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A COMPARATIVE STUDY OF NATURAL RUBBER MODIFIED WITH DEVULCANIZED GROUND TIRE RUBBER(CAR)

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ABSTRACT

As the number of waste tires or what so-called end of life tires in the world are growing, it is important to find a better way to recycle them. In this work, ground tire rubber from car (GTRc) was used. This GTRc have been undergo microwave treatment at different duration to devulcanize it. Sample of natural rubber with GTRc/dGTRc was prepared. It appears that the devulcanization time does not affect the tensile strength and elongation at break. For crosslink density, samples containing devulcanized GTRc have higher crosslink density compared with sample containing GTRc without microwave treatment.

1. INTRODUCTION

1.1. NATURAL RUBBER

Natural rubber, also can be known as India rubber. It consists of polymers of organic compound isoprene with minor impurities of other organic compound and water [1]. Natural rubber is classified as elastomers as they have viscoelasticity properties [1]. The one of leading country of rubber production is Malaysia [1]. The rubber production in Malaysia almost one and a half million tons per year. Natural rubber was harvested from a tree called rubber tree [2].

Figure 1.1.1: rubber tree plantation

Rubber is harvested in form of latex from the tree and it was later processed in to rubber ready for commercial processing [1].

Figure 1.1.2: latex being harvested from a rubber tree.

Figure 1.1.2: Natural rubber

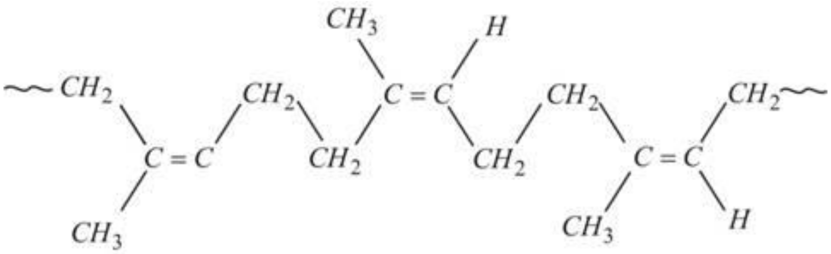

Figure 1.1.3: structure of Natural rubber (Cis Polyisoprene)

Nowadays, rubber has been used widely in industry such as adhesives, insulating material and more. Rubber also can be processed to increase its mechanical properties through vulcanization. This vulcanized rubber has numerous application thanks to its properties.

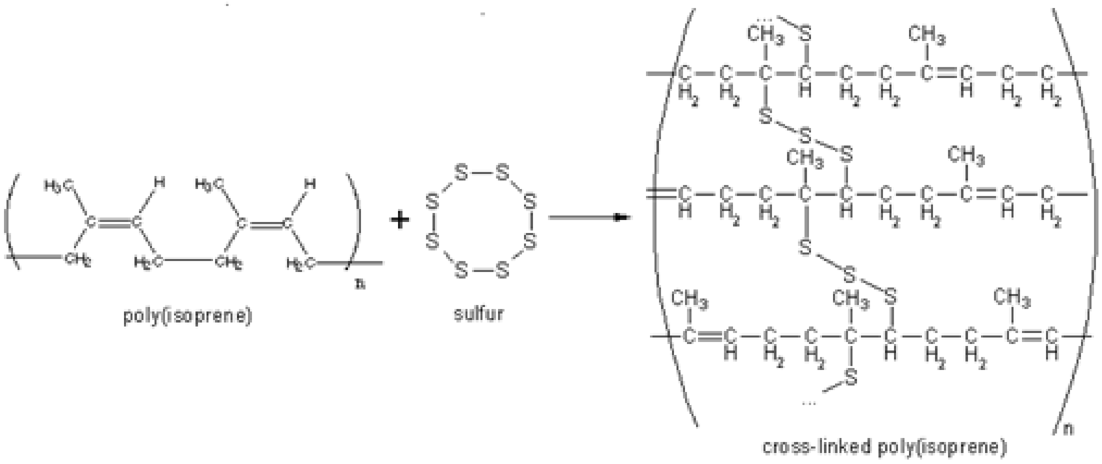

Figure 1.1.4:vulcanization of natural rubber reaction

This vulcanized rubber can be used to make hoses, conveyor belts, diving gear and more. Also, it also has been widely used to make tires for vehicles. With this reason rubber are important to our everyday life. Without it there will be no transport [3].

Carbon black is one of important component in rubber industry. It helps to improve the properties of the rubber [2].

But, the problem is now these tires will wear out after being used. It need to be replaced with a new one. These worn out tire cannot be recycled because of the vulcanization process. These tires were thrown into landfill or burned [3]. This disposal of waste tires is a serious problem as it involves high cost. Also, the rubber tree, also known as *Havea Brasiliensis* facing a great threat. In south America, the fungal disease of rubber trees is the South American leaf blight (SALB) caused by the ascomycete *Microcyclus ulei* [4]. Low rubber production in south America because of this disease. If this ascomycete spread to countries that is the main production of rubber, this might be a serious problem. Therefore, it is important to find a way how to reuse back this waste tire to decrease dependency towards rubber trees.

1.2. Tires

Tires are usually made of 30 types of synthetic rubber, eight types of natural rubber, eight types of carbon black, steel cord, polyester, nylon, steel bead wire, silica and 40 different kinds of chemicals, waxes, oils and pigments [3]. Different type of tire has different composition of components depending the type of vehicle and terrain. The common tires are car tire, truck tire and off road tire [3]. This are the typical composition of tire rubber.

INGREDIENTS	CAR TIRE (%)	LORRY TIRE (%)
RUBBER/ELASTOMER	47	45
CARBON BLACK	21.5	22
METAL	16.5	25
TEXTILE	5.5	
ZINC OXIDE	1	2
SULFUR	1	1
ADDITIVES	7.5	5

Table 1.2.1: composition of car tire and lorry tire. [5]

Usually lorry tires contain higher proportions of natural rubber than car tires [3].

1.3. Waste Tires/end-of life tires (ELTs)

A tire is considered at the end of its life when it can no longer be used on vehicles. It could be the tire has been retreaded or regrooved [3]. All tires including car, truck, airplane and other result in ELTs. It was approximated about 1 billion ELTs are generated globally each year. In 2008, it was estimated 4 billion ELTs in landfills and stockpiles worldwide [3]. Below shows amount of ELTs generated in some countries every year [3]:

	MILLIONS OF ELTS GENERATED PER YEAR
USA	292
EUROPE	250
CHINA	112
JAPAN	80
MEXICO	30
BRAZIL	27
SOUTH KOREA	23
CANADA	22
AUSTRALIA	20
MALAYSIA	14
SOUTH AFRICA	12
IRAN	10
ISRAEL	7
NEW ZEALAND	4

Table 1.3.1

Some of these ELTs will be export or to be retread. Those tire do not go this will be used for energy recovery [3]. Also, it will be used for civil engineering uses or material recovery. Else, it will send to landfill, stockpiled or discarded waste [3].

Some studies have been carried out to find a way to recycle back waste tire. One way to reuse the waste tire is to pulverized them first to make ground tire rubber (GTR). Next, this ground tire rubber is blended with a virgin rubber [6]. This way we can protect environment. But, there is a flaw. It is the bond between ground tire rubber and the virgin rubber is weak because of the crosslink of the GTR [6]. This will reduce its mechanical properties of this composites. Because of this, another way is to devulcanize the tire. The sulfur crosslinks making these tire unrecyclable. The purpose devulcanization process is to break the sulfur crosslinks. There are several techniques to devulcanize the ground tire rubber. Devulcanization strategies that can be used are mechanical, chemical, physical and biological processes.

1.4. Devulcanization of rubber

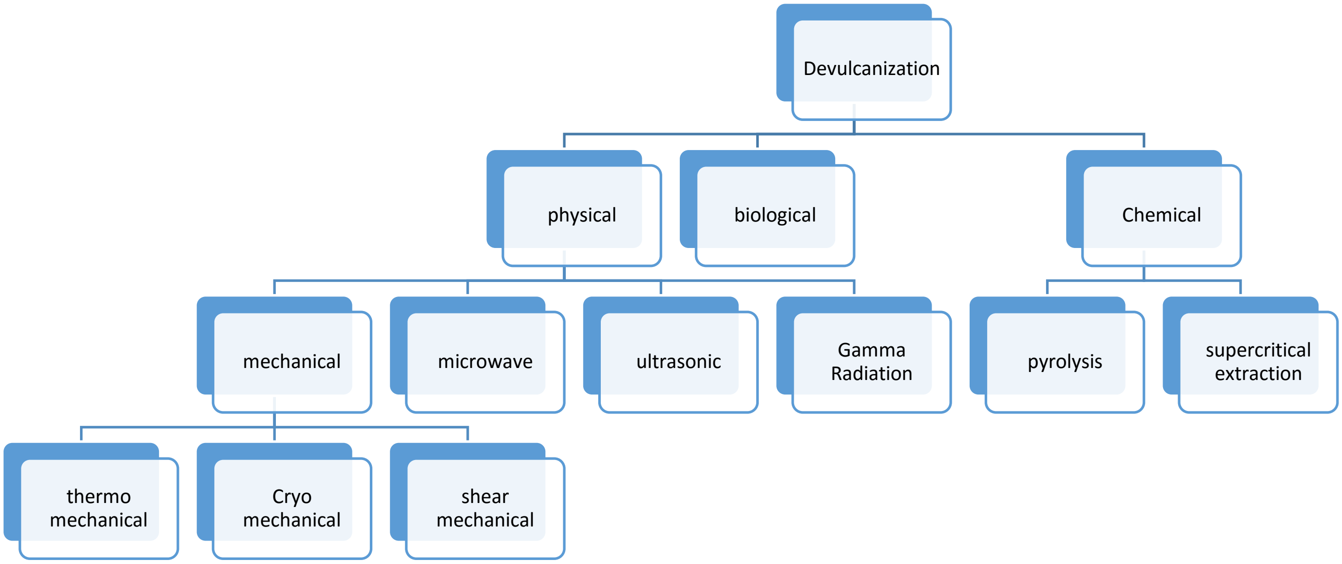

Figure 1.4.1: overview of devulcanization methods [7]

Devulcanization means the process is reversed from vulcanization. In vulcanization process, sulfur crosslink was form during the process. Therefore, for devulcanization process the objective is to break the s-s and c-s bond that responsible for the crosslink formation. So, ideally after devulcanization process, the material that undergo this process are expected to be used again like rubber before it undergoes vulcanization process. It makes the material easier to processed again. Tires that will be used for devulacanization are normally grounded to create a lot of surface area for ensuring the effectiveness of the devulcanization process.

1.4.1. Mechanical devulcanization

This method uses shear force and grinding to break the main backbone chain of rubber and some sulfur crosslinks. There has been a research in M. Mouri et al. [8] uses a modular screw type reactor, based on "Shear-flow stage reaction control technology". In this experiment, ethylene propylene diene monomer (EPDM) rubber was used. There are several part in the reactor. The crushed rubber will get smaller along the reactor due to high pressure and shear force exerted by the screw rotator [9] [10]. These method is classified as thermo-mechanical devulcanization as it also involves high temperature.

There is also a method called cryo-mechanical devulcanization. In this method, liquid nitrogen is used to cool down the rubber below its transition glass temperature. When a polymer is in a state below its transition glass temperature, it is brittle. Then the rubber is place in a mill to reduce its size [11] [12]. These two mention mechanical methods have no selective C-S and S-S bond break occur. In the first method which involves breaking of the backbone will reduce the mechanical properties of the vulcanizates because of degradation.

1.4.2. Ultrasonic Devulcanization

It was discovered that ultrasonic waves of certain levels, in presence of heat and pressure can break the three dimensional network in vulcanized rubber. The first study on ultrasonic devulcanization was done by okuda and Hatano by batch process [13]. In their study, the vulcanized rubber was exposed at 50 kHz of ultrasonic wave for 20 minutes. In A. Isayev study, a devulcanization reactor based on single screw extruder with the horn for ultrasonic wave placed before the die [14]. Devulcanization occurs due to dissipation of heat by the rubber because of the ultrasonic wave. The amplitude of the ultrasonic wave affects the degree of devulcanization. If the amplitude is too low, no devulcanization of rubber will take place. In Okuda and Hatano study, they claimed that selective bond breaking of s-s and c-s are proven and no effect on the c-c bonds [13]. Therefore, the mechanical properties can be preserved.

