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A Comparative Study of Natural Rubber Modified with Ground Tire Rubber of Truck

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ABSTRACT

The recycling of waste rubber has considerable significance in term of environmental protection and energy conservation. Considering that most of the relevant literature is concerned with tire recycling, the aim of this work was to develop and characterize the elastomeric samples of natural rubber (NR) composites filled with ground tire rubber of truck (GTR) devulcanized by microwave (DGTR). The tire rubber was ground under ambient conditions and subjected to microwave exposure for 3, 5 and 10 minutes. The samples were developed by the incorporation of 10, 30 and 50 phr (parts per hundred of rubber) of the devulcanized GTR-t into the rubber matrix and subsequent vulcanization. The physical-mechanical properties: tensile strength, elongation at break, shore A hardness and modulus were determined. The changes in the chemical characteristics were evaluated with cross-link density, sol fraction and Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) analyses. In addition, the samples have been investigated by thermogravimetric analysis (TGA) and scanning electron microscope (SEM). The results were compared with an unfilled sample of NR submitted to the same conditions.

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1 INTRODUCTION

Rubber is broadly used in our life and industry. As an elastic and flexible material, rubber is widely applied in manufacturing of tires, conveyors belts, shoes, pads and other products. Raw rubber cannot be utilized until it is vulcanized. Typically raw rubber is compounded with processing oil, fillers, antioxidants and other additives. Compounding can help to disperse additives, strengthen the rubber, reduce the cost, and lengthen its service life and so on. Vulcanization ingredients are also compounded with rubber, followed by the vulcanization of rubber. During vulcanization the crosslinks are formed to make rubber insoluble, infusible and in-flowable. After vulcanization the mechanical properties are further improved. Crosslinks play a crucial role in the application of rubber, but hinder its recycling. In recent years, the lack of recycling programs for scrap tire rubber has become an environmental, social and economic problem. The rubber tires in landfills and dumps can create serious problems to the entire municipal solid waste (MSW) management system because of their low degradability and large volume [1]. This is a huge waste of the valuable rubbers. One way to avoid this waste is to retread used tires. But this process is not easy to be automated, and requires a lot of human labor.

A more economical way is to grind used rubbers. Before the grinding of rubber products, the non-rubber composition, e.g., metals and fibers in tires, are separated. Rubbers are left, with carbon black, silica, zinc oxide and other chemicals which are not easy to be separated physically. Rubbers are then ground to small particles for further use. The ground rubbers can be blended with fresh rubber and used for new products. They can also be further processed to break the crosslinks, which may restore better properties. This process is called reclamation. Many reclamation methods have been developed [2]. Among them the microwave devulcanization is a very promising method with a feasibility to be scaled up for industrial production. This method enables to apply large amounts of energy rapidly and uniformly to the rubber, without using chemical reagents during the process [3, 4], which makes it an eco-friendly process [5]. The energy used to heat the rubber promotes the breaking of sulfur crosslinks [6]. Some studies have reported the use of microwave devulcanization in different types of elastomers [7–9].

There are several kinds of ground tire rubber (GTR) (e.g. car, truck) provided by manufacturers. In the truck tire loading, natural rubber composition is higher than in the car tire loading. A lot of study has revealed that ground tire rubber recycling should target the production of thermoplastic elastomers, and its reuse in the rubber industry. Thus, a comparative research of composites with different amount of devulcanized GTR, as well as different time treatment in microwave, is very useful for practical purpose. The treatment may have played an important role in the compatibilization of the elastomeric samples and implicitly affected the properties [10]. Accordingly, this thesis is focused on the devulcanized GTR from truck tires which was used as part of the natural rubber (NR) matrix.

The goals of this research were to obtain devulcanized rubber from waste tires and then to combine it with a natural rubber matrix to produce a new composite material. These composites were characterized physically and thermally.

2 LITERATURE SURVEY

2.1 THE CHEMISTRY AND COMPOSITION OF TIRE RUBBER

Natural rubber comes from the rubber tree (*Hevea brasiliensis*) and is white, milky liquid called *latex*. Most rubber comes from Malaysia and other nations in East Asia. Latex can also be seen as the white fluid in dandelion stalks. The latex from the tree is actually a suspension of rubber particles in water. Rubber is a polymer (long chain made of repeating units) of isoprene. Natural rubber is relatively reactive, and is especially vulnerable to oxidation.

Vulcanization is the process by which rubber molecules are cross-linked with each other by heating the liquid rubber with sulfur (Figure 1). Cross-linking and cure are used synonymously to the word vulcanization. Cross-linking increases the elasticity and the strength of rubber by about ten-fold, but the amount of cross-linking must be controlled to prevent creating a brittle and inelastic substance. The process of vulcanization was discovered accidentally in 1839 by the American inventor Charles Goodyear (1800-1860) when he dropped some rubber containing sulfur onto a hot stove. Goodyear followed up on this discovery and subsequently developed the process of vulcanization.

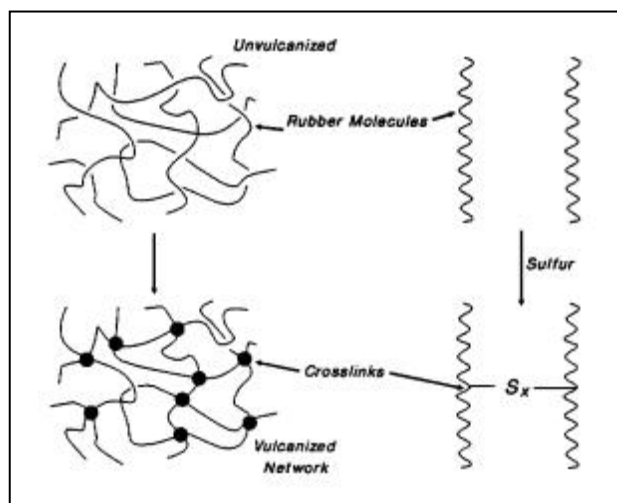


Figure 1. Sulfide network formation

Natural rubber, when vulcanized will form a three dimensional network of mono-, di-, and polysulfide bridges (Figure 2) [11]. The added sulfur allows some C-H bonds to be broken and replaced by C-S bonds. Also carbon-carbon bonds can be formed.

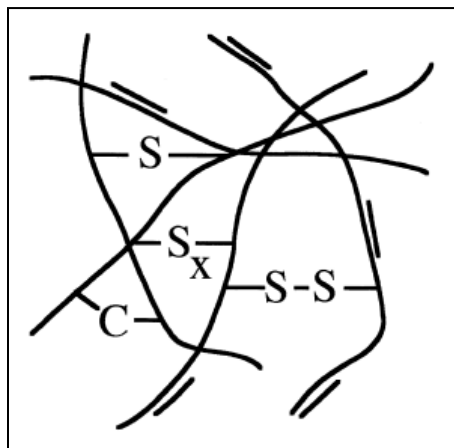


Figure 2. Structure of the vulcanized rubber materials containing mono-, di- and polysulfide crosslinks, as well as carbon-carbon bonds.

The vulcanization process has been and is being improved since then. The rubber industry had to wait until the first decades of the 20th century, when three discoveries greatly improved the quality and durability of rubber:

- organic accelerators,
- reinforcement by carbon black and silica, and
- activators such as zinc oxide, lead oxide and magnesium oxide.

The non-accelerated vulcanizing process uses elemental sulfur in the amount of 8 per 100 parts of rubber (phr), with a temperature of 142°C for 6 hrs. With the addition of some parts of the organic accelerator, vulcanizing time was greatly reduced. Furthermore, it was found that zinc oxide (ZnO) acts as an activator, increasing the effect of most organic accelerators [12].

Heideman *et al.* [13] studied the influence of ZnO during different stage of sulfur vulcanization. The use of accelerators in combination with zinc activators has a marked effect on the vulcanization rate and distribution of crosslinks formed. The advantage of organic accelerators lies not only in shortening the vulcanization time, but also in reducing curing temperature and reducing the required amount of sulfur. Furthermore, the durability of rubber articles as well as

the physical properties, particularly tensile strength, is improved by the use of these organic accelerators.

Carbon black is used as fillers. Curing characteristics are influenced by combination of surface area of carbon black and sulphur content on the filler surface, because carbon black enhances the physical cross-linking and sulphur introduces the additional chemical cross-linking, adding the strength of rubber [14].

Tires are classified as being:

- Passenger tires, including those used on passenger vehicles, motorcycles and caravans, as well as trailers for domestic use.
- Truck tires, including those used on buses, light and heavy commercial vehicles, prime movers, trailers and semi-trailers, and fire fighting vehicles.
- Off-the-road (OTR) tires, including those used on machinery or equipment used in areas such as agricultural, mining and construction and demolition.

Different rubber materials are used in different types of tires and also in different parts of the tires. Tires are made for their use on vehicles; they are not made as a recycling industry feedstock. Their composition makes them difficult to recycle. The common compositions of tires are given in the table below:

Table 1. Typical composition of passenger and truck tires based in North America [15].

Composition	Passenger tire	Truck tire
Natural rubber	14%	27%
Synthetic rubber	27%	14%
Carbon black	28%	28%
Steel	14-15%	14-15%
Fibre, fillers, accelerators, antiozonants, etc.	16-17%	16-17%
Average weight:	New 11 kg Scrap 9 kg	New 54 kg Scrap 45 kg

Passenger tires tend to contain more synthetic rubber than natural rubber; truck tires consist of more natural rubber; and OTR tires have nearly no synthetic rubber. The rubber composition may be due to the fact that passenger tires have to meet higher quality standards (low rolling resistance, improved skid resistance and good wear [16]) to succeed in the competitive market.

Truck and OTR tires, on the other hand, have to cope with heavy loads and longer distances more than operating under high speed conditions, and natural rubber can withstand much more higher workload demands than synthetic rubber. Other than that, natural rubber builds up less heat when flexed and has a great resistance from tearing at an elevated temperature [17].

2.2 END OF LIFE TIRES (ELT)

The development and rapid growth of the automotive industry as well as high demands of passenger and commercial vehicles around the world have contributed to positive impacts on the economy and job creation. However, there are also environmental problems that arise from this industry. One of them is the generation of End-of-Life Tire (ELT).

An estimated one billion tires worldwide (about 17 million tonnes) reach the end of their useful lives every year. This number has been growing steadily and this trend is expected to continue in the future. Tire production and use are expected to more than double in the next 30 years, with much of this growth in developing economies [18]. These scrap tires can also be responsible for the proliferation of mosquitoes and other disease-carrying vectors, besides potential soil contamination due to the presence of stabilizers, plasticizers and of other chemical substances leached from rubber. This situation could also impact the economic sphere due to higher sanitation and health system costs.

2.3 RECYCLING OF USED TIRE RUBBER

The reuse or recycling of waste rubber tires is a significant and world-wide problem. It is an important issue to optimize the recycling of this huge amount of used tires, which can both benefit human society economically and ecologically. Generally, there are three ways to recycle and reuse used tires: retreading, grinding and reclamation.

Retreading is a process to use new tread to replace the old one of a used tire, which is more economical compared to produce a new tire. But retreading process requires a lot of labor, which is becoming less and less economical considering the ever increasing labor cost.

Grinding is a process which physically reduces the particle size of used tires. The ground tires can be used to blend with fresh rubber and become raw materials for new rubber products. Grinding is an economical way to recycle used tires, but the rubbers are not chemically devulcanized, i.e. most of the crosslinks in the rubber are not broken. Thus, for safety consideration and quality control of products, especially for manufacturing of tires, only a small amount of ground rubber can be used to make new products.

The purpose of reclamation of used rubbers is to chemically break the crosslinks in rubbers and regaining their fluidity. In this case, a better dispersion of the reclaimed rubbers in fresh rubber can be expected; the interfaces between them can be improved. A larger amount of recycled rubbers can be used for new products, as well as better properties can be achieved.

2.4 RECLAMATION METHODS FOR USED RUBBER

The final purpose of reclamation is to break the chemical bonds (crosslinks). Thus, reclamation process can also be called as devulcanization process [19]. It is a physical or chemical method which has the objective to break the three-dimensional network present in the vulcanized rubber [20, 21]. However, it should also be noted that breaking the main polymer chains might occur, leading to polymer degradation [6, 22]. Hence, the key for successful devulcanization of used rubbers is to break the crosslinks in rubbers, while damage as less as possible the main chains. The following devulcanization methods have been developed for the reclamation of waste rubbers.

2.4.1 MECHANICAL METHODS

Mechanical devulcanization of used rubbers involves the using of mechanical force, especially shear force, to break crosslinks in rubber vulcanizates. This method is a very fast process, and it does not require any chemicals. This reduces the cost and saves the efforts of disposing used chemicals. But the mechanical devulcanization has the disadvantages of degrading polymers during the process, because the high shear stress in the devulcanization system can damage the macromolecular chains. Thus, the optimization of devulcanization conditions is very important.

Typically, pan mill or twin-screw extruders are used to apply the mechanical force to GTR. Zhang *et al.* [23] studied the devulcanization of GTR with a pan mill reactor. After revulcanization, the blend of devulcanized GTR with fresh NR showed significantly better mechanical properties than the blend of GTR and NR. This was attributed to the homogeneous distribution of devulcanized GTR in NR, which was confirmed by SEM. The devulcanization of waste tire using a twin-screw extruder was studied by Yazdani *et al.* [24]. The effects of the barrel temperature of extruder and screw rotation speed were studied. These parameters can be used for the optimization of the devulcanization conditions.

