Manufacture and characterization of composite materials obtained by reactivated GTR and elastomeric matrix (BR)

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Abstract

Incorporation of ground tyre rubber with the polymeric compounds is one of the initiative way in order to recycle and reduce the numbers of worn-out tires that rapidly increase nowadays all around the world and become one of the serious environmental problem that needs to be take into a serious consideration. Researches and environmental concern societies invented a lots of applications in order to make full use of these scrap tires. Because of excellent properties own by these tires, the process to decompose and transform them to another new product is one of the limitation and difficullty that needs to be overcome. In order to incorporate the crumb-formed ground tyre rubber (GTR) with matrix polymer, they need to undergo devulcanization process in order to attain a good interaction between GTR and polymer matrix other than to ease the process of making blends. So, by undergo this process, other than to break strong crosslinking bonds, they are able to incorporate much better with the virgin rubber matrix and attain a good interaction between these two main components. The interactions are improve also by the formation of sulphur crosslinkings during the revulcanization process involving GTR and the vulcanization process that involve virgin rubber. In this project, by using different devulcanization treatments that available and mostly being applied, we investigated the diffferent behaviours for each one of them including their mechanical properties, the stability of finished vulcanizates and also to observe the interaction that formed between the components of vulcanizates using scanning microscope.

Objectives

a. To study the effect of different devulcanization treatments of ground tyre rubber on the behaviour of butadiene rubber and ground tyre rubber vulcanizates.

b. Investigate the mechanical properties achieve by each vulcanizate from the different ground tire rubbers devulcanization process.

c. Determine the gel fraction of the vulcanizates which then can be relate with the crosslinking density that formed during vulcanization process.

d. Study and observe the structure and interaction between the particles and also the bonds resulted from the tensile test.

1. Introduction

Nowadays, tire industry has become one of the most crucial industries in the world. Huge demand on the tires cause the production of the them to increase day by day as we always find this kind of material whether on cars, trucks, motocycles, aircraft landing tires and even shopping carts. As we know, the number of the cars on the road raise up rapidly together with the world's populations on Earth trigger a huge number of tires to be produced in order to satisfy with this situation. The rapid growth of the automative industry also contribute to the high stacked production of the tires in any part in this world.

During the last decade, the disposal of used tires has become one of the major regulatory activity in Europe generally and Spain in particular. According to the European tyre and Rubber Manufacture Association (ETRMA), for European Union countries, about 3.4 million of total end-life tires were generated (1) while in Spain, according to the statistics almost 300,000 tonnes of scrap tires generated per year (2). Besides that, the number of used tires around the world reached about 800 millions units/year and this amount is expected to increase by 2% every year while according to the Siekiewicz et al. the production of tyres is approximately 1.4 billion units which means there will be 17 millions tonnes of discarded tyres anually (3). In accordance, the consumption of the rubber around the world either natural or synthetic rubber in 2010 was about 24.845 kt. From the total production of the rubber which is about 16-17 million tonnes per year, about 65% is use in the tire production (4) make it as the largest consumer for the existing rubber. Oregon Department of Environmental Quality stated that, Oregon generates about five million used tires, or 50,000 tons, every year and about 1.5 million of these tires were originated from the Portland area, United States (5). In addition, from the total 27 European Union members including Norway and Switzerland, 3273 kt postconsumer tyres were accumulated during 2010. Figure 1 show the ranking of countries according to the quantity of the used tyres that they generate.

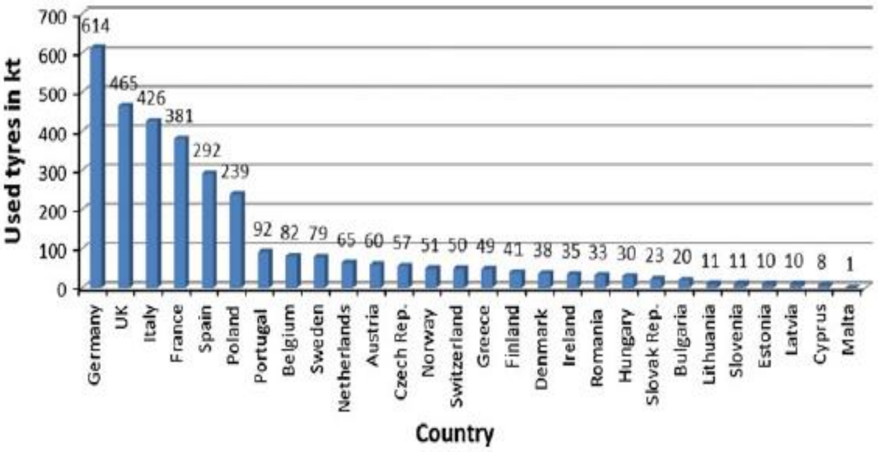


Fig. 1 The quantity of used tyres arisen in the EU countries completed with Norway and Switzerland in 2010 [5]

The advantages that the tires own induce many applications of them to be applied on our daily life. The main component of the tyres which is rubber (natural and synthetic) already have lots of abilities such as flexibility, toughness, impermeability, electrical resistor and etc. making them such a unique material by itself. In addition to the vulcanization or curing process which had been discovered by Charles Goodyear in 1839 (6) that used sulphur as a stabilising agent and any other additives in order to modify the property of the rubber as they cannot withstand high **temperature,** brought up lots of improvement to the rubber and they became a lot more resistants towards biodegradation, photochemical decompositons, reagents and as well as the ability to withstand high temperature (6) (7).

As being mentioned just now, tires are highly resistant towards biodegradation and that is why they cannot be decomposed easily by environmental means due to the strong formation of crosslinking bonds between the sulphur during their production process. As the numbers of tires around the world increases too much nowadays, various and proper waste disposals have been taken into actions in order to overcome this problem. Figure 2 shows the data from 2002 to 2011 for some of the tire decompositions (8) that commonly applied. The earliest method that used was land filling. (9)However, this method are not supported and being restricted to be applied nowadays as they bring lots of side effects and disadvantages rather than advantages for the disposal of those scrap tires. One of the significant effect is that they are prone to cause fire and once it occur, it is hardly to be extinguished. The releasing of pyrolitic oil to the soil result from the fire , caused the soil to aggravate which then bring up to the groundwater contamination (10). Besides, those burning of tires cause the releasing of thick smoke plumes to the air and hazourdous gases as well as the unburned hydrocarbons (10) that can cause serious respiratory problems to the humankind. Other than that, these stockpiles tyres provide a breeding sites for the insects and rodents and also trapped water which provide an ideal environment for the breeding of mosquitoes larvaes. Due to all these problems, the impilification of regulation by European Union in 1999 named as Directive on Landfill of the waste 1000/31/EC prohibited the stockpilling of whole tires starting from July 2003 and for the ground tires starting from July 2006 (11).

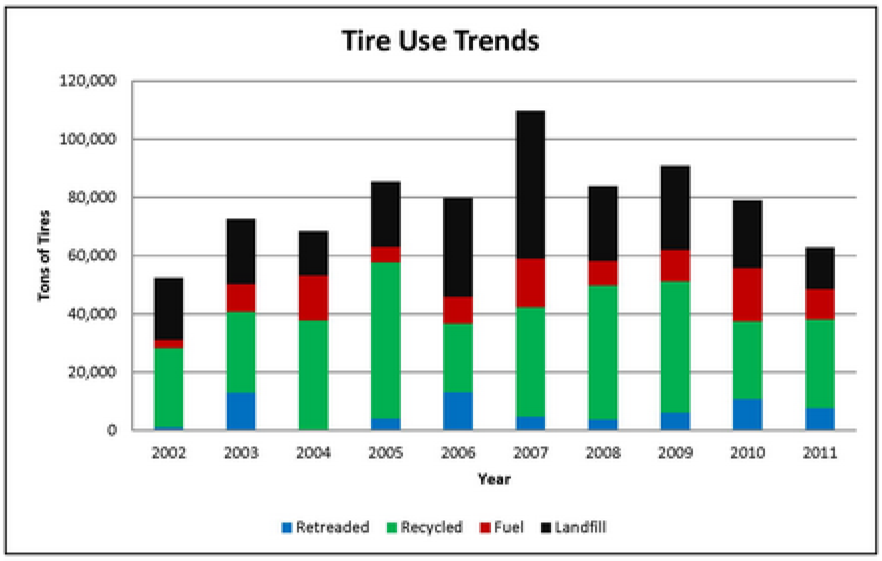


Figure 2 : Recycling of tires from 2002-2011

It has been recognized that the old tires represent as a resource (rubber, oil, steel, etc.) rather than being consider as a waste. Because of this, the reutilizations of the scrap tyres are vital. We can classify those scrap tires into two groups which are worn out tyres and end of life tires. Worn out tires normally can be reused and retreaded again as they are still fit to be used on the road while end of life tyres are the tires that are totally cannot be reuse anymore. Reusable tires are the tires that can be used again as there are some of tire treads remained which make the tyres to be able to reuse again on the road. Meanwhile, the retreaded tyres are the tyres that already worn out and new treads are bonded to the tire casing using a process similar to that of manufacturing for a new tires (12). A retreaded tire needs only seven gallons of oil, compared to 22 gallons of oil that are needed to make a new tire. The use of retreaded tires also prevents waste by diverting scrap tires from being stockpiled or disposed off in landfills (12). Moreover retreaded tires will cost 30 to 50 percent less than their traditional counterparts. As long as the tire casing is in good condition, it can be reused again and again, saving money by eliminating the need for disposal process and the performance are similar to the new tyres. But because of the cheap new tires that are imported from Far East and Eastern Europe make a competitive price as well as safety consideration by the consumers reduced the demand of these retreaded tires. The waste tires utilization flow can be seen from figure 3.

