	24.51	24.54	27.14	26.14	5	25.77
8	55.33	57.72	55.22	52.84	56.90	5	55.60
9	52.51	49.87	47.42	49.87	52.96	5	50.52
10	49.05	45.21	42.6	47.51	45.17	5	45.90
11	38.14	41.52	42.14	40.91	41.14	5	40.77
12	34.74	35.27	35.56	35.76	34.09	5	35.08
13	36.11	31.65	31.81	31.65	30.08	5	32.26
14	26.67	27.63	27.65	29.24	29.63	5	28.16

## APPENDIX B

**Table B 1** Tensile Strength of injection-molded polypropylene/reclaimed tire rubber/sawdust blends without weather resistance.

Entry	Tensile Strength (MPa)						X
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>	Data	
1	21.11	22.97	22.32	20.45	23.82	5	22.13
2	22.29	21.18	21.65	21.27	21.89	5	21.66
3	20.06	20.38	20.87	22.39	20.11	5	20.76
4	19.42	18.95	19.38	19.02	18.89	5	19.13
5	18.24	17.88	17.5	18.57	18.04	5	18.05
6	17.17	16.99	17.04	17.33	16.15	5	16.94
7	15.41	16.2	16.06	15.09	15.46	5	15.66
8	23.3	23.13	22.82	22.78	22.81	5	22.98
9	22.42	22.74	21.78	22.19	22.14	5	22.25
10	20.77	21.28	21.33	21.09	20.79	5	21.05
11	19.72	19.71	20.2	19.65	20.14	5	19.88
12	19.01	19.06	19.59	18.58	18.26	5	18.90
13	17.25	18.31	17.28	17.87	18.71	5	17.84
14	17.72	17.69	17.98	17.69	17.98	5	17.81

**Table B 2** Tensile Strength of injection-molded polypropylene/reclaimed tire rubber/sawdust blends with weather resistance for 100 h.

Entry	Tensile Strength (MPa)					Data	X
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>		
1	21.55	22.02	22.01	21.56	22.02	5	21.83
2	21.17	21.14	21.18	21.17	21.16	5	21.16
3	19.39	19.32	19.34	19.35	19.36	5	19.35
4	18.25	18.25	18.24	18.25	18.26	5	18.25
5	17.75	17.49	17.64	17.48	17.62	5	17.59
6	15.43	16.63	17.35	16.63	17.31	5	16.67
7	14.95	14.45	15.12	14.55	15.12	5	14.83
8	22.31	22.35	22.36	22.37	22.31	5	22.34
9	21.21	21.99	21.17	21.19	21.97	5	21.50
10	19.89	19.67	19.39	19.89	19.67	5	19.70
11	19.84	19.41	19.27	19.41	19.27	5	19.44
12	19.01	18.88	19.05	17.88	18.05	5	18.57
13	17.60	17.57	17.68	17.57	17.68	5	17.62
14	15.68	16.81	18.33	17.04	18.45	5	17.26

**Table B 3** Tensile Strength of injection-molded polypropylene/reclaimed tire rubber/sawdust blends with weather resistance for 200 h.

Entry	Tensile Strength (MPa)					Data	X
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>		
1	20.29	20.16	20.28	20.16	20.27	5	20.23
2	20.16	20.16	20.17	20.19	19.98	5	20.13
3	19.31	19.34	19.36	19.46	19.34	5	19.36
4	18.12	18.218	18.12	18.16	18.14	5	18.15
5	17.4	17.25	17.4	17.25	17.23	5	17.30
6	15.73	15.04	15.57	15.43	15.34	5	15.42
7	14.71	14.81	14.62	14.74	14.82	5	14.74
8	21	20.46	21.03	20.12	20.11	5	20.54
9	20.04	20.04	20.26	20.77	20.99	5	20.42
10	19.4	18.49	19.48	19.41	19.46	5	19.24
11	18.77	19.31	18.34	19.29	19.41	5	19.02
12	18.54	17.88	17.92	17.99	17.59	5	17.98
13	17.08	17.47	17.57	17.98	17.72	5	17.56
	16.31	17.47	17.08	16.39	16.74	5	16.79

### APPENDIX C

**Table C 1** Weight gain (%) of injection-molded polypropylene/reclaimed tire rubber/sawdust blends without weather resistance.