2.4.2 CHEMICAL METHODS

All reclamation methods are essentially chemical methods because the purpose is to break crosslinks. The chemical methods in this section are designed for those methods where certain chemicals are used as reagents or solvents.

De *et al.* [25] reported the devulcanization of GTR with tetramethylthiuram disulfide (TMTD). TMTD served as the reclamation reagent during the devulcanization of GTR with a two-roll mill. After devulcanization, TMTD was also used as a curative during the revulcanization process. The revulcanizates of reclaim rubber showed better aging properties than NR without reclaim rubber [26].

As a chemical process, the selection of reactants for chemical devulcanization methods is very important. For better delivery of the reclamation reagent to the crosslinks, proper organic solvents are needed. However, the using of organic solvents may cause environmental problems. Therefore, environment-friendly solvents are preferred. Supercritical fluids of carbon dioxide, which can penetrate solids while carrying certain chemicals is a proper candidate.

Kojima *et al.* [27] used supercritical carbon dioxide as a medium to carry the reclamation reagent, diphenyl disulfide, for the devulcanization of carbon black filled natural rubber and truck tires containing natural rubber. A loading up to 40 phr of devulcanized tire rubbers in fresh rubber restored 90% tensile strength.

Jiang *et al.* [28] also used supercritical carbon dioxide as the medium and diphenyl disulfide as the devulcanization reagent to study the devulcanization of butyl rubber vulcanizates, as well as its structure and mechanical properties.

2.4.3 CONTINUOUS ULTRASONIC METHODS

Continuous ultrasonic devulcanization of tire rubbers with an ultrasonic extruder was first introduced by Isayev [29] and his coworkers in 1995. GTR can be devulcanized in a short time. The devulcanized rubber was reprocessable and reshapable. It can be vulcanized again to produce new rubber products without adding any fresh rubbers.

A typical ultrasonic devulcanization reactor includes two critical parts: an extruder and an ultrasonic device. The extruder is used to heat rubber up and provide rubber flow to the ultrasonic device. The ultrasonic device is used to impose mechanical vibration wave at a frequency range of ultrasound to rubber through a metal horn.

A. Isayev et al. [30] managed to create a devulcanization reactor based on single-screw extruders with the horn for ultrasonic wave placed before the die. The factors that can affect the degree of devulcanization are the amplitude of ultrasonic wave, the exposure or residence time and the pressure inside the extruder. The breaking of bonds of the rubber is mainly due to the dissipation of heat by the rubber due to the ultrasonic wave. If the amplitude of wave and the pressure is too low, no devulcanization occurs.

Continuous devulcanization process have been studied by Jeong Seok Oh et al. [31] on butadiene rubber and the result of the study showed that devulcanization conditions are narrow and must be specific, or else significant degradation or no devulcanization occurred.

2.4.4 BIOLOGICAL METHODS

To avoid the unnecessary degradation of polymer main chains during the devulcanization process, highly selective methods are preferred. Besides chemical devulcanization, another method which can focus the breakage on the sulfur crosslinks was developed [32–34]. Certain microbial agents can change the sulfur at the crosslinks to another form. Although biological devulcanization process typically takes a couple of weeks, it provides another research direction for the disposal of used rubber.

2.4.5 MICROWAVE METHODS

Microwave is an electromagnetic wave with a frequency between 300 MHz to 300 GHz. It can interact with polar chemicals and induce their orientation. During the orientation process, the electromagnetic energy is transferred to thermal energy, which can be used as a heating source. Due to the fact that microwave does not interact with non-polar groups, the heat is localized at the vicinity of polar groups [35], which minimizes the thermal degradation of main chains. From the basic mechanism, the microwave devulcanization is very similar to the thermal devulcanization, but with the thermal energy delivered more accurately. As tire rubber being one of non-polar elastomers, they are unable to absorb the microwave energy due to their low absorption and scattering, which requires adding some particles to absorb the energy, such as carbon black [6, 36]. This filler is known to absorb electromagnetic radiation through a phenomenon known as Maxwell-Wagner polarization, and the devulcanization process can only be achieved through it [37–39].

Zanchet *et al.* [7] noted that the microwave devulcanization enhanced the interfacial adhesion between devulcanized styrene-butadiene rubber (SBR) in a virgin SBR matrix. The results showed that this mixture can be used in automotive profiles obtained by compression molding. Other papers analyzed the influence of the amount of carbon black in the rubber during the microwave devulcanization and concluded that the degree of devulcanization increases as a function of the increase in the amount of carbon black [9, 40]. Despite the fact that microwave devulcanization is a known method, there are few studies addressing the chemical and physical aspects of the GTR after being exposed to radiation for different periods [6]. According to the authors, with the technique, they were able to create a material with properties quite different from the original vulcanized rubber, due to the changes in the tire rubber structure and composition during the treatment.

3 EXPERIMENTAL

3.1 MATERIALS

Natural rubber (NR) was obtained from VIGAR Rubi, Spain.

Ground tire rubber (GTR) made from whole truck tires, was supplied by Gestión Medioambiental de Neumáticos S. L. (GMN) Maials, Spain.

Vulcanization accelerators (N-tert-butyl-2-benzothiazolesulfenamide (TBBS), tetramethylthiuram disulfide (TMTD)), carbon black, stearic acid, zinc oxide and sulfur with technical purity were supplied by VIGAR Rubi, Spain.

3.2 RECYCLING OF GROUND TIRE RUBBER: DEVULCANIZATION PROCESS

Vulcanized GTR samples were recycled by devulcanization using microwaves. In this work, samples were prepared using microwave model DAEWOO KOR-6L37 with microwave power of 700 W and nominal power of 1000 W. This microwave was modified with a stirrer attached. Stirrer type comb was used with rotational speed of 80 rpm. GTR is filled about 150 mL, approximately about 60 g, into a pot. This pot was then placed into the microwave. The plate was fixed so that it didn't move. The devulcanization process was conducted using different periods, where GTR samples were exposed to the microwaves for: 3 min, 5 min and 10 min.

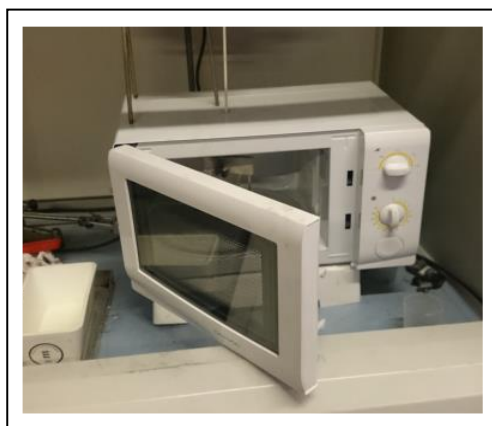


Figure 3. The setup of modified microwave oven with stirring system.

3.3 PREPARATION OF VULCANIZED SHEET

Devulcanized GTR (DGTR) obtained from the microwave process was blended with different proportions of virgin natural rubber using a Brabender plastograph batch mixer (Figure 4) at 70°C. The rotational speed of rotors was 100 rpm. The mixing time of 8 min; including 2 min of preliminary plasticization of natural rubber, 4 min of mixing with carbon black and 2 min of mixing the curatives (sulfur, stearic acid, ZnO, TBBS, and TMTD). The DGTR content in the samples was 0, 10, 30 and 50 parts per hundred rubber (phr). A sample with unfilled DGTR is a control sample. It should be pointed out that all samples were exposed to the same treatment conditions, same curing system and they were prepared the same way. The formulations of the composites are presented in Table 2.

Table 2. Formulation of NR composites.

Material	Weight/phr
NR	100
Carbon black	30
Zinc oxide	5
Stearic acid	3
Sulfur	2
Accelerator TBBS	1
Accelerator TMTD	0,25
DGTR	Variable (0, 10, 30 or 50)

Then, the batches of each sample were homogenized in an open Collin two-roll mill (Figure 5). The total mixing time was approximately 10 min for each sample. Subsequently, the samples were molded in the Collin P200E hot compression molding machine (Figure 6) at a temperature of 180°C and 4,9 MPa according to determined optimal curing time which is approximately 12 min. During molding, rectangular sheets weighed nearly 125 g having dimensions of 16 cm wide × 16 cm length × 0.3 cm thick were formed (Figure 7).



Figure 4. Brabender plastograph batch mixer.



Figure 5. Collin two-roll mill.



Figure 6. Collin P200E hot compression molding machine.



Figure 7. Before compression sheet.

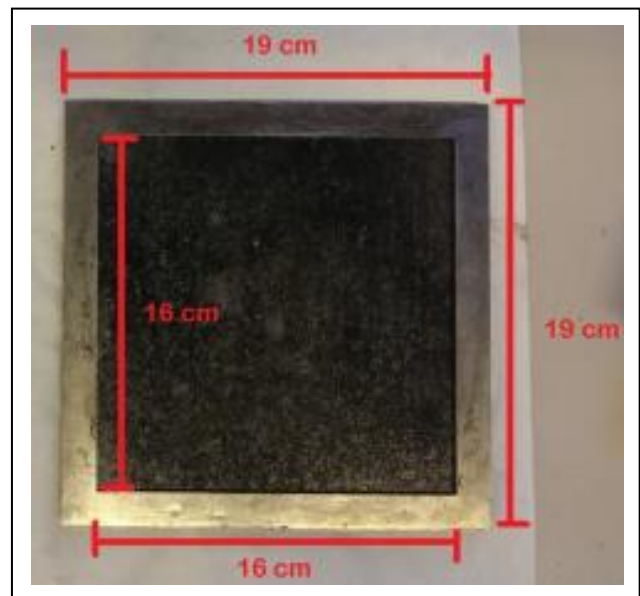


Figure 8. After compression sheet.

3.4 CHARACTERIZATION OF NR/DGTR COMPOSITES

3.4.1 MECHANICAL ANALYSIS

Dumbbell-shaped specimens were punched from the compression-molded sheets. Tensile strength and elongation at break of the obtained vulcanizates were done according to the standard ISO 37 method using Instron testing machine with cell load capacity of 20 kN (Figure 9). Tensile tests were performed at a cross-head speed of 500 mm/min at 25°C. Direct extension measurements were conducted periodically using an extensometer with sensor arms.

Hardness was determined using a Zwick 3130 durometer Shore A (Germany) in accordance with the standard ISO 7619-1. At least five samples for each composition were tested, and the average value is reported.



Figure 9. Tensile test machine.

3.4.2 CHEMICAL ANALYSIS

Fourier Transform Infrared Spectroscopy (FTIR)

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy analyses were performed on all samples to obtain information about chemical structure modifications on the GTR and elastomeric samples structure as a result of the revulcanization process. The spectra were recorded on a Nicolet iS10 FT-IR Spectrometer from Thermo Scientific (USA) (Figure 10). The device had an ATR attachment with a germanium crystal. Measurements were performed from 4000 to 550 cm^{-1} at resolution of 4 cm^{-1} .



Figure 10. ATR-FTIR spectrometer.

Swelling degree

Swelling degree of composites as function of time with approximately 2 g for each sample, were determined by equilibrium swelling in toluene at room temperature. Samples were soaked in a beaker filled with toluene and weighed at every 1, 2, 4, 8, 16, 32 and 72 hrs. Swelling degree was calculated in accordance with formula:

Equation 1. Swelling degree equation.

$$Q = \frac{m_t - m_0}{m_0} \times 100\%$$

Where: Q = Swelling degree
 m_t = Mass of the sample swollen after time t (g)
 m_0 = Initial mass of sample (g)

Crosslink density

In order to analyze the network structure of the vulcanized samples, the crosslink density was performed according to ASTM D 6814-02 standard method through swelling test. The samples were cut into tiny squares of approximately 0.2 g and were allowed to swell in a small container of cold toluene at 30 °C for 72 hrs (the equilibrium swelling time) and the solvent was refreshed every 24 hrs. The test pieces were then taken out, weighed and left to dry for 24 hours at room temperature. The weight of the dried specimen is recorded once again.