1.4.3. Chemical Devulcanization

On the ‘60s by Malaysian Rubber Producer Research Association (MRPRA) [15], they introduced the use of chemical reagent to break the sulfur crosslinks for sulfur vulcanized rubber. The reagent used were triphenyl phosphine, sodium di-n-butyl phosphite, thiol-amine reagent, lithium aluminum hydride, phenyl lithium and methyl iodide. Hunt and kovalak used 2-butanol at 150 °C and 3,4 MPa to devulcanize the rubber [16]. In this method, the is no significant change of microstructure of rubber devulcanizates and can be used the same way as the original rubber. Devulcanizing rubber chemically are dangerous for health and environment as they require reaction that uses organic compound, oils and solvent.

1.4.4. Biological devulcanization

We can devulcanize the ground tire rubber biologically. It uses microorganisms to break sulfur bonds inside the rubber. The use of chemolithautotrophs which gains energy from sulfur oxidation is an environmental friendly process [7]. It is also can be as called microbial desulfurization of ground tire rubber with microorganism [17]. Usually microorganism used for desulfurization are *thiobacillus ferrooxidans, thiobacillus thioparus* and more. The problem in this technique is to maintain the proper environmental conditions such as nutrients and temperature for the microorganisms to survive [17].

1.4.5. Microwave devulcanization

Microwave also been used to devulcanizing waste tire. This is a physical process. Microwave is an electromagnetic radiation which has a frequency between 300 MHz to 300 GHz which corresponds to 1 mm to 1 m of wavelength. Domestic microwave usually operates at 2450 MHz [18]. the factor that affect heating using microwave which is the power level of the microwaves and the material to be heated. The higher the power level of the microwaves the faster the heating of the material. And for the types of material, different material act differently in microwave radiation [19]. This means that some material will not heated in microwave like metal. They just reflect the radiation. The material heat by microwaves because it has dipole and water molecules inside. This molecule will arrange themselves in the direction of electric field. Because of this microwave has frequency which is high, these molecules will oscillate according this frequency. So, heat will build up as these molecules rotates.

The crosslink breaks by heating the vulcanized rubber by microwaves. This technology was developed by Goodyear Tire and rubber company in late 1970s [20]. This technique offers more advantage than other method for example treatment of large quantities of material at the same time and also environmental friendly. This devulcanized rubber became soft and can be reprocessed or also can be blended with other virgin rubber to be revulcanized again.

The objective of this study is to do a comparative study of Natural Rubber modified with devulcanized ground tire rubber from car (GTRcar) to see how the properties of the composite changes with different amount of devulcanized ground tire rubber (GTR).

2. EXPERIMENTAL

2.1. Materials

Natural Rubber

GTRcar was supplied by GMN Maials (Spain)

Vulcanization accelerators (TBBS – N-tert-butyl-2-benzothiazole sulfonamide, TMTD – tertramethylthiuram disulfide), carbon black, stearic acid, zinc oxide and sulfur with technical purity were supplied by Vigar (Spain).

2.2. Samples preparation

Elastomeric samples were prepared at 70°C using a Brabender plastograph batch mixer. The rotational speed of rotors was 100 rpm. The mixing time equaled 8 minutes included 2 minutes of preliminary plasticization of natural rubber, 4 minutes of mixing with carbon black 30phr the GTR and dGTR (3, 5 and 10 minutes) and 2 minutes of mixing the blend with the sulfur curing system. The GTR content in the sample was 0, 10, 30 and 50 parts per hundred rubber (phr). For all samples the same curing system samples was used. The curing system composition (phr): zinc oxide 5.0; stearic acid 3.0; TBBS 1.0; TMTD 0.25; sulfur 2.0.

Devulcanized GTR were prepared using a microwave model DAEWOO KOR-6L37 with microwave power 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 placed into the microwave. The plate was fixed so that it does not move. The microwave was started for 3 min, 5min and 10 min duration.

Figure 2.2.1: a microwave for devulcanization

Figure 2.2.2: Brabender Plastograph

Then these 2 batches are mix together using a two roll mill.

Figure 2.2.3: Two roll mill

the sample from the two roll mill is folded before compression molded.

Figure 2.2.4: the folded sample before compression molded

The obtained EcoRubber Composite were compression molded into 3mm thick samples at 160 °C at 4.9 MPa according to determined optimal vulcanization time. Unfilled natural rubber processed in the same conditions was used as a reference sample.

Figure 2.2.5: compression molding

Figure 2.2.6: obtained sample after compression molding

2.3. Measurement

Chemical structure of GTR and elastomeric sample was determined using Fourier transform infrared spectroscopy (FTIR) analysis by means of a Nicolet iS10 spectrometer from Thermo Scientific (USA). The device had an ATR attachment with a germanium crystal. Measurement was performed with 1 cm-1 resolution in the range 550-4000 cm-1.

Figure 2.3.1: FTIR device with an ATR attachment

Tensile strength and elongation at break of obtained vulcanizates were tested according the standard ISO 37 using a Instron testing machine with cell load capacity of 20 kN. Tensile tests were performed at a cross-head speed of 500mm/min. 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. The reported results are the mean of 3 measurements per sample.

Figure 2.3.2: Tensile test

Swelling degree of EcoRubber Composite (0.2 g samples) as function of time was determined by equilibrium swelling in toluene (room temperature). Swelling degree was calculated in accordance with the formula (2).

$$Q = \frac{m_t - m_o}{m_0} \times 100\% \quad (2)$$

Where: Q- swelling degree; m_t – mass of the sample swollen after time t, g; m_o – initial mass of sample, g.

The crosslink density was determined according to ASTMD6814-02 standard method through swelling measurement of EcoRubber composites (ER-C) was let to swell in cold toluene for 72 hours and the solvent was refreshed every 24 hours. The Flory Rehner equation [Flory PJ, Rehner J (1943) Statitiscal mechanic of crosslinked polymer networks I. rubber like elasticity. J chem phys 11:512-520.] (3) was used to calculate the crosslink density. The χ interaction parameter between rubber and swelling solvent was set equal to 0.39, considering NR as main polymer and toluene as solvent. The rubber density is 0.92 g/cm3; the Kraus correction model was applied due at the presence of carbon black as a filler [21] the carbon black density was chosen equal to 1.85 g/cm3 and the k constant was chosen to be 1.17 [22].

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

Where:

V_e – crosslink density, mol/cm^3; V_r – gel volume in the swollen sample; V_1 – solvent molar volume (toluene = 106.2 cm3/mol);

$$V_r = \frac{\frac{a_2}{\rho_2}}{\frac{a_1 - a_2}{\rho_1} + \frac{a_2}{\rho_2}} \qquad (4)$$

Where: a_1= weight of swollen sample

a_2= weight of dried specimen (24 hours at room temperature)

ρ_1= Density of solvent – toluene (0.8669 g/cm^3)

ρ_2= Density of the specimen

Cross-link density with Kraus correction was calculated according equation (5) and (6):

$$v_{after\ correction} = \frac{v_e}{1 + K + \Phi} \qquad (5)$$

$$\Phi = \frac{\phi_f \times \rho_r \times m_0}{\rho_f \times m_{dry}} \qquad (6)$$

V_e – the measured chemical crosslink density, mol/cm^3; $v_{\text{after correction}}$ – the actual chemical crosslink density, mol/cm^3; K – constant characteristic of the filler but independent of the solvent;

Φ_f – the volume fraction of filler in the sample which is calculated; ρ_r – the density of studied compound, g/cm^3; m_{dry} – the weight of the sample after extraction, g.

Sol fraction was determined as mass difference of elastomeric samples (ER-C) before extraction (W1) and after extraction (W2), according to equation (7):

$$Sol\ fraction = \frac{W_1 - W_2}{W_1} \times 100\% \qquad (7)$$

Figure 2.3.3: Schoxlet Extraction to measure sol fraction

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

Thermogravimetric analysis (TGA) was performed on Mettler Toledo TGA/SDTA 851 apparatus. Elastomeric samples (ER-C) weighing approx. 14 mg were placed in a corundum dish. The measurement was conducted in the temperature range 40 – 600 °C and under nitrogen atmosphere (30 ml/min), at a heating rate of 20 °C/min.

Figure 5: TGA device

The breaking surface of the sample from tensile test was observed with a Jeol 5610 scanning electron microscope. Before measurement, the samples were covered with a fine gold-palladium layer in order to increase their conductivity in a vacuum chamber.

Figure 2.3.5: an electron microscope

Figure 2.3.6: device to cover the sample with gold-palladium layer

Figure 2.3.7: samples which have been covered with gold-palladium layer

	sample												
NR	100	100	100	100	100	100	100	100	100	100	100	100	100
dGTRc0		10	30	50									
dGTRc3					10	30	50						
dGTRc5								10	30	50			
dGTRc10											10	30	50
Carbon black	30	30	30	30	30	30	30	30	30	30	30	30	30
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5
TBBS	1	1	1	1	1	1	1	1	1	1	1	1	1
TMTD	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Sulfur	2	2	2	2	2	2	2	2	2	2	2	2	2
Stearic Acid	3	3	3	3	3	3	3	3	3	3	3	3	3

Table 2: Sample's compositions in (phr); TBBS – N-tert-butyl-2-benzothiazole sulfonamide; TMTD – tetramethylthiuram disulfide.

3. RESULTS AND DISCUSSIONS

3.1. Fourier Transform Infrared spectroscopy (FTIR)

This analysis is used to study the chemical of the elastomeric samples. ATR attachment with a germanium crystal was used. With this attachment The penetration depth into the sample is typically between 0.5 and 2 micrometers, with the exact value being determined by the wavelength of light, the angle of incidence and the indices of refraction for the ATR crystal and the medium being probed.

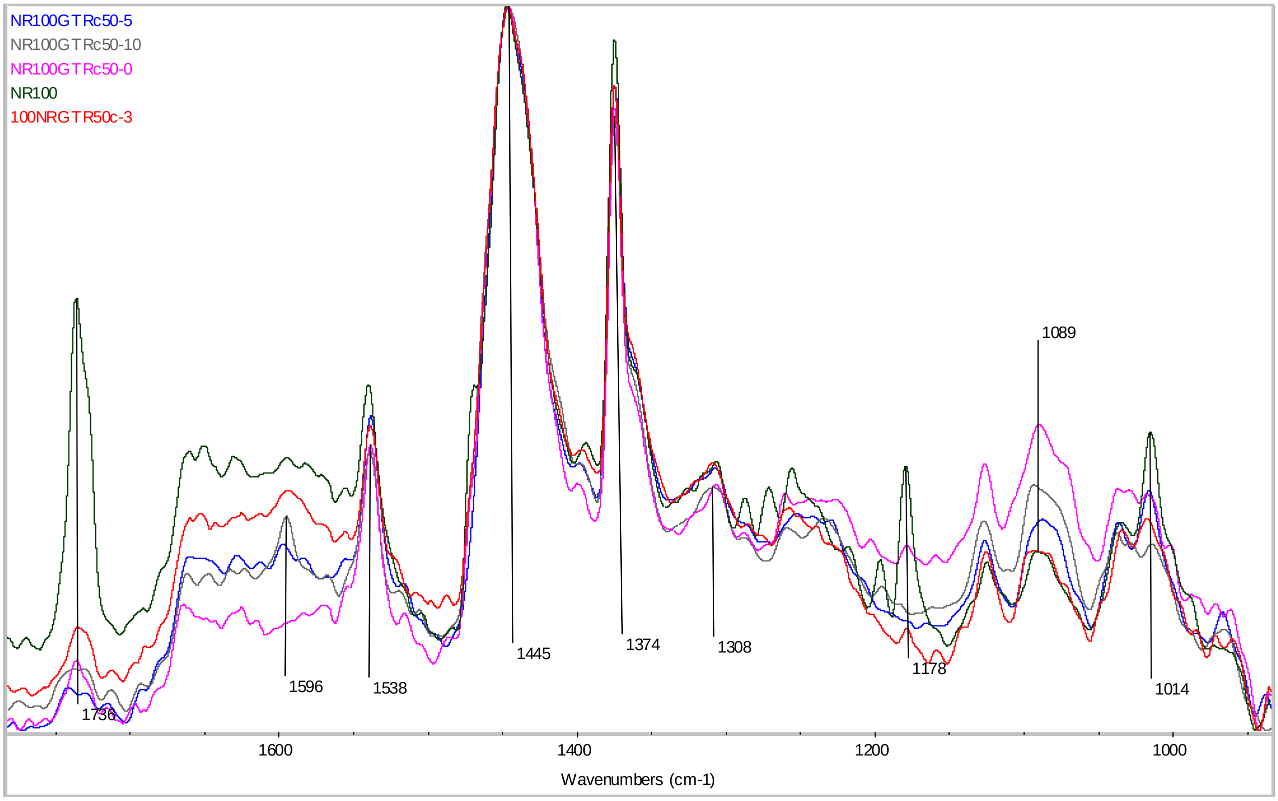

Figure 3.1.1: spectrum for NR100 with GTRc 50 phr at different devulcanization time

In figure above, it shows FITR result for samples containing GTRc 50 phr at different devulcanization time. from these spectra, there are several peaks. It was observed that all sample have very high peak at 1445 cm-1 and 1374 cm-1. There is also very little peak at 1308 cm-1.