The other ways in making use of the end of life tires are by recycling, recovery of energy and pyrolysis. The recycling of tires can be done for the whole tires and also for the shredded one. Scrap whole tires have been used as a fishing reefs, oyster bed and also as floatation breakwater (13) while the crumb rubber form are normally used for the production of mats, ground cover under playground equipment, running track material also in the rubberized asphalt for paving industries and rubberized concrete which have many advantages in addition to the shredded rubbers rather than conventional cement-concrete structures (13). The energy recovery using tires are used due to the energy content of the about 27- 39 MJ/kg and this amount of energy is higher than the bituminous coal and it more than twice the heating value given by the solid wastes and chipped wood waste (10). The energy generated is mainly used in the cement kilns which act as fuel (14) and it has lower emission of combustion than coal burning. Apart from this, they also use as a fuel in steam production also generate electrical energy to the pulp and paper mills and steel industry (15) (10).The recovery options available in 1998 for most of the EU members are shown in Table 1 for just an indicative view.

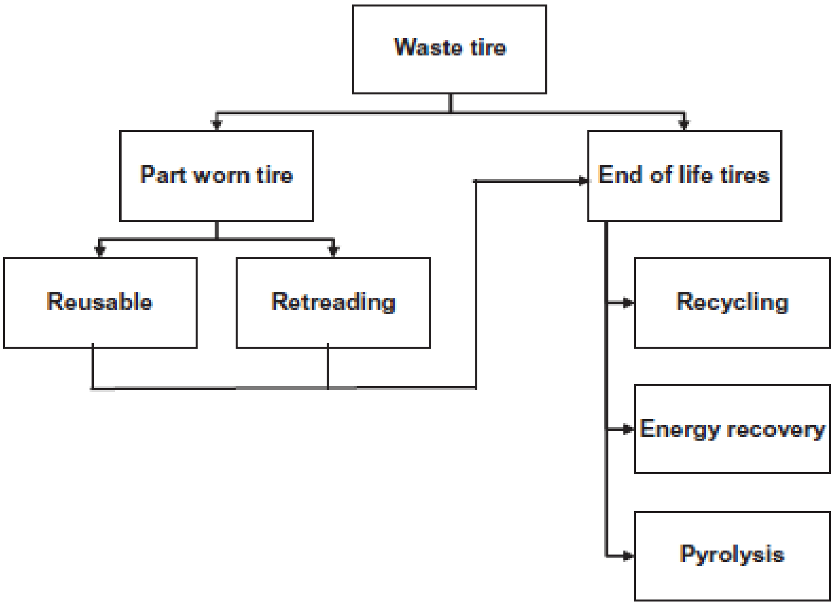


Fig. 3. Flow of waste tire utilization.

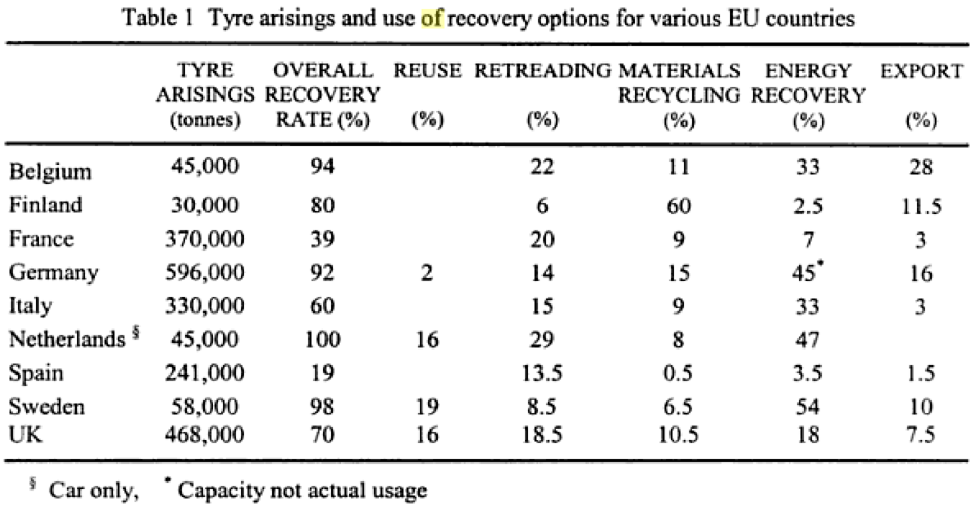


Table 1 Tyre arisings and use of recovery options for various EU countries

	TYRE ARISINGS (tonnes)	OVERALL RECOVERY RATE (%)	REUSE (%)	RETREADING (%)	MATERIALS RECYCLING (%)	ENERGY RECOVERY (%)	EXPORT (%)
Belgium	45,000	94		22	11	33	28
Finland	30,000	80		6	60	2.5	11.5
France	370,000	39		20	9	7	3
Germany	596,000	92	2	14	15	45*	16
Italy	330,000	60		15	9	33	3
Netherlands §	45,000	100	16	29	8	47	
Spain	241,000	19		13.5	0.5	3.5	1.5
Sweden	58,000	98	19	8.5	6.5	54	10
UK	468,000	70	16	18.5	10.5	18	7.5

§ Car only, * Capacity not actual usage

The other recycling way that we may applied is the incorporation of waste tires which act as feedstocks or fillers with the polymeric blends such as termoplastics composition, thermoset and rubbers compounds. Basically, combining these two compounds together improve the properties of the materials as those scrap tyres which are basically remained with some useful chemicals or components can be used up. This also may help reduced the consumption of petroleum where the synthetic rubber are originated as well as cut down the amount of virgin polymers used and reduced rubber product cost. In order to convert the whole tires into ground rubber tire (GTR), there are four few steps that need to be done which are shredding also known as downsizing process, separation (i.e steel, textile, etc), granulation and classification (16). The obtention of GTR in downsizing part can be done whether by mechanical grinding at ambient temperature, at ambient temperature under wet condition, at high temperature and at cryogenic temperature (17) (16). According to J.Karger et al. (16), cooling the rubber compound below its glass transition temperature helps in reducing the energy that needs during grinding process. Here also stated that the advantages of grinding at ambient temperature is that the surface area of the GTR obtained are double than the cryogenic one at equal size as greater surface area means a good adherence of GTR to a given matrix polymer. Thus, the GTR particles size and particles distribution effect much the properties (18) (16) (19) of the finished rubber product that they formed with polymeric compounds which can be see from Figure 4.

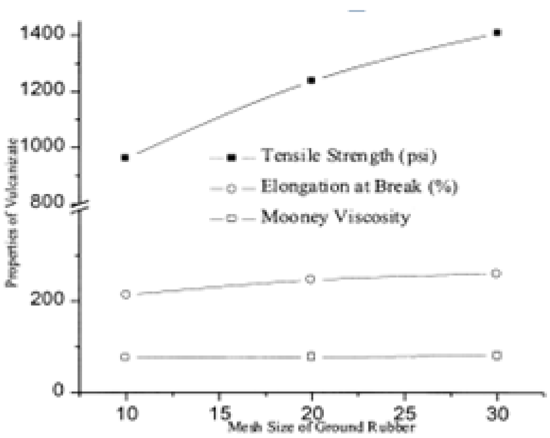


Figure 4 : The effect of mesh size on the mechanical properties

In accordance to a good incorporation of the GTR with the polymeric compounds known as upcycling process to be successful and efficient, the GTR obtained from the shredding process need to be modified due to the poor interaction between the GTR and matrix polymer (17). Blends that contained GTR typically has lower mechanical properties due to the insufficient bonding between

GTR and rubber matrix as the presence of crosslinking bond structure of GTR hinder the entanglement of GTR with rubber matrix. So, the increase in physical and/or physical interfacial interaction in the heterogenous blend are made possible by the surface modifications or the addition of compatibilizers (1). So, one example for this is by partial devulcanization of the GTR which can be considered in this case. General scheme of compatibilizatin between polymer and GTR phase is illustrated like in the Figure 5.