The volume fraction of the rubber in the swollen gel (V_r) was determined on the basis of simple additivity rule of volumes as follow [41]:

Equation 2: Formula to calculate the volume fraction of rubber.

$$V_r = \frac{\left(\frac{a_2}{\rho_2}\right)}{\left(\frac{a_1 - a_2}{\rho_1}\right) + \left(\frac{a_2}{\rho_2}\right)}$$

Where: a_1 = Weight of swollen specimen
 a_2 = Weight of the dried specimen (24 hours at room temperature)

$\rho_1 =$ Density of solvent – toluene (0,8669 g/cm³)

$\rho_2 =$ Density of the specimen

The apparent crosslink density (v_e) was calculated according to Flory-Rehner using the value of V_r as follows [42]:

Equation 3: Flory-Rehner equation.

$$v_e = \frac{-[\ln(1 - V_r) + V_r + \chi V_r^2]}{[V_1(V_r^{\frac{1}{3}} - \frac{V_r}{2})]}$$

Where: $v_e =$ Crosslink density (mol/cm³)

$V_r =$ Gel volume in the swollen sample

$V_1 =$ Solvent molar volume – toluene (106,2 cm³/mol)

The χ interaction parameter between rubber and swelling solvent was set equal to 0,39 considering NR as main polymer and toluene as solvent. Considering the content of sulfur, the rubber density was approximated to 0,92 g/cm³. The Kraus correction model was applied due to presence of carbon black as filler [43]. The carbon black density was chosen as 1,85 g/cm³ and the K constant was chosen as 1,17 [44]. Crosslink density with Kraus correction was calculated according equations:

Equation 4: Krauss correction equation.

$$v_{after\ correction} = \frac{v_e}{1 + K + \Phi}$$

$$\Phi = \frac{\phi_f \times \rho_r \times m_0}{\rho_f \times m_{dry}}$$

Where: $v_e =$ Measured chemical crosslink density (mol/cm³)

$v_{after\ correction} =$ Actual chemical crosslink density (mol/cm³)

$K =$ Constant characteristic of the filler but independent of the solvent

φ_f = Calculated volume fraction of filler in the sample

ρ_r = Density of studied compound (g/cm³)

m_0 = Weight of sample before extraction (g)

ρ_f = Density of filler – carbon black (g/cm³)

m_{dry} = Weight of sample after extraction (g)

The density of the samples was measured based on the Archimedes method, as described in ISO 2781. Accordingly, all measurements were carried out at room temperature in distilled water medium.

Sol fraction

The fraction of soluble matter (sol content) and insoluble matter (gel content) present in the sample of the materials were determined by extraction in a Soxhlet apparatus (Figure 11), using toluene as solvent.



Figure 11: The Soxhlet extractor (left) and the filter paper thimble used (right).

The vulcanized NR samples were extracted for 24 hrs in toluene in order to remove low molecular substances like remains of accelerators and curatives, oil and non-crosslinked polymer residues or soluble polymer released from the network by the vulcanization process. Approximately 4 g of vulcanizate is placed in a filter paper thimble which is then placed into the main chamber of the Soxhlet extractor. The toluene solvent travels into the main chamber and the partially soluble components are slowly transferred to the solvent. The sample remained under Soxhlet extraction for 24 hrs until the soluble fraction had been extracted by solvent. Then, the extraction was followed by drying the insoluble fraction of the sample in a vacuum oven at 80°C for 24 hrs and determining the weight loss until constant weight. The sol fraction was calculated by the following Equation 5 [45]:

Equation 5: Sol content determination.

$$\text{Sol fraction \%} = \frac{(W_1 - W_2)}{W_1} \times 100\%$$

Where: W_1 = Weight of sample before extraction (g)

W_2 = Weight of sample after extraction (g)

3.4.3 THERMAL ANALYSIS

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed using Mettler Toledo TGA/SDTA 851 apparatus (Figure 12). The samples weighing approximately 14 mg were placed in a corundum dish. The analysis was conducted in the temperature range 40°C to 600°C and under nitrogen atmosphere (30 mL/min), at heating rate of 20°C/min.



Figure 12. Thermogravimetric analysis machine.

3.4.4 MORPHOLOGICAL ANALYSIS

Scanning electron microscope (SEM)

The morphology of the elastomeric samples at their fracture surfaces was examined by JEOL 5610 scanning electron microscope (Figure 13). Before analysis, the samples were sputter coated with a fine gold-palladium layer in order to increase their conductivity in a vacuum chamber (Figure 14).



Figure 13. Scanning electron microscope.



Figure 14. Gold-palladium coated samples.

4 RESULTS AND DISCUSSION

The numerical results of the characterization of NR composites are presented in the following table.

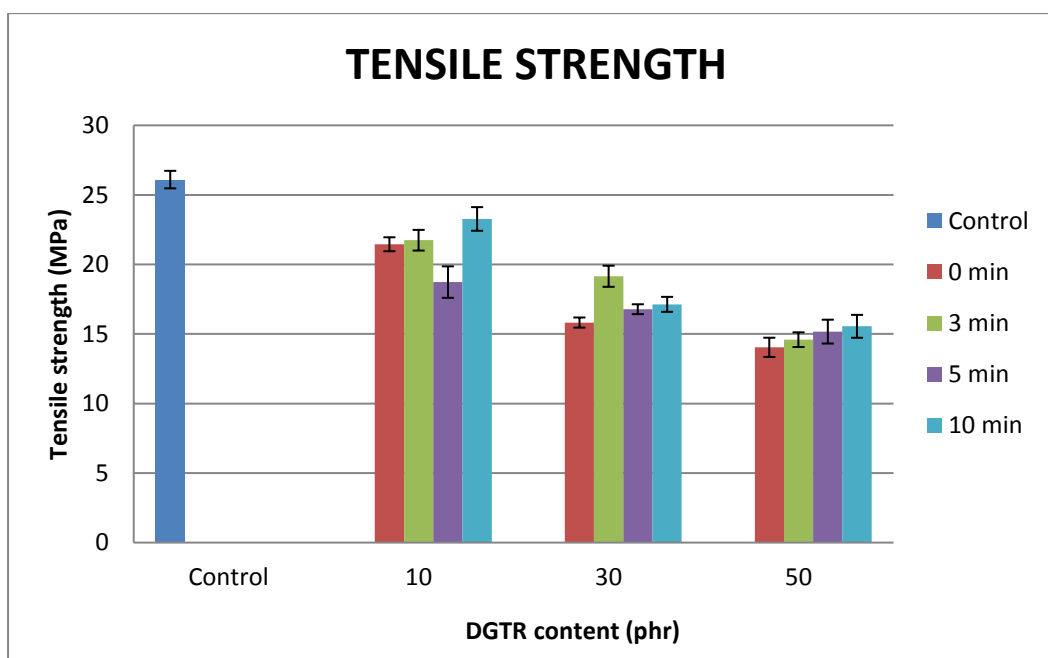
Table 3. Values of properties of NR composites.

DGTR (phr)	Samples												
	Control	0 min (Untreated GTR)			3 min			5 min			10 min		
	0	10	30	50	10	30	50	10	30	50	10	30	50
Tensile strength (MPa)	26,10	21,45	15,82	14,04	21,74	19,15	14,59	18,73	16,78	15,17	23,27	17,13	15,55
Elongation at break (%)	918	850	754,17	675	845,83	766,67	687,50	827,08	739,58	702,08	856,25	837,50	779,17
Modulus at 100% (Mpa)	1,41	1,41	1,23	1,39	1,38	1,49	1,29	1,26	1,42	1,30	1,44	1,07	1,29
Modulus at 300% (Mpa)	2,19	2,08	1,86	1,96	1,98	2,45	2,22	1,81	2,09	2,20	2,04	1,74	2,09
Hardness (Shore A)	49,20	48,66	50	45	48,00	47,66	46,50	48	48,16	46,66	48,50	46,83	47,33
Experimental density (g/cm³)	1,12	1,08	1,12	1,09	1,05	1,09	1,09	1,08	1,11	1,08	1,09	1,10	1,07
Theoretical density (g/cm³)	1,29	1,26	1,27	1,27	1,29	1,26	1,27	1,26	1,27	1,26	1,28	1,26	1,1,29
Porosity (%)	14	10	11	10	15	13	14	15	10	13	12	12	11
Crosslink density (mol/cm³ x 10⁻⁴)	1,41	1,385	1,114	1,079	1,425	1,259	1,22	1,265	1,219	1,218	1,323	1,125	1,213
Sol fraction (%)	3,72	6,02	8,09	8,15	6,47	6,65	8,21	6,13	11,06	7,37	5,17	7,9	7,49

4.1 MECHANICAL PROPERTIES

The tensile strength, elongation at break, modulus and hardness were used to evaluate the mechanical properties of the systems. The DGTR content and the exposure time were found to have a distinct effect on the mechanical properties of the DGTR/NR and GTR/NR composites. The mechanical properties of the NR composites with different concentrations of DGTR are shown in Table 3. Generally, these composites tend to become brittle and weak with increasing concentrations of DGTR and untreated GTR. A similar observation was reported by some studies [33, 45, 46]. The effects of the waste rubber contents on the tensile strength and the elongation at break are shown in Figure 15 and 16.

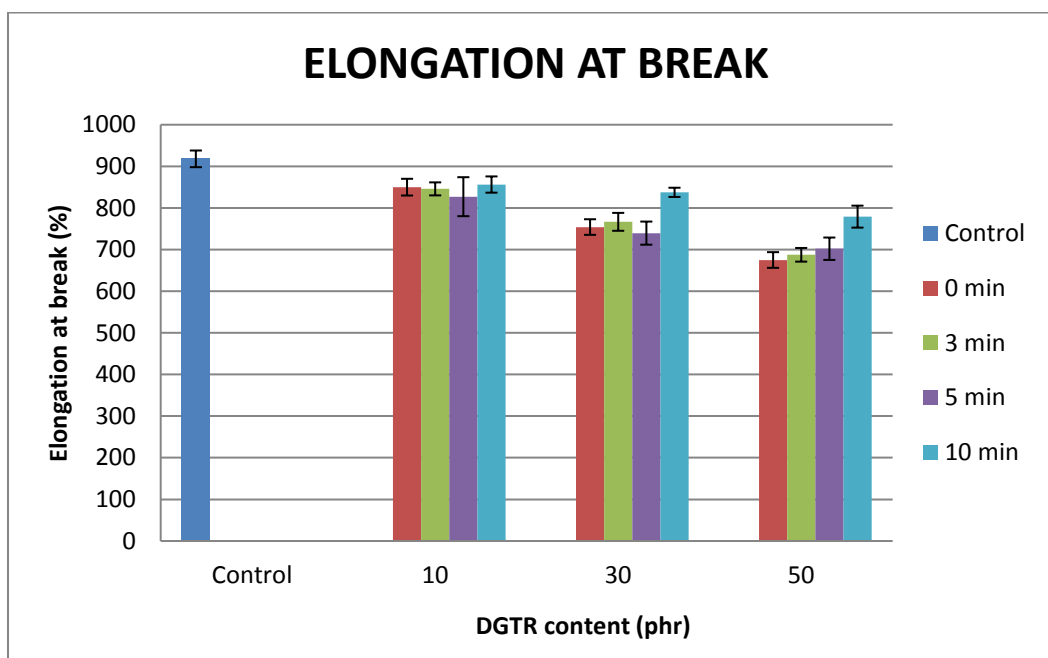
Figure 15. Variation of tensile strength for NR composites.



As shown in Figure 15, further increases of rubber powder loading led to a decrease in tensile strength. It is thought that, at 10 phr of rubber powder loading, the smaller proportion and uniform dispersion of recycled tire rubber in natural rubber compounds contribute to a higher tensile strength. However, as the loading increases, the weak interaction and bonding between the rubber powder particles and the natural rubber matrix is responsible for the deterioration in tensile strength. As the tire rubber concentration increases, agglomeration and hence particle-particle interaction of the rubber also increases.

The values of the properties for composites that contained DGTR were much better than for the composites with untreated GTR at the same loading, because of the treatment. Because DGTR takes part in the crosslinking reaction, there is strong interfacial bonding between the NR matrix and the DGTR that leads to good tensile properties. Although devulcanization reaction only occurred on the surface of GTR, better compatibility between the matrix and the DGTR led to better properties of DGTR/NR composites.

Figure 16. Variation of elongation at break for NR composites.



The elongation at break of natural rubber composites decreases with increasing ground tire rubber loading (Figure 16). The deterioration of the elongation at break is related to the weak interfacial adhesion between the GTR particles and the NR matrix. With higher GTR content, the particles are not well-dispersed in the matrix of NR. Hence, there are weak sites for stress-transmission and result in easily breaks of rubber and lower mechanical properties for the composite.

On the whole but with some exceptions, the values of tensile strength and elongation at break increased as the exposure time of GTR to microwave got higher. The higher tensile strength and elongation at break may be due to the decrease in number of crosslinked sites in the DGTR/NR specifically in 10 min and the strong interfacial bonds between the NR matrix and DGTR, which transmit stress very well in the composite structure.

It can also be observed that the tensile strength and elongation at break for all the rubber matrices has lower values than the control NR sample. The deterioration of tensile strength and elongation at break could be caused by less homogenous and uncontinuous structure blend. GTR/DGTR contains crosslinked gel that can act as stress concentrating point since the gel cannot be dispersed as continuous matrix in the virgin rubber [47]. This obstruction can prevent smooth stress transfer on the rubber surface. Thus, the control sample has better dispersion and homogeneity which makes it withstands higher loading.

Variation in tensile modulus, the GTR and DGTR content effects on the stress at 100% and 300% elongations, which is a measure of stiffness, are presented in Figure 17A and B.

Figure 17A. Effects of DGTR content on 100% modulus.

