UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Preparation and Characterization of Transesterified Waste Cooking Oil as Processing Oil for Sustainable Rubber Compound

by

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FACULTY OF MANUFACTURING ENGINEERING

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This report is submitted in accordance with requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Hons)

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DECLARATION

I hereby, declared this report entitled "Preparation and Characterization of Transesterified Waste Cooking Oil as Processing Oil for Sustainable Rubber Compound" is the result of my own research except as cited in references.

Signature :

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Date : 13th September 2021

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfillment of the requirement for Bachelor Degree of Manufacturing Engineering (Hons).
The member of the supervisory committee is as follow:

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(TS. DR. JEEFFERIE BIN ABD RAZAK)

ABSTRAK

Bahan getah banyak digunakan dalam kehidupan seharian manusia. Penggunaan bahan getah yang paling biasa berlaku pada industri tayar, pembinaan dan automotif. Komponen utama sebatian getah ialah getah, pengisi penguat dan minyak pemprosesan. Salah satu tujuan utama memproses minyak adalah untuk mengurangkan kelikatan dan meningkatkan kualiti sebatian getah. Minyak aromatik yang mengandungi hidrokarbon aromatik poliklik digunakan secara meluas dalam menghasilkan banyak jenis sebatian getah kerana kesesuaiannya dengan bahan tak jenuh. Walau bagaimanapun, minyak aromatik mempunyai potensi karsinogenik dan cenderung diganti dengan pilihan lain yang mesra alam. Oleh itu, kajian ini memaparkan potensi minyak masak sisa yang dirawat secara kimia sebagai minyak pemprosesan untuk pengeluaran sebatian getah. Isu pembuangan sisa menggoreng atau minyak masak sisa telah banyak menyumbang kepada masalah persekitaran yang serius. Penggunaan minyak masak semakin meningkat dan bekalan yang konsisten menjadikan minyak masak sebagai bahan makanan komersial. Kira-kira, terdapat kira-kira 3 bilion liter minyak masak yang digunakan di Malaysia setiap tahun yang mana sekitar 30% minyak masak sisa tersedia untuk pengeluaran biodiesel atau pelupusan alam sekitar. Ciri penyembuhan bagi sebatian dan sifat mekanik pemvulkanan akan diukur dan dibandingkan dengan getah berasaskan minyak pemprosesan rujukan. Penyediaan dan ciri minyak masak sisa transesterifikasi akan diukur dengan menggunakan ujian mekanikal dan fizikal iaitu ujian tegangan, pemerhatian fraktur mikroskop SEM, ujian kekerasan, ujian lelasan, ujian termal (TGA, DSC), dan ujian penyerapan.

ABSTRACT

Rubber materials are widely used in human daily life. Most common usage of rubber material is mostly in tires, construction and automotive industry. The main components of rubber compounds are rubber, reinforcing fillers and processing oils. One of the main purposes of processing oils is to decrease the viscosity and to raise the quality of rubber compounds. The aromatic oils which containing polycyclic aromatic hydrocarbon is widely used in producing many type of rubber compound due to their compatibility to unsaturated materials. However, aromatic oils have carcinogenic potential and tend to be replaced with other environmentally friendly option. Therefore, this study presents the potential of chemically treated waste cooking oil (WCO) as processing oil for rubber compound production. Waste management issues of frying or waste cooking oil have led greatly to severe environmental problems. Moreover, around three billion liters of cooking oil consumed in Malaysia yearly which about 30% of WCO accessible for biodiesel production or disposal to environment. In this study the waste cooking oil was modified through the transesterification process to be used as the processing oil for rubber compound. The cure characteristic of the rubber compound and the mechanical properties rubber vulcanization were measured and compared than commercial processing oil based rubber. The resulted NR compounds processed by using the WCO as PO at varying collect (0, 10, 20, 30 grams) has shown promising and comparable cure characteristic, physical and mechanical performances than commercial parafinic as processing oil added to industrial NR compound. This study was significant as WCO used in this study, able to replace parafinic oil as sustainable candidate of processing oil for manufacturing of rubber compound.

DEDICATION

Dedicated to

my beloved country Yemen

My beloved father, Mohammed Alkahlani, my beloved mother, Nadia Alsrori

my beloved family,

my beloved friend, Abdulsalam Khaled

my beloved cousin. Dr. Sahker Alshibani

For giving me honest support, encouragement, cooperation, money, and also understanding.

Thank You So Much & Love You All Forever.

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In the name of Allah, the most generous, gracious, with the greatest thanks to Allah that I succeed achieve this FYP 2.

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LIST OF ABBREVIATIONS

AO - Aromatic oil

PO - Processing oil

PCA - Polycyclic aromatic compounding

VO - Vegetable oil

VVO - Vulcanized vegetable oil

IIR - Isobutylene rubber

Mc - Cross-Links

NR - Natural rubber

SR - Synthetic rubber

PAHs - Polycyclic aromatic hydrocarbons

WCO - Waste cooking oil

CB - Carbon black

FFA - Free Fatty Acide

FAME - Fatty acid methyl ester

HA - Highly aromatic

BR - Butadiene rubber

ENR - Epoxidized natural rubber

SBR - Styrene butadiene rubber

TDAE - Treated distillate aromatic oil

ODR - Oscillating disk rheometer

DSC - Differential scanning calorimeter

SEM - Scanning selection microscope

SMR - Standard Malaysia rubber

CHAPTER 1

INTRODUCTION

This chapter has emphasized a background of study, problem statement, objectives, scope, and significance of study, report organization and summary of study. Moreover, the research scope also encompasses the scope and depth of research, although the real requirements of performing this analysis were specifically explained in problem statement part.

1.1 Research Background

Highly aromatic oil derives from petrochemical industry derivatives, historically been commonly used as rubber compounding extender oils. Their success is attributed to strong ability with most of the natural elastomers. In the manufacturing process of rubber based products, extender oils also referred as softening oils and are applied to rubber compounds in order to ensure acceptable process ability (Chandrasekara *et al.*, 2011).

The main aim of this research is to maneuver the treatment of waste resource to balance the ecosystem and develop alternative processing oil for producing the sustainable rubber compound. There are several choices of bio-based resources with higher possibility to substitute petrochemical resources such as vegetable oil, castor oil, palm oil, and many others. However, waste cooking oil is chosen as processing oil for producing the sustainable rubber compound due to their abundant accessibility. As well as, this initiative also will help to eliminate massive disposal issue of WCO and to protect the environment.

Lately, enormous quantities of waste cooking oil are created and discharged. This could seriously added to serious environmental problems (Ibrehim *et al.*, 2014). In 2013, in Petaling District of Selangor State, Malaysia, a study was conducted for 352 households to examine the awareness, attitudes and best practices into WCO recycling. In this research, it was recorded that the average waste cooking oil generated per household is about 2.34 kg/month (Ibrehim *et al.*, 2014). Thus, this quantity of waste could make a huge disposal problem which later may led into serious pollution issues.

In this research, waste cooking oil was filtered to minimize the highest number of contaminates and particles. Then, the filtered WCO was characterized by using FTIR spectroscopy to evaluate the presence of organic functional groups as well as the chemical substances. By having the understanding from waste cooking oil results, the WCO was modified into processing oil for producing the sustainable rubber compound through transesteification process. The transesterified WCO was then utilized as green processing oil for NR based rubber compound. The resulted compounds were characterized for their cure characteristic behavior, physical and mechanical properties. This research provides obvious of sustainability element by converting waste into wealth and provides the platform into resolving never ending story of waste cooking oil disposal issues.

1.2 Problem statement

The rising attention in environmental issues had maximized the needs for developing new applicant of superior materials that are environmental friendly. Literally, demand of rubber compound resources are enhanced dramatically. Most of existing processing oil to produce the rubber compound is the aromatic types processing oils.

However, most of the aromatic oils have higher content of potential carcinogens which containing polycyclic aromatic hydrocarbons (PAH). On 13-Febrauary 2004, the council of the European communities (2005) has adopted a resolution to prohibit the use and selling of PAH-rich extender oils. Moreover, since viable substitutes are not present in the market, the restriction has not been strictly applied to date (Chandrasekara *et al.*, 2011).

Since WCO is derived from a vegetable source, no hydroxyl group has been found (Fan *et al.*, 2011). In due to that, great effort to find the best replacement for aromatic oil as processing oils should be taken into consideration utilizing of green resources from the household waste that could be the best idea for replacing all those synthetic type of processing oils. Therefore, special step of structural adjustment must be taken in order to introduce the hydroxyl group at the structure of WCO. This can be actualized by performing the transesterification process.

Although the process of transesterification could introduce the hydroxyl group (OH^-) into the WCO structural unit, there are some challenges that must be addressed. Monomer heterogeneity, caused by the existence of double bonds in the triglyceride structure, is a key problem that often occurs in the transesterification process (Maisonneuve *et al.*, 2016).

In addition, until now, there are no specific study to prepare and characterized the NR rubber compounds which produced by using the WCO based processing oils as the extenders. Hence, up until now, there are no ideas about their compatibility, the cure characteristic and even their resulted physical and mechanical properties results that can be referred.

1.3 Objectives

To ensure the success of this research, there are three objectives which are:

1- To modify WCO into usable PO for rubber compound using transesterification method.

2- To evaluate the potential WCO, to be used as PO for NR based compound.

3- To test the mechanical and physical performance of NR based compound by performing related testing.

1.4 Scope of study

1- Prepare rubber compound by using transesterified WCO as extender to replace the aromatic toxic based synthetic oil.

2- Analysis the presence of hydroxyl group (OH^-) in transesterified WCO and compounded natural rubber using Fourier Transform Infrared (FTIR) spectroscopy method.

3- Evaluate the physical and mechanical properties of transesterified WCO based natural rubber compounds.

1.5 Significant of study

WCO is used in this study due to its capability to restore the petrochemical resources. Waste cooking oil contains required molecular structure and could be customized in order to produce the processing oil. This study is significant due to its own advantages.

The use of transesterified WCO in this study is one of the great efforts to minimize the massive quantity of WCO disposal in Malaysia, which decreases the use of non-renewable energy.

At the same time, it is also beneficial to evaluate the potential of WCO as new source of sustainable processing oil for NR based compound manufacturing using standard Malaysia rubber grade (SMR-L 20).

1.5 Organization of study

This report consists of five chapters which are introduction, literature review, methodology, result and discussion as well as conclusion and recommendation. First chapter is introduction; it provides an overview of history and background of this study, problem statement relating to this study, objectives and scope of study concerned as well as the significance of study.

Chapter two outlines on the literature review of previous related studies and articles on this topic. This chapter concerned primarily on the procedure to make processing oil for sustainable rubber compound. This chapter concerning on the waste cooking oils and its applications, collections, and its properties. Moreover, highlights the transesterification process with its classification and applications. Chapter three which is the methodology had modified the method concerned in order to prepare and to characterization waste cooking oil as processing oil for developing sustainable rubber compound and also the physical and mechanical testing performance as the resulted NR based compounds. All of the findings and results are described and evaluated in Chapter 4, which under the "Results and Discussion". Finally, chapter five provides summarization of findings and results, as well as suggestions for further study.

1.6 Summary

In conclusion, there is a need to modify waste cooking oil by inventing the suitable method to manufacture rubber compound by using transesterified waste cooking oil as processing oil for natural rubber applications. The importance of this research had been explained in subtopic of background. The problem statement of this study has fully justified. There are three objectives stated for this study. It was expected that the waste cooking oil could be utilized into as processing oil using for sustainable rubber compound development.

CHAPTER 2

LITERATURE REVIEW

This second chapter highlights the concept and application of processing oil (PO) as extender for rubber compound. Commonly in literature review, it discussed further on rubber compound, its applications, and its properties. Furthermore, this chapter has summarized the transesterified waste cooking oil as sustainable replacement for synthetic processing oil for rubber compound development.

2.1 PO for rubber compound

Processing oils are often utilize to minimize the rubber compound viscosity to improve the compound process ability (Ren et al., 2020). Also Dasgupta et al., (2009) had stated that, the processing additives were added to promote the interaction between rubber and dispersion of the added filler.

Processing aids are organic materials that when applied to polymers, developed their flexibility and enhance their process ability. They are primarily used to reduce or lessen the viscosity and elasticity of pre-vulcanized materials, while improving the ability to blend with other additives in the elastomeric matrix and their fluidity during molding (Zanchet *et al.*, 2016).

Plasticizers has important role in rubber factory due to their ability to minimize the viscosity of rubber, improve the processing ability, improve the elasticity, and minimize processing energy utilization. In addition, the best plasticizers for different rubbers are plant oils. For example, soybean oil, cashew oil, and castor oil (Xu et al., 2020).

Rubber materials are widely used in human daily life especially in tire, construction, textile, and biomedical applications. Most common ingredients of rubber compound are processing oils (PO), oil softeners. The roles of processing oil are to decrease the viscosity and increase the process ability of rubber compound (Öter et al., 2011).

Highly aromatic (HA) oils are usually used in rubber compound processing. In order to enhance the process ability and efficiency of the rubber compound, such as encouraging wet grip and wear resistance, this kind of processing oil was applied to the rubber compound beside other additives (Mohamed *et al.*, 2017).

According to Dasgupta et al., (2007), the Swedish National and Chemicals Inspectorate in 1994, KEMI, has declared that the aromatic oil with higher content of polycyclic aromatic compounds (PCA) as poisonous or carcinogenic. It was also supported by Li *et al.*, (2015) had stated that, the polycyclic aromatic hydrocarbon (PAH), which is the main elements of aromatic oil for tire rubbers, having the potential to cause cancer. Also, it can cause harmful to the community or human health and significant pollution to the environment. The following Table 2.1 demonstrates the commercial PO for rubber that are commonly used for compounding process.