These peaks correspond to the hydrocarbon chain. 1445 cm-1 and 1308 cm-1 correspond to (-CH_2-). 1374 cm-1 corresponds to (CH_3-).

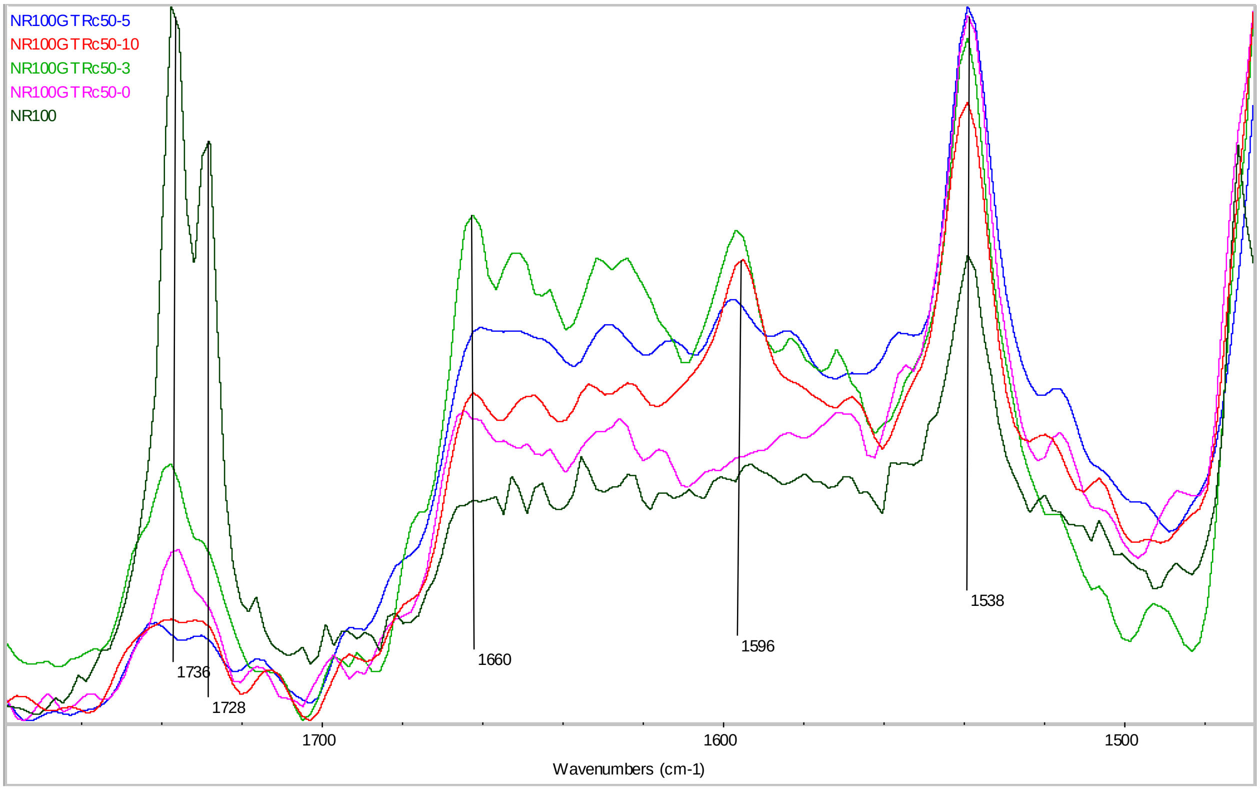

Figure 3.1.2

This are the amplified spectrum ranging from 1480 cm^{-1} to 1780 cm^{-1}. It was observed that the reference sample have high peak at 1736 and 1728 cm^{-1}. These peaks correspond to carbonyl group. Samples containing GTRc have lower peak. It was also observed that there is a peak at 1538 cm^{-1}. This peak correspond to carboxylate of zinc. This compound came from the reaction of zinc oxide with the stearic acid. This compound act as an activator for vulcanization. At 1538 cm^{-1}, the reference sample has lower peak compared to sample containing GTRc. Because of the ATR allow us to analyze on the surface, it can be inferred that the existence of GTRc in the sample helps migration of carboxylate of zinc to the surface. Also, the peak is the highest for sample with

GTRc devulcanized for 3 min and without treatment and the peak is smaller with sample containing GTRc devulcanized for 10 min.

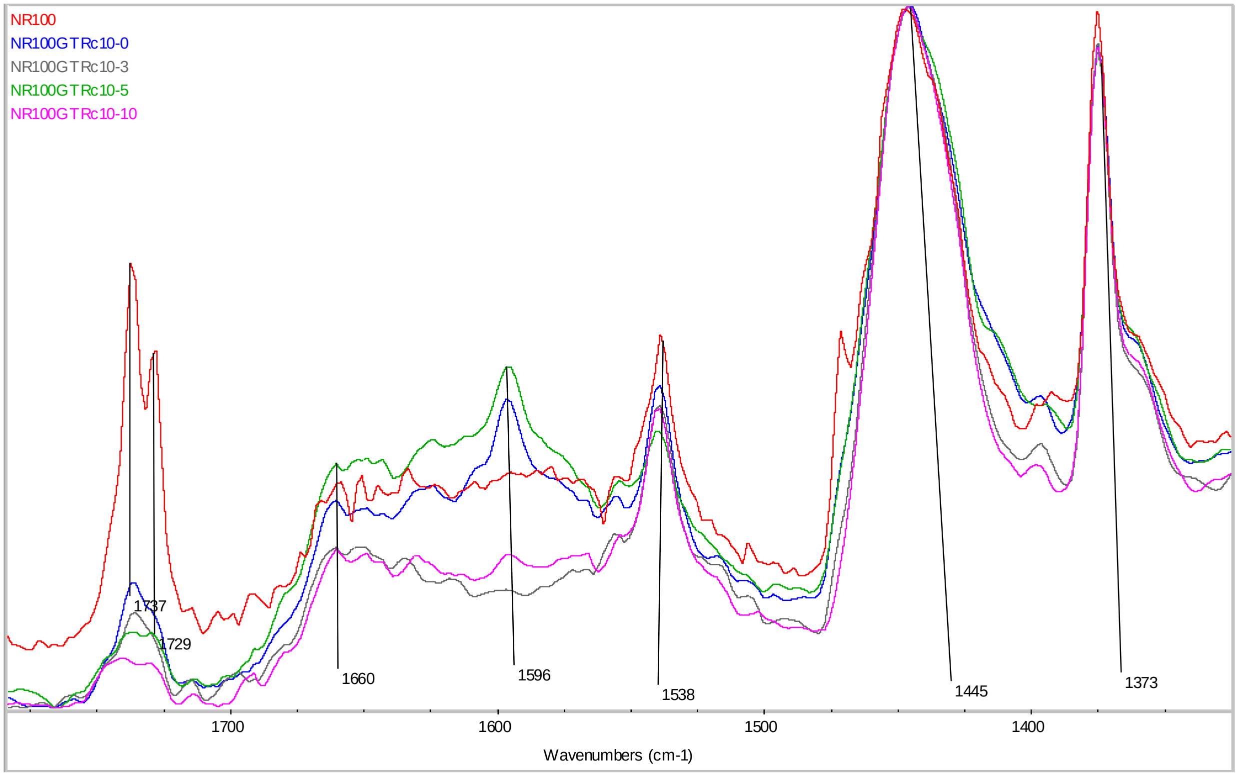

Figure 3.1.3: spectrum for samples NR100 with GTRc 10 phr

From figure above, it is observed at 1538 cm^{-1}, the peaks for sample containing GTRc have been reduced below the reference sample. This probably due to amount of GTRc can affect the amount of zinc carboxylate on the surface. In this case the amount of GTRc is at 10 phr. Therefore, higher amount of GTRc with promotes the migration of zinc carboxylate towards the surface.

3.2. Mechanical Properties

The mechanical properties result is summarized in the table

Mechanical Properties	**NR100 GTRc*** **(amount and devulcanization time)**												
GTR*	0	10	30	50	10/3	30/3	50/3	10/5	30/5	50/5	10/10	30/10	50/10
Tensile strength (MPa)	26.1	21.1	17.3	15.5	21.1	17.4	16.4	21.5	17.0	15.8	19.4	16.5	16.0
Elongation at break (%)	918	802	740	695	831	739	705	793	749	671	766	727	722
Modulus at 100 % (MPa)	1.41	1.51	1.43	1.43	1.31	1.43	1.47	1.56	1.42	1.48	1.52	1.50	1.47
Modulus at 300 % (MPa)	2.19	2.13	1.94	2.11	2.17	2.15	2.07	2.24	1.94	2.18	2.04	1.76	2.18
Hardness (Shore A)	49.2	47.7	46.3	48.0	47.8	48.5	48.0	48.8	48.3	47.8	48.0	49.0	47.8
Experimental density (g/cm^3)	1.12	1.16	1.12	1.13	1.06	1.11	1.08	1.07	1.14	1.10	1.12	1.11	1.12
Theoretical density (g/cm^3)	1.29	1.29	1.27	1.26	1.29	1.27	1.26	1.29	1.27	1.26	1.29	1.27	1.26
Porosity (%)	14	10	12	10	17	13	14	17	10	13	13	13	11