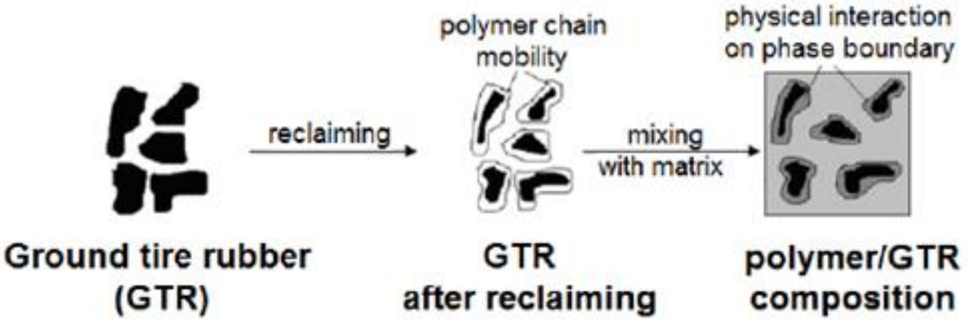


Figure 5 : Schematic view of polymeric compound and GTR

This modification also termed as compatibilization, result in a significant improvement in mechanical properties of the blends. There are two oldest methods that are used to modify the GTR which are devulcanization and reclaimation. Both are these are the methods that used for the scission of bonds that are originated from the tire formulations. The only different is the type of bonds that each of them breaks. Reclaimation is defined as the scission of the carbon-carbon bonds that formed on the rubber backbone with the aimed to reduce the molecular weight of the GTR in order to gain plasticity (20) while devulacanization process is the process at which the the sulphur-sulphur and carbon-sulphur bonds are cleavage in order to break the three dimensional structure formed during vulcanization process. We can consider both of the process to occur simultaneously as it is difficult and almost impossible (11) to distinguished and target the cleavage of the bonds that occurred during the process of modification. The scission of bonds by these two methods are shown in figure 6 (11).

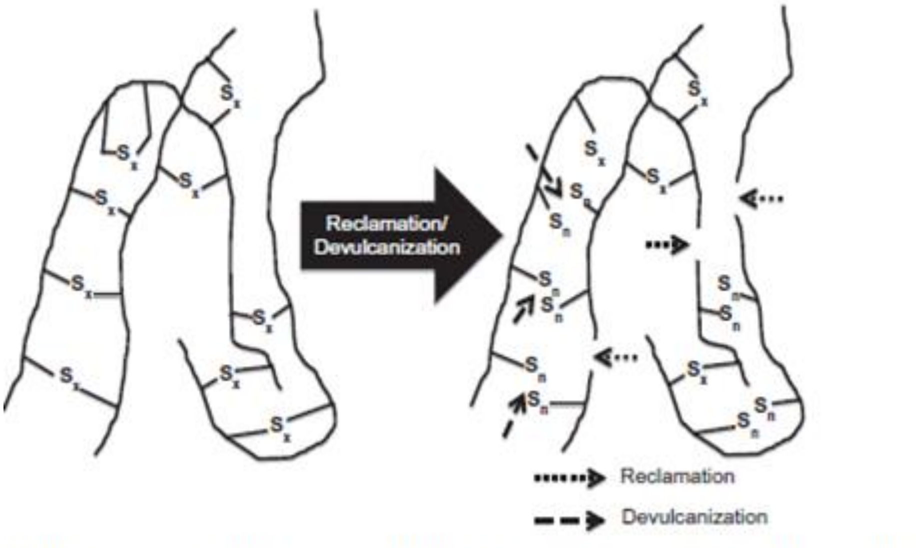
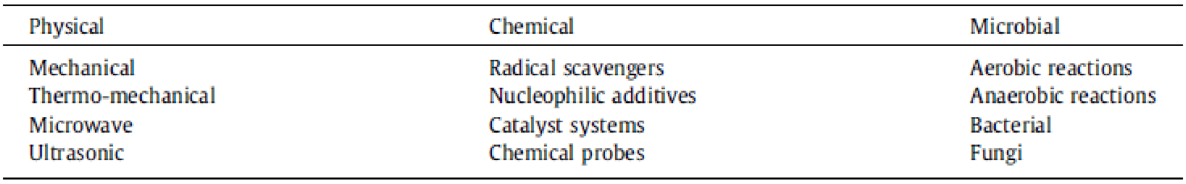


Figure 6 : Schematic representation of reclaiming and devulcanization

According to Wilma et al. (20), the improvement of devulcanization process can be done by swelling process. In their work, they use diphenylsulfide (DPDS) and TDAE oil as the solution. GTR was then swollen in this solution prior to the devulcanization and result in a significant improvement in the devulcanization efficiency as there are higher decrease in the crosslinking density compared to the unswollen GTR (20). In Table 1 (21) (16), there are some of the modification process which commonly applied whether through the physical, chemical or biological method.



Physical	Chemical	Microbial
Mechanical	Radical scavengers	Aerobic reactions
Thermo-mechanical	Nucleophilic additives	Anaerobic reactions
Microwave	Catalyst systems	Bacterial
Ultrasonic	Chemical probes	Fungi

Table 1 : Rubber reclaiming/devulcanization process

Under the *physical method* of devulcanization, we can divide this process into four other treatments which are mechanical, microwave, ultrasonic and thermo-mechanical (21). Basically, we will mainly focus on just three of the treatments available which are thermomechanical, thermochemical and microwave devulcanization in continuation also some of the explainations on microbial process.
In both *mechanical recycling*, the crumb rubbers are treated into a suitable equipment such as two-roll mill and twin screw extruders. Normally, this process is done at ambient and high temperature. Due to the mechanical shearing together with the presence of heat reduce the molecular weight of the of the rubber (16) (21). High shearing effect helps in effectively pulverize with an improved surface activation (21). The devulcanized GTR are characterized by the equipment used, local shear rate and processing parameters (e.g residence time). The difference between these two mechanical process is that the *thermo-chemical* needs the presence of reclaiming agents such as organic disulfides or mercaptans (18) and also the needs of high temperature during its process. The role of the reclaiming agents is to cleave the sulfuric crosslinks between the rubber chains and terminate the free radicals formed. The digester process reclaim the rubber crumb in a steam vessels equipped with agitators, which continually stir the crumb rubber while steam is applied. The disadvantage of the both processes is the generation of the heat which may degraded the rubber and may bring a potential of combustion. This cause the properties of the GTR that produced to be slightly reduced compared to the initial vulcanizate (21).

For the *microwave devulcanization*, the energy needed for the process can be easily obtained and controlled as this technique is based on the application of a controlled amount of microwave energy to the material at a certain energy level which is sufficient to cleave carbon-sulfur (302 kJ/mol) and sulfur-sulfur bonds (273 kJ/mol), but insufficient to cleave carbon-carbon bonds, which have a higher bond energy (349 kJ/mol) (9). Besides, heating process by microwave improved and has better efficiency than conventional method (21) as the devulcanized rubber
is not degraded when the material being recycled which normally takes place in the other commercial processes currently being practiced (18). Heat is generated within the material itself rather than obtained from external sources. The presence of black carbon and also the properties of having high thermal conductivity and heat capacity ensures the accumulation of internal energy and its uniform distribution in the material (16). Moreover, major characteristics by this process are the reduction of waste volume, is rapid, selective heating, low cost, safe and energy saving (21). However, one vital requirement of the microwave process is the presence of polar groups or

components in the polymer (9) while the presence of apolar groups will bring a negative impact on the devulcanization process (16). The presence of carbon black in nonpolar rubbers makes the rubbers receptive to microwave energy. This makes possible the use of the microwave heating to devulcanize waste tire rubber (22). Therefore, microwave technique is an unique method of reclaiming in terms of properties and fastness of the process.

While by *microbiological devulcanization*, we use bacterias and researchers believed that these bacterias are able to break the polysulfide linkage. According to the work done by Jim Kuk et al. (23), two different treatments were applied; chemical treatment with di-(cobenzanidophenyl)disulfide and microbial treatment with T. peromatabolis. The experimental results indicate that the processing of crumb rubber, as well as the end-product properties, were enhanced by both these treatments, with the microbial treatment being the most effective. Other than that, this process can be regulated by temperature, pH and etc. (16) (23) as the bacteria cannot withstand very low and very high temperature environment. Unfortunately, the devulcanization can be done only on the surface of the rubber. Besides, the toxicity of additives in the rubber inhibit the function of the of bacterias and hindered the devulcanization process to occur efficiently.

Due to the incompatibility of GTR and the dispersed of phase that formed in the finished vulcanizates, there are two common practices that applied which are by addition of compatibilizer and formation of crosslinking between GTR with the polymer matrix (11). Both of these are believe to improve the mechanical properties as they help to compatibilize the blend components. Magdalena et al. (1) incorporated maleic anhydride grafted polyethylene (PE-g-MA) to the blend of HDPE/GTR while Yewen et al. (24) used bitumen and maleic anyhydride-grafted styrene-ethylene-styrene (MAgSEBS) as the compatibilizer for the PP/GTR blend. Another attempt was done using maleic anyhydride grafted polyethylene for acrylamide modified GTR and HDPE by Kim et al. (25) which showed an improvement in tensile and impact properties of the blend. The addition of compatibilizer is normally used in the thermoplastics and thermoplastics elastomer blends.

The other possibility that we may applied is by formation of crosslinking bonds between the components of the blends. This practice is frequently done for the rubber blends and preferred to be done in thermoplastics elastomer blends. There are two types of crosslinking process which are sulphur crosslinking which is the commonly used and peroxide crosslinking which depends on the type of substances used in the blends (11). This formation of crosslinking also helped to increase and improve the properties of blends and ensure a good interfacial adhesion between the incompatible GTR and polymer matrix as the dispersed phase that both of them own.