In addition, Flanigan *et al.* (2011) had stated that, the European Union (EU) had prohibited a highly aromatic oils (DAE) which contain more than 10 mg/kg of the sum of eight listed polycyclic aromatic hydrocarbons (PAH) or more than 1 mg/kg. However, the prospective replacement oils for (DAE) has included the naphthenic oils, residual aromatic extracts (RAE), and treated distillate aromatic extracts (TDAE).

Table 2.1: The commercial PO for rubber which used for compounding process (Öter et al., 2011)

Type of Oil	Commercial name	Code
DAE	Aromatic Oil	DAE
MES	Vivatec 200 Nytex 832	MES-1 MES-2
TDAE	Vivatec 500 Nytex 840	TDAE-1 TDAE-2
NAP	Nytex 4700 Octopus N317	NAP-1 NAP-2

2.1.1 Types of PO

Dasgupta et al., (2007) had stated that, the most importance PO for rubber processing purposes is linseed oil, soya bean oil and castor oil which could afford fast drying and good color confinement properties. Soybean oil is known as a rubber plasticizer because the double bond in it will interact in the cross-linking stage along the dual bond of the rubber molecular chains.

All in all, soybean oil is regarded as one of the important vegetable oils that mostly utilized while; soybean oil consumption in 2018 only was over than 56 million tons (Xu et al., 2020).

The bio-based oil was soy oil, beaver oil, olive oil and vulcanized vegetable oils, as reported by Flanigan et al. (2011). Previously, the petroleum based oils used as processing oils for rubber compounds as plasticizers to minimize the compound viscosity and maximize the flexibility at lower temperature. The PO for rubber formulations is summarized as in Table 2.1.1.

For automotive application, due to higher output and lower emissions compared to other preferred methyl esters, linseed oil based methyl ester is the best performing engine fuel. Compared to diesel at rating load, brake specific fuel consumption for linseed oil is increased and is the result of delays in the ignition process (Antony *et al.*, 2017).

Table 2.1.1: PO used for rubber (Flanigan et al., 2011)

Oil Type	Raw Source
Aromatic Oil	Crude Oil
Naphthenic Oil	Crude Oil
Soy Oil	Soybeans
Tall Oil	Pine Trees
Linseed Oil	Flax Seeds
Castor Oil	Castor Plant
Orange Oil	Orange Peel
Vulcanized Vegetable Oil	Soybeans

2.1.2 Properties of PO

Boontawee *et al.* (2013) had stated that; the vegetable oils are plentiful natural products that used for greater performance in rubber compounds processing. Types of vegetable oils (VO) as the following, coconut, palms, and soybean oils can be relevant for rubber compound. By this way, the carcinogenic risk of processing oil, specifically petroleum based aromatic oils may be excluded.

Processing oils possessed several properties such as lower viscosity and good compatibility with rubber. It had deemed that the processing oils have a good compatibility with rubber and able to improve their process ability (Grosser, 2015) .

Processing oil as plasticizers are chosen on the basis of their chemical compatibility with the elastomer matrix and glass transition temperature, which influences the complex mechanical properties of the compounded rubber (Flanigan et al., 2013). Figure 2.1.2: present the properties of NR compound with types of PO.

Table 2.1.2: Properties of NR compound with types of PO (Flanigan et al., 2013)

Types of PO in the NR compound	Mixing energy [kJ]	Mooney viscosity [ML(1+4),100°C]	Scorch time [min]	Cure time [min]	MH-ML [dNm]
Without oil	775	41.5	2.59	10.4	14.76
Coconut oil	626	34.4	3.31	11.36	9.85
Palm oil	574	30.0	3.32	10.09	8.95
Soybean oil	557	25.2	3.37	10.02	8.71

2.1.3 Production of rubber compound

Dario *et al.* (2018) has claimed that, the disposal of waste cooking oil was considered as problem for the humankind. Thus, the feasible solution is to produce raw material for biodiesel production. Nevertheless, to analyse a process for waste cooking oils (WCO), via filtration with a cellulose filter, drying with silica gel, and esterification with methanol, for removing particles as standard procedure for WCO refining by employing a filter paper.

Higher aromatic oils are commonly used as extender oils for rubber compounding. Their success is because of strong compatibility with the most modern natural and synthetic elastomers. In addition, extending oils are also defined as processing oils which are added to the rubber compounding in the manufacturing process of rubber products to ensure reasonable process ability. They are also important to ensure the mechanical consistency of the tires, in particular their conformity to the road surface (Chandrasekara *et al.*, 2011).

Fillers are known as chemicals that are not functioning as a curative agent. The primary aim of their addition is to increase or maximize the mechanical properties of the resulted rubber vulcanizes, such as the tensile strength, tearing, abrasion and flexing resistance. Carbon black (CB) is considered as the most common filler for the manufacturing of different kinds of rubber products, and CB is usually used to strengthen the compound of rubber (Surya *et al.*, 2017).

Usually, fillers, additives, and other strengthening materials are applied to reinforce the rubber compound properties. The processing oils, is one of the compounds that are commonly applied during the manufacturing process of rubber copounds process, which serves as compatibility agent that increasing the process ability of them (Mohamed *et al.*, 2017).

2.2 Rubber compound

Compound refers to the science of selection and combination of elastomers and other additives to achieve the constant mixture and improving the importance physical and chemical properties of finish the products. The aim of rubber compound is to satisfy the end of properties, better processing, and cost reduction and economic processing (Sisanth *et al.*, 2017).

The growth of industry had made the use of rubber materials becoming widespread, and also brings out the higher standards for rubber properties as well as manufacturing techniques (He *et al.*, 2019).

The drawbacks which restrict the application of natural rubber are includes of being instable at higher temperature; being difficult to process into oil-based and organic solvents because of its unsaturated hydrocarbon chain structure and non-polar mechanical properties of cross-linked rubber that must changed via addition of fillers to confirm their final applications. Petroleum-based fillers are used in the preparation of natural rubber (Bao *et al.*, 2016).

Rubber and elastomers is considering as are of the most common materials that are substantially known for their versatility and capability to contain particles such as CB, silica and clay in order to enhance and achieve the required properties for particular applications wherever impact tolerance or hardness is required (Mohamed *et al.*, 2017).

The integration of reinforcing fillers from alternative sources into polymeric materials could result in new materials development of improved properties and biodegradability. The alternative sources, such as rice husks, palm oil, and chitin are popularly used in place of widely used CB, and synthetic fibers. This strategy has becoming of significant importance in recent year (Ismail *et al.*,2011).

Silica is incompatible with non-polar rubbers such as NR. In the other hand it was suitable with polar rubbers such as polychloroprene rubber, butadiene rubber (BR) and styrene butadiene rubber (SBR). Using silica in nonpolar rubber require compatibilization to solve weak dispersion of filter that could resulted for ultimately inferior properties (Sengloyluan *et al.*, 2014).

A typical production processes in the rubber factories are as following; storing, handling and weighing of raw materials. Raw rubber milling, rubber mixing and chemical rubber mixing. Also, methods such as sheeting, extruding and calendaring are intermediate. Vulcanization of rubber compound or curing, and finishing product, inspection and testing. Lastly, followed by the storage, packing and dispatch (Jagadale *et al.*, 2015).

2.2.1 NR compound

Natural rubber (NR) is considered as one of the most common elastomers that usually used in factories, engineering field and technological purpose because of its superior and exceptional mechanical properties. These are the main reasons or their importance utilization for several applications, such tires, gaskets and mountings (Carli *et al.*, 2011).

Natural rubber (NR) remains as a significant general purpose rubber owing to its outstanding cost-effectiveness ratio. Natural rubber plays a particularly important role in an automotive tires applications, where its dynamic properties are necessary (Yang *et al.*, 2010c).

The main component of Hevea brasiliensis natural rubber (NR) is polyisoprene. However, separate non-rubbers component such as proteins, lipids, and inorganic compounds are also made of NR. Depending on several variables such as clones, soils, season and environmental conditions, the amount of non-rubbers is variable (Tuampoemsab *et al.*, 2015). Figure 2.2.1 present NR chemical structure (polyisoprene).

Epoxidized natural rubber (ENR) is more polar as compared than virgin NR because of the epoxide groups in its molecular structure. The physical and chemical characteristics of ENR are affected by the epoxide components, such as heat and swelling resistance. ENR has interacted at beside of hydroxyl group on silica surfaces through its polar functional groups (Sengloyluan *et al.*, 2014).

NR has properties such as higher strength, oil resistance, enhanced wet grip and excellent rolling resistance. NR getting from latex is mainly polymerized isoprene beside a low percentage of contaminant on it. Also, the vulcanization and sulfur are usually used to enhance their properties (Ulfah *et al.*, 2015).

The NR rubber bulk is commonly used in anti-vibration and shock absorbance applications includes tires, rubber insulators and seismic bearings, since their energy dissipation ability and viscoelasticity is usually superior to that of other engineering material. Rubber capability to adapt to any object on which it falls into contact where it is allowed to be an efficient seal in engine, window seals and sea waterproof (Kamaruddin *et al.*, 2017).

An approximate about 10 million tons of natural rubber and latex are manufactured each year, with 70% of the production are dominated for the tire factories. With higher demands and price spikes of up to $6/kg for natural rubber, alternatives for improving latex and natural rubber from Hevea trees have earned overwhelming attention (Flanigan et al., 2013).

Carbon black (CB) is commonly added to strengthen the NR. In NR/CB compounding, filler-polymer interpenetration network is constituted based on the interfacial interactions and the dispersion of the CB filler (Xu *et al.*, 2019).

With similar amounts of CB the commercial organclay (OC) has been compounded with natural rubber nanocomposites via a new technique of incorporating nanofillers onto solid rubber by a conventional two-roll mil (Carli *et al.*, 2011).

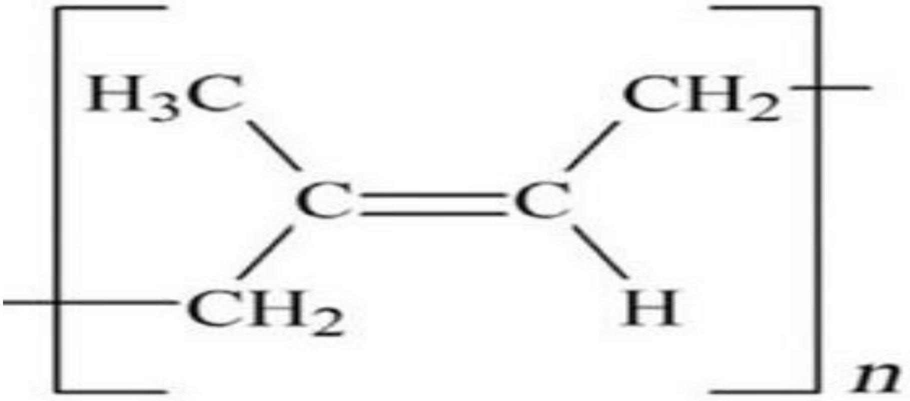


Figure 2.2.1: NR chemical structure (polyisoprene) (Tuampoemsab et al., 2015)

2.2.2 Vulcanization of NR rubber compounds

Almost any rubber product undergoes a vulcanization phase. The fundamental concept of vulcanization is through establishment of chemical cross-links among rubber macromolecules, that leads into the creation of 3D network of rubber matrixes through reactions between functional groups of elastomeric chains with suitable curing agents (Kruželák *et al.*, 2016)**.** Figure 2.2.2 present the cross-linking network structure of rubber vulcanization.

Rubber compound rubbery behavior are consists of rubber additives such as plasticizers that is commonly used to minimize the viscosity, increase deformability and change its properties; vulcanizing or curing agent that will cross-link the rubber chains and accelerators agent to accelerate the rate of curing during vulcanization process (Surya *et al.*, 2017).

ENR rubber was used as a compatibilizer for silica-filled natural rubber blend to further improve their mechanical properties. The usage of arylonitrile butadiene rubber (NBR) has improved the tensile strength, tear strength and the abrasion, as well as lowering the tangent loss. The ENR behaves as a coupling agent so it can cross-link with NBR and connected beside the silica filler at the temperature of vulcanization (Sengloyluan *et al.*, 2014).

In addition, the use of bifunctional organosilanes as binding agents is widely used to improve the reinforcing performance of silica. Under optimum conditions, during the mixing of silanes can chemically bond into silica and then reacted with rubber while vulcanization stage (Diani and Gall, 2006).

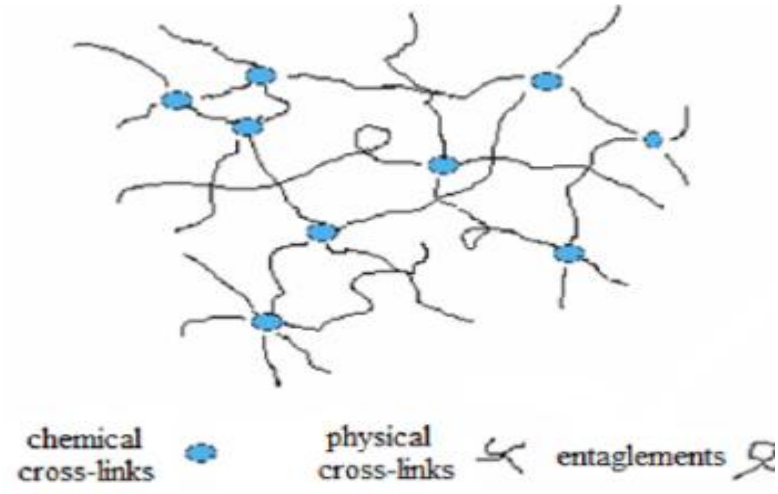


Figure 2.2.2: The cross-linking network structure of rubber vulcanization (Kruželák et al., 2016)

2.2.3 Rubber compound ingredients

Basic polymers and ingredients have been used to produce rubber compound, either separately or after blends, has produced some carcinogenic vapor and fumes during mixing, vulcanizing and even while storing. When the chemical or dust comes into contact with the environment, some gets contaminated in water and thus, directly or indirectly influences living organisms (Jagadale et al., 2015).