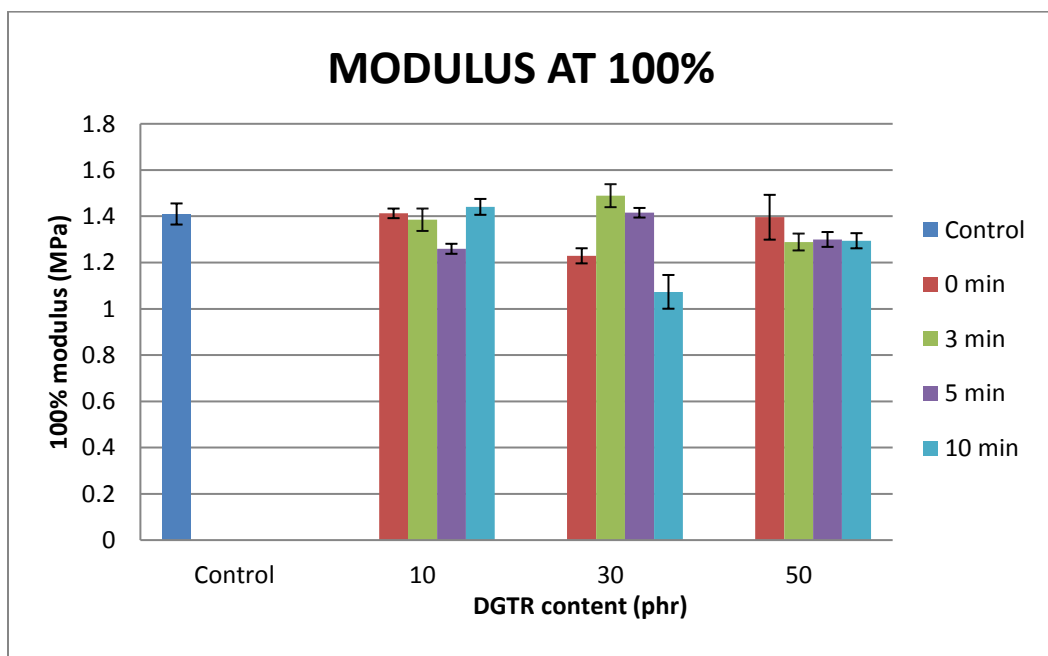
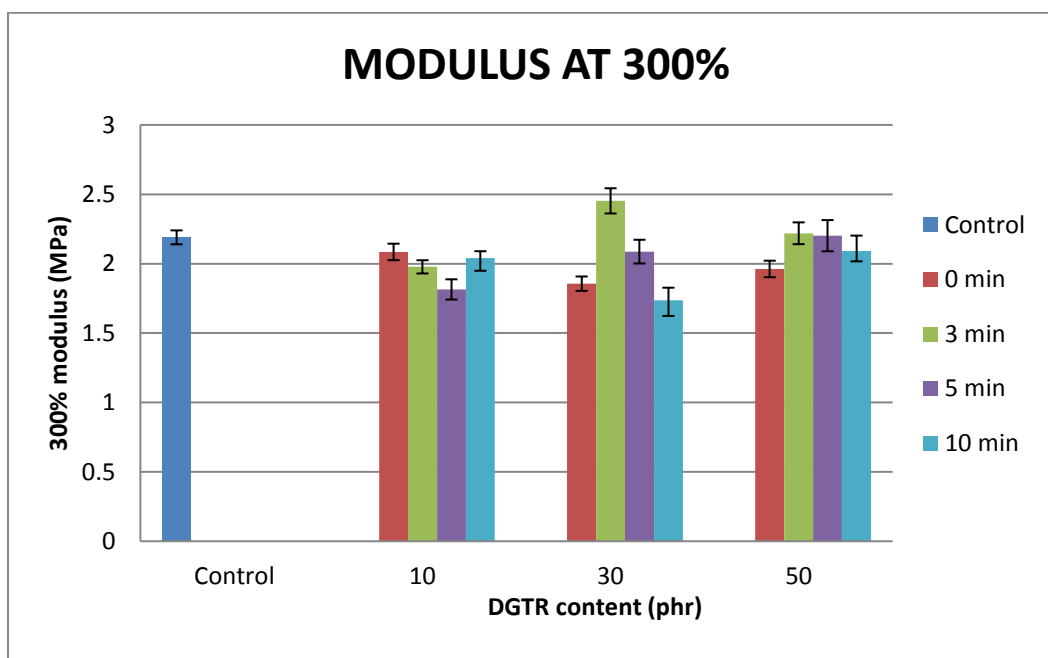


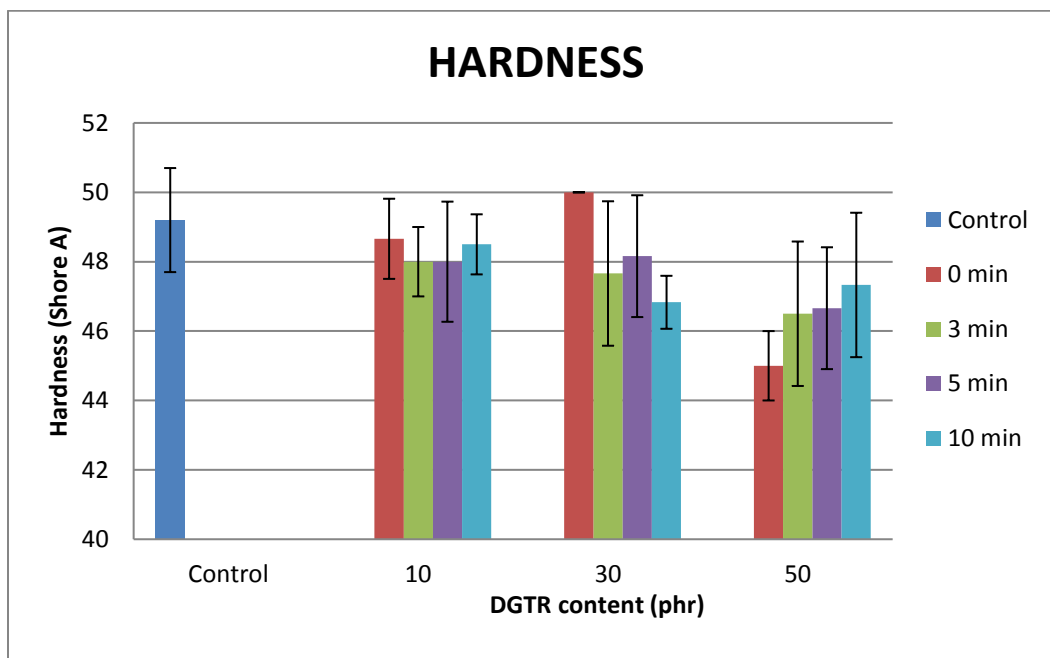
Figure 17B. Effects of DGTR content on 300% modulus.



In general, a clear trend was not observed for the values of modulus. According to some review studies [45, 46], the values of modulus would increase with increases of GTR content, indicating that the GTR behaves like a rigid particulate filler in the rubber matrix and enhanced the rigidity of the composite. Since GTR has a higher modulus than the natural rubber matrix, it cannot be deformed easily.

The Shore A hardness (Figure 18) of the composites did not present a clear trend with the increase of the exposure time of the GTR to microwaves. However, there are slightly decreasing when GTR content got higher, in comparison to original NR sample. The decrease in the hardness of the composites is most likely due to the decrease in the crosslink density of the composites, which will be analysed later. The presence of reinforcing filler such as carbon black may also contribute to the hardness of the composites [47].

Figure 18. Effects of DGTR content on Shore A hardness.



Other variation graphs of tensile strength versus elongation at break for each GTR loadings are shown in Figure 19A-C.

Figure 19A. Tensile strength vs. elongation at break with 10 phr loading.

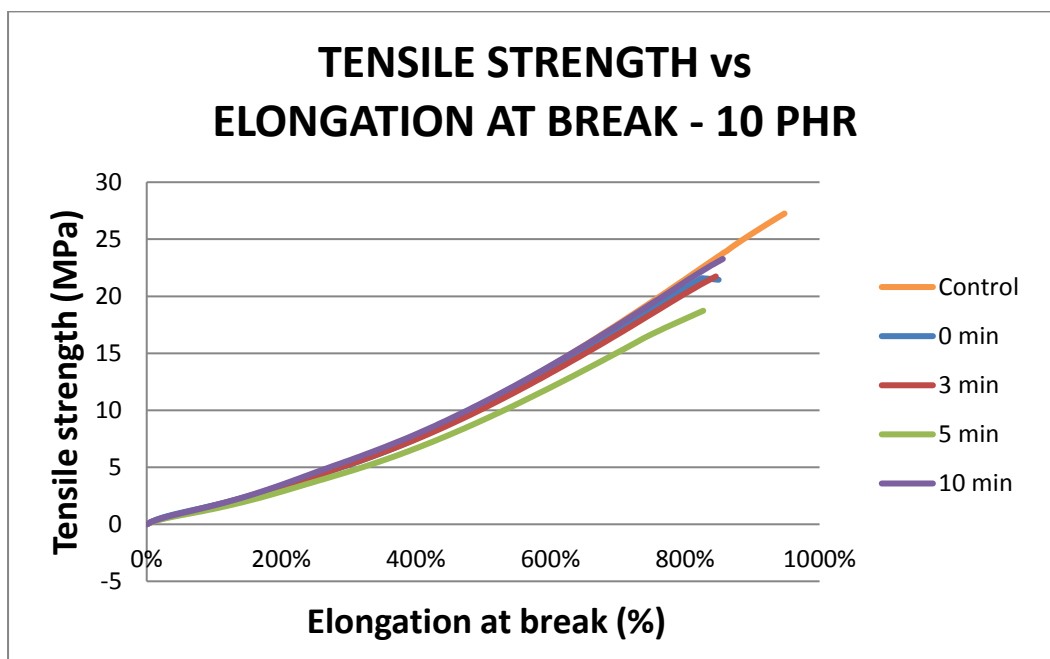


Figure 19B. Tensile strength vs. elongation at break with 30 phr loading.

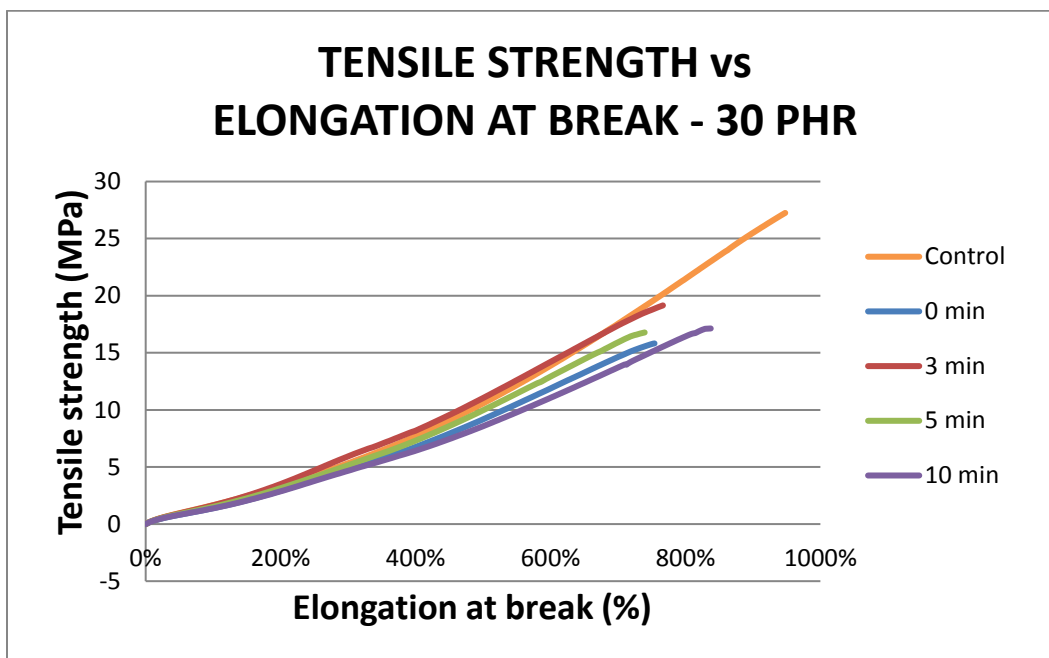
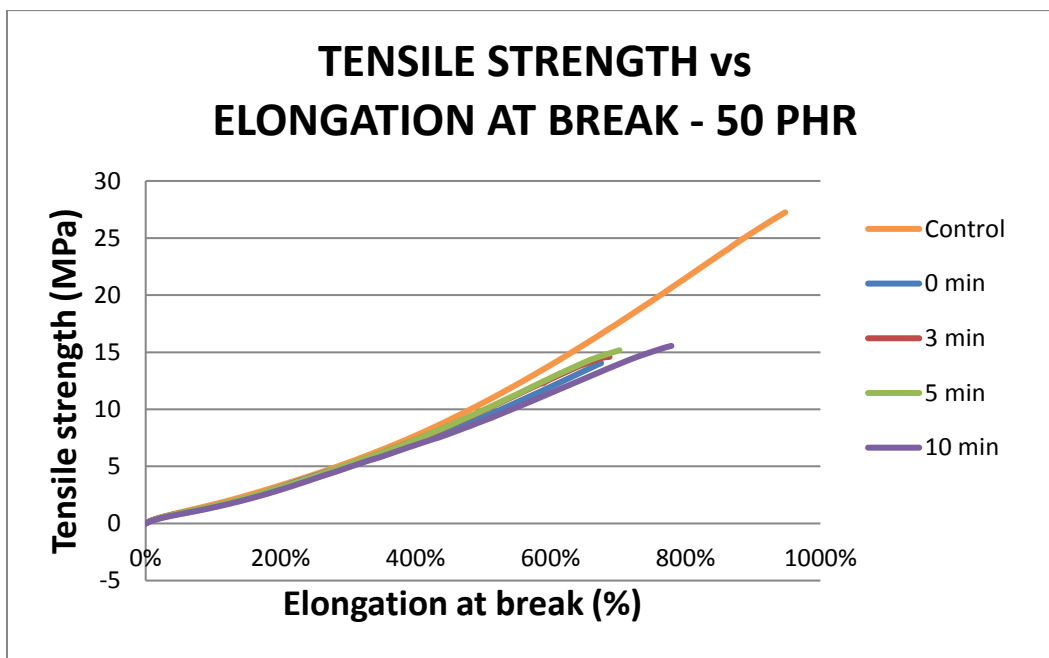


Figure 19C. Tensile strength vs. elongation at break with 50 phr loading.