In this project, we investigate the properties and behaviour of the butadiene rubber matrix polymer incorporated with GTR. The revulcanization of this blends results into a new properties created in combining both of these compounds. We used GTR that undergo different treatments of devulcanization which are mechanical, chemical-mechanical, and microwave also with the GTR which do not undergo devulcanised process (i.e non-devulcanised GTR). Also, we practiced the crosslinking formation by the addition of sulphur during the vulcanization process in order to promote a better compatibilization. After that, we investigate the effect of different treatments in determining the properties of the sample or vulcanizate followed by the explainations on the mechanical properties such as tensile strength, young modulus, elongation at break and etc.. Later we discussed on the termogravimetric analysis (TGA), Scanning Electron Microscopy (SEM), the hardness and also the gel-fraction contain in each of the sample with different proportions of GTR for each of the treatments used. By this, we could investigate and analyse which one of these devulcanization process is better and good to be applied.

2. Experimental

2.1 Materials

Untreated GTR of car nominated as non-devulcanised (nd), treated GTR by mechanical devulcanization (dm) of 50% truck tyre and 50% car tyre, chemical-mechanical devulcanization (dcm) of unknown source of GTR, chemical-mechanical microwave devulcanization (dmw) of unknown GTR, microwave devulcanization of truck GTR (dmwA1) and microwave devulcanization of car GTR (dmwA2). All of the GTR were obtained from Environmental Management of Pneumatics, LLeida,Spain. The sizes of shredded GTR done by downsizing process were ranging from few microns to a few millimeters. Butadiene rubber (BR), zinc oxide(ZnO), strearic acid($C_{18}H_{36}O_2$), sulphur (S) and Redozon added together as complement to make the vulcanizate, received from Michelin Company, Valladolid,Spain. Acetone (Chemical Laboratry of UPC) used as the dissolvent for gel fraction determination test.

2.2 Experimental Procedure

Preparation of BR/GTR vulcanizates

Fresh BR was being mixed with the various proportions of GTR of untreated one and of different devulcanization treatments which were dm, dcm, dmw, dmwA1 and dmwA2. They were combined together using the open two roll mixing mill for about 30 minutes at around 55 °c to 65 °c which was under their melting point temperature. The formulations for each of the samples prepared was shown in the Table 2. The other compounds like zinc oxide(ZnO), strearic acid, sulphur and redozon were combined together during the mixing process based on the 100g of BR irrespective of the GTR introduced as we assumed that the additives in GTR did not involve in the reaction process (27).

Open two-roll mixing mill

The first sample which was the reference sample was made without any GTR added while the sample 2 to 7 were combined with the nd GTR for the proportions between 5% to 50% respectively. Same goes to dm,dcm and dmw treatments, with 5% to 50% proportions named as sample 8 to 13, sample 14 to 19 and sample 20 to 25 respectively. For the the sample with dmwA1 and dmwA2, the amount of GTR used were ranging from 5% to 40% which dedicated as the sample 26 to 30 and finally the sample of 31 to 35 respectively. The mixing process became harder as the amount of GTR used increases and the incorporation of GTR into the rubber matrix took a longer time in order for the blends to be well mixed together.

The samples were then treated by vulcanization process using compression molding machine at 160°c for about 10 minutes at the pressure of 10 MPa. At this time we assumed that all the crosslinking bonds, the sulphur-bonds formations and the treating process for the samples were completely done and reached maximum. The mold was then cold down with running water, known as quenching to stop the curing process. The sheet was then taken out from the mold and left to cool down at room temperature.

Compression molding machine

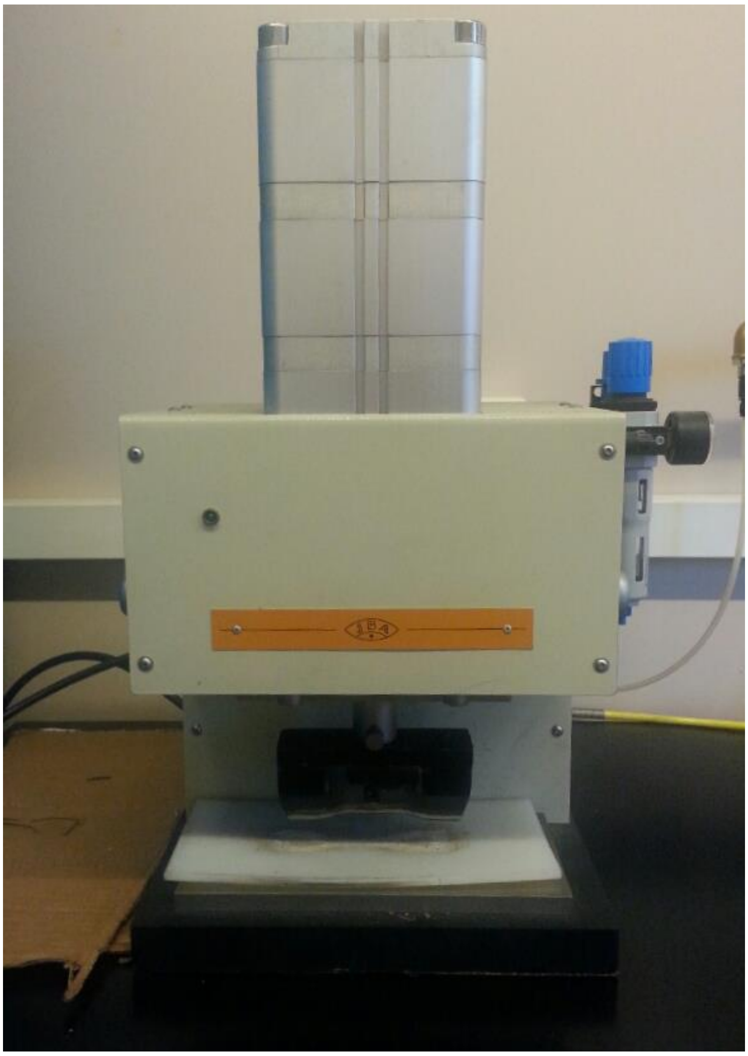
GTR TREATMENTS	PROPORTIONS, phr	BR, %	ZnO, phr	STEARIC ACID , phr	SULPHUR, phr	REDOZON, phr
-	0	100	5	2	2	4
nd	5	100	5	2	2	4
	10	100	5	2	2	4
	20	100	5	2	2	4
	30	100	5	2	2	4
	40	100	5	2	2	4
	50	100	5	2	2	4
dm	5	100	5	2	2	4
	10	100	5	2	2	4
	20	100	5	2	2	4
	30	100	5	2	2	4
	40	100	5	2	2	4
	50	100	5	2	2	4
dcm	5	100	5	2	2	4
	10	100	5	2	2	4
	20	100	5	2	2	4
	30	100	5	2	2	4
	40	100	5	2	2	4
	50	100	5	2	2	4
dMW	5	100	5	2	2	4
	10	100	5	2	2	4
	20	100	5	2	2	4
	30	100	5	2	2	4
	40	100	5	2	2	4
	50	100	5	2	2	4
dmwA1	5	100	5	2	2	4
	10	100	5	2	2	4
	20	100	5	2	2	4
	30	100	5	2	2	4
	40	100	5	2	2	4
dmwA2	5	100	5	2	2	4
	10	100	5	2	2	4
	20	100	5	2	2	4
	30	100	5	2	2	4
	40	100	5	2	2	4

phr- per hunderd rubber

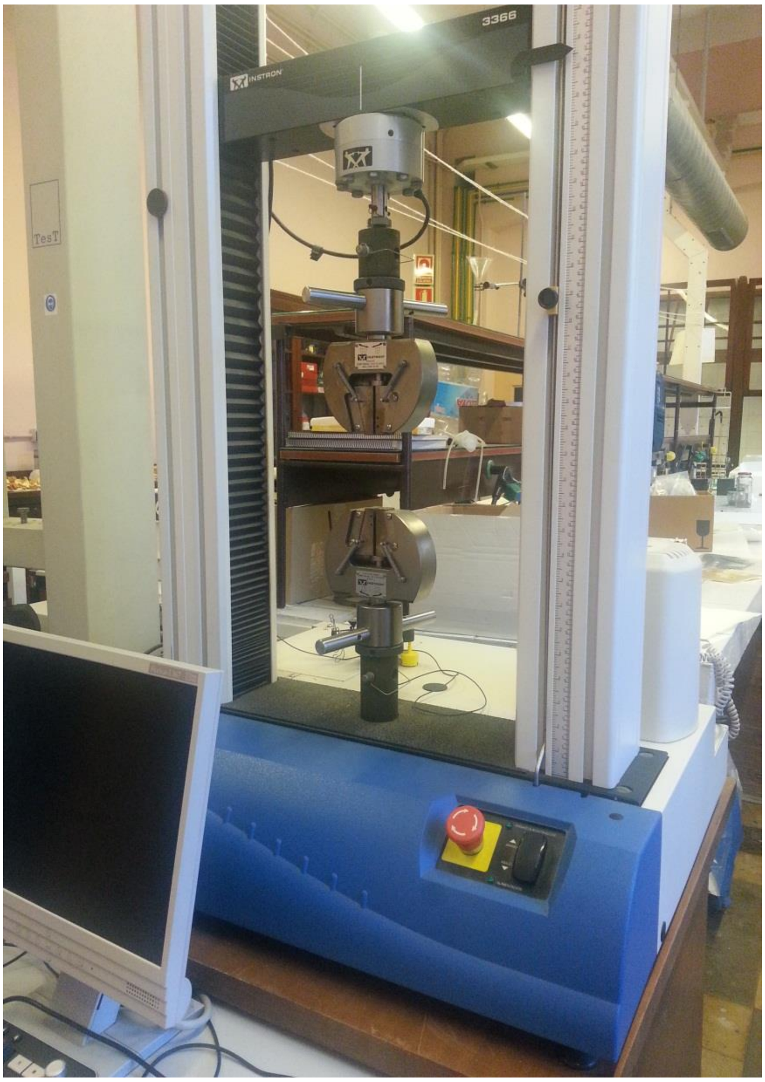
Table 2: Formulations of the samples with different GTR treatments

Test of the mechanical properties

Using the cutting machine, the sheet was cut into 8 pieces of dumbbell shaped sample with 2 mm thick and 33 cm length. In order to test for the properties such as Young modulus, tensile strength and elongation at break, we used Bluehill Instron 5569 tensile machine of ASTM D412-51T at the speed of 500mm/min at normal room temperature. The average value of the mechanical parameters were obtained using at least five of the samples.