Tires contain vulcanized rubber with the rubber fabric; together with reinforced textile cords, and steel-wire support beads. With various natural and artificial rubbers and other elements are included within the tire; CB, extender oil, sulfur, and other additives. For example, accelerators, organo-sulfur compounds, zinc oxide and stearic acid (Sadaka *et al.*, 2012).

Plasticizers are considered as a special group of ingredients. They are commonly used in the rubber factory as processing additives. They are very helpful in enhancing the process ability of rubber as well as to change the chemical and physical properties of rubber compound (Jagadale *et al.*, 2015).

2.2.4 Properties of rubber compound

Fillers are essential additives that are used in rubber compound. They are relevant to the rubber mixture in order to maximize the properties which are necessary for end service purposes. Product benefits could resulting from filler which hardened the rubber through vulcanizations which include the structural stability, enhanced physico-mechanical properties, strength and manufacturing efficiency (Onyeagoro, 2012).

Reinforcing rubbers with commercially available fillers has been typical applies to yield properties needed for specific applications. In recent years, there are several studies about nano-sized reinforcing fillers because of the perfect demand for enhancing the material properties (Ismail *et al.*, 2011).

2.2.4.1 Mechanical properties of rubber compound

Elastomers filled composites are commonly employed in number of engineering applications like structural engineering, mechanical engineering, and automative engineering because of higher elasticity, high damping and greater elongation at failure. NR properties can be suited to this requirments, by adding of carbon black (CB) fillers of different surface chemistry and accumulation size ratio (Luo *et al.*, 2010).

In addition, NR is renowned for its excellent efficiency across a wide range of applications. While NR has outstanding properties, in certain situations the reinforcing fillers are normally added to NR to acquire the suitable properties for different applications. A wide range of particulate fillers are usually utilized in the rubber factory for various reasons. The most important of which are stabilization that minimize the cost and maximize process ability in manufacturing (Yang *et al.* 2010).

CB has several disadvantages, such as converting the hue of rubber to charcoal, causing waste and depleting profit due to its roots from petroleum. For this cause, diverse research activities have been focused on the production of new rubber compounds (Bao *et al.*, 2016).

In addition, Sampath *et al.*, (2015) had stated that the mechanical properties of rubber can be developed by using filler addition through minimizing the particle size or through modification treating it with an effective binding agent.

Silica and CB are used as the main reinforcing agents in rubber compounds but their surface chemistry is totally different. Silica has higher value of hydroxyl groups on their surface, which produced in strong filler interactions and adsorption of polar materials via hydrogen bonds (Ulfah *et al.*, 2015). Moreover, CB and silica are used beside a nanoscale fine structure to reinforce the composites, but their amount is highly than nanofillers (Carli *et al.*, 2011).

2.2.4.2 Dynamical properties of rubber compound

The reinforcement of polymers by means of clay filler addition has long drawn significant interest due to the possible nanodispersion of silicate layers of clay and increasing of polymer filler ratio (Yang *et al.*, 2010a).

As far as dynamic viscoelastic characteristics are concerned, if the mobility of rubber molecules are constrained by-rubber interactions, then higher energy is required to transfer the rubber molecules (Park *et al.*, 2018).

During complex vulcanization in the midst of liquid thermoplastic under shear stress, the rubber is vulcanised. As crosslinked rubber is unable to coalesce, although at higher rubber content, rubber particles are scattered in the thermoplastic matrix (Xu *et al.*, 2013).

Epoxidized natural rubber (ENR) beside various mole % of epoxide groups are commonly used as compatibilizers in a specific range of 2.5-15 phr for virgin NR and silica compounds. Interaction of epoxide groups with the silanol groups of silica could enhance silica rubber compatibilization (Sengloyluan *et al.*, 2014).

2.2.4.3 Physical properties of rubber compound

The physical properties of rubber compound can be converted depending to their particular application (Flanigan *et al.*, 2013)**.** In the other hand, NR is attractive material because of its perfect physical properties, especially its higher mechanical strength, low heat build-up, resistance to impact, and excellent durability (Onyeagoro, 2012)**.**

Physical properties of polymer blends are primarily influenced by the nature of their structure of compound mixture and the interfacial adhesion between polymers. (Sampath *et al.*,2015).

2.3 WCO as sustainable PO

WCO can be defined as the vegetable oil which derived through repeatedly cooking food and other food preparation that makes the edible vegetable oil is no longer appropriate for use because of its higher free fatty acid (FFA) amount (Sarno and Iuliano, 2019).

Edible vegetable oils such as canola, soys and corn were used for the production of biodiesel and have been described as for diesel alternative. However, the high-rise cost of conversion is the greatest obstacle to the commercialization of biodiesel production from edible vegetable oil.

WCO that is much cheaper than edible vegetable oil is a promising alternative to edible vegetable oil (Patil *et al.*, 2010). Figure 2.3 depicts the biodiesel production from various feed stocks.

The higher energy request in the developed world country and in the domestic sector and the pollution issue caused by the widespread used of fossil fuels made it important to establish alternative energy sources with a lower environmental influence than traditional ones (Hingu *et al.*, 2010).

Cooking oil sources vary across the globe and their raw resources are plant-based lipids such as margarine, coconut oil, olive oil, and palm oil, or animal-based lipids such as butter and kermanshahi oil. In Malaysia, the commonly used cooking oil is made from palm oil due to its cheap cost compared than other sources (Yaakob *et al.*, 2013).

Vegetable oil (VO) is a possible fuel supply that is classified as edible and non-edible oils on the basis of its properties. The edible VO is a triglyceride derived from the plant sources (Nanda *et al.*, 2019).

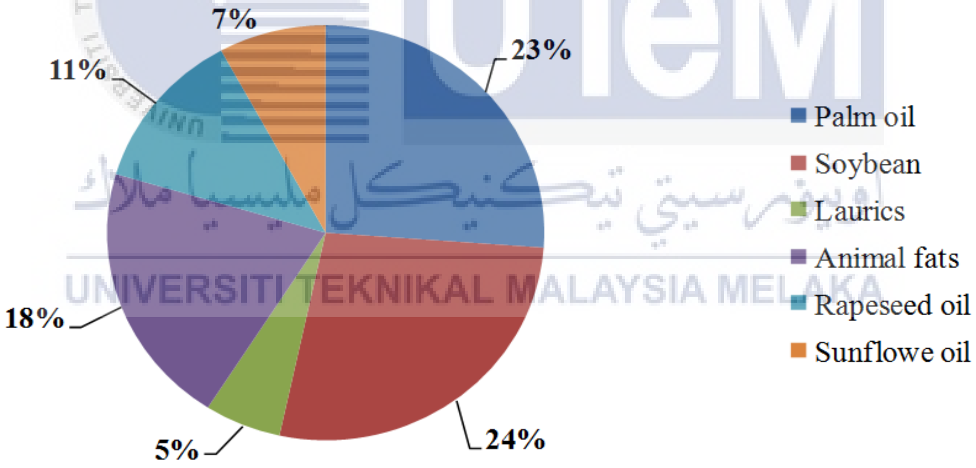


Figure 2.3: Biodiesel production from various feed stocks (Gnanaprakasam *et al.*, 2013)

2.3.1 Introduction of WCO

According to Gnanaprakasam *et al.* (2013)**,** the production of biodiesel has been increased tremendously in order to cope with the depletion issue of fossil fuels. Biodiesel production around the world has increased in recent years. The benefit of using vegetable oil as raw material for manufacture of biodiesel with lower free fatty acid content.

WCO possessed some significant environmental impacts, including unpleasant odors. It may say that one liter of oil poured into natural waters could pollute about 500,000 liters of water. Mainly, it raises the microbial load on the water sources and often creates a thin layer over the water that decrease the importance concentration of dissolved oxygen for aquatic living beings (Panadare and Rathod, 2015).

During frying, several volatile compounds are produced as a result of mixture of highly oxygen and temperature, which facilitates the oxidation processes and other transformations (Don et al., 2013).

Malaysia has produced more than 17.7 million tons of palm oil and used around 4.5 million hectares of land, and it was the second largest country to produce palm oil. Malaysia was considered as the largest exporter of palm oil in the globe. In addition, around 40 % of palm oil made into cooking oil, specialty fats (Sengloyluan *et al.*, 2014).

Transesterification is a common method to manufacture biodiesel. Due to the lower price of methanol in contrast to other alcohols, it was considered as the most widely used alcohol for this process. The reaction is considered as methanolysis. Basically, this reaction is catalyzed by an acid catalyst. The most widely used are alkali catalysts, since they make the phase smoother and the conditions of reaction condition are milder (Kiliç *et al.*, 2013).

Several researchers had investigated alcohols, liquefied petroleum gas, vegetable oils, biofuels, and hydrogen as renewable fuels. Alcohols are emerging as good alternatives because they are part of the oxygenated fuel unit. Methanol, fructose, propanol, and butanol are the most favored alcohols for use. The temperature of auto-ignition, vaporization heat and stoichiometric air-fuel ratio are equivalent to those of traditional mineral diesel (Halek *et al.*, 2009).

Methanol is one of alcohol types that can be used for biodiesel processing as a part of methanol recovery. The biodiesel yield from methanol-based WCO is higher. The biodiesel viscosity obtained with methanol is less than that obtained with other alcohols (ethanol) and the biodiesel viscosity is lower than that obtained with other alcohol (Gnanaprakasam *et al.*, 2013).

2.3.1.1 Collections and refining of WCO

Approximately about three billion liters of cooking oil are consumed annually in Malaysia, with about 30% improvement in biodiesel output that equal to 10% of diesel output (Gupta *et al.*, 2017).

In China, some restaurants also export their surplus cooking oil (CO) to unlawful or illegal farmers who then turn it into low quality oil with significant health threats. However, using WCO to create electricity consider as a good deal with main difficulties. For example, Japan uses biodiesel which processed from WCO to power its garbage trucks and encourages the use of biodiesel with consumption taxes (Zhang *et al.*, 2017).

According to Panadare and Rathod (2015), China had produced about 4.50 million tons of WCO per year. In India, referring to 2009-2010 oil consumption trend, about 0.167 million tons of WCO can be expected. Japan and Ireland has generated about 0.45-0.57 and 0.153 million tons of WCO per year respectively.

Palm oil is the most effective biological source of oil-based hydrocarbon and is considerably very competitive than any other commercial oil based crops. Palm oil has a yield capacity usually of around 4-6 tons of oil per hectare per year for the best commercial plantation (Arniza et al., 2015).

2.3.1.2 Applications of WCO

Oil can be used in chemical factory for the manufacturing of soap, detergents, paint, lubricants, grease and among others. Also, the storage and disposal of this form of waste has lead into the combined solution of three environmental problems which are the reduction of waste by goods recovery, reduction of energy dependency on fossil fuels and reduction of pollutants (Ramos et al., 2013).

In certain nations, such as the USA and Japan, the WCO disposal regulation was very strict. There are several private companies that are currently collected the WCO and process it primarily for the manufacture of biodiesel or also for production of electricity. Kumar Polcher uses WCO obtained from the restaurants to produce approximately about 1.9 million liters of biodiesel per year (Panadare and Rathod, 2015).

The conversion of waste cooking oil usually used as key raw materials in several manufacturing processes, such as bio-lubricant or fuel processing, or as additives for asphalt (Don et al., 2013).

2.3.2 Properties of WCO

Analysis of various properties of WCO, such as acid value, viscosity, and fatty acid profile, shows a surprising values based on its sources and mode of usage (Panadare and Rathod, 2015). Figure 2.3.2 present the general properties of WCO.

WCO is mainly a combination of triglycerides and fatty acids, some of which are contaminations or impurities. Derivatives through the frying process such as FFA, heterocycles and metal traces, emanated from food leaching. The basic structure of WCO can also be used as valuable sources of chemicals for the manufacture of bioplasticizers, syngas and sorbents (Don et al., 2013).

In WCO, the water content can speed up the hydrolysis reaction and minimize the value of ester formation at the same time. To achieve 90 % of biodiesel production, the water level should not more than 0.50 % and it is important for an acid-catalyzed reaction than a based catalyzed reaction (Gnanaprakasam *et al.*, 2013).

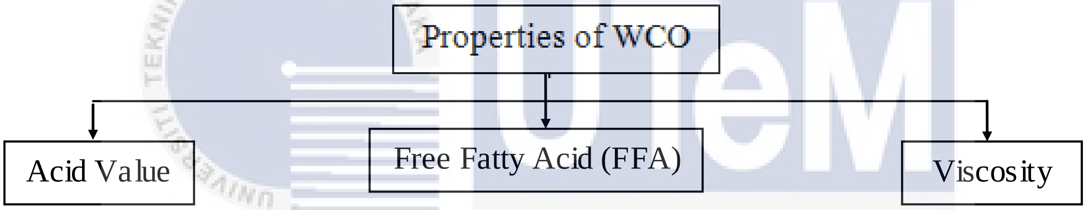


Figure 2.3.2: The general properties of WCO (Panadare and Rathod, 2015)

2.3.2.1 Acid value

The acid value of oil was measured by titrating an oil solution in a diethyl ether with an acidic solution containing sodium. It was expressed as a volume of KOH (in mg) to neutralize 1g of oil (Dijkstra, 2015).