Entry	Weight (oven dry) (gram)		Weight (immersion) (gram)		Weight gain (%)	
	X:Before	X:after	X:1 day	X:7 day	X:1 day	X:7day
1	16.70	16.69	16.74	16.78	0.30	0.54
2	17.70	17.67	17.71	17.72	0.23	0.28
3	15.9	15.89	15.93	15.93	0.25	0.25
4	15.99	15.98	16.01	16.01	0.19	0.19
5	15.84	15.83	15.85	15.85	0.13	0.13
6	15.82	15.82	15.83	15.84	0.06	0.13
7	15.69	15.68	15.69	15.70	0.06	0.13
8	15.93	15.92	15.98	16.00	0.38	0.50
9	15.92	15.91	15.94	15.95	0.19	0.25
10	15.84	15.83	15.86	15.87	0.19	0.25
11	15.63	15.63	15.66	15.66	0.19	0.19
12	15.64	15.44	15.46	15.47	0.13	0.19
13	15.34	15.33	15.34	15.35	0.07	0.13

14	15.30	15.30	15.31	15.31	0.07	0.07
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**Table C 2** Weight gain (%) of injection-molded polypropylene/reclaimed tire rubber/sawdust blends with weather resistance for 300 h.

Entry	Weight (oven dry) (gram)		Weight (immersion) (gram)		Weight gain (%)	
	X:Before	X:after	X:1 day	X:7 day	X:1 day	X:7day
1	16.72	16.7	16.75	16.84	0.30	0.84
2	17.74	17.73	17.78	17.84	0.28	0.62
3	16.9	16.89	16.93	16.98	0.19	0.25
4	15.87	15.86	15.9	15.95	0.19	0.19
5	15.62	15.61	15.65	15.68	0.14	0.17
6	15.91	15.9	15.93	15.96	0.10	0.17
7	15.7	15.69	15.72	15.74	0.06	0.07
8	15.83	15.82	15.87	15.92	0.37	0.78
9	15.65	15.64	15.68	15.71	0.29	0.39
10	15.43	15.42	15.46	15.48	0.19	0.37
11	16.04	16.03	16.07	16.1	0.19	0.35
12	15.69	15.68	15.71	15.74	0.15	0.31
13	15.31	15.3	15.32	15.34	0.11	0.20
14	15.15	15.14	15.16	15.18	0.06	0.07



**Table C 3** Weight loss (%) of injection-molded polypropylene/reclaimed tire rubber/sawdust blends without weather resistance and with weather resistance for 300 h.

Entry	Weight (oven dry) (gram)		Weight loss (%)	Weight (oven dry) (gram)		Weight loss (%) *
	X:Before	X:after		X:Before	X:after	
1	17.58	17.52	0.34	17.57	17.49	0.46
2	18.35	18.29	0.33	18.38	18.30	0.44
3	17.05	16.99	0.35	17.09	17.02	0.41
4	15.89	15.84	0.31	16.04	15.97	0.44
5	15.95	15.93	0.13	16.01	15.95	0.37
6	15.97	15.96	0.06	15.98	15.93	0.31
7	15.95	15.94	0.06	15.96	15.92	0.25
8	15.93	15.92	0.07	15.81	15.74	0.44
9	15.92	15.91	0.06	15.99	15.93	0.38
10	15.84	15.83	0.06	15.87	15.82	0.32

11	15.63	15.62	0.06	15.65	15.61	0.26
12	15.64	15.63	0.09	15.66	15.62	0.26
13	15.34	15.33	0.04	15.45	15.41	0.26
14	15.11	15.10	0.04	15.13	15.10	0.20

\*With weather resistance for 300 h

#### APPENDIX D

**Table D 1** Thickness Swelling (%) of injection-molded polypropylene/reclaimed tire rubber/ sawdust blends without weather resistance.