Table 3.2.1: Comparison of mechanical properties

First we compare the tensile strength with the same amount of GTR in the sample

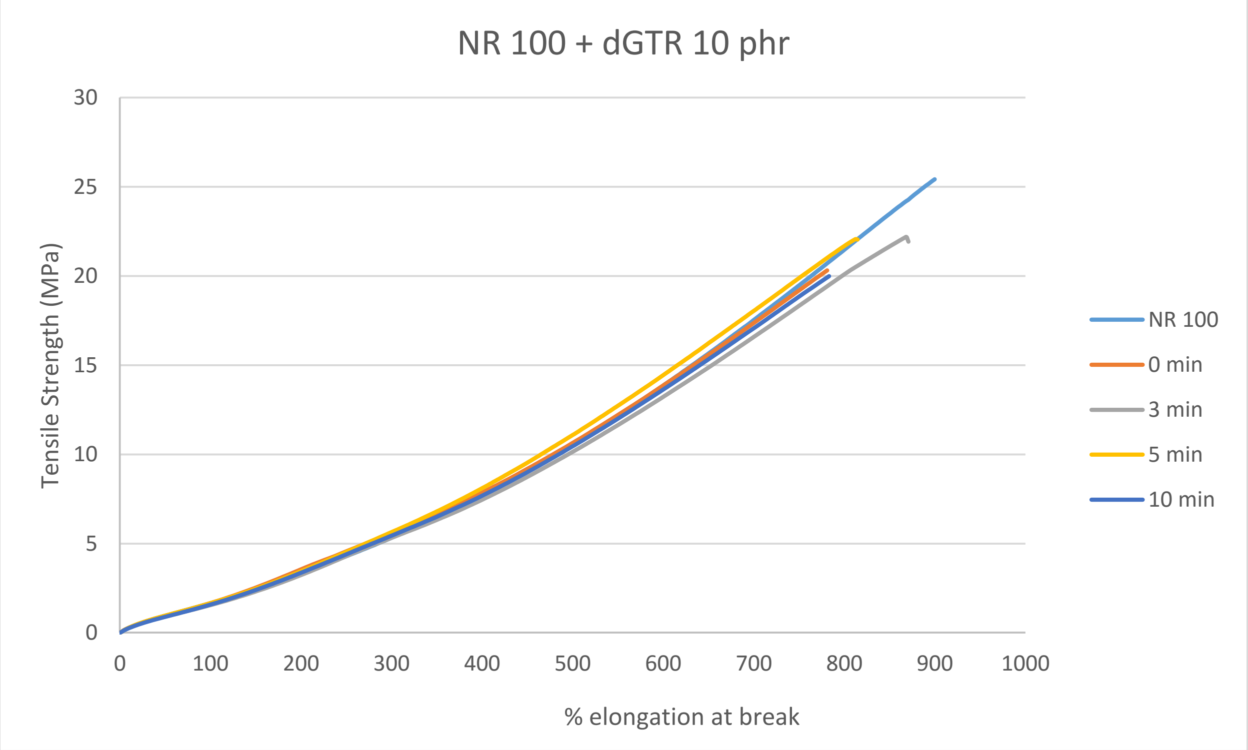

Figure 3.2.1

On the graph above shows the result of tensile test with 10 phr of GTRcar. Generally, by comparing to the reference sample that is NR 100, the tensile strength decreases by 18 to 20 % approximately. The elongation at break also decreases. in function of devulcanization time, it does not really effect anything. But at 3 min devulcanization time, it has the highest tensile strength and elongation at break. Interestingly, at 10 min devulcanization time, the tensile strength and the elongation at break is the same as with non-treated gtr which is 0 min devulcanization time.

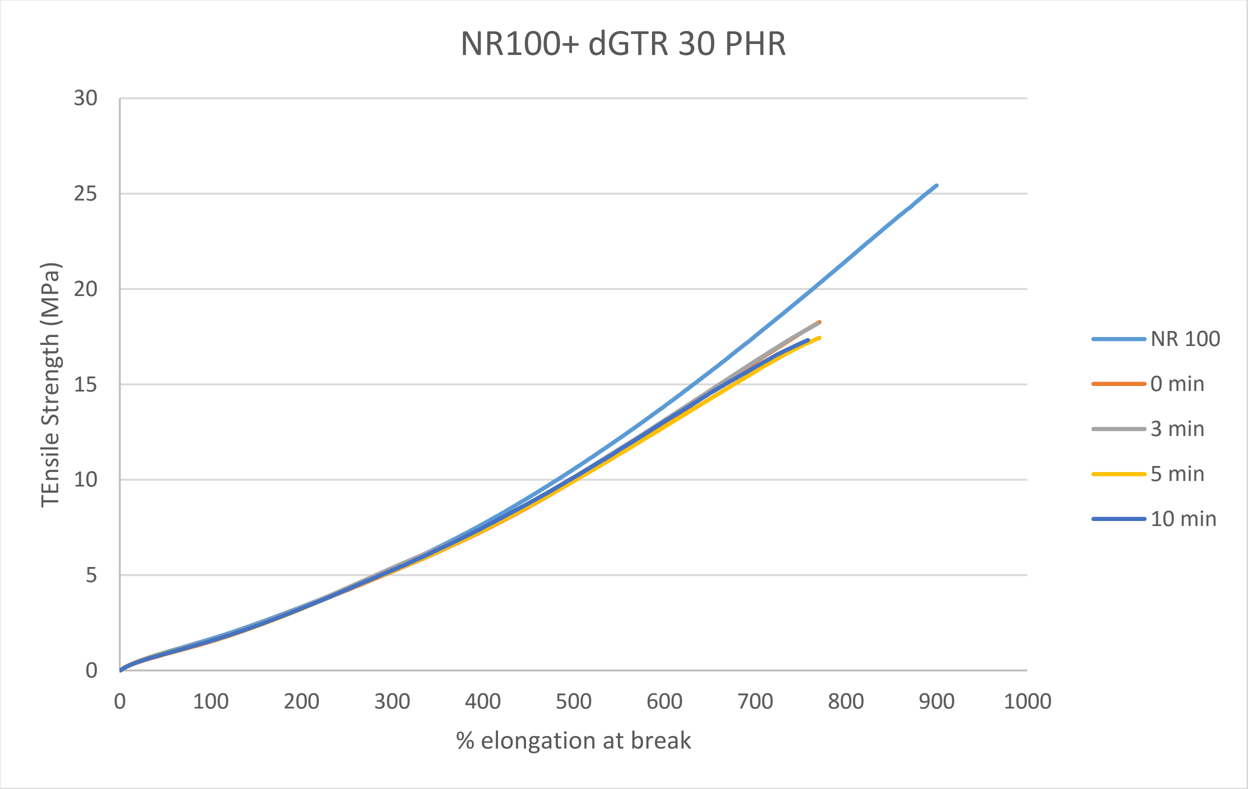

Figure 3.2.2

For the case of samples containing 30 phr of GTR in the figure above. The tensile strength decreased about 25 % for all the sample compared to reference sample. the elongation at break also decreased about 18 percent. We can see that the devulcanization time have no effect on this case as the tensile strength and elongation at break is almost the same for all the sample containing GTR regardless its devulcanization time.

Figure 3.2.3

Similarly, like 30 phr and 10 phr GTRc content in the sample, for 50 phr shown in figure also have decreased value of tensile strength compared to the reference sample. it about 38% less than the tensile strength in the reference sample. the elongation at break also decrease. It is about 18% less than the reference sample. in this case also the devulcanization time does not affect the tensile strength and the elongation at break as these values are almost the same.

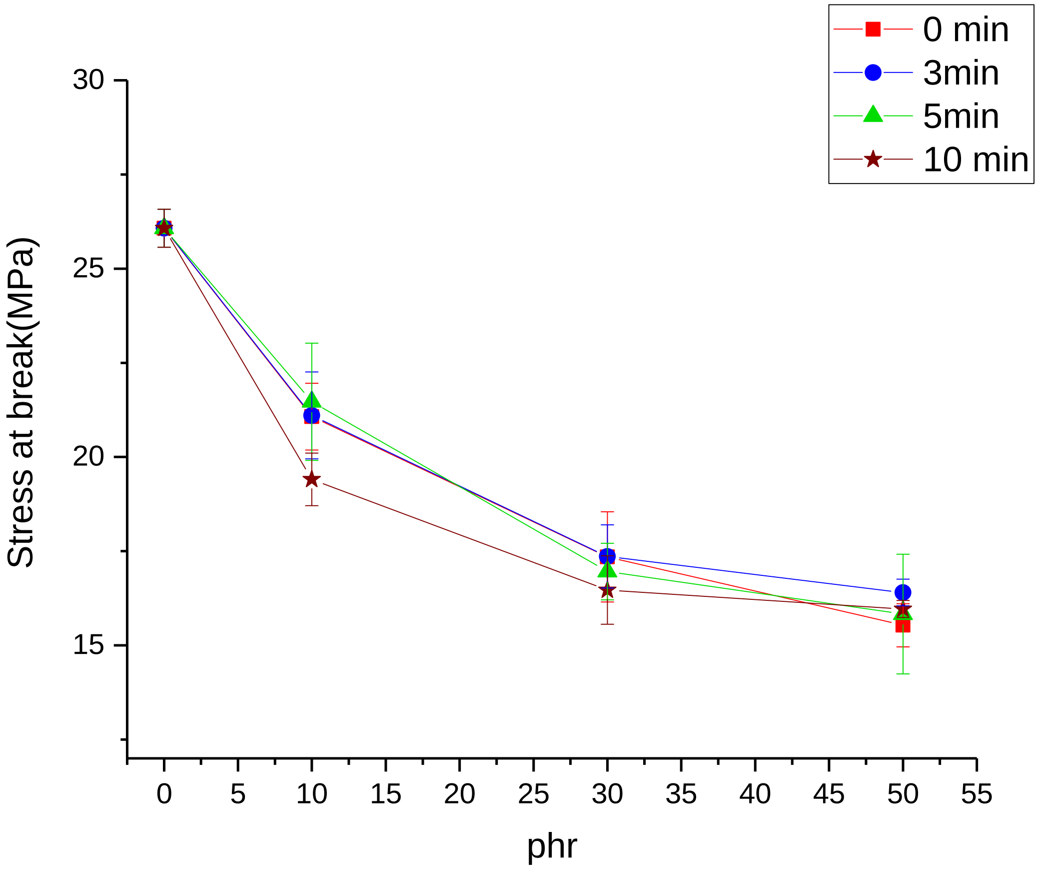

Figure 3.2.4.

Now, in the figure above shows stress at break (tensile strength) in function of different GTR content in the sample for each devulcanization time. The sample with 0 phr in the figure indicates the reference sample because it does not have any GTR. Generally, as the GTR content increase, the tensile strength of the material decreases. In terms of devulcanization time, it does not affect the tensile strength. the tensile strength almost the same with other sample with different devulcanization time.

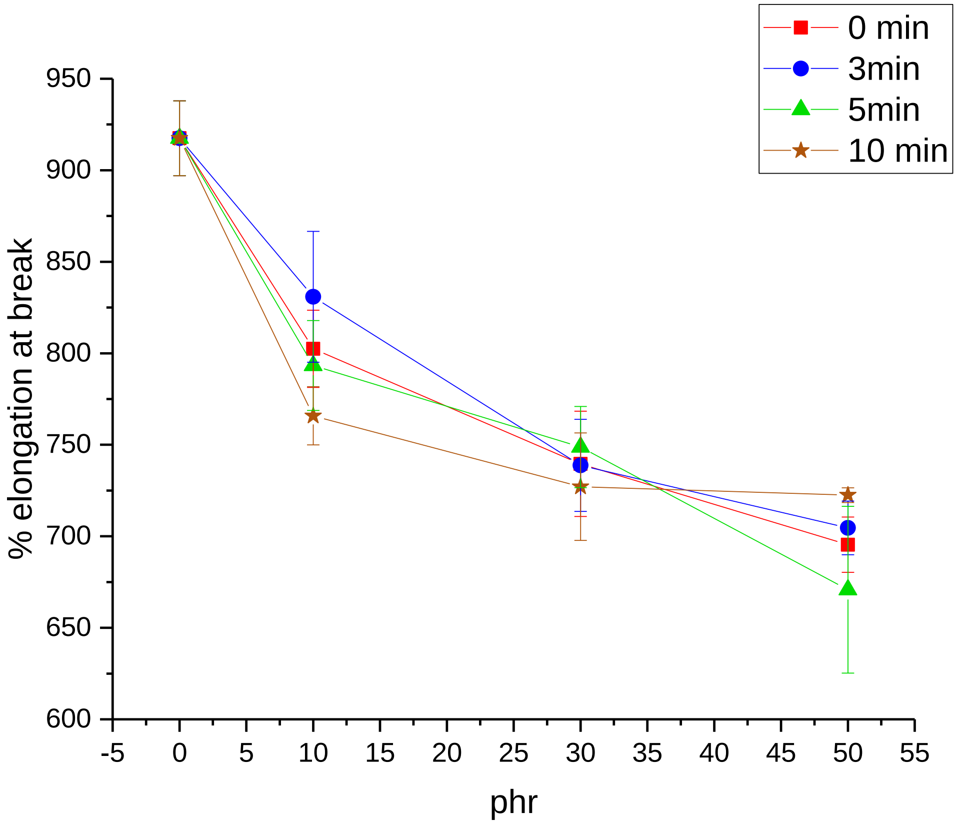

Figure 3.2.5.