Acid value is an example of how an esterification reaction can be followed via a chemical analysis. Esters and acids have various physical properties and it was vital to know what is the chemical structures of estolides when mixture their physical properties (Cermak *et al.*, 2017). Acid performance, like kinematic viscosity, is a simple way to track the fuel consistency that was used as dilution (Knothe *et al.*, 2010).

The acid value is a systematic way to describe the free fatty acid content of a lipid raw material that are typically expressed as magnesium potassium hydroxide used to neutralize the acidity of gram of raw material. In the case of waste lipids, the acid levels are considerably higher than in the case of other traditional biodiesel feedstocks such as Palanga and Jatropha (Iglesias and Morales, 2012).

Any sources of fatty acid may be used to produce biodiesel. Moreover, any plant lipid must be ready substratum for the manufacturing of biodiesel. Animal fats and vegetable oils for biodiesel production has not long ago been perfect concern due to between the food supply of the long term (Sengloyluan *et al.*, 2014).

2.3.2.2 Viscosity

Viscosity index is a concept that is used lubricating oil subjected to consistency measurement to measure changes in kinematic viscosity at certian temperature. The lower the viscosity index, the higher the changes in temperature viscosity of oil. The viscosity of lubricant is closely linked to its capability to minimize the friction. In all cases, the viscosity index is very high (Cermak *et al.*, 2017) .

The minimization of viscosity is the main objective for alkyl esters in vegetable oils. The limits on this property are thus beyond the spectrum of most typical vegetable oil (methyl) esters and help to avoid vegetable oils as fuel. Highly viscosity of the oil triggers operational problems, such as engine deposit (Knothe *et al.*, 2010).

2.3.2.3 Free fatty acid (FFA)

FFA is primarily defines as the properties and usage of vegetable oils. Optimum applicability has includes the personalized free fatty acid profiles. Strong acid content is harmful to health. On the other hand, oils with higher oleic acid content are quite expensive (Bart *et al.*, 2010).

The proportion of unsaturated to saturated fatty acids in edible oils is very usful for human nutrition. Although, high-rise of saturated FFA are desirable to maximize oil consistency, they are also nutritionally unfavorable (Kostik *et al.*, 2013).

The higher content of FFA could lead into higher soap and water formation. Comparably, even with a homogenous base catalyst, transesterification reaction will not begin if the FFA content has reached into 3.00 %.

This problem could be solved via utilization a heterogeneous catalyst and also pretreatment of FFA into FFA based ester with an acid homogenous catalyst (Gnanaprakasam *et al.*, 2013).

2.4 Transesterification of WCO

Transesterification referred to as alcoholysis, is the reaction of butter beside alcohol in the presence of solvent for esters and glycerol. Cycle involved is usually a series of three consecutive steps, which are reversible reactions converting the triglyceride into diglyceride into monoglyceride and finally into glyceride which release esters at each step (Hingu et al., 2010).

Mid-glycerol, mono-and diacylglycerols are constructed during the trasesterification process, small quantities of which can remain in the final biofiesel (methyl) substance. Besides the small glycerol, unreacted triaylglycerols as well as non-separated glycerol, FFA, residual alcohol and catalysts can remain in the final product (Knothe *et al.*, 2010).

A short-chain alcohol is used in transesterification also called as methanolysis of glycerol in triglycerides. The cycle begins beside a series of three successive reversible reactions in which triglycerides are transformed to diglycerides then transformed to monoglycerides then turned to glycerol. Each step results in an ester, producing three ester molecules from one triglyceride molecule (Yaakob et al., 2013). Figure 2.4 present the overall transesterification chemical equation.

Biodiesel consists of methyl and ethyl esters of fatty acids which may created by totally many lipid sources through a trasesterification method. However, throughout transesterification, the lipids has reacted beside a short-chain alcohol with the presence of a solid catalyst, which might be acid (Cordero-Ravelo and Schallenberg-Rodriguez, 2018).

Methanol has been used for the transesterificaton of sunflower waste oil and being researched by using a different alcohol to oil molar ratios beside NaOH and found that the 6:1 alcohol to oil molar ratios gives the maximum yield of 99.5 % methyl ester formation. However, when the transesterification of waste canola oil by using one molar methanol to oil ratio was studied, the yield has reported to be 49.5% (Gnanaprakasam *et al.*, 2013).

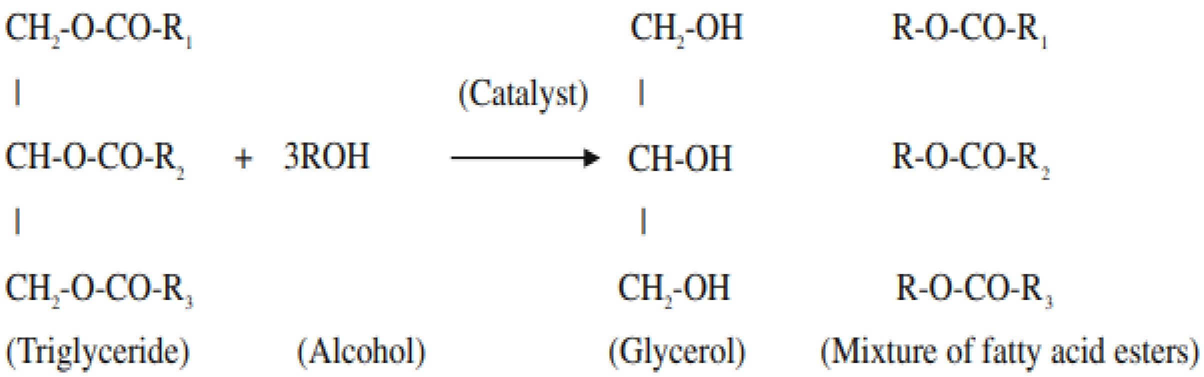


Figure 2.4: Transesterification chemical equation (Leung et al., 2010)

2.4.1 Transesterification process of WCO

Gupta et al., (2017) has stated that, the transesterification process is the method by which biodiesel would be generated. In any scenario, the triglycerides and alcohol has produced in the presence of catalytic reactions to the synthesis of esters and glycerin. Figure 2.4.1: present a flow chart to produce biodiesel from WCO.

Once FFA in WCO is < 2% the method can immediately to transesterification process, but if the (FFA) is > 2 % it needs to esterification method to minimize FFA in WCO. The acid value in WCO in order to approximate FFA satisfy and provide an indication of acid value acid catalyst and methanol will be required to drive the chemical for acid esterification towards the development of methyl ester, it was decided (Abdullah, *et al.*, 2013).

Biodiesel defines as the long-chain methyl, or ethyl comes by transesterifying vegetable oil with an alcohol. Usually, the procedure of intensification of natural triglyceride transesterification is achieved commercially by using a mechanical agitation system for homogenization (Aghbashlo *et al.*, 2017).

Biodiesel is a methyl ester extracted from vegetable oils or WCO via transesterificatlion method. However, transesterification method or usually referred to as alcoholic beverages, is the reaction among hydroxyl groups of triglycerides to form esters (Puspa Asri and Puspita Sari, 2015).

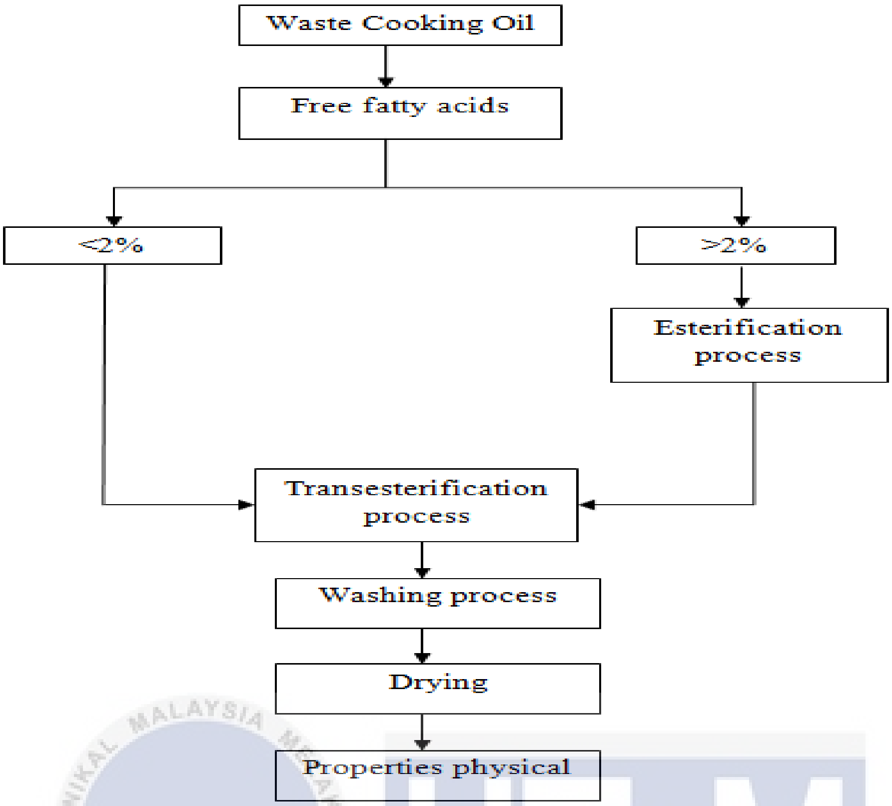


Figure 2.4.1: A flow chart to produce biodiesel from WCO (Abdullah, *et al.*, 2013)

2.4.2 Characterization of transesterification

The best method to manufacture biodiesel via homogeneous base catalysts such as sodium hydroxide is by performing transesterification. The homogenous state of the catalytic method is milder than an accelerated transesterification. However, there are drawbacks to the homogeneous catalyst, mainly in the separation step (Tan *et al.*, 2017).

Moradi *et al.*, (2012) had stated that, a series of transesterification reactions with processed soybean oil were conducted under set operating conditions at different durations. The compounds were then studied to see how the conversion is varied through the reaction. Viscosity, pour point, cloud point, and refractive index were calculated as chosen physical properties to determine the strength of transition.

Transesterification used to minimize viscosity in biodiesel. This method can be used if the free fatty acid (FFA) is less than 2 %. Sodium hydroxide usually used as catalyst in this method. The value of catalyst had effect the conversion of esters through the transesterification process (Abdullah, et al., 2013). Figure 2.4.2: Shown the WCO to biodiesel.

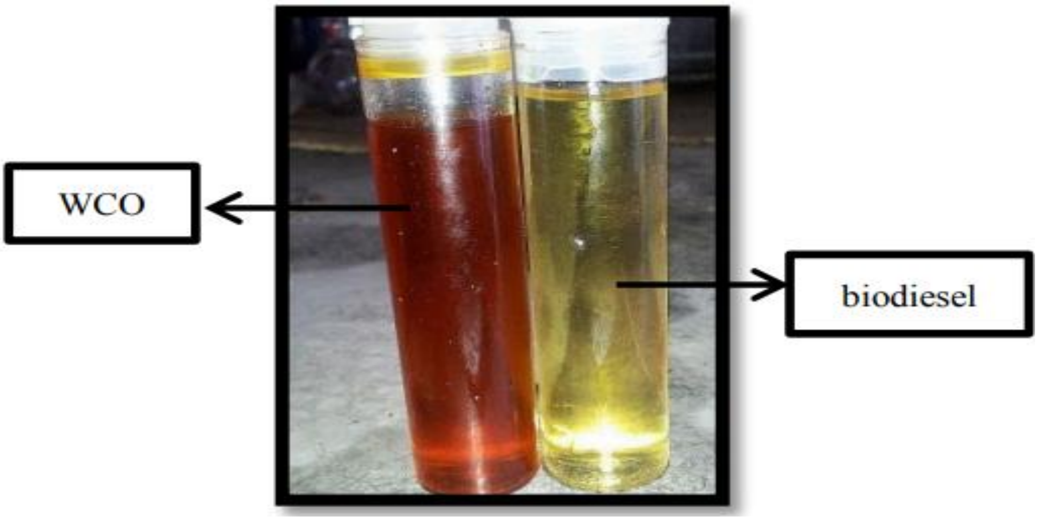


Figure 2.4.2: WCO and biodiesel (Abdullah, et al., 2013)

2.4.3 Advance applications of transesterification

Transesterification is the most widely used method for biodiesel production. It was a procedure that uses oils that obtained from cow, oleaginous microorganisms to react with alcohol that are mainly methanol for the synthesis of fatty acid methyl esters or FAMEs as biodiesel (Sadaka *et al.*, 2012).

Direct transesterification refers to the conversion of biodiesel of algal oils which are found in biomass. Direct transesterification, here, requires both free fatty acid esterification and triglyceride transesterification from microalgae. As compared to traditional extraction, this method simplifies the process and increases the biodiesel yield due to the absence of an oil extraction stage that causes oil loss (Park *et al.*, 2015).

The reaction that is usually catalyzed by an acid or base occurs at the interfaces of two immiscible processes, i.e. in traditional transesterification of triglycerides (TG) with methanol to manufacture biodiesel, With TG and methanol. The interfacial surface area between these two immiscible phases must be maximized to increase the overall reaction rate and product conversion (Ho *et al.*, 2016).

Composed of long-chain FAME, biodiesel can be given in the presence of catalysts via transesterification of triglycerides and methanol. Conventionally, acid and alkali catalysts, such as phosphoric acid, sulphonic acid and sodium hydroxide, can catalyze transesterification. These catalysts, however, produce by-products, induce machinery deterioration, generate a significant volume of waste water and are complicated to retrieve (Ding *et al.*, 2018).