Cutting Machine



Bluehill Instron 5569 tensile machine

Hardness test

In order to test for its firmness, the Zwick shore A ASTM D676 machine was used. This test was done for all samples of each of the treatment. The average value of at least 5 readings at five different positions were then recorded.

Zwick shore A ASTM D676 machine

Determination of gel fraction

Small sample with about 1cm x 1cm x 1cm size with certain weight determined previously was extracted by using soxhlet apparatus for 24 hours using acetone as the dissolvent. The sample was then dried at room temperature until it reached a constant weight. The gel fraction in the sample was calculated by the following formula (20);

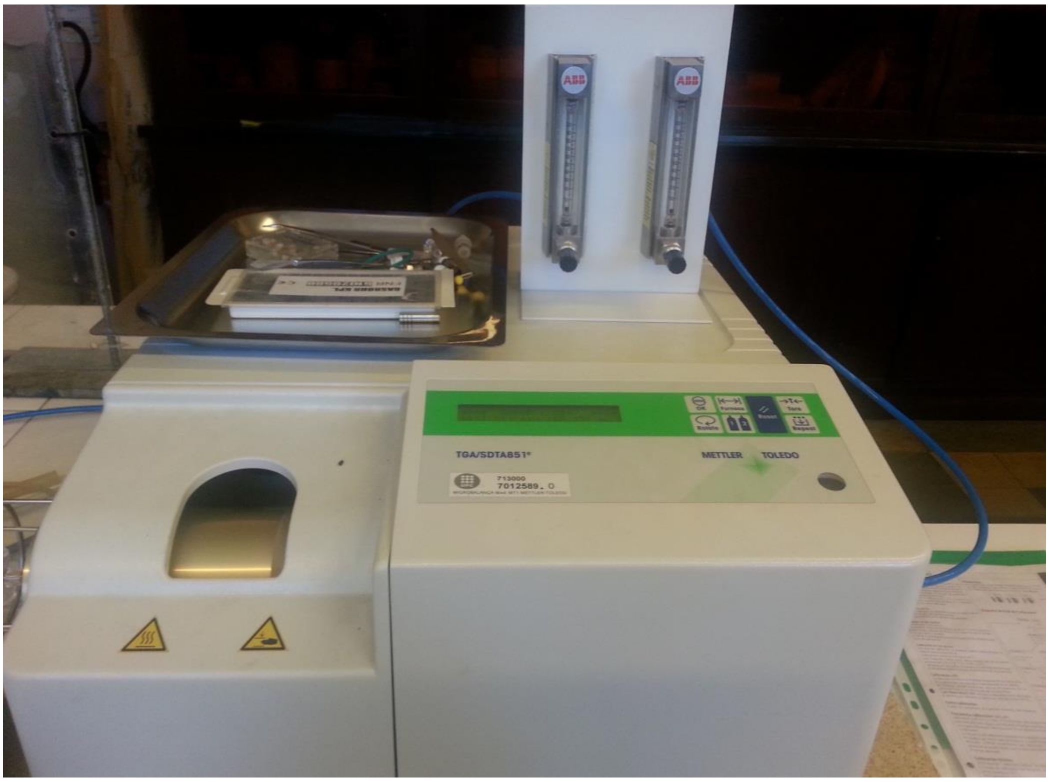
$$\text{Gel fraction} = 1 - \frac{\text{weight of rubber dissolved in solvents}}{\text{weight of pure rubber in the compound}}$$

where weight of rubber dissolved in solvents is the difference of weight at the initial and after the sample reached its constant weight while weight of pure rubber in the compound is the intial weight of sample introduced into the soxhlet.

Soxhlet extraction apparatus

Thermogravimetric analysis (TGA)

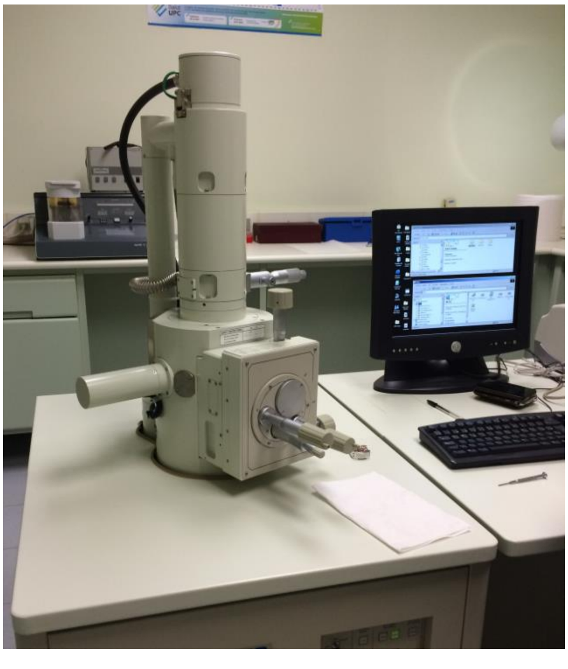
The thermal stability of the sample was determined by the TGA test and it was carried out using the METTLER TGA in the nitrogen atmosphere of 20mL/min from the temperature of 40°c to 600°c. The heating rate is 20°c/min with the weight introduced was about 16mg. This test was done for the pure BR matrix, the reference sample of 0% GTR, 20% GTR and the highest proportions for each of the GTR treatments.



METTLER TGA

Scanning Electron Microscopy (SEM)

The fracture surface of the samples from mechanical testing was examined with a JEOL JSM 6480 scanning electron microscope. Dry samples were coated with a thin layer of gold before observation under the microscope, to increase the sample conductivity.



3. Observations

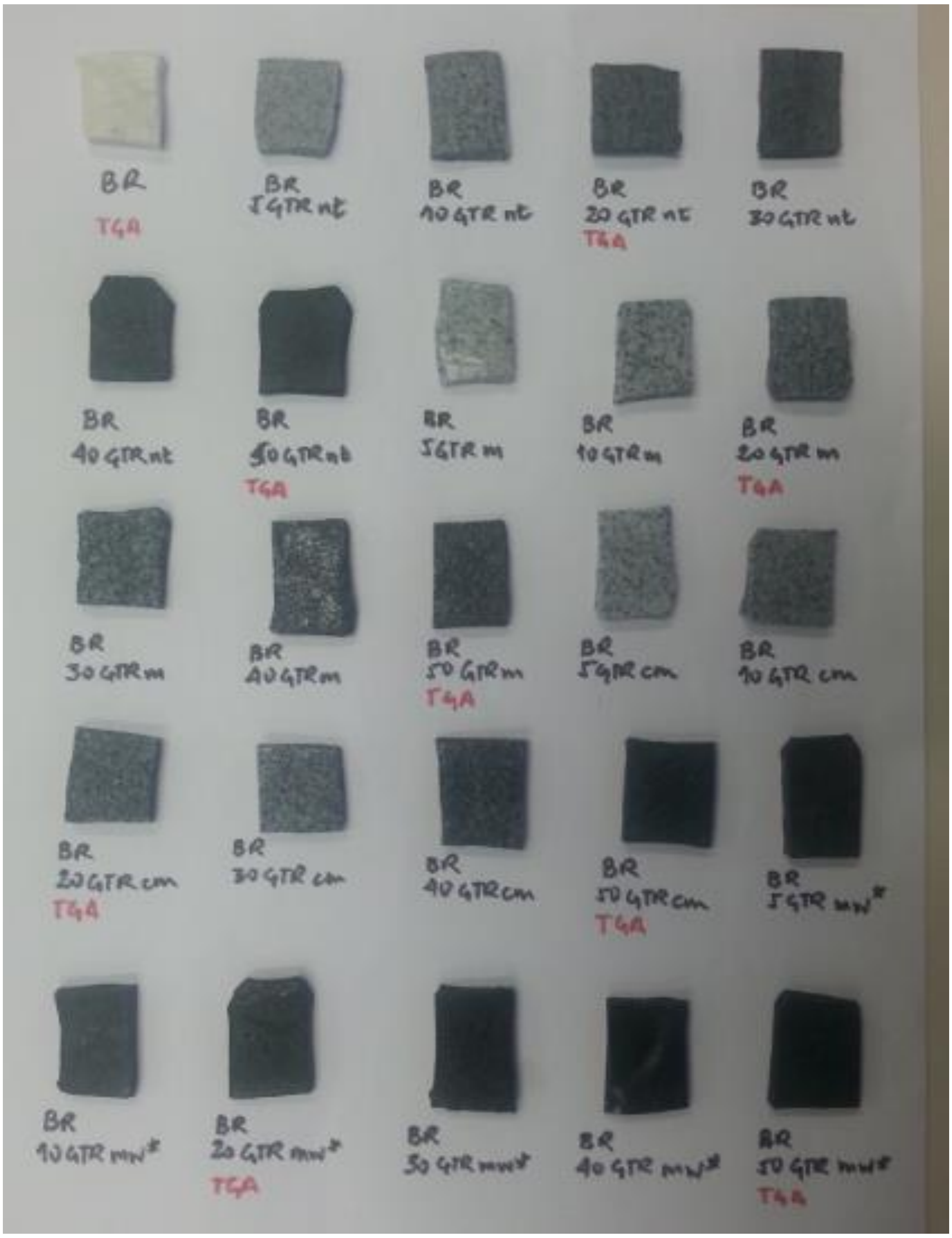
a. The colour for each vulcanizate was different. The colour given by BR/dmw GTR was the darkest and the blackest compared to the others.