4.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

To obtain information about the structure and functional groups after vulcanization, FTIR spectra are presented in Figure 20A-C. It is well known that the bond energy of S-S (227 kJ/mol) and C-S bond (273 kJ/mol) is lower than that of the C-C bond (348 kJ/mol). During the process of microwave devulcanization of GTR, the amount of energy released is utilized for breaking S-S bonds instead of C-C main chain bonds, because the S-S bond energy is lower than the energies of various organic bonds. However, a few C-C and C-S bonds may break along with the S-S bonds at higher temperatures after longer duration of heating [45].

For all samples, the peaks in the region of 1450 and 1370 cm^{-1} , are assigned to CH_3 and CH_2 bonds, relative to the rubber structure. They did not show significant differences between different GTR loadings or time exposure of treatment.

The prominent absorption at 1736 cm^{-1} was due to the carbonyl group ($\text{C}=\text{O}$). The presence of this polar group on the surface of GTR enhances the interaction with polar polymers [47]. This peak was more pronounced in the control sample for all concentrations of GTR. Samples containing ground tire rubber have lower peaks.

The peak at 1538 cm^{-1} was assigned to the zinc carboxylate bond (COO^-). This bond was come from the reaction of zinc oxide with the stearic acid which both acts as an activator. According to Delor-Jestin *et al.* [48], carboxylic acids are converted into zinc carboxylates as an effect of the presence of zinc oxide in the formulation. Untreated GTR peak has higher peak than the devulcanized GTR peaks. For the devulcanized GTR, the peak value of the bond decreased especially for the 10 min sample, which showed the devulcanization of GTR during the microwave devulcanization. However, no significant difference appears with 50 phr GTR content. ATR allows an analysis on the surface, which can indicates the existence of GTR content in the sample helps the migration of carboxylate of zinc to the surface.

Figure 20A. Fourier transform infrared spectroscopy (FTIR) spectra of 10 phr loading.

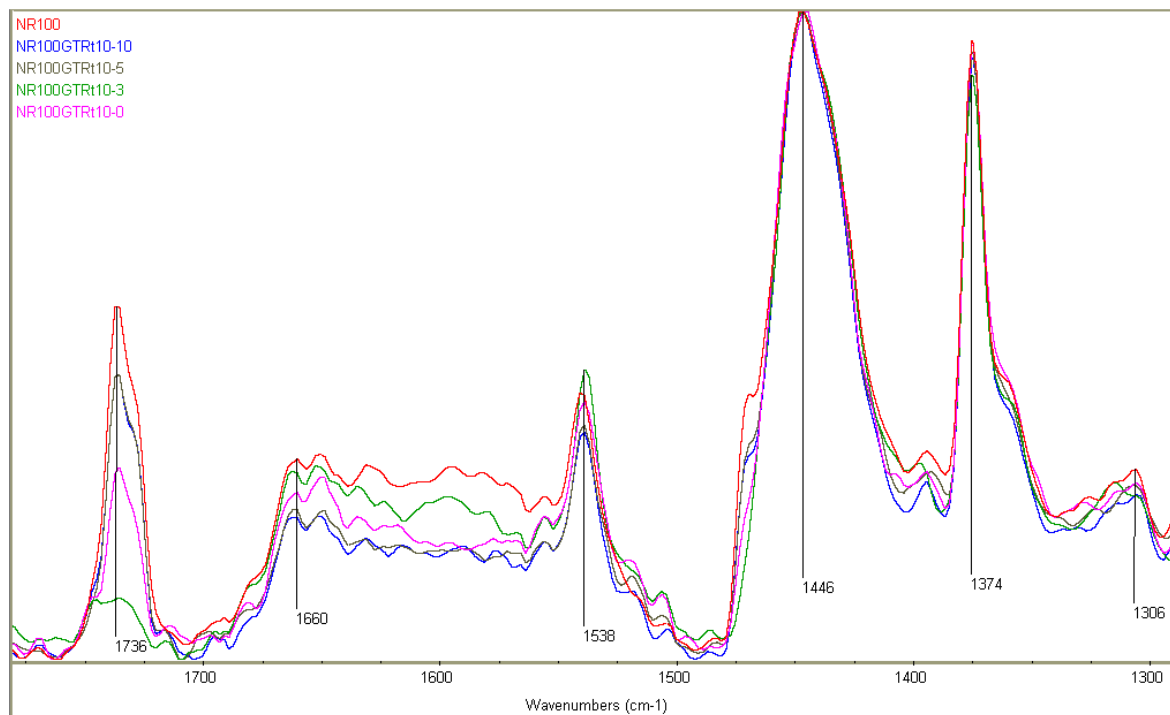


Figure 20B. Fourier transform infrared spectroscopy (FTIR) spectra of 30 phr loading.

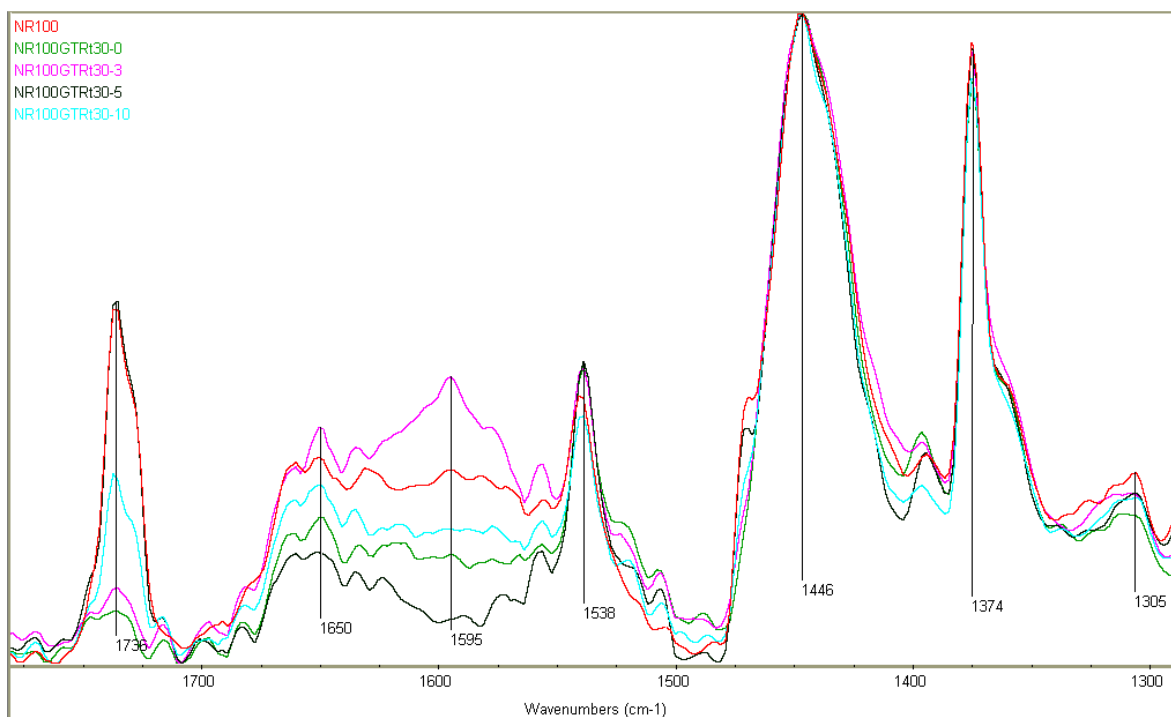
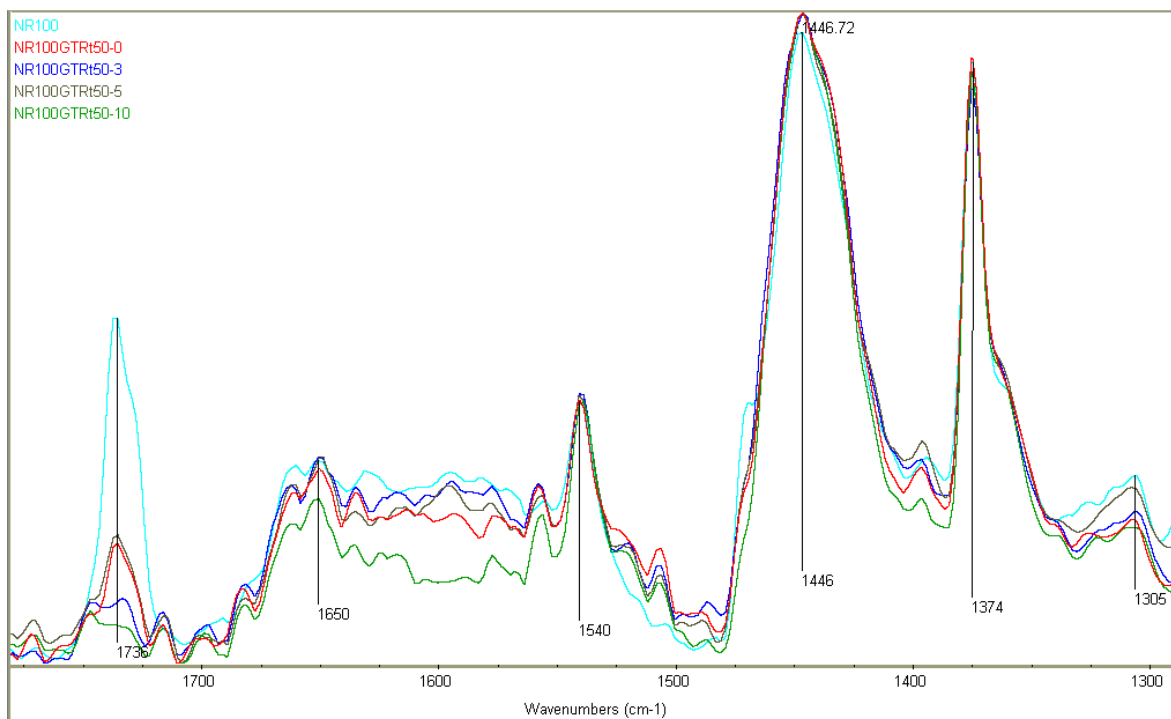


Figure 20C. Fourier transform infrared spectroscopy (FTIR) spectra of 50 phr loading.



4.3 SWELLING DEGREE

Swelling describes the sorption and desorption behavior of polymer in solvent, in this study it is a toluene. The swelling behavior of NR composites with different proportions of GTR was observed in the Figure 21A-C accordingly. All graphs have similar pattern in which; the uptake of toluene in GTR composites was found to increase relatively fast in the initial stage and reaches an equilibrium state thereafter.

Comparing between those three graphs, it can be seen that increasing the GTR concentration in natural rubber compounds results in slightly higher degree of swelling. Thus, gives poor swelling resistance.

Swelling is inversely related to crosslink density. Lower crosslink density as for 50 phr loading samples, would yield higher degree of swelling due to free molecular movement, making it easier for the solvent to penetrate through the rubber [47].

Figure 21A. Effect of 10 phr of GTR concentration on swelling degree in NR composites.

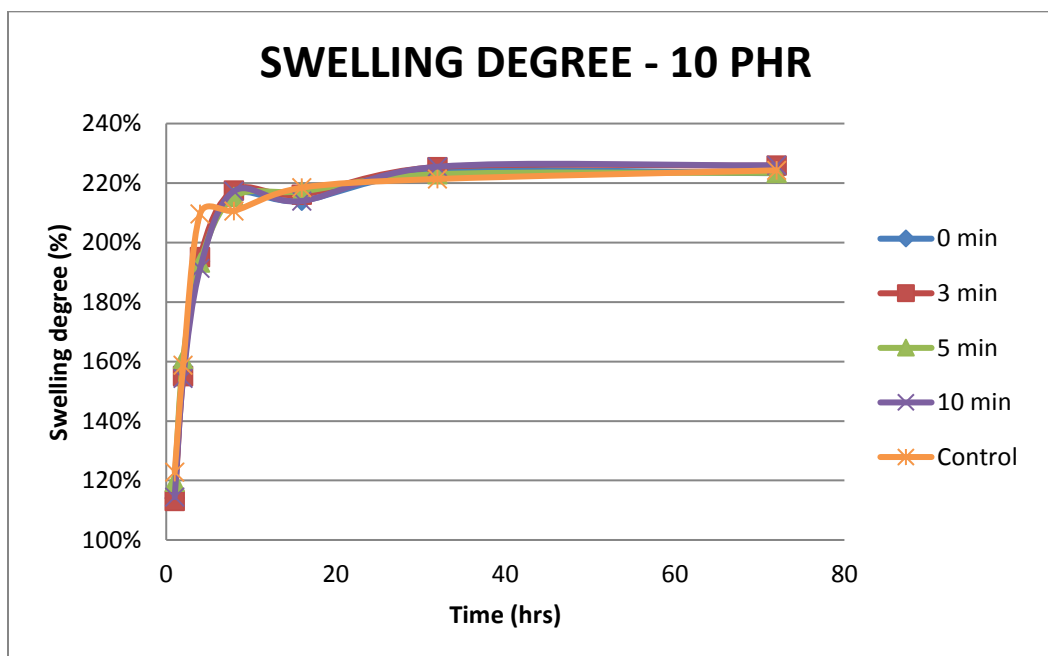


Figure 21B. Effect of 30 phr of GTR concentration on swelling degree in NR composites.