2.5 Review on rubber compound using sustainable PO

Polyisoprene was the first commercially manufactured elastomer in the world. Usually obtained from the latex of the Hevea Brasilienis rubber tree, and during World War 2, a synthetic form was developed for an industrial scale. Nevertheless, both natural (NR) and synthetic (IR), polyisoprene compounds are economical and have a variety of acceptable physical properties, including low dynamic response, low hysteresis and high longevity. (Kind and Hull, 2012).

For nations around the world, the relentless rise in rubber waste has been a significant environmental problem. This is attributed to the growing rise in demand for rubber goods, such as the outgrowth of the development of automobiles and also higher demand for the use of rubber in automotive, medical, stem, goods for homes and much more Due the number of recycled rubber products grows (Nuzaimah *et al.*, 2018).

High aromatic oils, which derive as petrochemical industry derivatives, have historically been commonly used as rubber compounding extender oils. Their success is due to the strong ability with both natural and synthetic elastomers that are available. In the manufacturing process of rubber articles, extender oils are also mentioned to as processing oils and are applied to rubber compounds in order to obtain acceptable process ability. (Chandrasekara *et al.*, 2011).

2.6 Summary

This second chapter outlines the fundamental and the main concept of processing oil (PO) and rubber compound. This chapter discussed the literature review and the previous articles on rubber compound, its applications, its uses and its properties. Furthermore, this chapter summarized the transesterified waste cooking oil as sustainable replacement for synthetic processing oil. However, this chapter will be helpful and gives for executing the experimental stage.

CHAPTER 3

METHODOLOGY

This third chapter highlights the entire experimental phase flow that is needed to accomplish the objectives of study. The methodology of this research was included the principle that was carried out to complete the research. The methods that discussed were consist of raw material characterization and experimental procedure for sample preparation and testing the associated measures are all pointed to the standard of the American Society for Materials and Testing (ASTM).

3.1 An overview of methodology

Three separate experimental steps in the overall methodological process are based upon the specified objectives as stated in Chapter 1. Reference to Figure 3.1, the first stage was started with raw material preparation and characterization of transesterified waste cooking oil. Next, production of sustainable rubber compound analyzed by using standard Malaysian rubber-SMR-20, added WCO as extender processing oil. Last stage, the confirmed sample production was tested physically and mechanically by referring.

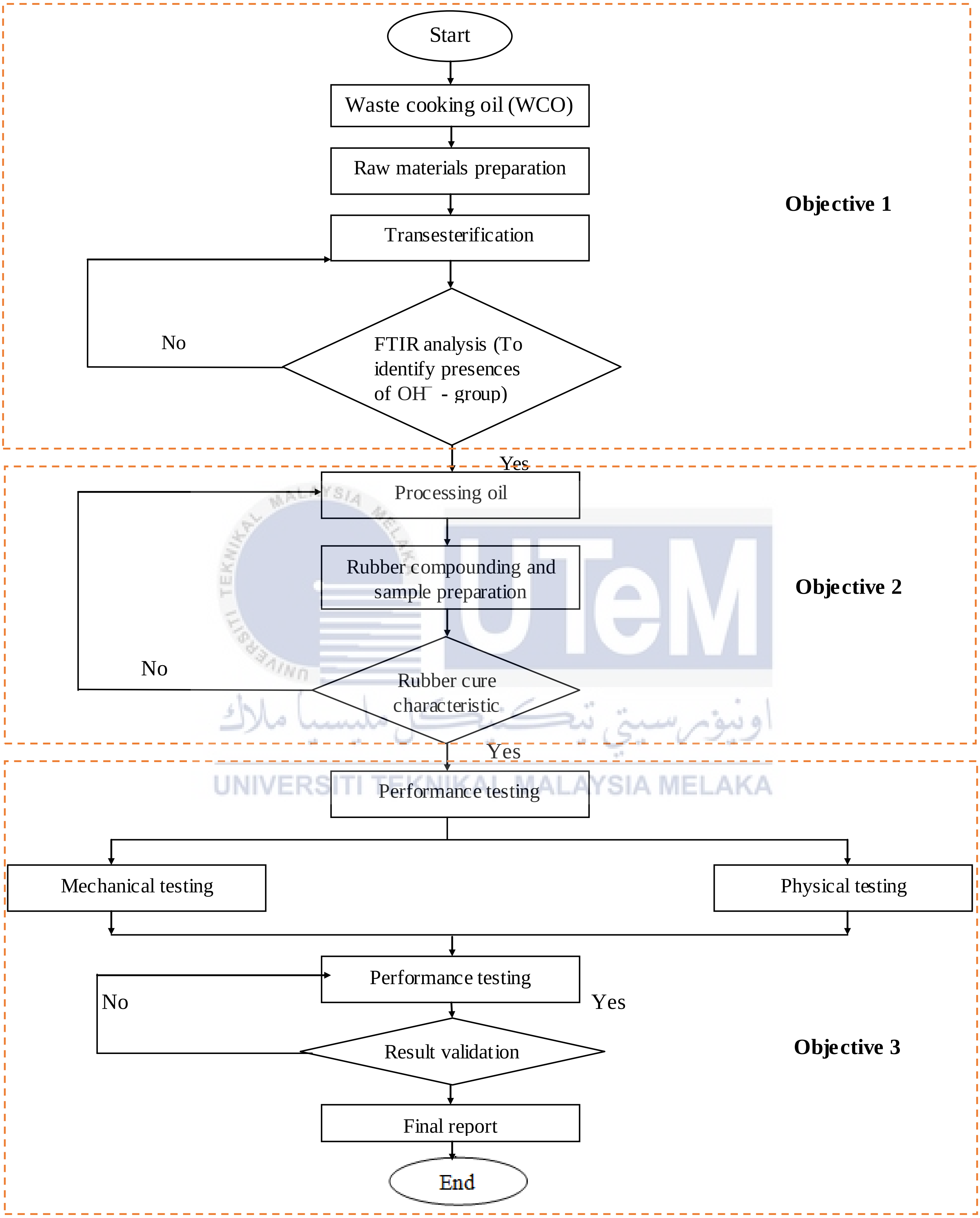


Figure 3.1: Methodology flow chart

For the first objective, the research goal was to treat the WCO using transestrification process into useable processing oil (PO) for rubber compounding purpose. In order to produce rubber compound from the usable (PO), some preparation should be carried out such transestrification process with the purpose to reduce the viscosity of WCO. The procedure was continued by two main stages of transesterification. Those stated process was highly important to introduce hydroxyl (OH^{-}) group in the molecular structure of WCO.

The next goal was to determine waste cooking oil WCO's ability as extender for natural rubber compound. This evaluation was helpful to verify the processing oil (PO) and testing the characteristics of rubber cure characteristic.

After the producing processing oil and testing of rubber cure characteristic, testing the performance of NR compound was compounded. Also, the sustainable rubber compound was tested for their physical and mechanical properties by analyzing the effect of PO content addition.

In this chapter, the following sections provide detail on the process and testing performed to complete this study.

3.2 Raw materials preparation

Preparation of raw materials has three types of feedstocks such as waste cooking oil (WCO), unused cooking oil (UCO) and filtered waste cooking oil (FWCO).

3.2.1 Waste cooking oil (WCO)

The production of WCO is considered as the functional of the frying temperature and period time of utilization the material used for frying. WCO were composed from a local restaurant (Yathreb restaurant) in Melaka, which produced French fries as well as sea food. It was decided to utilise oil from a fryer that was previously used for frying potatoes and other food products for this experiment. 25 litters of oil samples were acquired from a storage drum in which WCO was collected once a day for one week, resulting in a total of 25 litters of oil samples collected. It is expected that the sampling oils would be representative since they were collected from various batches of waste oil that were stored for 8 to 10 weeks. The temperature noticed while frying was in the variety of 130^{0}C - 175^{0}C. This temperature is similarity with the temperature (140^{0}C - 180^{0}C) to prepare the French fries.

Nevertheless, it was too hard to examine the temperature in boiling oil that gives about 5 to 10% error. Based on the amount of food used for frying, the oil was minimized from time to time at the end of every day and once in three days. Figure 3.2.1: Present the waste cooking oil (WCO).

Figure3.2.1: Waste cooking oil (WCO)

3.2.2 Natural rubber (NR)

NR grade of SMR-L 20 supplies from Rubber Leisure Company Sdn - Bhd, Melaka. The natural rubber (NR) was masticated in an internal mixer for about 65 min. The main compound and sulfur were added and milling was carried out about 5 min. The molding of rubber sheets was carried out using a laboratory hydraulic press at a temperature of 160^{o}C and a pressure of 150 kg/cm^2.

3.2.3 NR compound ingredients

Zinc oxide (ZnO) and stearic acid were combined and added to the combination. Following thorough mixing, the mixture was allowed to cool in ambient conditions. The mixture was then transfer into the two-roll mill, where it was thoroughly mixed once again. Sulfur and polyethylene glycol were combined and put to the two roll mill.

Several mill runs lasting approximately 5 minutes were necessary to ensure proper mixing. A thin compounded rubber sheet was produced by regulating the nip between the rollers.

3.3 Transesterification of WCO

3.3.1 Transesterification method

Firstly, condition of WCO has to be examined whether it is still fresh or already used. Then, it was filtered by using a vacuum filtration as shown in Figure 3.3.1 in order to reduce the contamination or any dust. The filter paper used in Whatman brand 47 mm of diameter. After vacuum filtration process is completely performed, filtered WCO is obtained. After that, the pre-treatment stage to eliminate the free fatty acid (FFA). In the beginning heat up the filtered WCO into 220°C using “hotplate magnetic stirrer” at 1000 rpm with adding 33 g of ginger with 3 mm thickness for 10 minutes. Then, remove the ginger by using spoon and leave it for 24 hours.

Figure 3.3.1: Vacuum Filtration

Next, Filtered WCO is going to undergo some procedure of chemical modification in order to introduce hydroxyl (OH^-) group. Firstly, mehanolysis was conducted.

In 1000 ml of reaction flask, a mixture of 1000 ml of WCO, 7.0092 mole of methanol and 2.25 g of sodium hydroxide (NaOH) are stirred using “hotplate magnetic stirrer” at 1000 rpm with 50° C of temperature. The mixing process is conducted within 90 minutes.

Next, it is transferred into separation funnel and allowed to precipitate overnight. Lastly, final product was washed using 100 ml of bicarbonate sodium solution at 5% and sodium chloride at 5%. Again, it was rewashed with water until it is completely neutralized. Finally, processing oil produced after being overporated at 90°C for 4 hours. The whole experimental is summarized in flowchart in Figure 3.3.1.1.

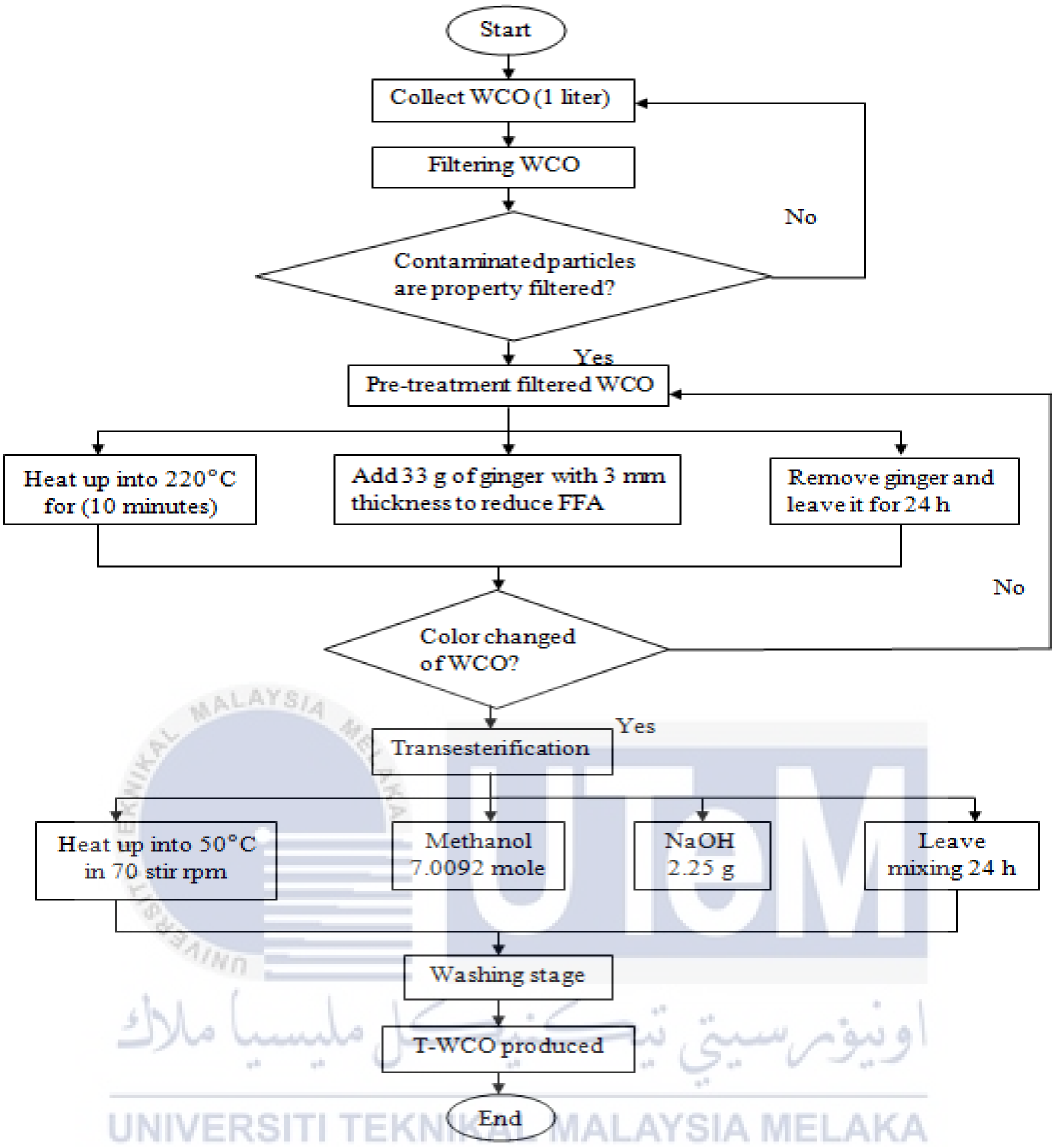


Figure 3.3.1.1: Transesterification process flow chart

3.3.2 FTIR spectra analysis

The presence of hydroxyl group in molecular structure of waste cooking oil (WCO) was characterized by using FTIR (FT/IR-6100, JASCO) as displayed in Figure 3.3.2. Hydroxyl group is critical to be presented in waste cooking oil in order to produce the processing oil.