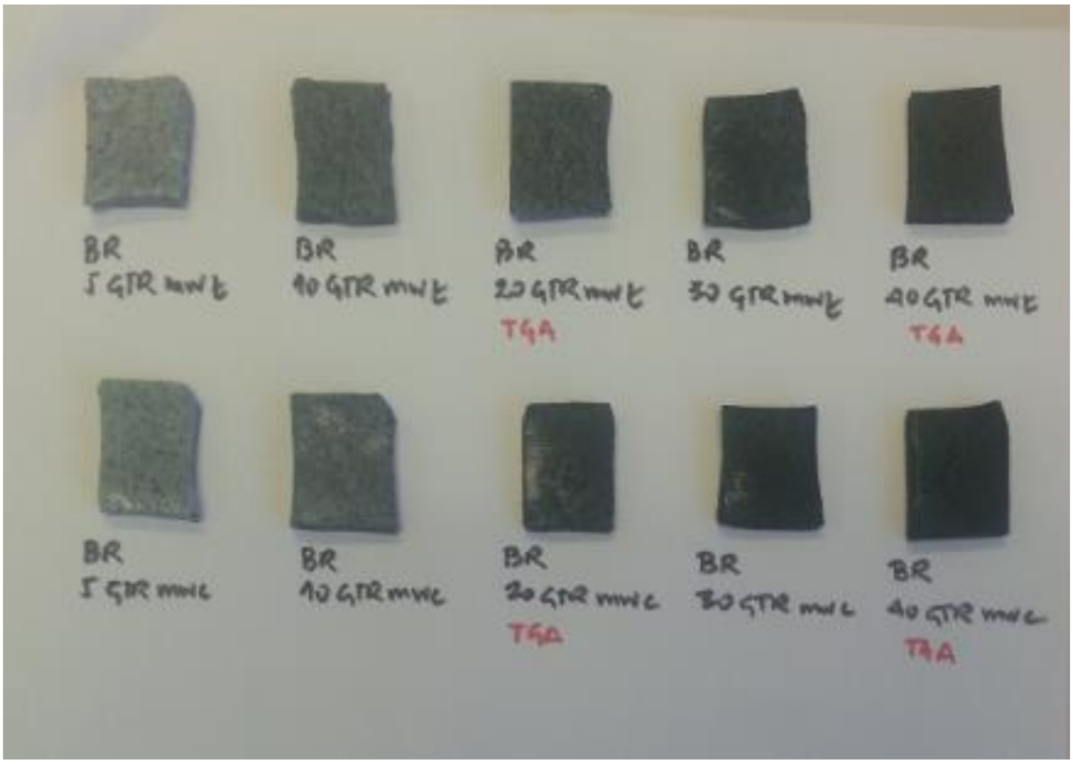
b. The need of some oil spreaded on the mold in order to avoid the sticking of the finished vulcanizate to the mold surface make it hard to take the sample out.

c. Holes formation inside the vulcanizate and on the surface as well.

d. The samples were easily stick and attached to each other, different from the SBR/GTR vulcanizates that loosely unstick to each other.

e. The samples changed their colour and create dusty feel-like surface when exposed to the open air environment.





SAMPLES OBTAINED FROM DIFFERENT BR/GTR VULCANIZATES

4. Results and discussions

Basically, we focused in all of the following for our next discussions which were:

1. **Tensile and mechanical properties**
2. **Relation between the elongation at break and toughness**
3. **Co-related sol fraction with crosslinking-density**
4. **Thermogravimetric analysis**
5. **Sem study**

i. Tensile and mechanical properties

From all the test that we had done and the results that we obtained, we could see the behaviour of each of the vulcanizate at increasing amount of GTR when it was incorporated with the matrix polymer of BR corresponds to each of the GTR treatments considered in this experiment. In this part, we mainly focussed on the important basic properties like maximum tensile strength, young modulus and elongation at break, also 100% and 200% elongation. Although there were many other properties that we might considered in this work but they were not in our main interest to deeply studied on them in this project.

Generally, as we can see from figure 7 and figure 8, the value of tensile strength (TS) as well as young modulus (YM) given by each of the treatment showed an increase in their values when the amount of GTR introduced increases. Both of these properties were determined by the material used by the objects which means different object with the same material have same TS and YM values. Basically, properties of the finished vulcanizates were determined by the type of virgin rubber that used. For example, NR/GTR vulcanizate showed a deterioration in both of TS and YM values while SBR/GTR vulcanizate have conflicting results, some show improvements and some show deterioration (11). In our case, BR/GTR vulcanizate showed an improvement in both of these. So, we could say that the crosslinking that formed during the vulcanization process create a strong suphur-sulphur bond formation which cause a restriction in the movement and elongation of the blends as the GTR introduced to the blend increases. High modulus values determined that the material was hardly to deform. As the results, high force needs to be applied during the test in order to elongate and pull the material away. In accordance to the increasing of YM values is the increasing of TS values given by each of the vulcanizate. The ability for the blend to withstand high loads during the elongation which then resulted in the increase of YM values, means that the high TS values were also achievable in accordance to this ability. As we know, GTR that we used contained some carbon black which were originated from the previous tire formulations. So, as the amount of GTR increase, the amount of carbon black that presenced also increases. By this, we could relate the presence of this component inside the vulcanizate to the high values of both TS and YM that have been obtained as the vulcanizates that formed exhibit strongness, rigidity and also stiffness (11). This increase in the stiffness means that there would be reduction in the elasticity behaviour of the vulcanizates itself compared to the reference sample.

Meanwhile, the increment of GTR introduced as well as carbon black content means that the amount of them inside the matrix also increase. As the values of TS and YM increase proportional to the GTR added, we can conclude that the presence of higher amount of GTR also known as elastomeric waste allowed the distribution of the stress applied during the tensile test to be even better. Consequently, we could relate this distibution of the stress by the matrix to the elastomeric waste with the dispersion of them inside the matrix. The well transferred of the stress make the sample to be hard to pull apart and higher force was needed in order to overcome the bond that formed between those molecules. In addition to that, the high crosslinking density results in the higher value obtained for 100% and 200% moduli (Figure 8i and 8ii), which restrain the mobility of the chain making high load was required in order to cause the sample to elongate. According to the S.Ramarand et al. (11), the presence of the carbon black act as the reinforcing characteristics to the styrene butadiene rubber and also to the acrylonitrile butadiene rubber resulting to the increase of TS. We assumed that, this behaviour also applied to the BR like in this case.

In figure 9 showed the average hardeness value of vulcanizates for each of the GTR treatments. The increase of this value with %GTR was supported with the increase of YM values as we mentioned before and also to the high crosslinking bonds that formed. This increment might also got affected due the presenced of the reinforcing material as mentioned also just now (11).

Now, let focussed on the influence of the type of GTR used in the determination of the mechanical properties. Based on all the properties that we considered, we could see that dcm GTR treatment showed the highest value of TS, YM and also withstand high stress at 100% and 200% elongation at 40% amount compared to the other at 50%. So, this means that dcm treatments showed in contrary behaviour from what that had been explained. At the initial (i.e lower %GTR) from 5% to 40%, the behaviours are similar to the GTR from other treatments but as it reached 50%, both of the TS and YM showed some reduction in values compared to the 40% but still higher than the other proportions and the other treatments. This irregularities might due mainly to the inhomogenous blend that cause the transfer of the stress cannot be done properly to the whole blend during the test. Also, this caused the stress concentration to occur at certain points that make it break easily and resulted in the reduction of TS and YM values as well. Other than that, the deterioration of the properties might due to the increasing of GTR amount and also the size of GTR (19). The aggregation of GTR in the BR matrix caused the size of GTR that present inside the matrix to increase which caused an uneven flow of the stress along the sample. High amount of GTR that introduced reduce the mechanical properties of the vulcanizates that result from the lower adhesion between BR/GTR phase (1). From this, we could say that the BR/dcmGTR vulcanizate has its best and possess a high TS and YM only until 40% GTR. The reduction in both of these affected also the hardness value as shown in Figure 9.