The same case for % elongation at break in function of GTR content in the sample. Compared to reference sample the elongation at break is lower for sample with GTR. The elongation at break decreases as the GTR content increases. The same case like with tensile strength, the elongation at break for the samples with the same GTR content but different devulcanization time is almost the same with each other.

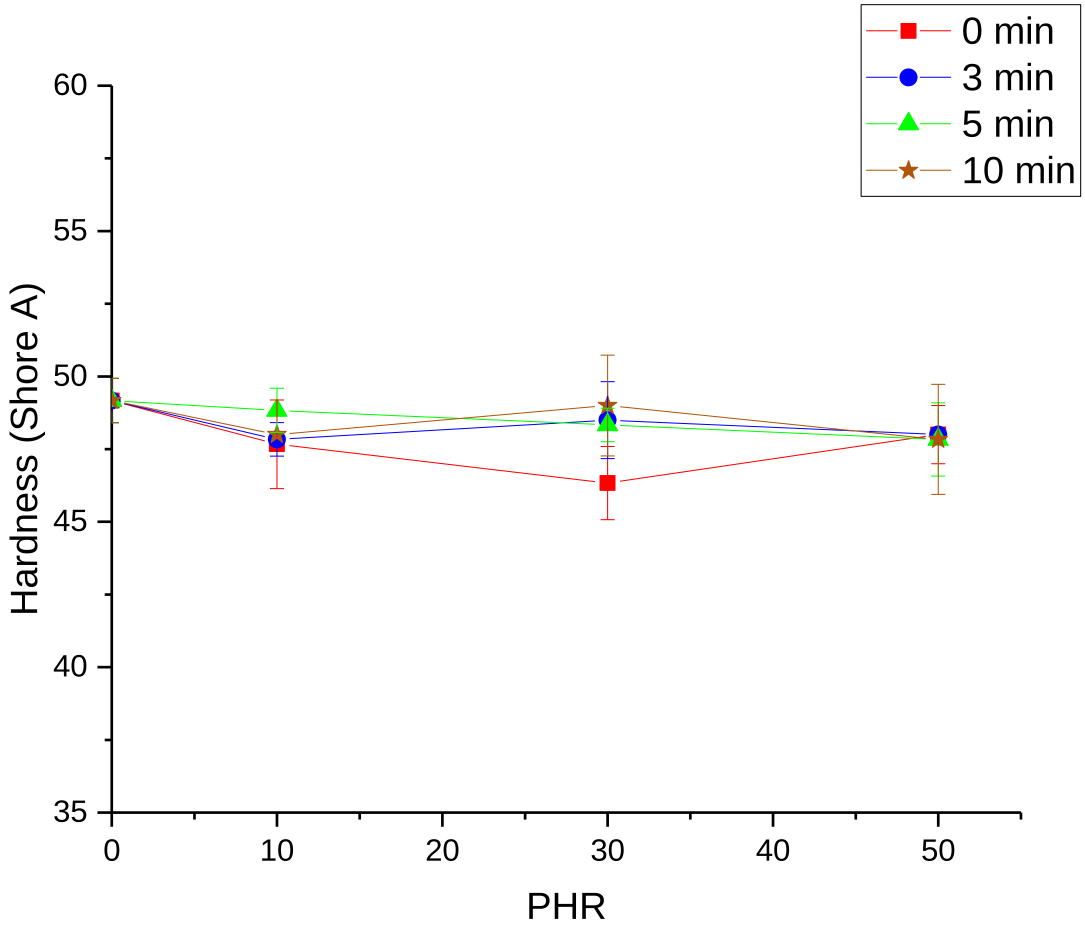

Figure 3.2.6

Figure above shows result of hardness of material in function of GTR content in the sample (Phr). It shows that the hardness is almost the same for all sample. the devulcanization time of GTR and GTR content in the sample have no effect on the hardness.

For young modulus, at 100% elongation it was observed that the young modulus does not change very much for all the samples but for sample that GTR 10 with 3 minutes' vulcanization time have the lowest young modulus at 100%. For young modulus at 300%, in sample with GTR without microwave treatment, the young modulus decrease as the GTR content increases. This is the same trend for sample with GTR treated with microwave for 3 minutes. But it is different for sample with GTR treated in microwaves for 5 and 10 minutes. The young modulus seems to decrease from 10 to 30 phr of GTR and the modulus increase back from 30 phr to 50 phr. Also, the young modulus for sample with GTR content of 10 phr devulcanized for 5 minutes have the highest value which is about 0.05 MPa more than the reference sample.

The result of mechanical test, the reduced mechanical properties of sample with GTR like tensile strength and elongation at break most probably caused by the amount of the GTR content inside the sample. the GTR inside the sample exhibit the continuity of the matrix which is natural rubber. The more GTR content less continuity of the matrix. As a result, the tensile strength and the elongation at break decreases as the GTR content increases. Another reason is also because the compatibility of GTR and the matrix. The weak interaction of GTR with the matrix will reduce the mechanical properties. The devulcanization time of GTR have less effect on the tensile strength and elongation at break as the result mostly depend on the GTR content and the values is almost the same for all devulcanization time.

3.3. Swelling degree

In swelling degree, it shows the consequence of interaction between a solvent and a matrix. When a cross-linked polymer was kept in a good solvent, it will swell rather than dissolve. The dimension of the sample will change in the solvent. Therefore, theoretically the swelling degree can tell how good or bad the crosslink in the polymer. A highly cross-linked polymer shows less Swelling degree.

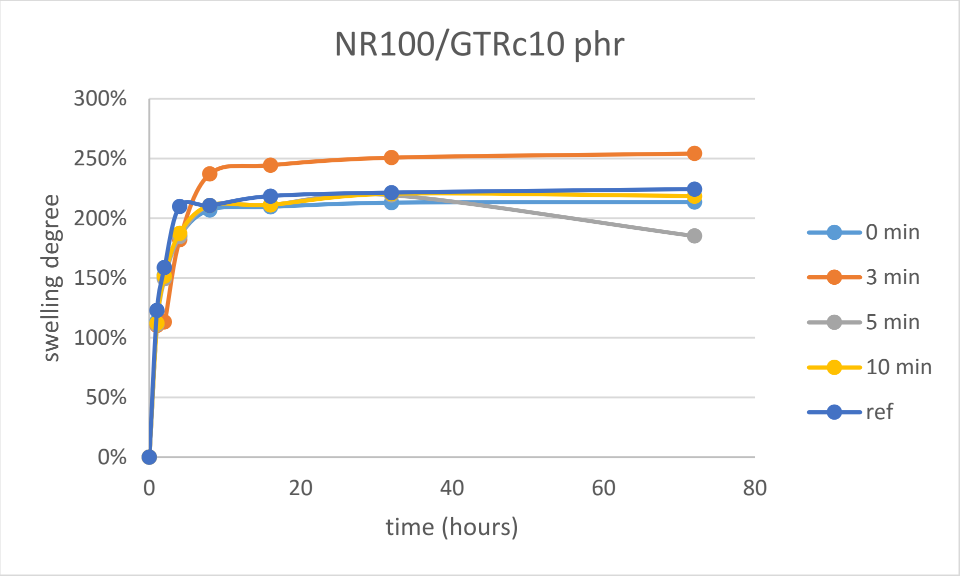

Figure 3.3.1

From the graph in figure above, shows the swelling degree for sample containing 10 phr of GTRc with different devulcanization time in function of time in hours. Generally, the swelling degree increases as the time increases and the value will remain almost constant at certain time. For samples containing 10 phr of GTRc, the swelling degree increase fast in first 8 hours and after that the values stabilize for next 64 hours. For the sample with GTRc with 3 minutes devulcanization, the swelling degree is higher than other sample. it is about 30 % more. This is probably due to less cross-link in the sample. for the sample containing GTRc with 5 min devulcanization time, at 72 hours the data is an anomaly. The value supposed to be near or a little bit higher than the value at 32 hours.

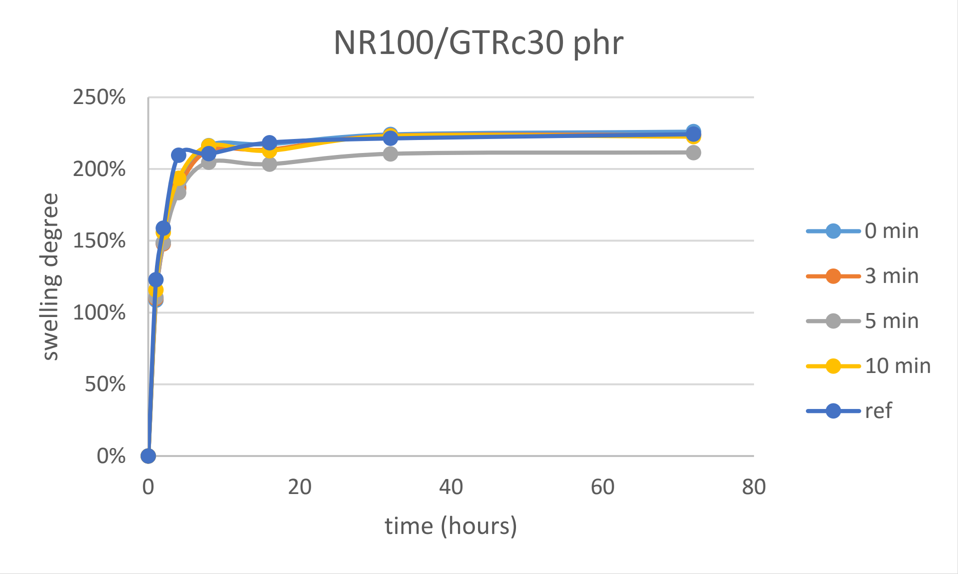

Figure 3.3.2

For sample with 30 Phr of GTRc almost all sample have the same swelling degree. Except the sample that contains devulcanized GTRc for 5 minutes. It has lower swelling degree which is about 5% lower than other sample. other sample have almost the same swelling degree as the reference sample.

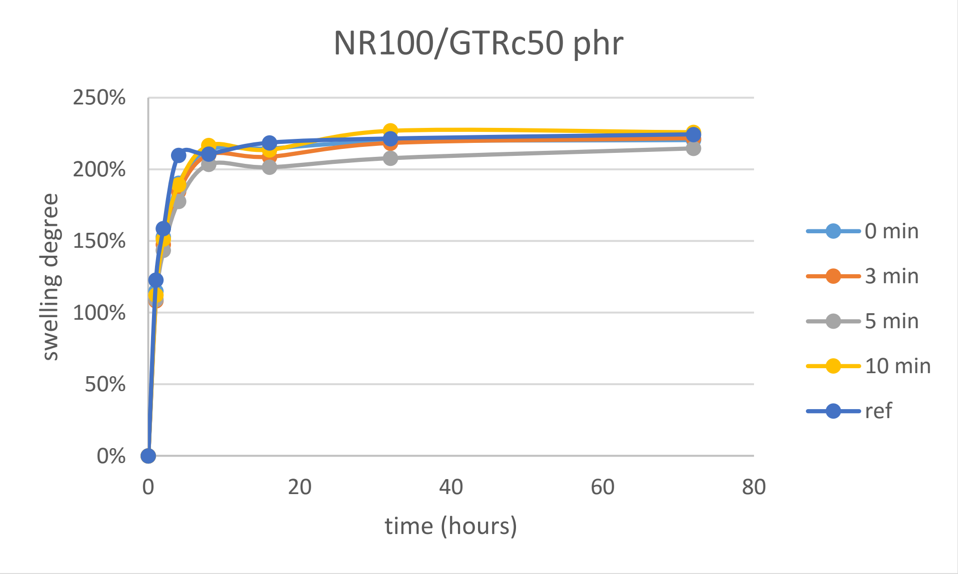

Figure 3.3.3

Like 30 phr and 10 phr of GTRc, the swelling degree for all sample with 50 phr of GTRc have almost the same value. Their swelling degree value does not deviate much with swelling degree value for the reference sample. but, for sample containing devulcanize GTRc for 5 min has a little bit lower value.