FTIR is one of the most important characterization tools which created the spectrum of infra-red absorption of the chemical bonds and functional group. Both spectrums with a wavelength range of between 1000 cm^{-1} to 4 000 cm^{-1} are registered at 2mm/s scan speeds with a width of 7.1 mm.

Figure 3.3.2: Fourier Transform Infrared (FTIR) Spectroscopy

3.4 NR rubber compounding

3.4.1 Compounding method and NR formulation

There are various different formulations of natural rubber compound as shown in Table 3.4.1. Compounds were prepared in an open two-roll mixing mill as shown in Figure 3.4.1. At 35°C and a friction ratio of 1:3. The mixing period of the rubber formulations was about 20 minutes; complete composite weight was 1.5 kg. In the same mixer after 24 h the variations were accelerated.

Figure 3.4.1: Two-roll mixing mill

Table 3.4.1: NR formulations

NO	Ingredients	Weight (g)	PPhr
1	SMR L	1000	100
2	Polyphenolic antioxidant	20	2
3	Calcium carbonate	300	30
4	Zno	30	3
5	Stearic acid	15	1.5
6	Polyethylene glycol	4	0.4
7	DPG	2	0.2
8	MBTS	18	1.8
9	Titanium dioxide	1	0.1
10	Sulfur	15	1.5
	Total	1405	140.0

3.4.2 Sample preparation

The specimens used in physical and mechanical research test compressing moulding was fabricated of curing temperature at 160°C and at a pressure of 10 MPa, and the hot press hydraulic presses were electrically heated at the right time for the procedure determined by an oscillatory disc rheometer, Tech Pro-Rheotech OD+. All fine mixing procedure and sample preparation are performed at the research and development (R&D) laboratory of Rubber Leisure Company Sdn – Bhd. Located in Serkam, Merlimau, Melaka.

3.4.3 Cure characterization using Rheometer

The vulcanization reaction has been tested from data obtained from an oscillating disk rheometer (ODR). In addition, the effects on the vulcanization reaction to the added processing oil into NR compounds were measured. The SMR – L 20 rubber compound was vulcanized at the 160°C vulcanization temperature. The ODR Tech Pro-Rheotech OD+ rheometer, ASTM D 2084–06 was used. Figure 3.4.3: present Oscillating disk rheometer using for cure characterization.

Figure 3.4.3: Oscillating disk rheometer using for cure characterization

3.5 Performance Testing

3.5.1 Mechanical Testing

3.5.1.1 Tensile Testing

The sheet thickness 2 mm was accomplished using a Wallace die cutter by moulding the compression onto the dumbbell shape. Tensile testing was performed using the Instron model 3366 at room temperature (25 ± 2 °C) at 500 mm/min crosshead speed level.

3.5.1.2 Tear strength testing

Tear strength is defined as the resistance force that a rubber sample, which has been changed by cutting or slitting, provides to the propagation of a tear during its formation. For the tear test, a large number of different specimen configurations have been given. The value of tear strength is defined as the product of the force (kN) required to tear the sample divided by the thickness (m) of the sample, where thickness is measured in millimetres.

3.5.2 Physical Testing

3.5.2.1 Hardness Test (Shore-A hardness)

In accordance with the shore hardness – A standard ASTM D 2240, the hardness test for the vulcanized rubber materials were performed. A pointing conical indenter was pushed back into the case of the tester against a spring by pushing against a sample and this motion was turned into a pointer action on the dial. At least 5 mm from each other, five measurements were taken from different sites. Figure 3.5.2.1: Present the hardness meter.

Figure 3.5.2.1: Shore-A hardness identer

3.6 Summary

This chapter illustrates the whole flow of the experimental process that is required to achieve the main objectives of this study. The theory that was applied to complete the analysis was used in the methods of this research. Finally, all methods had been discussed consisted of the classification of raw materials and the experimental technique for sample processing and testing of the relevant steps, both referring to the American Society for Materials and Testing standard (ASTM).

CHAPTER 4

RESULT AND DISCUSSION

The fourth chapter represents discussion and analysis of experimental data for sample preparation and their related conducted testing. Supporting by previous researches, the experimental findings data was analyzed with further justification to reinforce the discussion.

4.1 An overview

The main objective of this study is to modify WCO into usable PO for rubber compound using transesterification process. There are two main stages involved in this study. In order to produce PO based WCO, the presence of OH^- group is mainly required. Their existence could be proven by identifying it through Fourier-transform infrared (FTIR) spectroscopy technique.

The second objective was to evaluate the potential WCO, to be used as PO for NR based compound. However, an oscillating disc rheometer (ODR) was used to do this evaluation, which was beneficial in verifying the processing oil (PO) and evaluating the features of rubber curing characteristic.

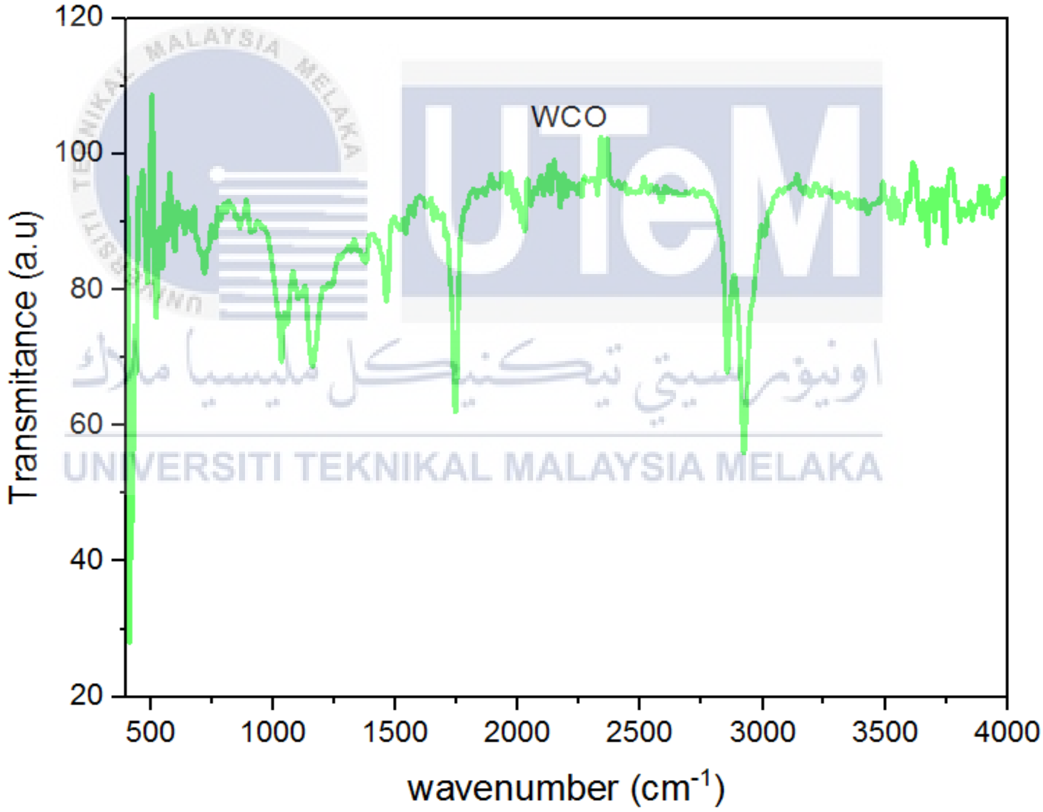
Following the production of PO and the testing of rubber curing characteristics, a compound for evaluating the performance of NR compound was analyzed. In addition, the mechanical and physical characteristics of the sustainable rubber compound were evaluated by examining the impact of the addition of PO content to the rubber compound.

The next sections of this chapter provide the findings of the testing that was carried out in order to finish this study.

4.2 FTIR analysis for raw material

Raw material characterization covered three different types of raw materials which are raw waste cooking oil (RWCO), filtered waste cooking oil (FWCO) and unused cooking oil (UCO). They are measured for their hardness and tensile strength that influences the quality of sustainable rubber compound samples that would at the end affect the final property of the rubber compound.

There was no evidence of the O-H bond in the initial spectra of WCO stretching, which was needed to produce the signal for processing oil. According to the band, WCO contains the same bond stretching as other materials, with the exception of the C-C triple bond at 2800cm^{-1}, as shown in Figure 4.2. The FTIR spectra of WCO contained the highest inverted peak, which could be a result of waste contaminants generated during frying and cooking activities. The C-C bond stretching is shown by the inverted peak at 2300cm^{-1}.



4.2: FTIR for the raw material

4.3 Cure characteristic analysis

Scorch time and cure time increase when the amount of – processing oil added is increase due to diluents effect of the plasticizer and lower mixing shear for the oil-loaded samples compared to the control. Higher cure rate for the oil-loaded samples is an advantage for higher production output, especially for the cooking oil types as shown in Table 4.3. However, waste cooking oil shows good plasticizing effect to facilitate mixing supported with lower compound viscosity (ML), especially significant for the 30g amount of PO added to SMR.

The lubrication effect decreases the inter-chain forces and increases the inter-molecular free volume, which soften and reduce the viscosity of rubber. At an equivalent level of 10g, its plasticizing effect is better than the common industrially used paraffinic oil. Oil proportionally reduces the cured modulus revealed by MH. This effect also relates to a reduction trend of crosslink density (delta torque) (Knothe *et al.*, 2010).

The plasticizing effect decreases the inter-chain forces and increases the inter-molecular free volume, which soften and reduce the rubber viscosity, without involving any chemical change and low mixing shear with a reduction on heat history that could contribute to these results on the oil-loaded samples. Due to the higher plasticizing effect of the cooking oil, its 10g sample shows more prominent in these effects than the sample loaded with 10g paraffinic oil. After-cured discoloration no significant differences across the samples loaded with the oils compared to the control. It is an advantage for the cooking oil used in the non-black vulcanized.

Table 4.3: Cure characteristics analysis

Sample	T_2 (min.sec)	T_2 (min)	T_{90} (min.sec.)	T_{90} (min)	ML (dNm)	MH (dNm)	Delta Torque	CRI (1/min)
0	1.23	1.39	2.15	2.24	5.10	26.73	21.63	116.96
5	1.24	1.39	2.14	2.23	4.44	24.25	19.82	119.76
10	1.25	1.41	2.14	2.23	4.53	23.28	18.76	122.74
20	1.28	1.46	2.14	2.24	4.37	21.34	16.98	129.04
30	1.28	1.46	2.15	2.25	3.70	18.62	14.93	125.79
10P	1.27	1.45	2.18	2.30	4.84	24.36	19.52	117.65

Using ODR, the development of crosslinking over time was examined, and the results are shown in Figure 4.3. The observed torque is proportional to the viscosity and elasticity of the system, and it is anticipated that the crosslinking process would increase the torque as the vulcanization time progresses, as shown in the graph.

This network has clearly defined phases, which are the induction phase, the cure response phase, and the network maturity phase.

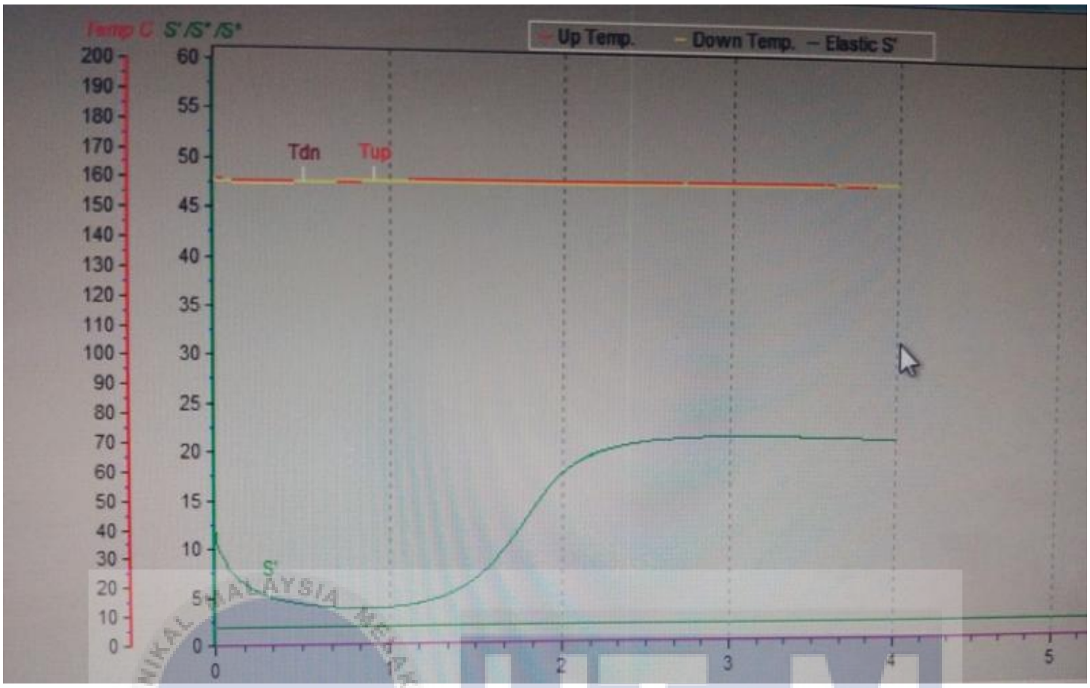


Figure 4.3: Rheometric curves of cure characterization analysis

4.4 Mechanical testing result

The plasticizing effect of the cooking oil decreases the modulus but enhances the elongation at break (EB) of the vulcanizates. The decreasing trends on the modulus values are corresponded well with the reductions of MH and hardness values when increasing the amount of processing oil added. Waste cooking oil at the level of 10 g is lower in modulus than the 10 g added paraffinic oil, which supports its better plasticizing effect.