Entry	Size before immersion (mm)			Size after immersion for 1 day (mm)			Size after immersion for 7 day (mm)		
	High	Long	Wide	High	Long	Wide	High	Long	Wide
1	24.00	213.00	3.38	24.00	213.00	3.38	24.00	213.00	3.39
2	24.00	211.00	3.32	24.00	211.00	3.32	24.00	211.00	3.34
3	24.00	210.00	3.16	24.00	210.00	3.16	24.00	210.00	3.18
4	24.00	210.00	3.15	24.00	210.00	3.15	24.00	210.00	3.17
5	24.00	210.00	3.15	24.00	210.00	3.15	24.00	210.00	3.17
6	24.00	210.00	3.16	24.00	210.00	3.16	24.00	210.00	3.17
7	24.00	210.00	3.16	24.00	210.00	3.16	24.00	210.00	3.17
8	24.00	213.00	3.17	24.00	210.00	3.18	24.00	210.00	3.19

9	24.00	213.00	3.16	24.00	213.00	3.18	24.00	213.00	3.19
10	24.00	211.00	3.16	24.00	211.00	3.18	24.00	211.00	3.18
11	24.00	210.00	3.16	24.00	210.00	3.19	24.00	210.00	3.19
12	24.00	210.00	3.13	24.00	210.00	3.14	24.00	210.00	3.16
13	24.00	210.00	3.11	24.00	210.00	3.12	24.00	210.00	3.13
14	24.00	210.00	3.08	24.00	210.00	3.10	24.00	210.00	3.10

**Table D 2** Thickness Swelling (%) of injection-molded polypropylene/reclaimed tire rubber/ sawdust blends with weather resistance for 300 h.

Entry	Size before immersion (mm)			Size after immersion for 1 day			Size after immersion for 7 day		
	High	Long	Wide	High	Long	Wide	High	Long	Wide
1	24.00	211.00	3.33	24.00	211.00	3.33	24.00	211.00	3.39
2	24.00	211.00	3.36	24.00	211.00	3.36	24.00	211.00	3.40
3	24.00	210.00	3.16	24.00	210.00	3.16	24.00	210.00	3.27
4	24.00	210.00	3.17	24.00	210.00	3.17	24.00	210.00	3.27
5	24.00	210.00	3.14	24.00	210.00	3.14	24.00	210.00	3.15
6	24.00	210.00	3.13	24.00	210.00	3.13	24.00	210.00	3.14
7	24.00	210.00	3.16	24.00	210.00	3.16	24.00	210.00	3.17
8	24.00	213.00	3.18	24.00	213.00	3.18	24.00	213.00	3.19

9	24.00	211.00	3.16	24.00	211.00	3.16	24.00	211.00	3.17
10	24.00	210.00	3.15	24.00	210.00	3.15	24.00	210.00	3.17
11	24.00	210.00	3.16	24.00	210.00	3.16	24.00	210.00	3.18
12	24.00	210.00	3.13	24.00	210.00	3.13	24.00	210.00	3.14
13	24.00	210.00	3.10	24.00	210.00	3.10	24.00	210.00	3.11
14	24.00	210.00	3.09	24.00	210.00	3.09	24.00	210.00	3.10

#### APPENDIX E

**Table E 2** Swell ratio of injection-molded polypropylene/reclaimed tire rubber/ sawdust blends vulcanized using sulphur system and additives system.

Entry	Without weather resistance			With weather resistance *		
	Weight of sample (gram) (X)		Swell ratio	Weight of sample (gram) (X)		Swell ratio
	Before	After**		Before	After**	
1	2.65	2.72	2.76	2.57	2.90	12.95
2	2.26	2.31	2.27	2.58	2.92	13.11
3	2.15	2.19	1.91	2.34	2.64	12.89
4	2.70	2.73	1.50	2.35	2.65	12.40
5	2.78	2.82	1.33	2.39	2.65	11.27
6	2.78	2.82	1.28	2.33	2.59	11.11
7	2.67	2.70	0.92	2.32	2.57	10.69
8	2.31	2.35	1.73	2.27	2.55	12.19
9	2.41	2.45	1.67	2.27	2.56	12.73
10	2.66	2.70	1.51	2.28	2.57	12.67
11	2.43	2.46	1.49	2.30	2.57	11.79

12	2.58	2.61	1.24	2.32	2.57	10.46
13	2.50	2.52	0.99	2.36	2.61	10.50
14	2.37	2.39	0.86	2.32	2.55	9.68

\*With weather resistance for 300 h

\*\*Sample were immersed in toluene for 7 days.

### **VITAE**

Miss Sunaree Sriboonrung was born on August 06, 1987 in Srisaket, Thailand. She graduated with a Bachelor's Degree of Science in Material from Maejo University in 2008. In 2009, she received a Master's Degree of Science in the Program of Petrochemistry and Polymer Science, Chulalongkorn University, Bangkok, Thailand since 2008 and finished her study in 2011.