Likewise, for the non-devulcanized GTR (i.e non-treated GTR), as we could see they showed quiet the same behaviour like the other treated GTR as the results obtained are more or less equal to the others. They have a good evolution both in TS and YM values as well as the hardness. The crosslinking that formed due to the present of sulphur during the vulcanization of BR/ndGTR contribute to the increase of these values although the GTR used are not treated. Other than that, we can state that the carbon black that remained in the GTR may probably helped to increase these values (27) irrespect whether the GTR are priorly treated or not.

Now, lets take a look on the results of tensile test for dmwA1 and dmwA2 which were the GTR that undergo microwave treatment and originated from truck and car respectively. Clearly, the TS and YM values for dmwA1 were higher than dmwA2 as well as the stress values that achieved at 100% and 200% elongation. By this, we saw that the truck tires have a better properties than the cars as different amount of components and the type of elastomers were used depending on the type of tires. During devulcanization process of GTR, different parameters were applied which were the best compromise of parameters for just the single type of elastomer used in the tires. According to S.Saiwari et al. (21), the outer layer of the particles are believed to be devulcanized and peeled off while retain the inner cores of the particles to stay more or less unchanged. Due to the different type of elastomers as well as their amounts used in cars and trucks, the finished GTR that formed showed a contrary in behaviour which then results in the different values obtained in the tensile test of the vulcanizates.