The results also tantamount with the increases of EB values for those samples loaded with plasticizer. The lower modulus and higher EB for the cooking oil-loaded sample at 10 g compared to the 10P suggest better plasticization of the cooking at an equivalent loading. Moreover, for tensile and tear strengths, the oil-loaded samples are obviously showing detrimental effects, especially when the waste cooking oil was loaded at the highest 30 g as shown in Table 4.4.

The anticipated low crosslink density and plasticizing effect that affecting the macromolecular structure of the rubber chains impair the ability of the samples to resist fracture under the uniaxial stress strain force loading.

Table 4.4: Mechanical properties

Sample	200 % Modulus (MPa)	300 % Modulus (MPa)	EB (%)	Tensile Strength (MPa)	Tear Strength (N/mm)
0	1.217	1.704	1243.000	21.305	30.729
5	1.079	1.513	1225.667	18.534	25.595
10	1.006	1.403	1312.333	19.209	26.756
20	0.923	1.293	1275.667	16.903	23.349
30	0.792	1.124	1286.000	14.858	21.545
10P	1.097	1.568	1280.000	21.088	26.486

4.4.1 Tensile strength analysis

Referring to Figure 4.3.1, there are two patterns on tensile strength behavior with the rising of Transesterified (T-WCO) loading. The initial pattern is an increase in tensile strength with increasing sample weight from samples containing 0 gram of Transesterified (T-WCO) to samples containing 10 gram of Transesterified (T-WCO), as seen in Figure 4.3.1. This is where the Transesterified (T-WCO) works as a plasticizer in the compound, increasing the interface at phase borders and improving the flexibility of blends as a result of its presence.

Due to significant interphase interaction, the stress concentration point on the sample is reduced when a tensile load is applied, which results in increased mechanical strength for the sample. When compared to the other samples, T-WCO 10, which contains 10 gram of T-WCO, demonstrates the greatest tensile strength rating by far. The second pattern that can be seen is the reduction in tensile strength from T-WCO10 to T-WCO30, which can be observed from T-WCO10 to T-WCO30.

Typically, a plasticizer will soften the rubber, and it is expected that the tensile strength would decrease when the amount of T-WCO is increased. The explanation for this behaviour is most likely related to the fact that there has been no development in the interface between rubber and T-WCO.

An additional hypothesis is that the significant reductions in tensile strength from T-WCO10 to T-WCO30 are due to the plasticizer-plasticizer interaction, which is more prevalent at higher T-WCO concentration and contributes to the large drops in tensile strength. Tensile strength is diminishing as a result of intermolecular contact and cohesion, which both have an impact on tensile strength in a crystalline structure.

When the force is given to the sample, the rubber molecules begin to rotate and move, and the T-WCO, which acts as a plasticizer, is required to lubricate and diminish the cohesion forces that exist between the rubber molecules. As a result, T-WCO filled up the gaps between rubber molecules, allowing them to glide more smoothly. Figure 4.4.1: present the result of incorporating T-WCO to the tensile strength.

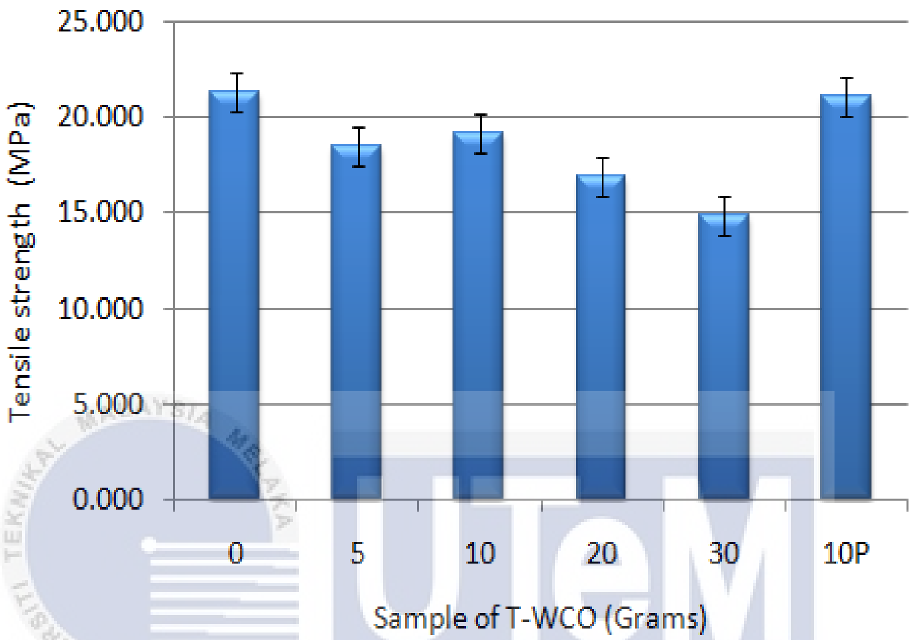


Figure 4.4.1: The tensile streangth result of incorporating T-WCO into NR compound

4.4.2 Elongation at break

Figure 4.4.2 shows steadily maximize of elongation at break with maximize of T-WCO. This is made feasible by the presence of more polymer chain entanglements per chain, which results in greater elongation at the point of break. A second hypothesis is that T-WCO lowers the intermolecular interactions between rubber chains and improves the mobility of rubber chains, thus increasing the flexibility of the rubber and T-WCO mixes together. Furthermore, the increase in T-WCO loading was attributable to the decreased stiffness associated with high concentrations of plasticizer, which results in a significant elongation at break when the load was increased.

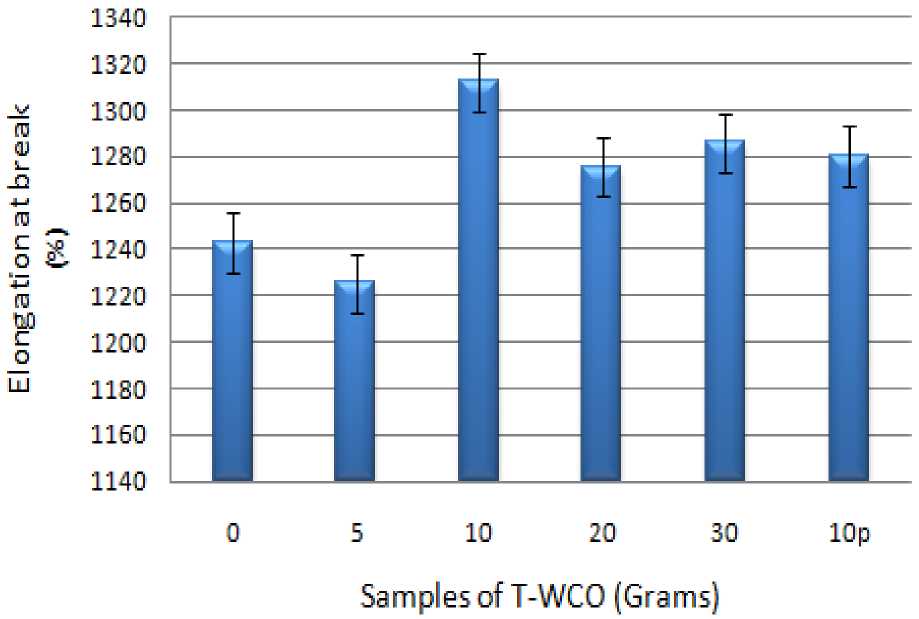


Figure 4.4.2: The result of incorporating T-WCO to the elongation at break 1

4.4.3 300 % Modulus

It is believed that a high tensile modulus indicates that the material is stiff, and that more stress is needed to generate a given amount of strain. This indicates that the material is resistant to deformation or stretch. Instead, modulus is linked to stiffness, or the ability to resist being deformed when subjected to a force. As shown in figure 4.4.3, the first style showing a slight increased from T-WCO0 to T-WCO5 and also from T-WCO10 to T-WCO30. The first rising style is likely due to the blends having the stiffness of rubber and the rubber-plasticizer interface which made the blends more rigid.

T-WCO0 shows the maximum value in Young's modulus while the lowest value for Young's modulus is T-WCO30. There is a phrase known as antiplasticization, which refers to a mechanical phenomenon defined by an increase in the stiffness of the rubber as a result of the inclusion of a tiny quantity of T-WCO. Strong interactions between plasticizer molecules and rubber chains cause antiplasticization to occur, which is associated with a decrease in free volume in the rubber chain.

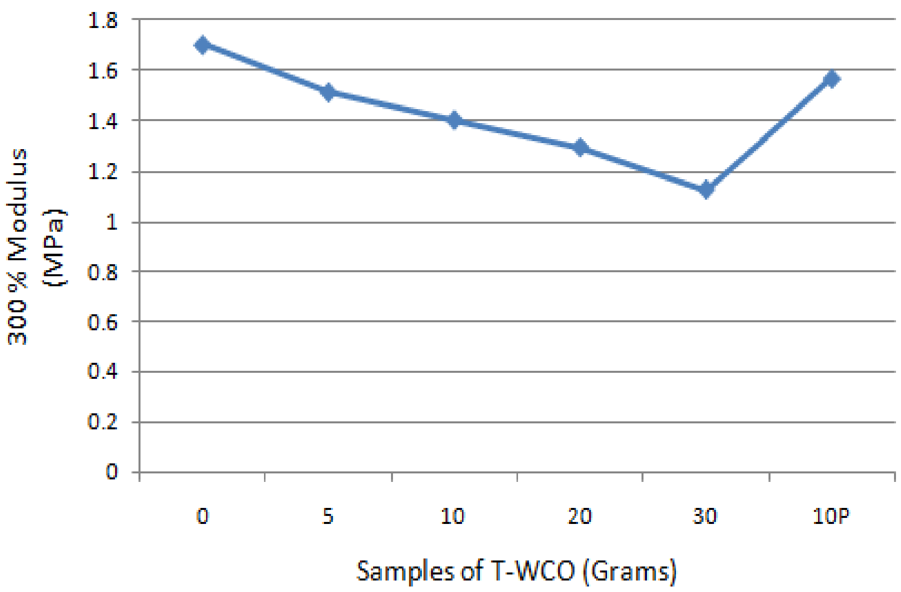


Figure 4.4.3: The result of incorporating T-WCO to the 300 % Young's Modulus 1

4.4.4 Tear strength

The tear strength value, as shown in figure 4.4.4, revealed that T-WCO0 has a greater tear strength value (30.729 N/mm) than the other formulae and that T-WCO30 has the lowest tear strength value (21.545 N/mm). Affecting the binding between the rubber composite molecules is the addition of softener ingredients to the rubber composite. The movement of the filler and the addition of the additive take up space in the rubber composite chamber at the same time. The quantity of additives and fillers that are used to fill the space between the rubber composite molecules has an effect on the difference in tear strength values between the two samples.

In terms of tear strength T-WCO0 which is a comparative formula that does not include synthetic rubber, has a number that is equivalent to T-WCO5 but is lower than T-WCO30. It was the ratio of natural rubber to synthetic rubber that caused the difference in tear strength between each T-WCO sample, whereas the addition of softener material and filler material affected the mechanical properties of rubber, especially when compared to the value of tear strength, in each sample.

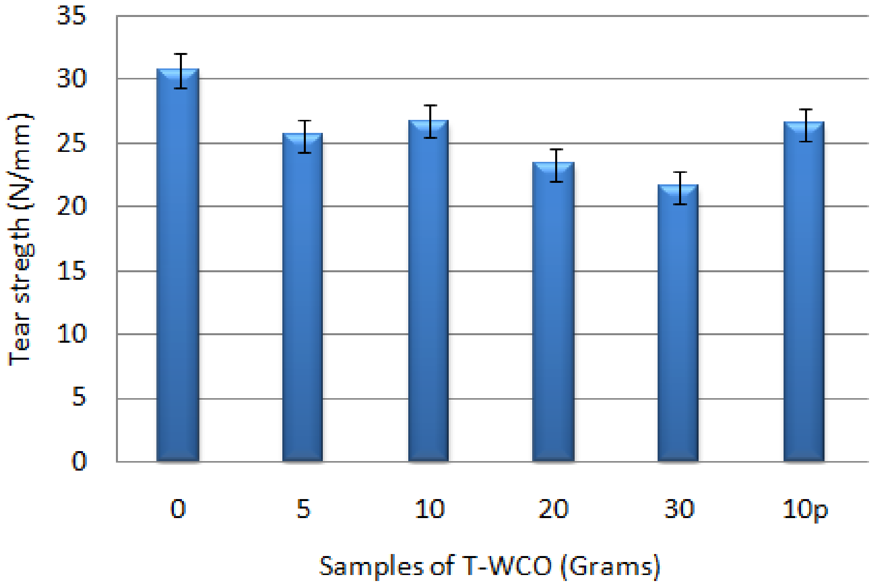


Figure 4.4.4: The tear strength of rubber (SMR) 1

4.5 Physical testing

4.5.1 Hardness analysis

Average hardness values taken from 5 data for every sample decrease in line with the increasing dosages of the cooking oil. It corresponds well with the reduction of modulus revealed by lower MH. This supports the effective plasticizing effect of the cooking oil. The hardness reduces from 41 Shore A to 36.6 Shore A after the rubber is loaded with 10g cooking oil, higher in decreasing degree compared to the sample loaded with 10 g paraffinic oil at 38.0 Shore A. Again, the results show the cooking oil is more effective in plasticizing rubber than the paraffinic oil. Table 4.5.1: present the hardness analysis.