From this result we can see that the swelling degree does not change much between sample containing GTRc and the reference sample. Almost all sample have the same swelling degree except sample with 10 phr of GTRc devulcanize for 3 min, it has higher swelling degree. For sample containing GTRc devulcanized for 5 min the swelling degree appears to be smaller and it increases as the GTR content increases. The swelling degree for reference sample appears to increase faster than other sample containing GTRc for the first 4 hours. From the result, except samples with 10 phr of GTRc devulcanized for 3 min and other samples that contain GTRc devulcanized for 5 min, we can see that the devulcanization time and the GTR content in the sample does not affect the swelling degree.

3.4. Sol Fraction

Figure 3.4.1.

The fraction of soluble matter (sol content) can indicate the efficiency of vulcanization process. In general, the lower sol fractions the more efficient the vulcanization. In can be observed that the GTRc content affect the sol content. For sample with GTRc and DGTRc for 5 min, the sol fraction appears to decrease from 10 phr to 30 phr and increase a little bit from 30 phr to 50 phr. For GTRc devulcanized for 10 min, at 30 phr, it has the highest value of sol content. For samples with GTRc devulcanized for 3 minutes, it can be observed that the steady increase of sol content as the GTRc content increase. In general, it can be observed that the amount of GTRc content affect the sol content as we compare it with the reference sample. In reference sample, it has the lowest value of sol content.

3.5. Crosslink Density

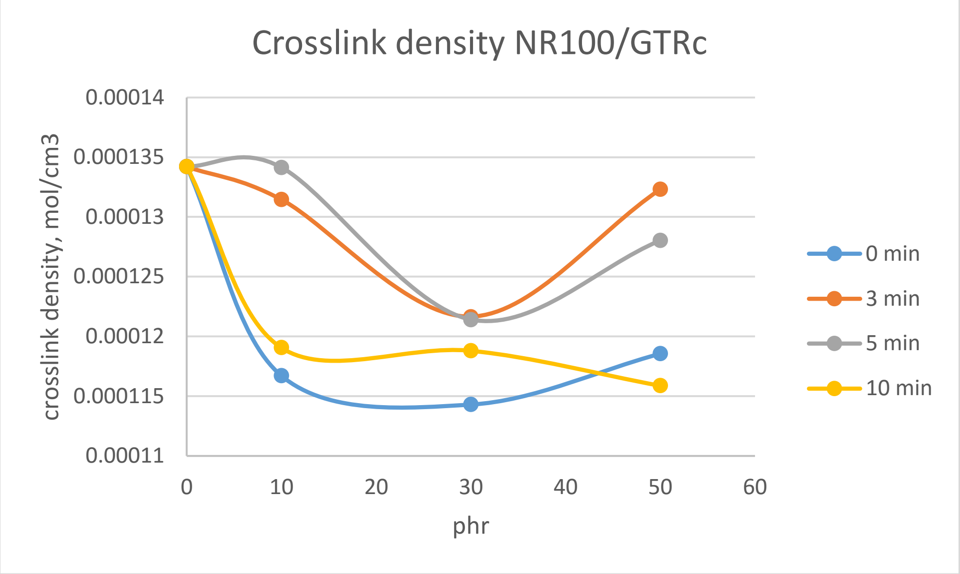

Figure 3.5.1

The cross-link density of samples with GTRc appears to be lower than the reference sample except sample with 10 phr of GTRc devulcanized for 5 minutes. It appears that this sample have the same cross-link density as the reference sample. It was observed that the cross-link density decrease from 10 phr to 30 phr. However, this value increase from 30 phr to 50 phr except sample with GTRc devulcanized for 10 minutes. It appears that from 30 phr to 50 phr, the crosslink density decreases. from this result, the cross-link density decrease as the amount of GTRc increases, this probably due to the GTRc particles in the restrict the formation of sulfur crosslink in the matrix. However, at a certain composition of the GTRc in the sample, in this case composition higher than 30 phr, the crosslink increase again. This probably due to revulcanization of the DGTRc. There is no observable pattern to relate the devulcanization time of GTRc with the cross-link density. If it was considered that the result GTRc devulcanized for 10 minutes at 50 phr as an anomaly, the cross-link density for non-devulcanized GTRc is lower than sample with GTRc treated with microwave. It was observed that microwave treatment has an effect on the crosslink density because it appears that microwave treatment have increase the crosslink density.