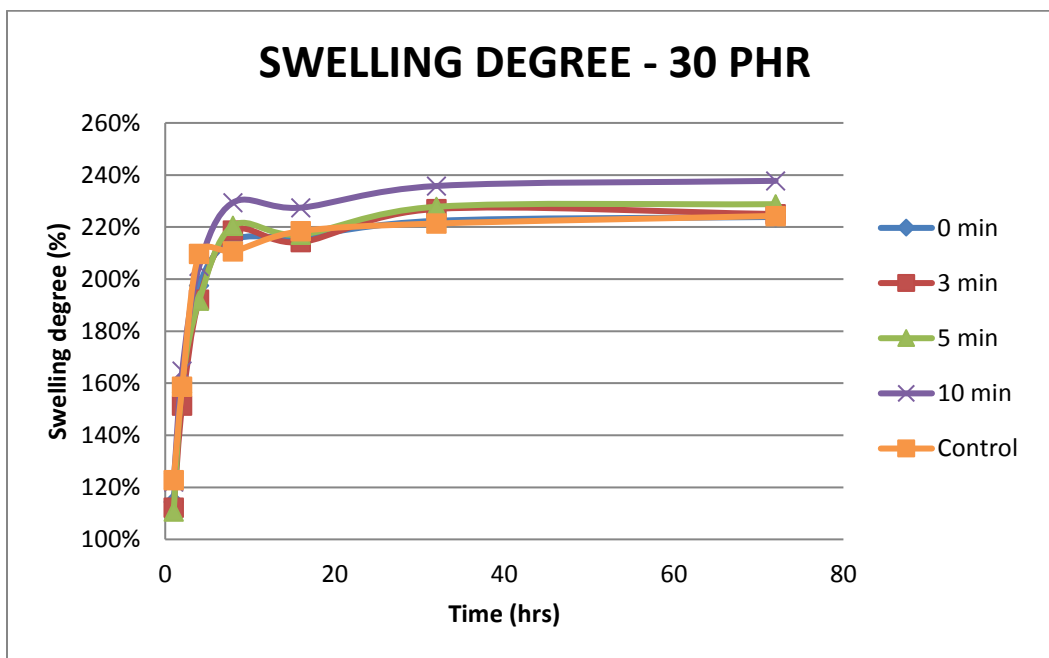
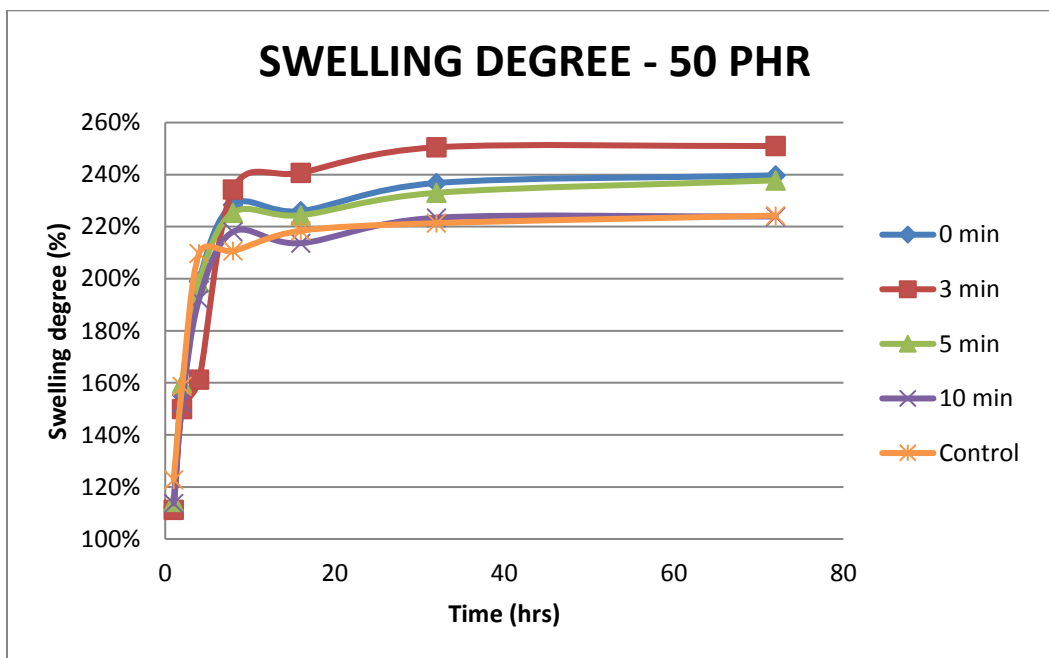


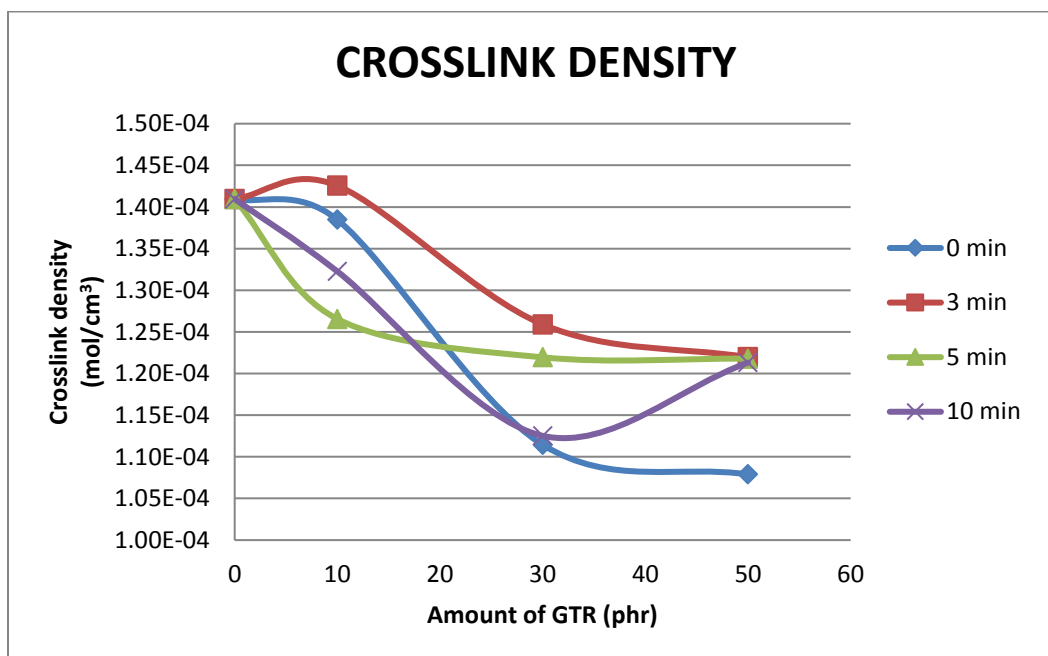
Figure 21B. Effect of 50 phr of GTR concentration on swelling degree in NR composites.



4.4 CROSSLINK DENSITY

The crosslink density of NR vulcanizates filled with DGTR and GTR content were shown in Figure 22.

Figure 22. Crosslink density vs. GTR loading in NR matrix.



It can be seen that the crosslink density decreases with increasing amount of ground tire rubber filled. They appear to be lower than the control sample. This might be because migration of sulfur from NR matrix during the revulcanization process due to the higher sulfur content on gum NR, result in a decline in the crosslink density [33]. During devulcanization, sulfur content and crosslinked structure on GTR surface have been reduced, so sulfur migrating from matrix to DGTR became much easier.

With increasing amount of devulcanized ground tire rubber, the value of volume fraction of rubber in the swollen gel (V_r) also decreases (Annex 2) indicates more breakage of C–S and S–S linkages present in the rubber occurred during the microwave treatment. At same loadings of 30 and 50 phr, a trend could be observed where as the exposure time to microwave increases, the crosslink density decreases.

Compared with untreated GTR (0 min) vulcanizate, crosslink density of DGTR vulcanizates were higher in 30 and 50 phr rubber loadings. Devulcanized GTR has more active sites existing on the surface, but untreated GTR contains surface that was not modified. This lessens the compatibility between GTR and rubber matrix. As the surface was not modified, GTR particles have lower surface area to interact with sulfur. Devulcanized GTR is favoured in blending with rubber as the devulcanized section (soluble fraction) of DGTR could form a good interphase as well as allowance for co-crosslinking between DGTR and rubber matrix.

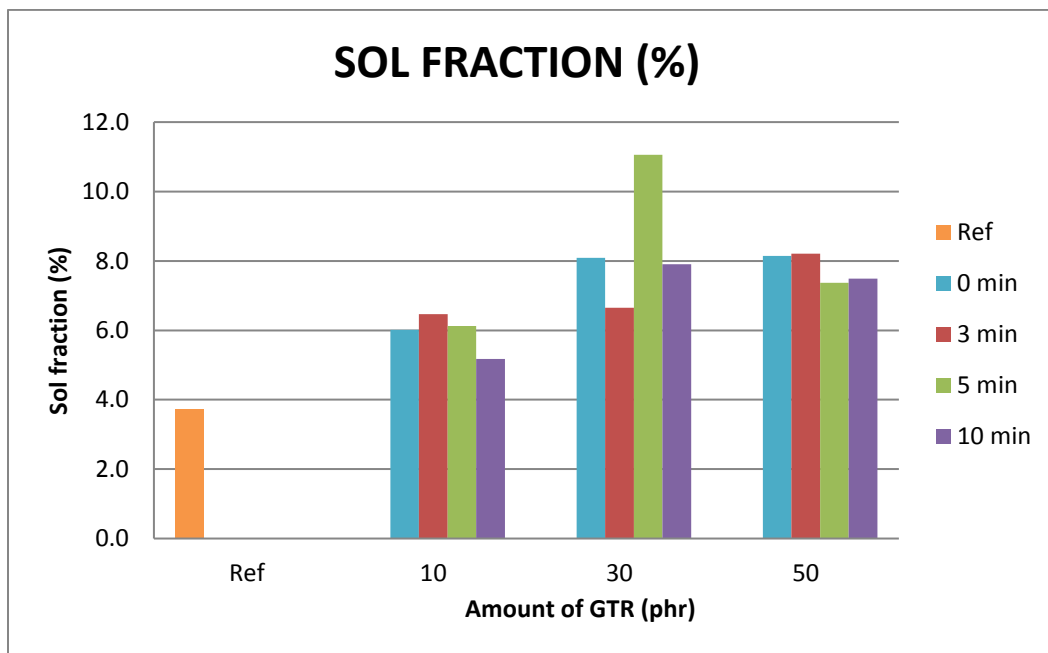
4.5 SOL FRACTION

The vulcanization transforms the majority of the free polymeric chains in a reticulated chemical structure, which is insoluble in toluene and forms a gel structure in the presence of this solvent. As mentioned before, extraction technique is able to separate the insoluble fraction of the rubber (known as gel fraction - vulcanized part) of the soluble fraction (sol fraction - devulcanized part). Thus, the gel content is an index to evaluate the degree of vulcanization of the rubbers [17].

The content of insoluble material (gel) increases with the increasing of vulcanization degree, due to the forms of the cross-linkings and, consequently, the capture of these molecules to exhibit the three-dimensional network of vulcanized rubber. Although the soluble part (sol) still makes part of the network, typically the vulcanization process tends to increase the cross-linkings density, making even this part more hardly moldable and breakable. In other words, the lower the sol fraction, the more efficient the vulcanization process is.

The sol content of the control sample which contains no GTR was 3,72% (Table 3), and it was the lowest amongst all. Regarding the NR control sample, a small amount of soluble materials could also be measured due to two possible reasons: either the additives from rubber were solubilized in toluene and/or there were small amounts of polymer chains that were not cured [10].

Figure 23. Graph of sol fraction in function of exposure times and GTR content.



It was noted that, the exposure time of the sample to the microwaves and the GTR content had a strong influence on the sol content compared to the reference sample, in which all sol content values are increasing.

According to the Figure 23, in general, it could be observed that the sol content increased with the increasing of GTR content present in the sample. The high sol content value indicates there is more main chain breakage or scission in the samples prepared with more devulcanized GTR.

When we compare samples of 0 min and 10 min, it was noted that, the sol content values get lower with higher treatment time in the microwave. The lower sol content showed that the vulcanization process was more efficient. This was expected because when the starting material was treated for longer exposure times, it reached higher temperatures and generated materials with lower sol contents.

4.6 THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetry analysis is an essential tool to characterize thermal stability of a blend. It is even more crucial in studies utilizing untreated GTR and devulcanized GTR as they are degraded material and will be influencing the resulting blends thermal stability significantly. Thermal stability of different composites was analysed in nitrogen atmosphere and the results are shown in Figure 24A, 25A, 26A. The DTGA curves for corresponding samples are shown in Figure 24B, 25B, 26B. The amount of residual is given in Table 4.