Table 4.5.1: Hardness analysis

Sample	1	2	3	4	5	Average
0	41.1	40.9	41.1	41.0	40.9	41.0
5	38.9	39.0	38.8	39.0	39.1	39.0
10	36.7	36.4	36.6	36.6	36.6	36.6
20	33.8	34.0	33.8	33.7	33.9	33.8
30	30.4	30.3	30.1	30.0	30.4	30.2
10P	38.0	38.0	37.9	37.9	38.1	38.0

The maximum hardness value (41.0) of T-WCO 0, as shown in Figure 4.41, is higher than that of the other T-WCO (5,10,20,30, and 10P). T-WCO 30, on the other hand, has the lowest hardness test score (30.2) of all of the models. The amount of filler, additives, and softeners used in rubber vulcanizates has an impact on the hardness of the rubber vulcanizate. The hardness of rubber vulcanizates is influenced by the filler materials kaolin and silica, which have different properties depending on the kind of filler material used. The distribution of additives and fillers in rubber composites is affected by the amount of softener used and the density of bonds between the molecules of the composite. The softener material's function is to extend the connection between the composite rubber molecules, allowing the additional material to be dispersed uniformly throughout the composite matrix molecule during the moulding process.

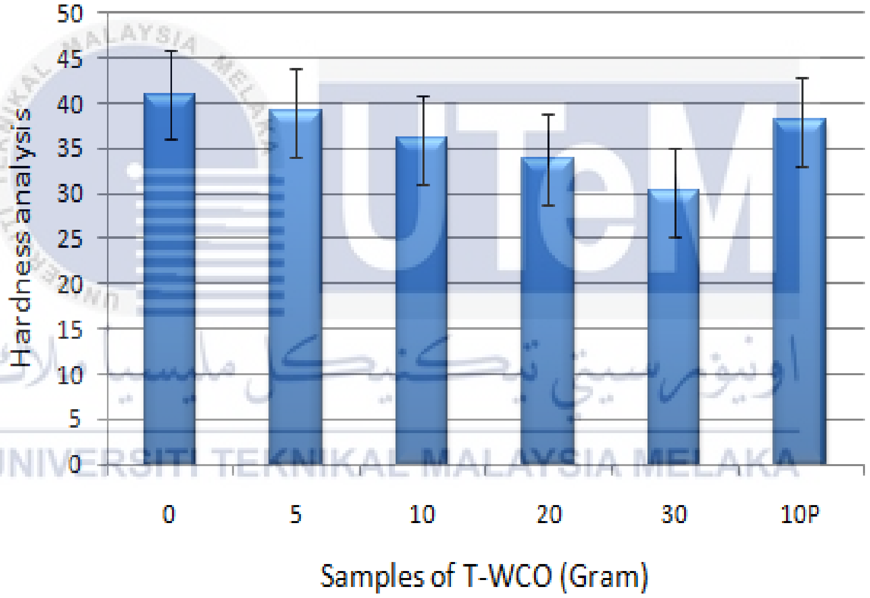


Figure 4.5.1: The hardness of rubber (SMR) 1

4.6 Fourier Transform Infrared (FTIR) Spectroscopy analysis

Figure 4.5 depicts the results of an investigation into the chemical structure of WCO using Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra, a wide distinctive peak was practical in the wave number region of 3396–3406 cm^{-1} that was evident in all of the FTIR spectra. Possibly, the stretching vibrations of hydroxyl groups (OH^{-}) in WCO molecules are responsible for this phenomenon.

Additionally, absorption peaks at about 2923 cm^{-1} and 2849 cm^{-1}, which correspond to stretching vibrations of C–H in methyl and methylene groups, respectively, have been detected and quantified. This effect may be caused by the stretching vibrations of hydroxyl groups (OH^{-}) in WCO molecules, which are responsible for the occurrence (Nasruddin and Susanto, 2020).

There have also been detection and quantification of absorption peaks at about 2923 cm^{-1} and 2849 cm^{-1}, which correspond to the stretching vibrations of C–H in the methyl and methylene groups, respectively. In accordance with C–O stretching vibrations in syringyl rings, the peak at wave number 1374 cm^{-1} corresponds to C–O stretching vibrations in guaiacyl rings, while the peak at wave number 1192 cm^{-1} corresponds to C–O stretching vibrations in guaiacyl rings (Nasruddin and Susanto, 2020).

In addition, the absorption peak at wave number 1035 cm^{-1} was attributed to the interaction of C–H in guaiacyl rings with C–O from primary alcohol, while the absorption peak at wave number 1112 cm^{-1} was assigned to the stretching of the C–H in syringyl rings. Their stretching vibrations of C–H bonds have been linked to these phenomena (Anis Nazurah *et al.*, 2013).

As shown in Figure 4.5, the absorption peaks at wave numbers of 778 cm^{-1} and 619 cm^{-1} were found, which corresponds to the findings obtained. Two earlier studies had shown similar findings and a third study had found similar results. Because of this, it is possible to infer from the proposed molecular structure of the WCO molecule that the extracted WCO. Specifically, it was discovered that variations between the instances were found to be in the intensities of the distinctive peaks.

The stretching vibrations of the CH3, CH2, and CH groups in cis-1,4 - polyisoprene macromolecules are represented by the strong peaks with the greatest intensities, which are located at 2963, 2921, and 2850 cm^{-1} respectively. The WCO particles, on the other hand, produced a slight change in the wave number range in this region. Several WCO macromolecules, including C=C and C–H, exhibit symmetric aromatic skeletal vibrations, which may be ascribed to the intense peak at 1539 cm1.

The peak at 1448 cm1 has been attributed to deformations of methyl groups C–H, and it is associated with the WCO as well as the natural rubber chain structure. It is possible that the asymmetric vibrations of methyl C–H groups in natural rubber are responsible for the band around 1371 cm^{-1}. According to the researchers, in-plane stretching of the paraffinic oil C–O group in WCO was the cause of the rising intensity peaks at 1039 cm^{-1}.

This may be due to hydrogen bonding between the C–O group of WCO and the hydrophilic group of non-rubber material in natural rubber, such as protein and lipid, which could explain the phenomenon. Specifically, the vibrations of C–H groups in the rubber chains are responsible for the peak at 834 cm^{-1}. According to the suggested hypothesis, the minor changes observed in various wave numbers imply some interactions between C–H groups of WCO and rubber, as well as the proposed theory.

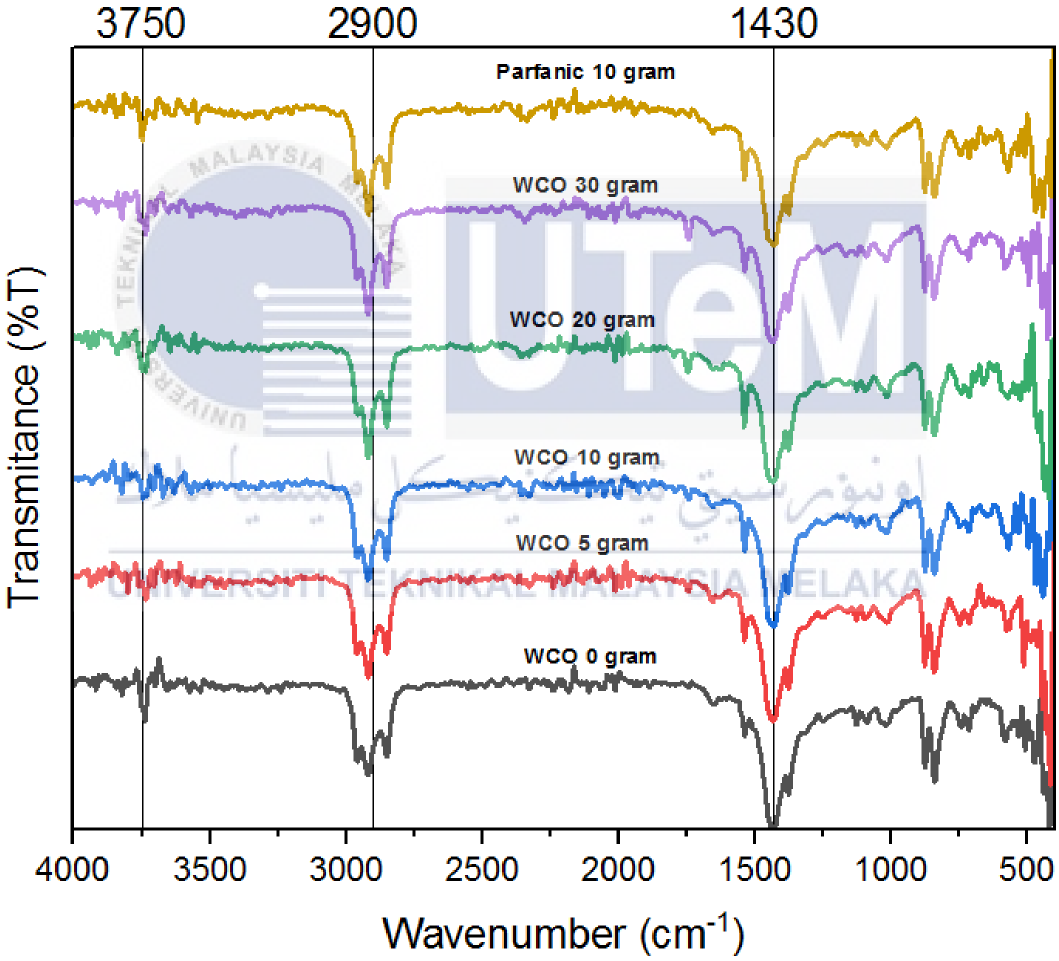


Figure 4.6: The results of an investigation into the chemical structure of WCO using FTIR 1

4.7 Summary

After careful analysis to overall experimental data finding, it can be concluded that raw material characterization such as hardness analysis and tensile properties was helpful to identify the behavior of raw material before conducting the experimental procedures.

Using FTIR analysis, the presence of hydroxyl group in rubber compound was analyzed and confirmed. Using FTIR spectra, it can be proven that the different types of rubber compound possessed distinct infrared spectra which due to dissimilar bond stretching.

The tensile strength value of T-WCO 0 (21.305) is higher than T-WCO (5,10,20, and 30) samples. The elongation at break (EB) with a value of T-WCO10 (1312.333%) is heights value compare with T-WCO (0,5,10,20,30, and 10P). Modulus 300% with a value of T-WCO0 (1.704 MPa) is higher than all other samples of T-WCO. Tear strength of T-WCO0 (30.729 N/mm) is higher than T-WCO (5,10,20,30, and 10P) samples. Lastly, hardness analysis with value of T-WCO (41.0) is higher than T-WCO (5,10,20,30, and 10P) samples.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In conclusion, transesterified WCO (T-WCO) was effectively used as processing oil in the production and characterisation of a sustainable rubber compound, which was generated via the transesterification method.

The first objective of this research is to modify WCO into PO by transesterification process has been productively achieved with some outlines as the following:

I. WCO are the raw material was used in this study since it contains triglyceride structure that can be modified chemically.
II. The experimental procedure such as transesterificatin method that was implemented to WCO feedstock is compatible.

The second objective of this study is to evaluate the potential WCO, to be used as PO for NR based compound. The following main points are the summary of significant findings that reflecting the achievement of the second objective.

I. The presence of hydroxyl group is analyzed by using FTIR spectroscopy since FTIR spectroscopy able to scan the presence of functional groups in samples.
II. In order to produce WCO-based rubber compound, existence of peak of hydroxyl group (OH^-) in infrared at wave number ($3441cm^{-1}$) is confirmed and proven.

For the last objective, physical and mechanical properties of WCO based rubber compound.

I. All the dissimilar types of rubber compound have different characteristic of physical properties and affecting their mechanical properties.
II. It is proven that WCO-based rubber compound possessed higher mechanical properties then non added compound

5.2 Recommendations

There are many more suggestions that may be proposed in order to improve the overall quality of this study. The following are the most prominent among them:

1- In order to apply WCO - based rubber compound, this research should provide with more than one liter of raw material WCO to get more samples.

2- This research would be more successful if provide scanning selection microscope (SEM) fracture observation during mechanical testing. Also, provide abrasion test and thermal test (TGA, DSC) as well as water absorption test during physical testing.

5.3 Sustainability element

It is anticipated that this study will have a positive impact on the environment by recommending rubber compound manufacturers that are interested in using waste materials. This research project is one of many options for providing assistance for recycling operations, which turn trash into money and wealth into garbage. At the same time, it is one of the measures that can be taken to address the issue of waste cooking oil disposal by controlling the use of waste resources in order to maintain the balance of the environment.

From the side view of economy, mission of producing rubber compound with lower cost can be accomplished by implementing this research closely within the related industry. The price of rubber compound is quite expensive due to the use of non-renewable resources such as crude oil as to minimize the depletion of natural resource. Recently, the rubber compound is made up of WCO which would provide high impact to the user health. It is suggested to eliminate the dependency.

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