3.6. Thermogravimetric Analysis

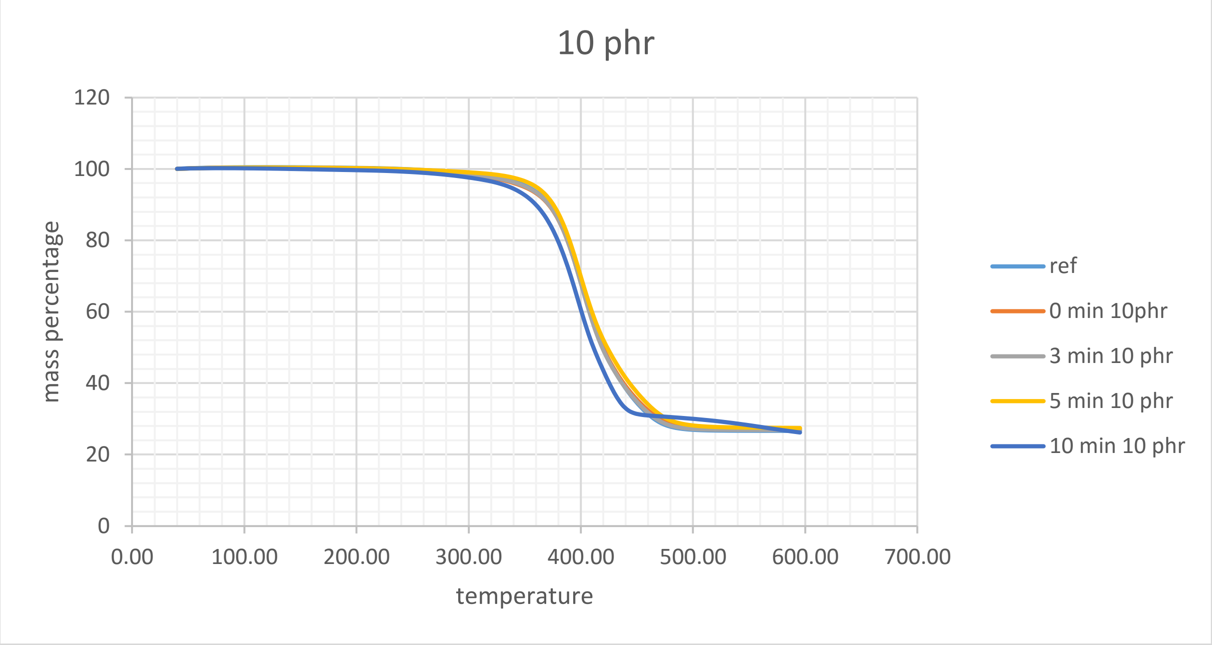

Figure 3.6.1

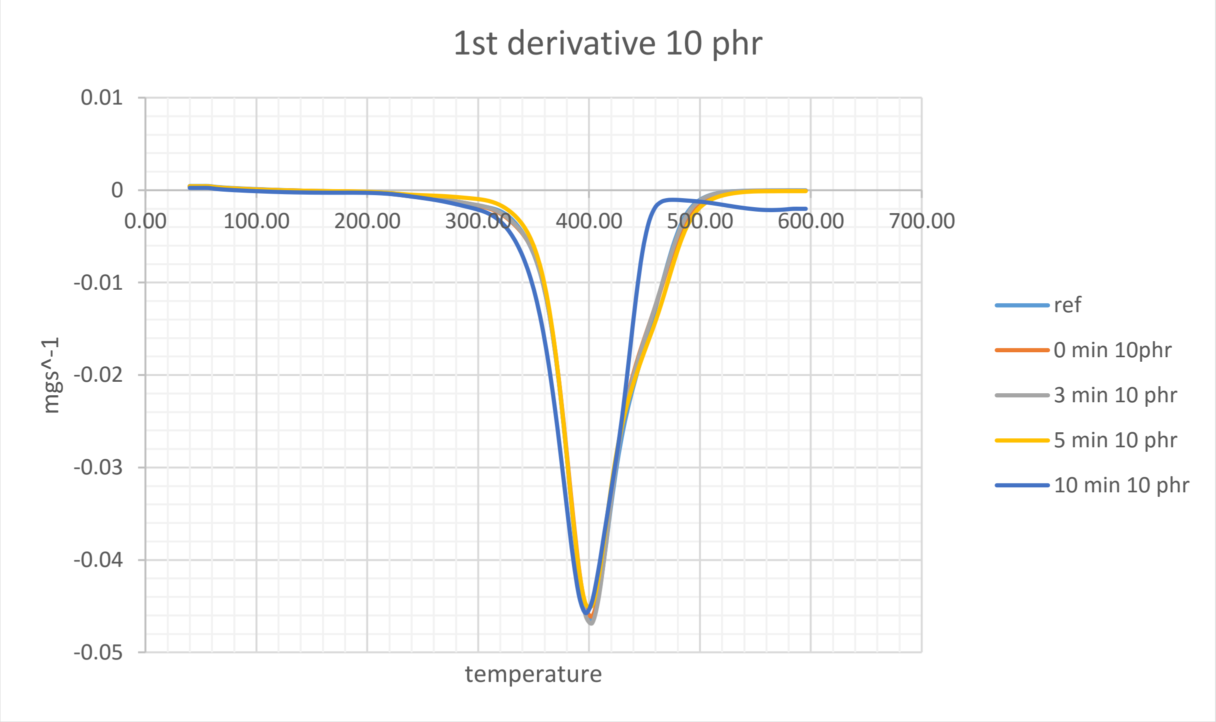

Figure 3.6.2

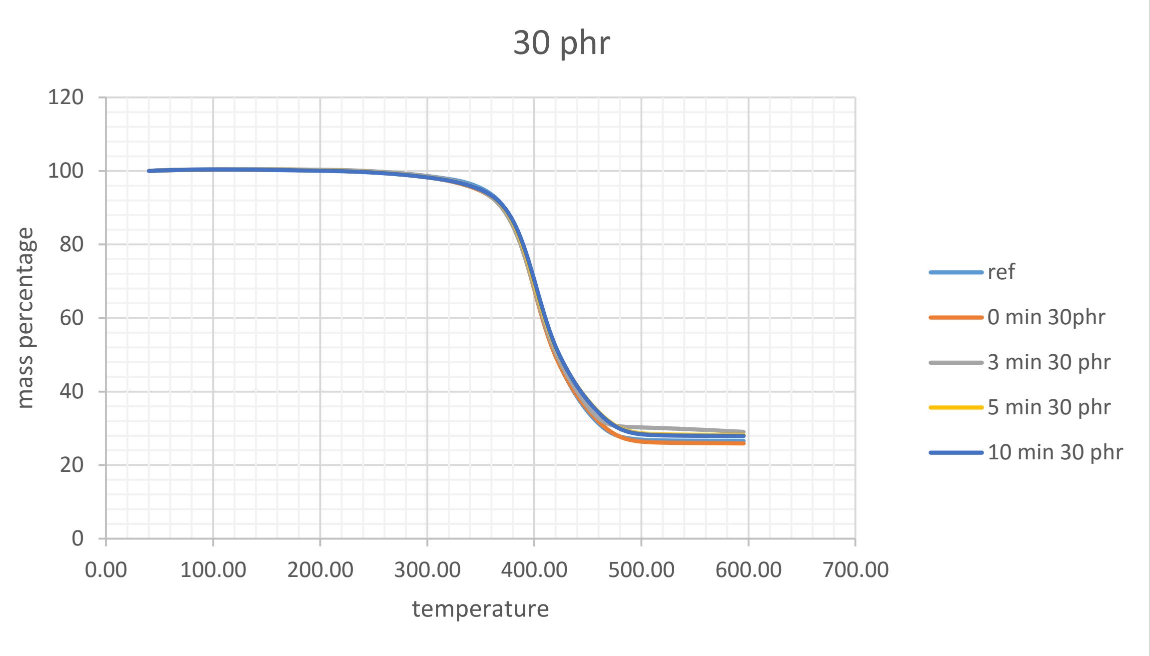

Figure 3.6.3

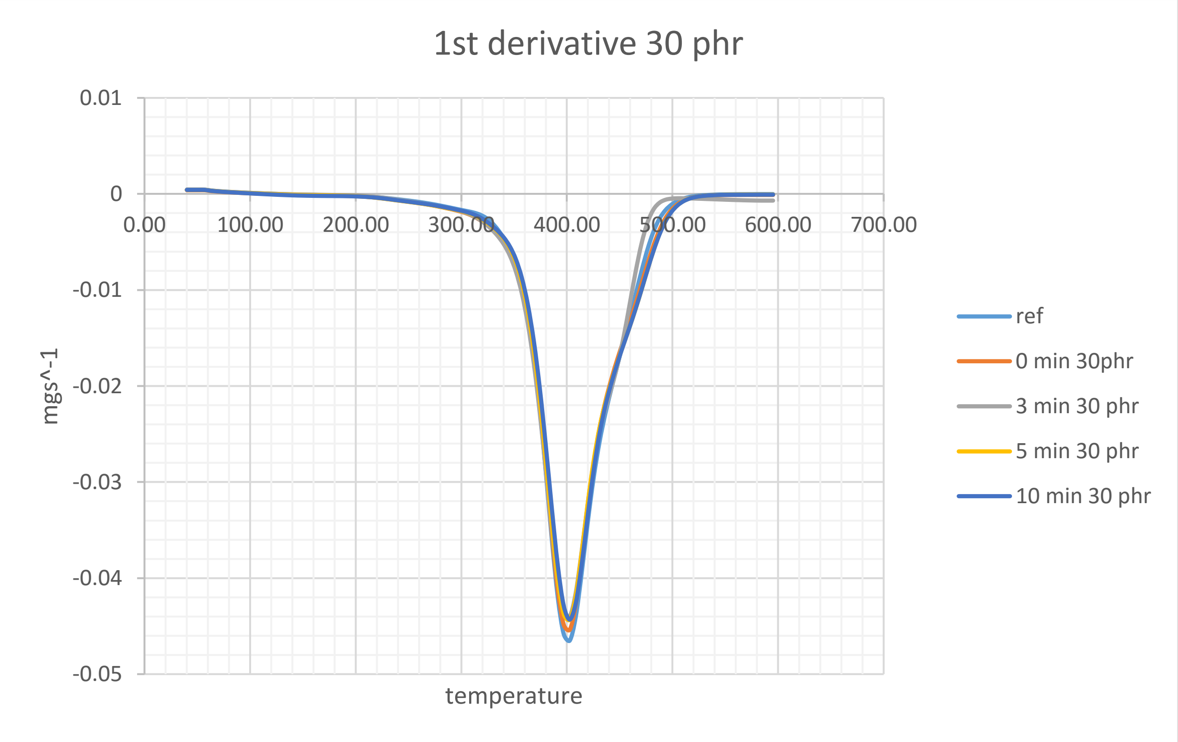

Figure 3.6.4

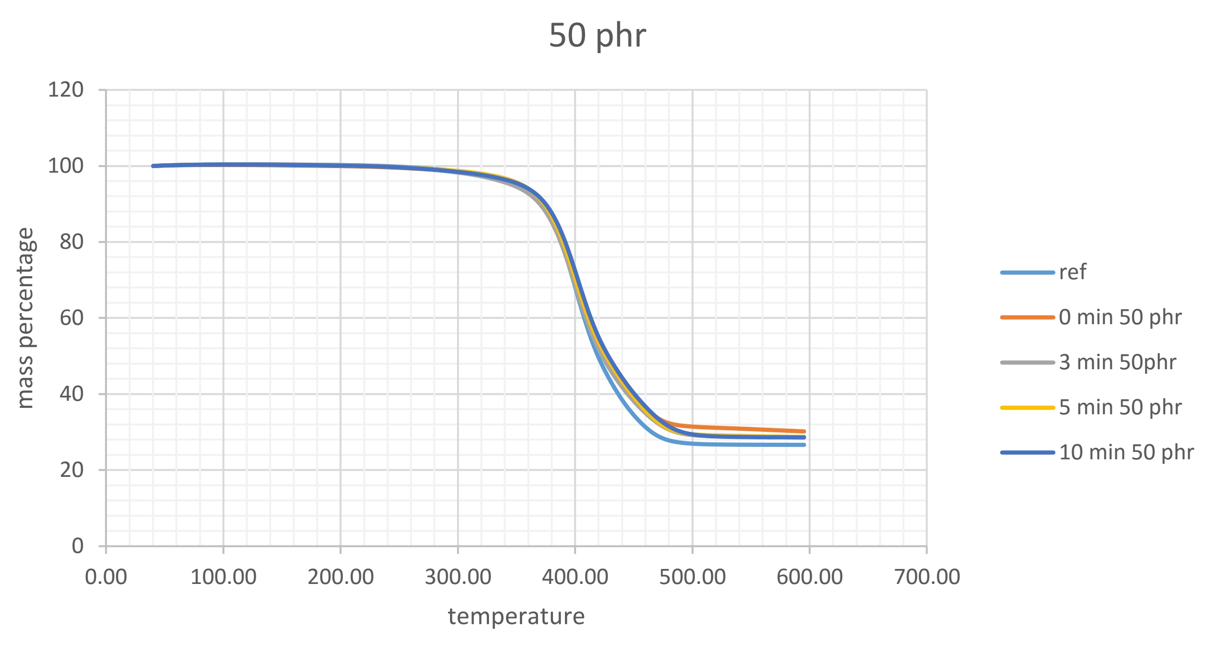

Figure 3.6.5

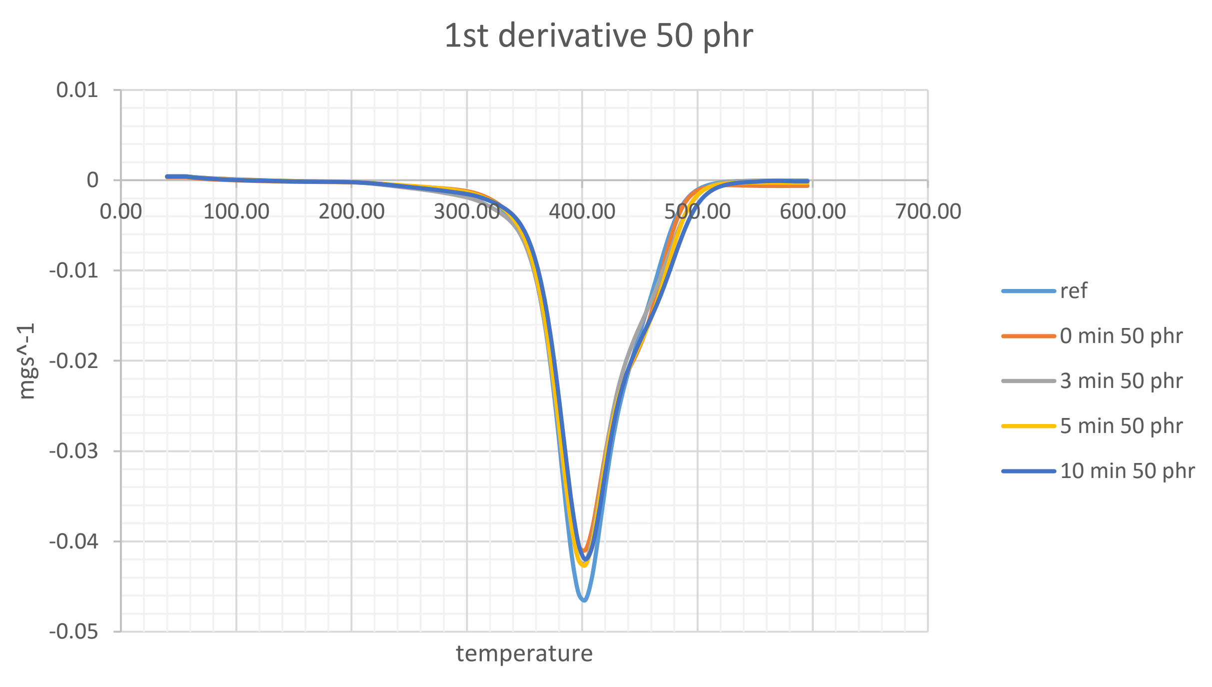

Figure 3.6.6

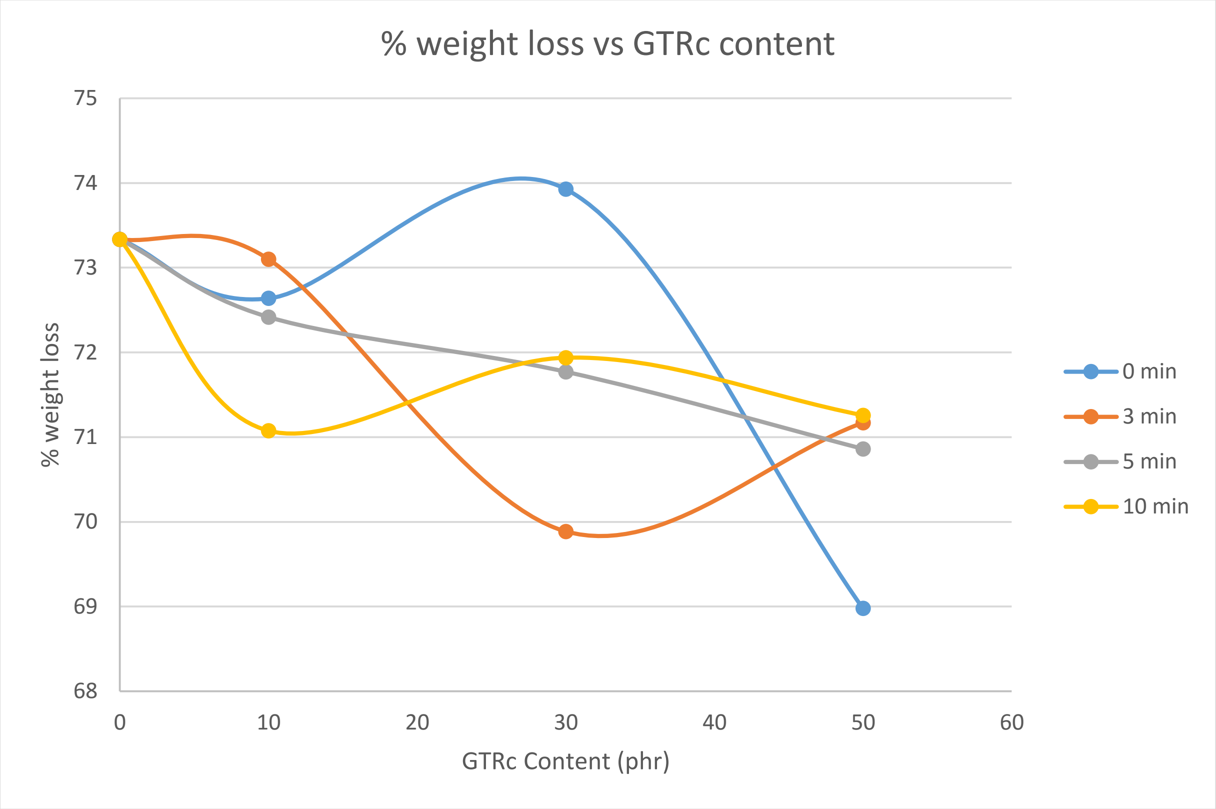

Figure 3.6.7

From thermogravimetric analysis results, all samples including the reference sample has peak when the temperature is at 402.7 °C. This peak correspond to degradation of Natural Rubber. This peak always appears for other sample. Therefore, the thermal stability remains the same as the GTRc content in the sample and the devulcanization time increases. Also, all samples show initial weight loss between 200°C – 340°C. This probably due to the volatilization of low boiling component in the sample. If we compare with samples with the same GTRc content with different devulcanization time, at 10 phr the weight loss is between 71.1%- 73.1%. For 30 phr, the weight loss is between 69.9%- 73.9%, and for 50 phr, the weight loss is between 69.0%-71.3%. Even though there is no observable trend in weight loss for samples with 0 min, 3min and 10 min devulcanization, for 5 min devulcanization, it was observed that as the GTRc content increase the percentage of weight loss decreases. It was also observed that in the derivate graph, as the GTR content increases the peak decreases. Samples with 10 phr, the peak at which degradation of natural rubber occur is almost the same with the reference sample. as the composition of GTRc increases, the peak decreases respect to the reference sample. This shows that the rate of the degradation decreases as amount of natural rubber matrix in the sample are smaller.