The vulcanizates first undergo weight loss at temperature below 350°C which corresponds to highly volatile materials such as oil, plasticizers and waxes that were used for tire manufacture [49]. The second weight loss occurs around 350°C to 550°C which corresponds to the thermal decomposition of polymers [49]. Unlike other review studies [45], there is no weight loss above 550°C that represents carbon black. This is because to observe the weight loss in this area, the analysis has to be done in the presence of oxygen.

All samples have same maximum degradation temperature which is 402,7°C. Hence, vulcanizates did not show any difference in thermal stability, regardless its difference of rubber proportions and time treatment.

The result also shows that as GTR content increased, the amount of residual increased. Residual could be the component that is not volatilized such as zinc oxide.

Figure 24A. Thermogravimetric analysis (TGA) curve of 10 phr loading.

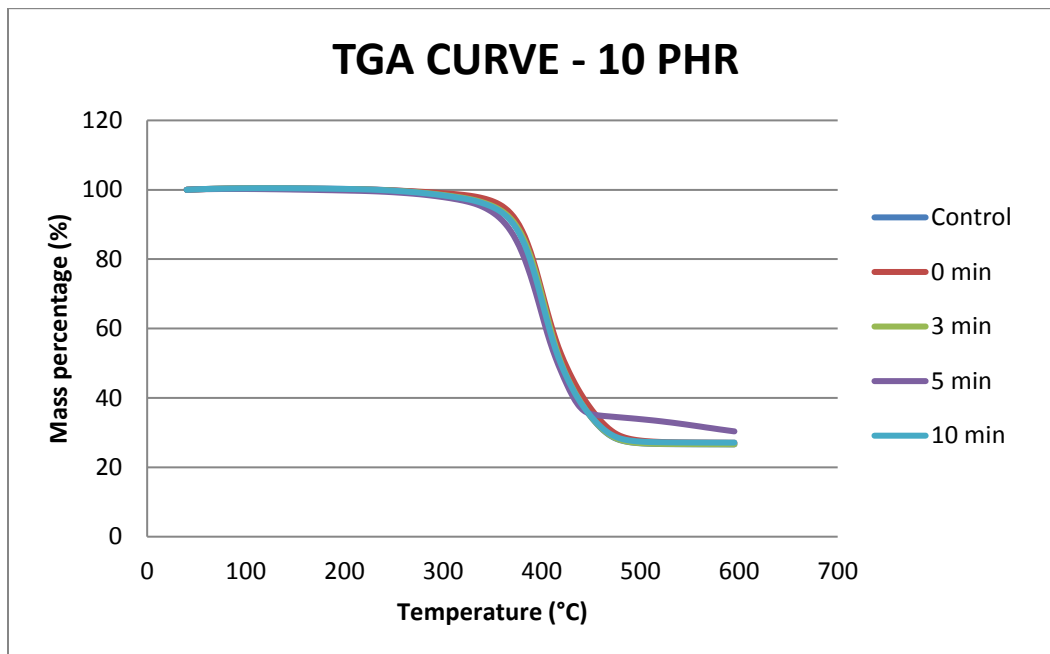


Figure 24B. DTGA curve of thermogravimetric analysis (TGA) of 10 phr loading.

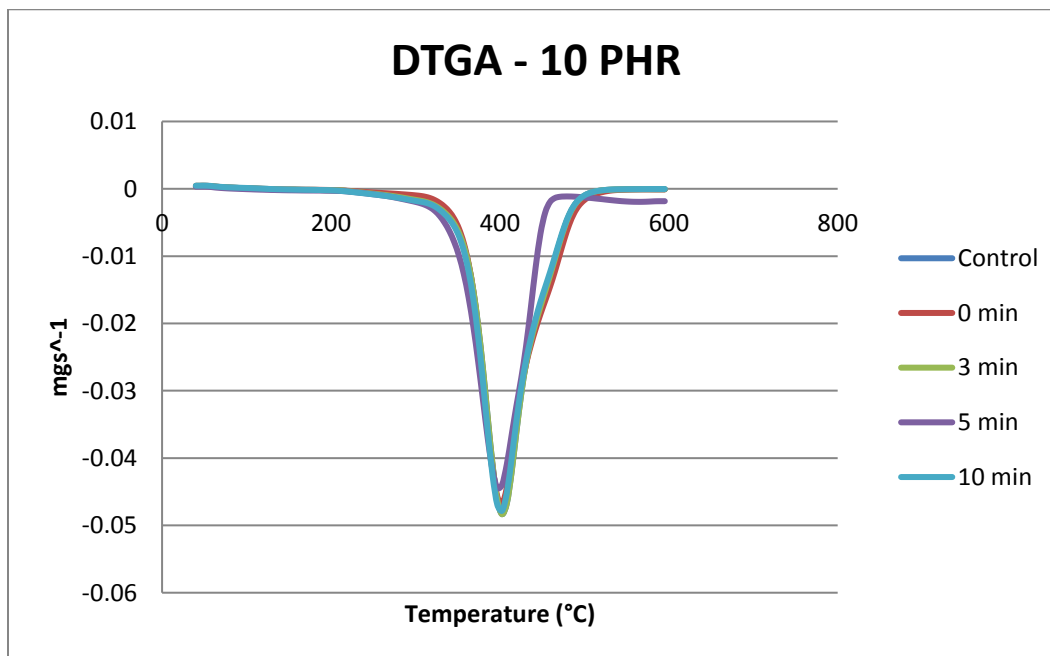


Figure 25A. Thermogravimetric analysis (TGA) curve of 30 phr loading.

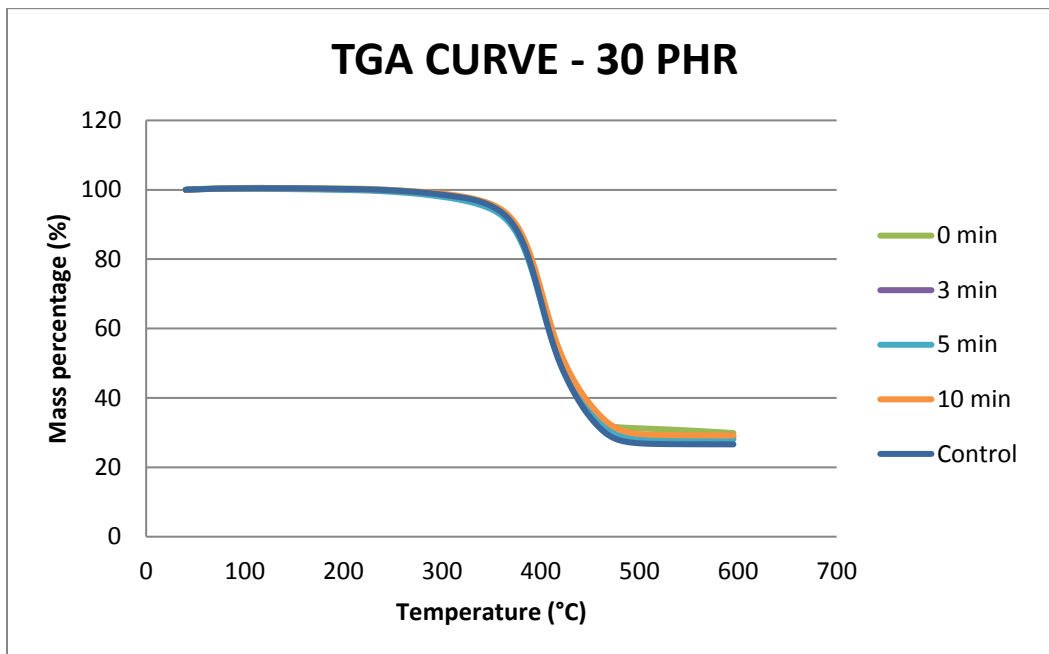


Figure 25B. DTGA curve of thermogravimetric analysis (TGA) of 30 phr loading.

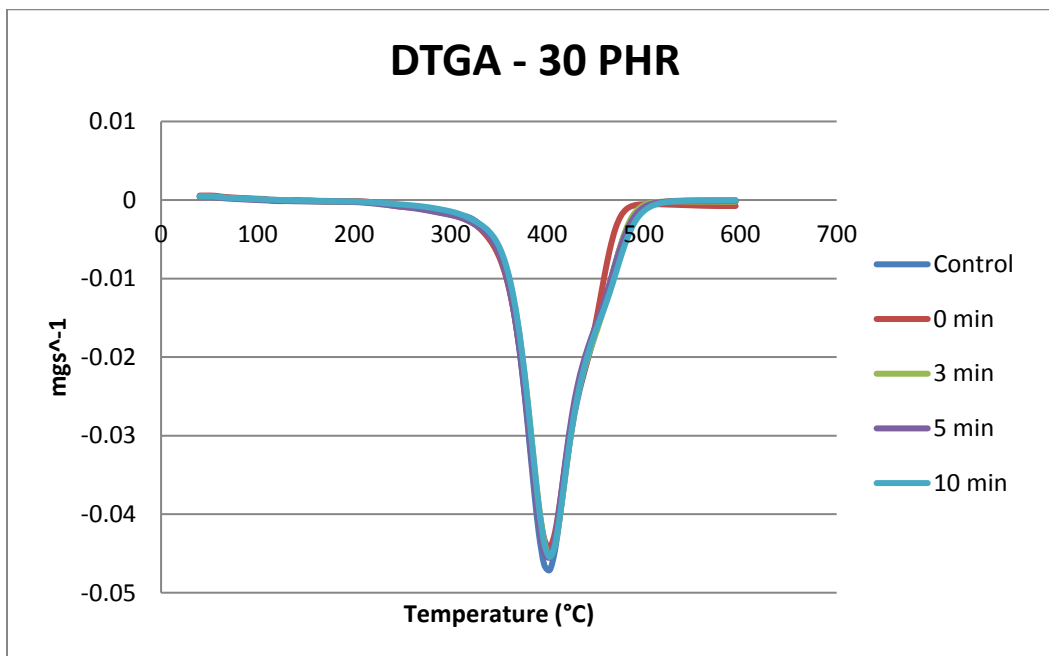


Figure 26A. Thermogravimetric analysis (TGA) curve of 50 phr loading.

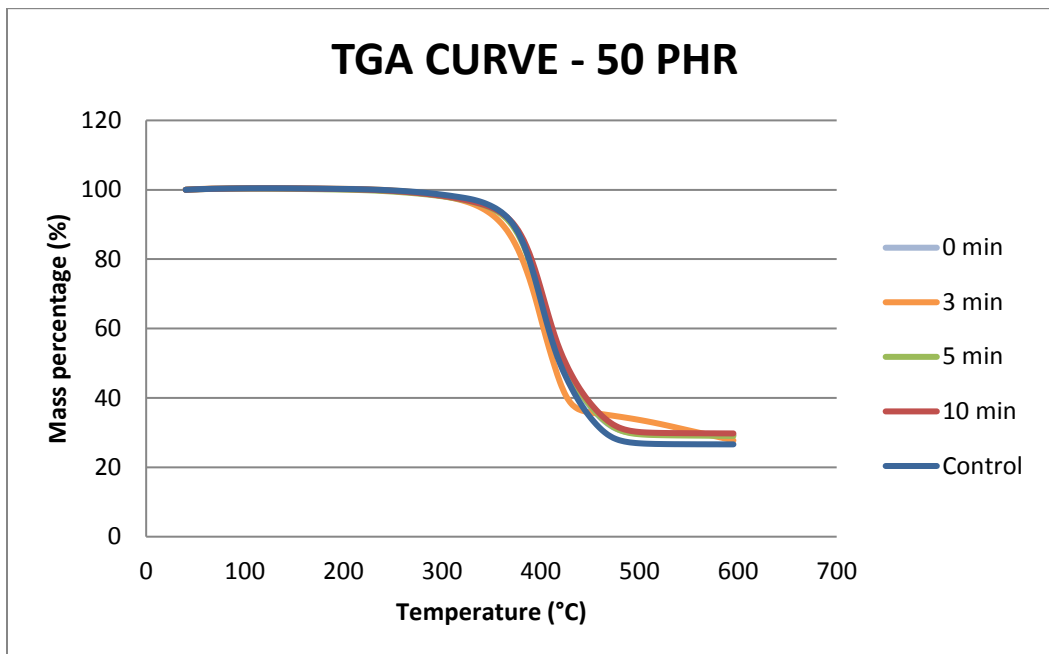


Figure 26B. DTGA curve of thermogravimetric analysis (TGA) of 50 phr loading.