3.7. Scanning Electron Microscope (SEM)

The sample from tensile test were used in this observation.

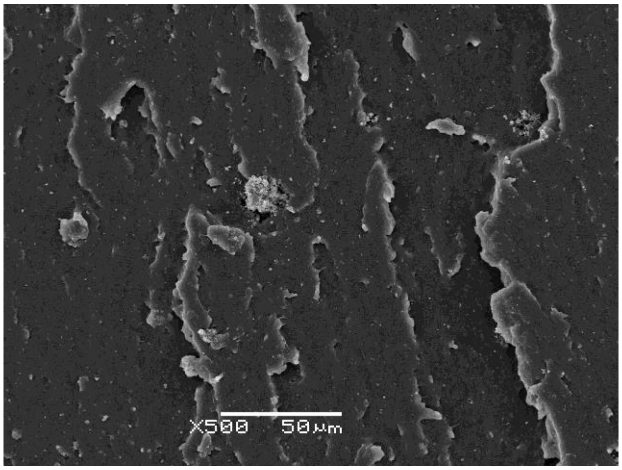

Figure 3.7.1: SEM of reference sample (NR100)

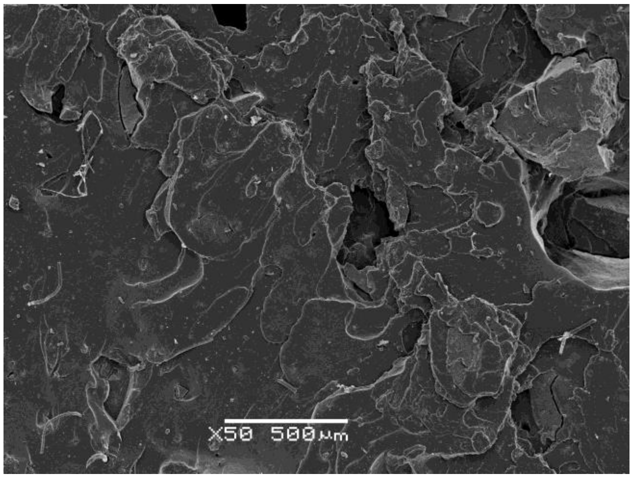

Figure 3.7.2: SEM of sample NR100+GTRc 10 phr, 10 min devulcanization

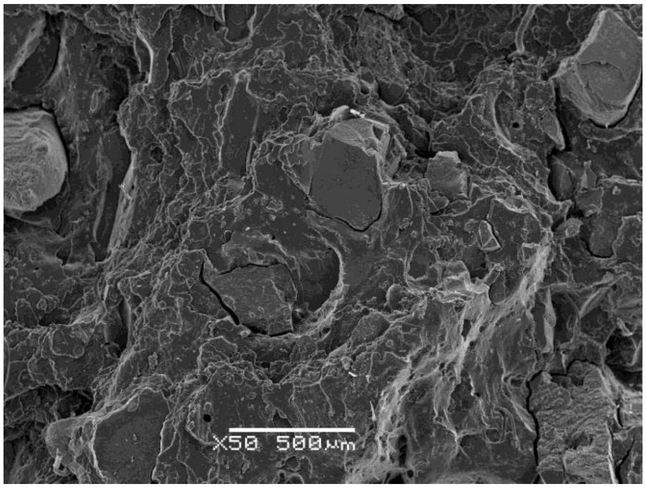

Figure 3.7.3: SEM of sample NR100+GTRc 30 phr, 10 min devulcanization

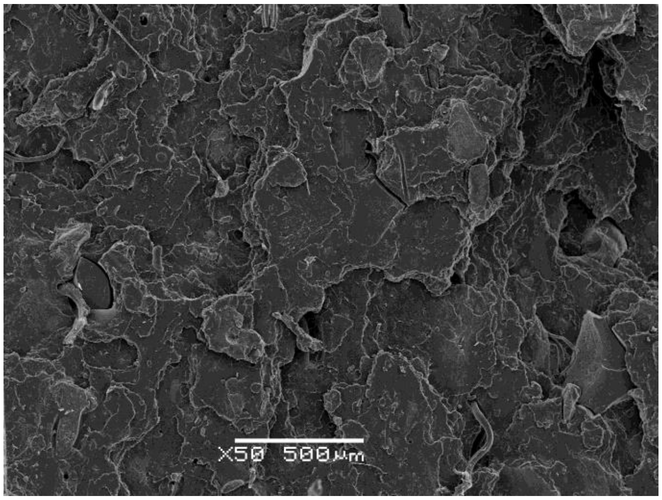

Figure 3.7.4: SEM of sample NR100+GTRc 50 phr, 10 min devulcanization

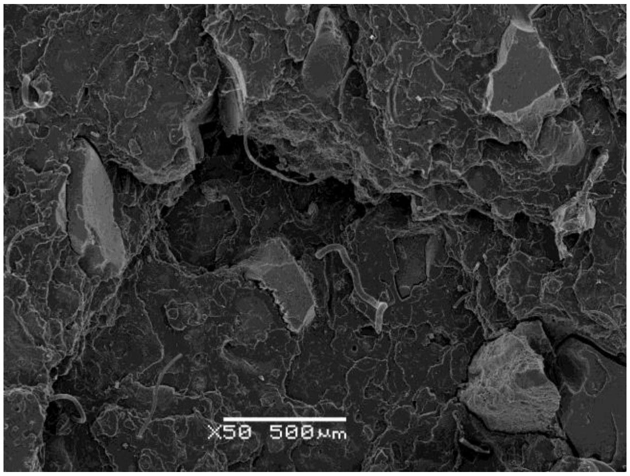

Figure 3.7.5: SEM of sample NR100+GTRc 50 phr, 3 min devulcanization

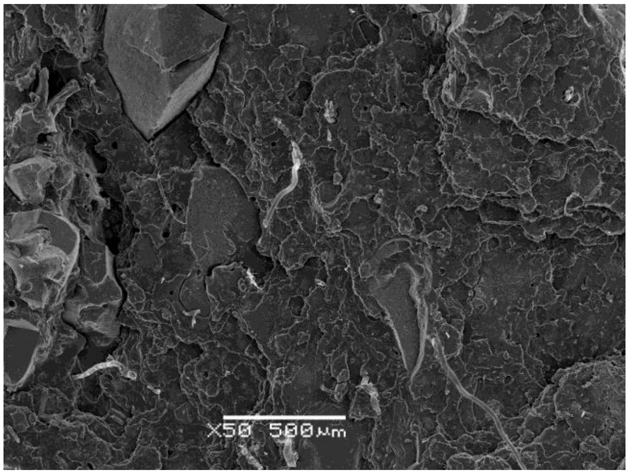

Figure 3.7.6: SEM of sample NR100+GTRc 50 phr, 5 min devulcanization

There is clear evidence to show the differences between the reference sample and sample filled with GTR/dGTR. The reference same shows quite flat surface with no void. Samples with GTRc shows some roughness on the surface. There are also some voids in them. This probably cause from the GTR particles that have been ripped out. By comparing sample filled with DGTR but at different vulcanization time. We can see small differences between them. In sample filled with dGTR 50 phr devulcanized for 10 minutes, we can see there is less void compared to 3 minutes and 5 minutes. Therefore, we can say that the devulcanization time has an effect on the adhesion between dGTR with the matrix.

4. CONCLUSIONS

The conclusions that we obtained from this study are, first of all about the mechanical test. The GTRc content affect the tensile strength and elongation at break. As the GTRc content increases the tensile strength and elongation at break decreases. This probably cause by the GTR particles reduces the continuity of the matrix which is natural rubber. This can be seen from the pure sample containing only natural rubber without GTR, it has the highest value for tensile strength and elongation at break compared to other sample containing GTR/dGTR.

Then, we can also see that the devulcanization time does not affect the tensile strength and elongation at break. Samples containing same GTR content have almost the same value of tensile strength and elongation at break. However, in case of sample containing 10 phr of GTRc devulcanized for 3 minutes have higher value of tensile strength and elongation at break compared to other sample with the same amount of GTR/dGTR.

For swelling degree, we can say that the values are the same for all sample including reference sample. However, sample containing 10 phr GTRc devulcanized for 3 minutes has slightly higher swelling degree.

Then, the crosslink density. It appears that the sample containing devulcanized rubber have higher crosslink density compared to sample containing GTRc without microwave treatment. So, the devulcanization increases the crosslink density.

In thermogravimetric analysis, for sample containing GTRc devulcanized for 5 minutes has a trend that as the GTRc content increases the weight loss decreases. we can conclude that this probably depends on the amount of natural rubber inside the sample.

Lastly, we can see from the electron microscope that the surface of samples containing GTRc devulcanized for 10 minutes have smoother surface compared to other devulcanization time. This is probably the interaction between the matrix and the GTRc is better.

5. BIBLIOGRAPHY

[1] Wikipedia, "Natural Rubber," [Online]. Available: https://en.wikipedia.org/wiki/Natural_rubber.

[2] S. H. Khudhair, "A Study of Some Rheologyical and Mechanical Properties for Natural Rubber Reinforced with Black Carbon from Apricot Stones by Ultrasonic Technique," 2013.

[3] "Managing End-of-Life Tires," 2008.

[4] R. Lieberei, "South American Leaf Blight of the Rubber Tree (Hevea spp.): New Steps in Plant Domestication using Physiological Features and Molecular Markers," 2007.

[5] A. &. R. Evans, "The Composition of a Tyre: Typical Components," 2006.

[6] J. T. H. Krzysztof Formela, "Curing characteristics, mechanical properties and morphology of butyl rubber filled with ground tire rubber (GTR)," *Iran Polym J ,* 2014.

[7] S. K. K. a. A. B. Yves Grohens, "Recycling And Reuse Of Materials And Their Products," 2013.

[8] e. a. M. Mouri, "New Continuous Recycling Technology For Vulcanized Rubbers".

[9] e. a. Guoliang Tao, "The Effect Of Devulcanization Level On Mechanical Properties Of Reclaimed Rubber By Thermal-Mechanical Shearing Devulcanization," 2012.

[10] M. C. a. J. T. H. Krzystof Formela, "Thermomechanical Reclaiming Of Ground Tire Rubber Via Extrusion At Low Temperature: Efficiency And Limits".

[11] "Evaluation Of Waste Tire Devulcanization Technologies," 2004.

[12] D. D. a. S. M. B. Adhikari, "Reclamation And Recycling Of Waste Rubber," vol. Progress In Polymer Science, 2000.

[13] M. a. Y. H. Okuda, "Method Of Desulfurizing Rubber By Ultrasonic Wave," 1987.

[14] A. I. I. a. S. Ghose, "Ultrasonic Devulcanization Of Used Tires And Waste Rubber," *Rubber Recycling,* 2005.

[15] W. C. Warner, "Chemical Methods Of Devulcanizing Thermoset Rubber," 1995.

[16] K. H. L. a. R. K. Ronald, "Devulcanization Of Cured Rubber," 1999.

[17] S. Z. Y. W. Yuanhu Li, "Microbial desulfurization of ground tire rubber by Thiobacillus ferrooxidans," *Polymer Degradation and Stability,* 2011.

[18] B. K. a. D. W. Tredinnick, "Industrial Microwave Technology," 2002.

[19] J. Moore, "EBSciences," [Online]. Available: http://www.ebsciences.com/papers/moore.htm.

[20] R. L. M. F. C. M. a. D. N. T. D. S. Novotny, "Microwave Devulcanization of Rubber," 1977.

[21] K. GJ, "swelling of filler-reinforced vulcanizates," *J Appl Polym Sci ,* 1963.

[22] H. A. B. B. E. Bilgili, "pulverization of rubber granulates using the solid state shear extrusion process: Part 11. Powder characterization," *PowderTechnology 115 ,* 2001.