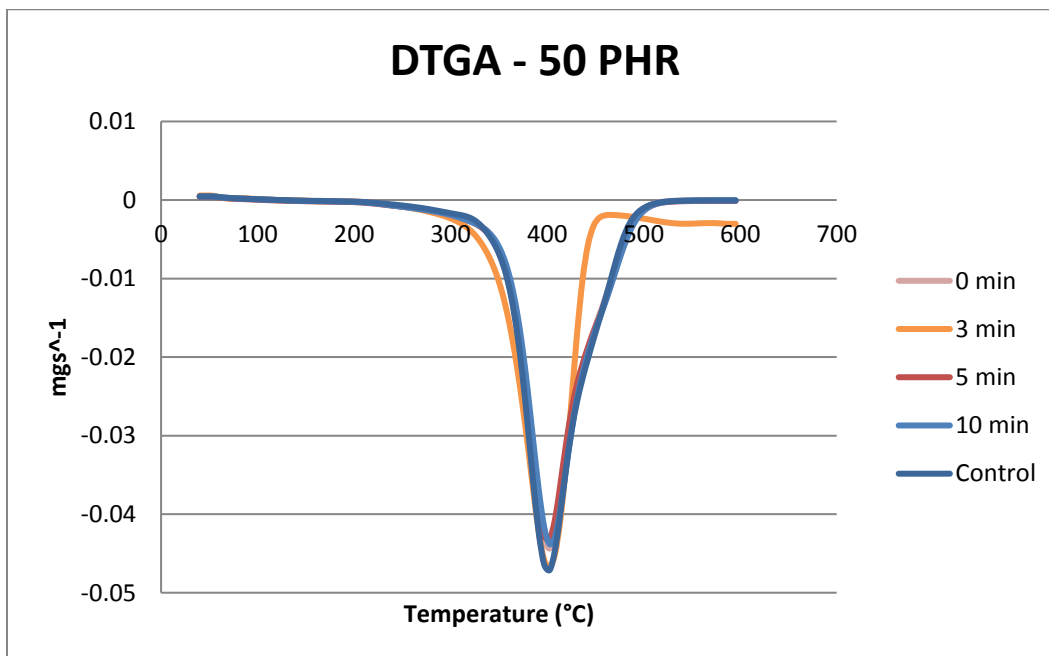


Table 4. Amount of residual after TGA analysis.

Time exposure (min)	Amount of GTR (phr)	Residue (%)
0	10	27,07
	30	29,88
	50	29,37
3	10	26,63
	30	28,81
	50	27,75
5	10	28,36
	30	28,06
	50	29,04
10	10	27,12
	30	29,16
	50	29,76
Control sample		26,61

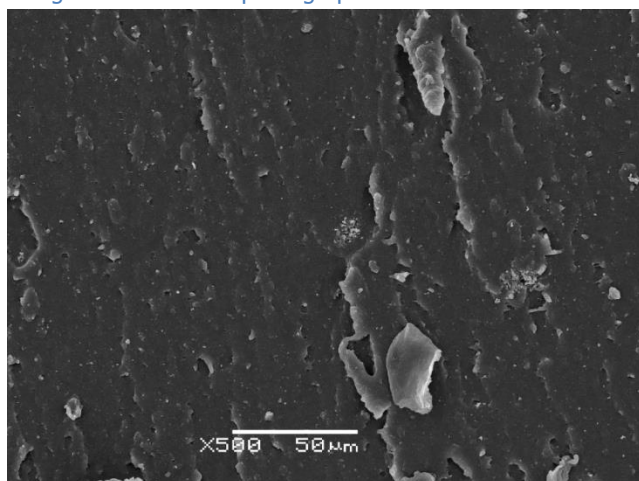
4.7 SCANNING ELECTRON MICROSCOPY (SEM)

The physical properties of the polymer blends are always affected by the resulting morphology of the blends [50]. SEM photographs with x50 magnification of tensile fracture surfaces of NR composites are shown in Figure 27A–F below. It could be seen from Figure 27A, the control sample has quite smooth surface since the particles are well-dispersed. Opposite with samples containing GTR, they show the presence of crack paths and fractured surfaces. This made the samples vulnerable and susceptible under mechanical stress.

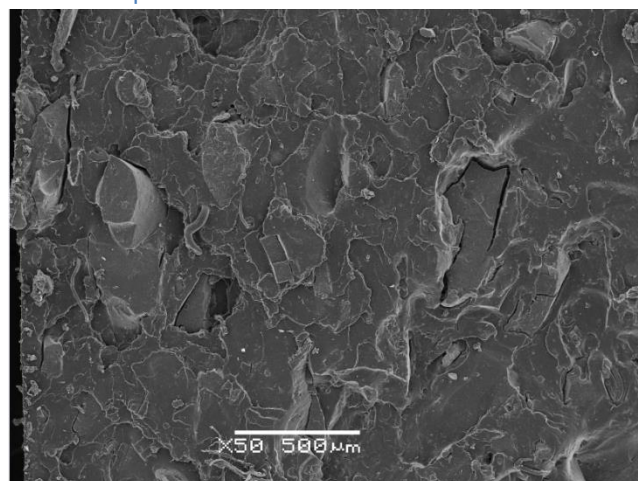
Sample of 5 min with 50 phr (Figure 27C) showed that some particles have been pulled out and gaps could be observed between DGTR and the matrix. The result indicated that the adhesion of the DGTR to the NR matrix was poor due to crosslink structure of GTR.

In sample of 10 min with 10 phr (Figure 27F), it could be seen that there was less void between DGTR and the matrix. This composite had much better compatibility. So the interface region between DGTR and the matrix could withstand a higher strength and deformation. It was agreement with the results of tensile strength and elongation at break that show higher microwave treatment and less proportion of GTR show best mechanical properties.

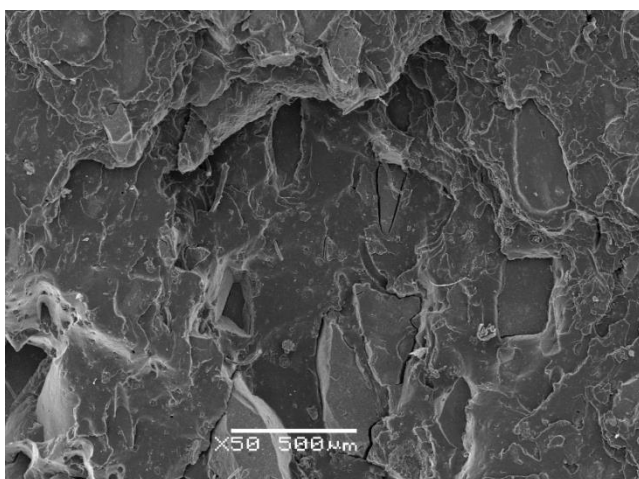
Figure 27A–F. SEM photographs of tensile fracture surfaces of NR composites.



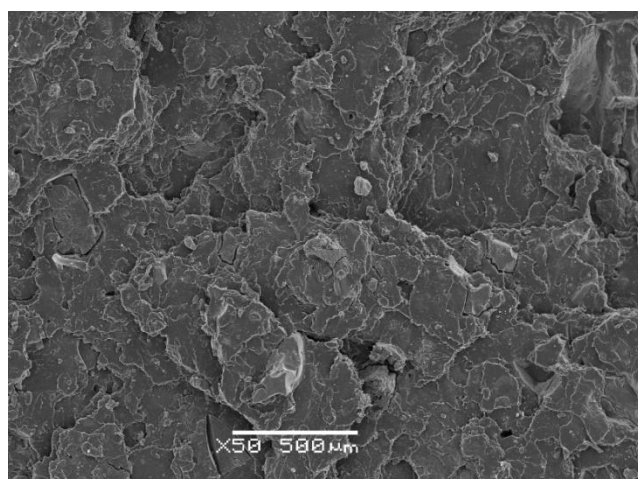
A. Control sample



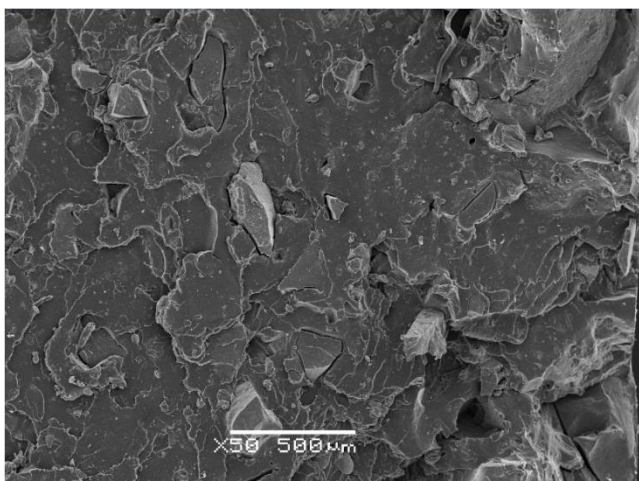
B. Sample of 3 min with 50 phr



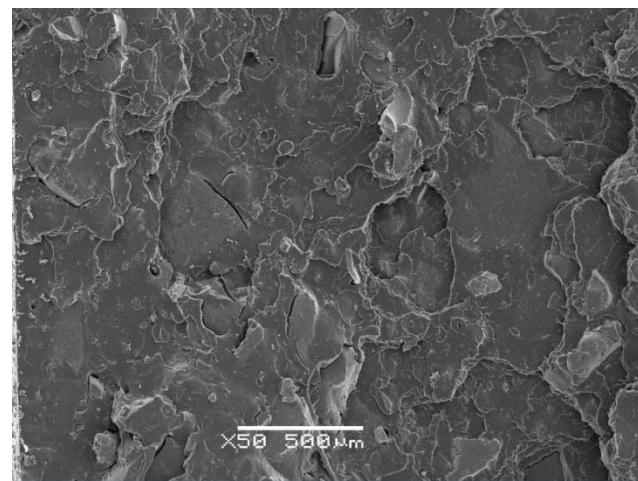
C. Sample of 5 min with 50 phr



D. Sample of 10 min with 50 phr



E. Sample of 10 min with 30 phr



F. Sample of 10 min with 10 phr

5 CONCLUSIONS

In a nutshell, DGTR was produced by a microwave technique with different treatment time then DGTR and untreated GTR were blended with virgin NR in different proportions. For mechanical properties, the lowest proportion of DGTR and the longest treatment time has the best mechanical properties, which is sample 10 phr with 10 min. As a result of microwave devulcanization, the tensile properties of the DGTR/NR vulcanizates were much better than those of the GTR/NR. However, all samples showed deterioration in comparison to the virgin NR, as virgin rubber is more homogenous. For swelling degree, even though the difference values of result are small, it can be concluded that the higher proportion of GTR has poor swelling resistance. For crosslink density, it was appeared that samples containing DGTR have higher crosslink density than those containing untreated GTR. This might be due to the compatibility of GTR with natural rubber matrix. The TGA indicates same thermal stability for all samples. SEM proves that the samples were vulnerable and susceptible under mechanical stress due to presence of fractured surfaces. At longer treatment time, sample shows well-dispersed and better homogeneity on the surface. This research has shown that the microwave treatment can be used as a convenient technique for rubber recycling studies.

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7 ANNEX

Annex 1: Table of swelling degree.

Time dev.	GTR content (phr)	Time (hrs)							
		0	1	2	4	8	16	32	72
0 min	10	0.206	114%	158%	194%	216%	214%	224%	223%
	30	0.201	114%	161%	198%	215%	216%	222%	224%
	50	0.204	112%	155%	199%	228%	226%	237%	240%
3 min	10	0.205	113%	155%	195%	218%	216%	225%	226%
	30	0.204	112%	151%	192%	219%	214%	227%	225%
	50	0.204	111%	150%	161%	234%	241%	250%	251%
5 min	10	0.209	120%	161%	193%	215%	217%	223%	223%
	30	0.205	111%	160%	192%	220%	217%	228%	229%
	50	0.209	114%	160%	199%	225%	224%	233%	238%
10 min	10	0.208	114%	154%	191%	217%	214%	225%	226%
	30	0.204	122%	165%	205%	229%	227%	236%	238%
	50	0.205	114%	152%	192%	218%	214%	223%	224%
Ref		0.206	123%	159%	210%	211%	218%	221%	224%

Annex 2: Table of crosslink density.

Sample	a1	a2	p2	Vr	ve	φf	m0	mdry	φ	v after correction
0_10	0.621	0.199	1.075491	0.2754171	0.000315	0.1983	3.99	3.75	0.104925	1.38E-04
0_30	0.671	0.203	1.117586	0.2517567	0.000252	0.1752	4.08	3.75	0.094794	1.11E-04
0_50	0.708	0.207	1.086259	0.2479719	0.000243	0.1569	4.05	3.72	0.084948	1.08E-04
3_10	0.645	0.206	1.053053	0.2786539	0.000324	0.1983	4.02	3.76	0.105433	1.43E-04
3_30	0.655	0.204	1.090264	0.2645215	0.000285	0.1752	4.06	3.79	0.093333	1.26E-04
3_50	0.682	0.210	1.093555	0.2607379	0.000275	0.1569	4.02	3.69	0.085004	1.22E-04
5_10	0.658	0.204	1.076923	0.2656284	0.000288	0.1983	4.08	3.83	0.105051	1.27E-04
5_30	0.664	0.205	1.094359	0.2613351	0.000277	0.1752	4.07	3.62	0.097957	1.22E-04
5_50	0.674	0.210	1.113468	0.2605546	0.000275	0.1569	4.07	3.77	0.084235	1.22E-04
10_10	0.631	0.199	1.077767	0.2703508	0.000301	0.1983	4.06	3.85	0.103993	1.32E-04
10_30	0.663	0.198	1.091398	0.2527382	0.000255	0.1752	4.05	3.73	0.094601	1.13E-04
10_50	0.661	0.204	1.100552	0.2601465	0.000273	0.1569	4.03	3.728	0.084347	1.21E-04
Ref	0.630	0.203	1.072417	0.2776146	0.000321	0.2124	4.03	3.88	0.109709	1.41E-04