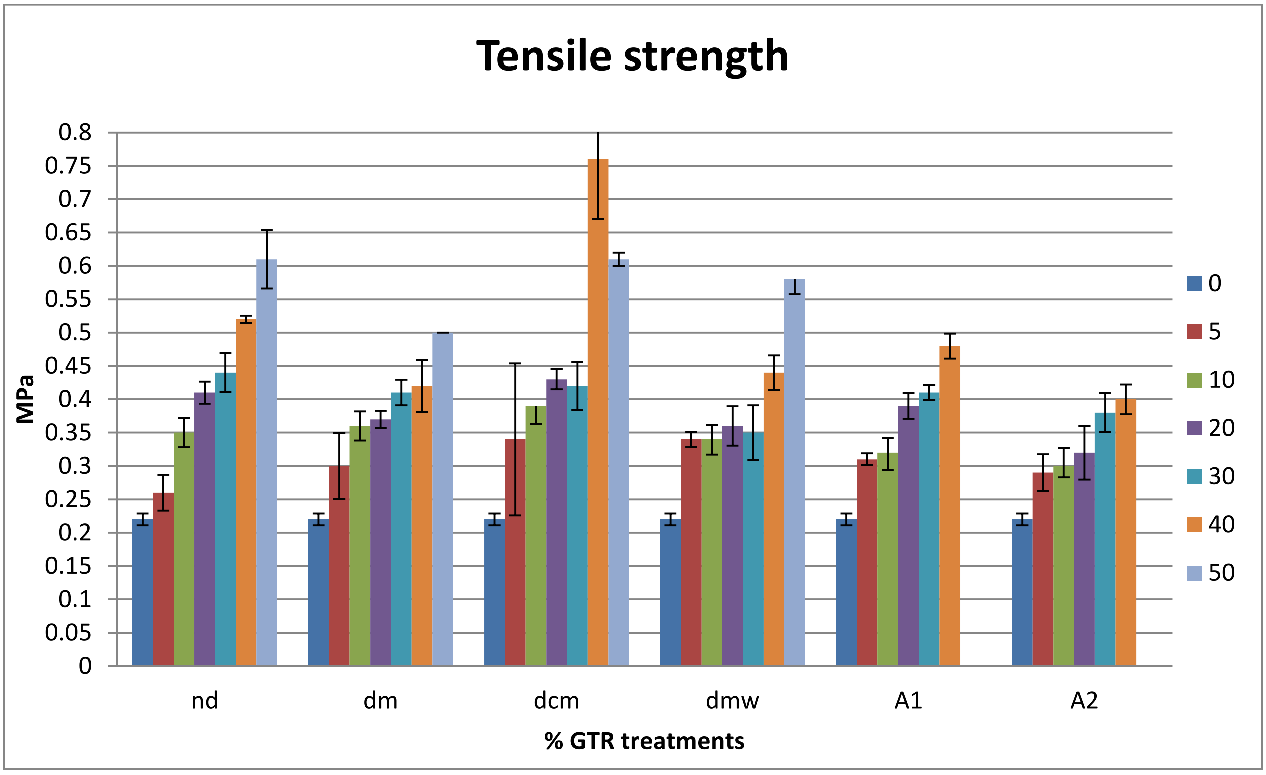


Figure 7 : Tensile strength values for BR/GTR of different GTR treatments

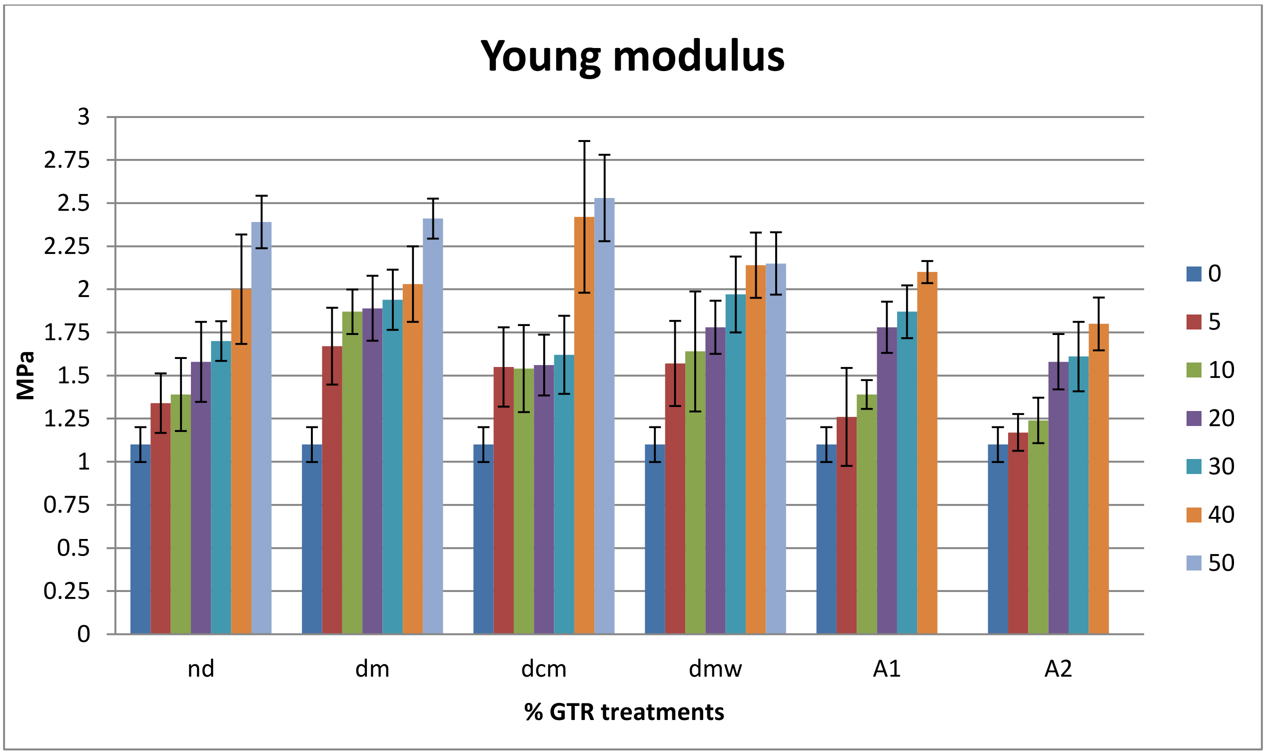


Figure 8 : Young Modulus values for BR/GTR of different GTR treatments

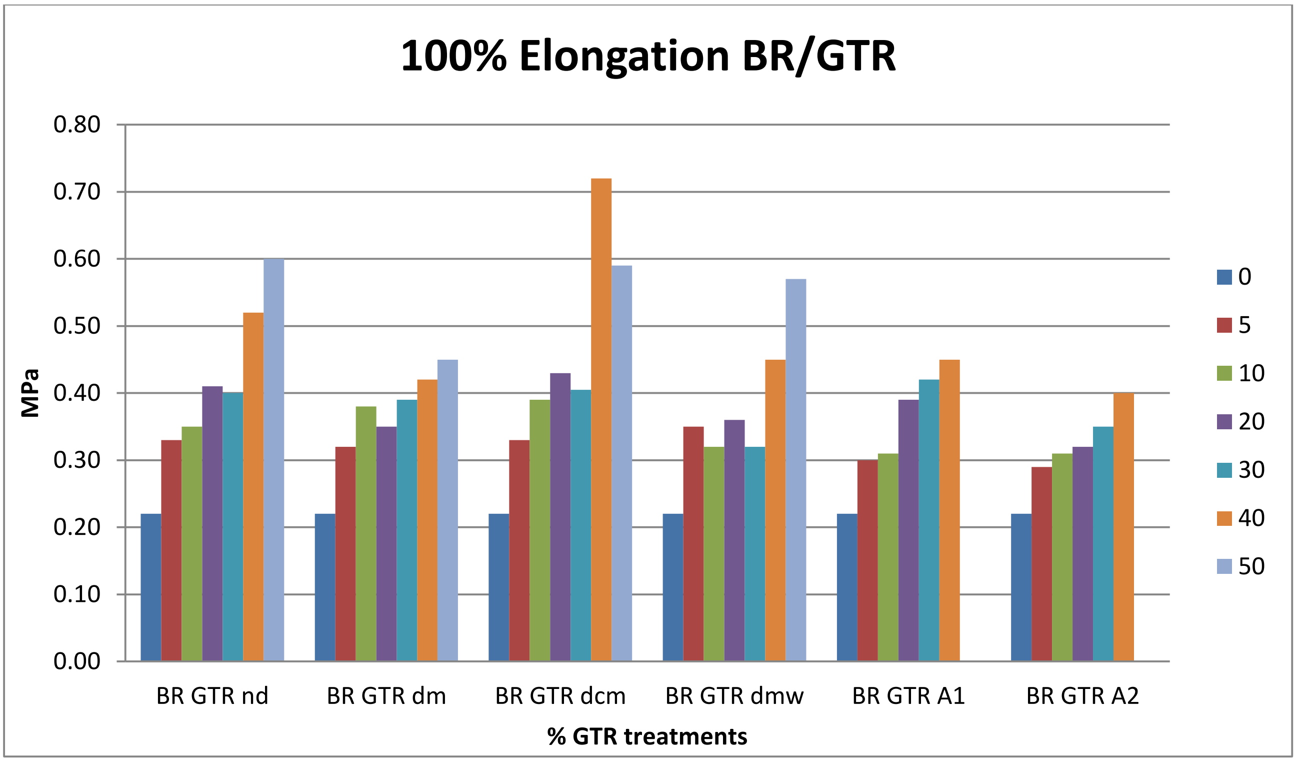


Figure 8i : Stress values for BR/GTR of different GTR treatments at 100% elongation

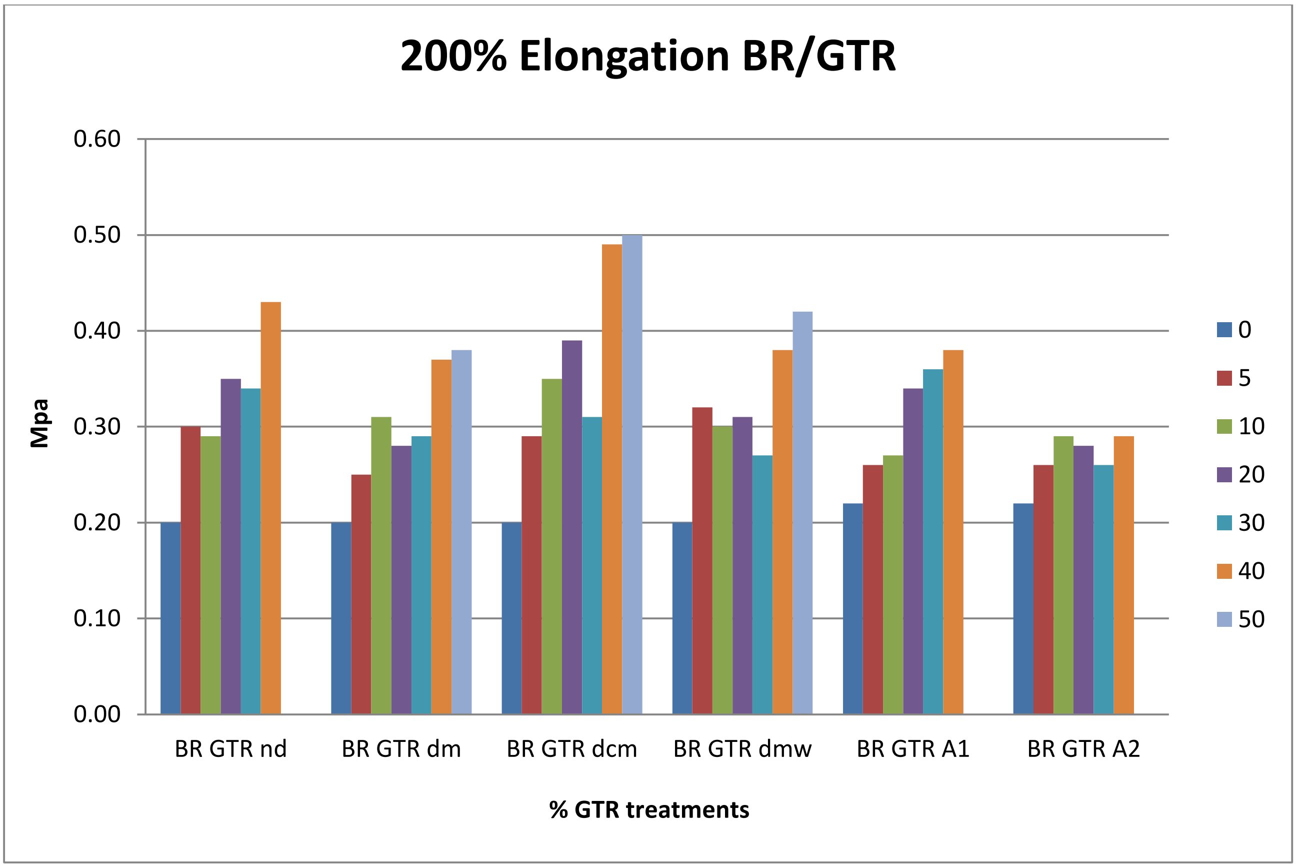


Figure 8ii : Stress values for BR/GTR of different GTR treatments at 200% elongation

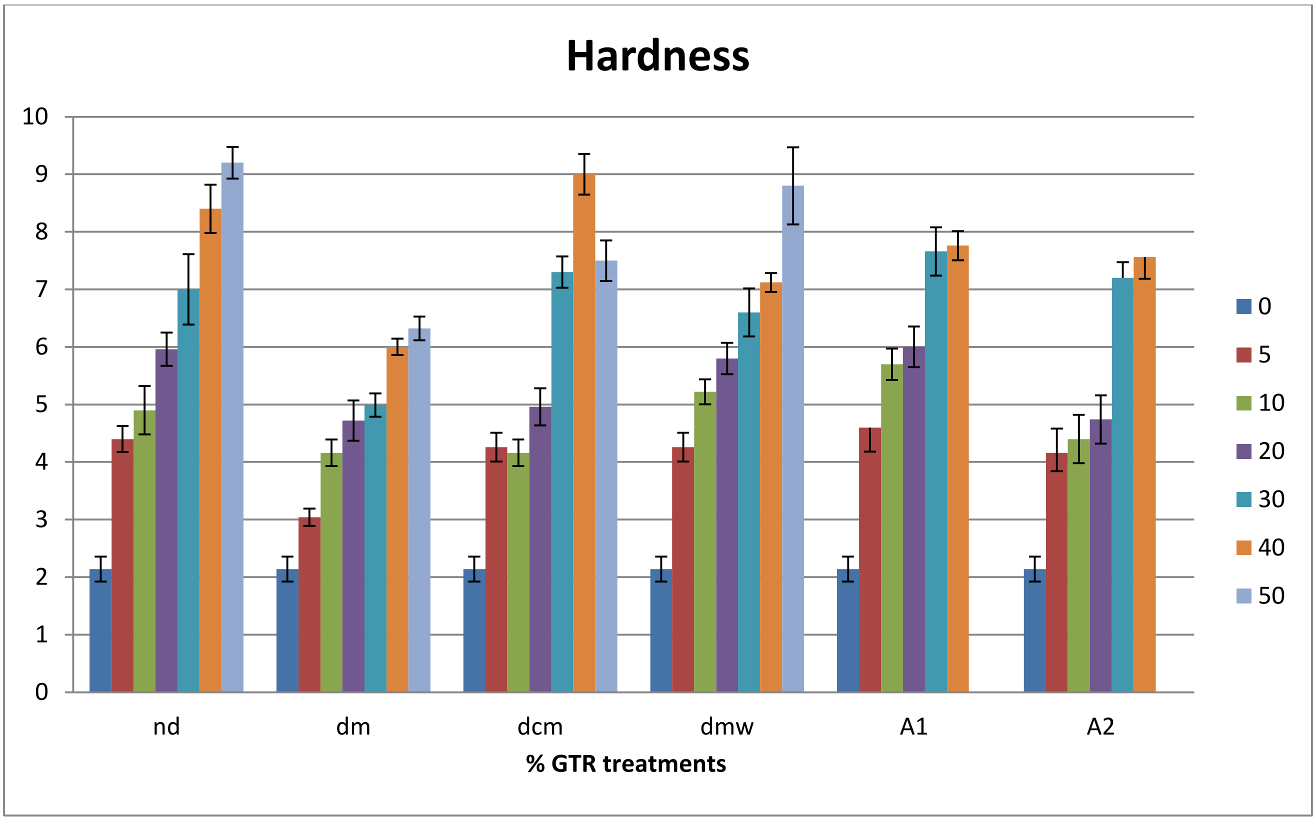
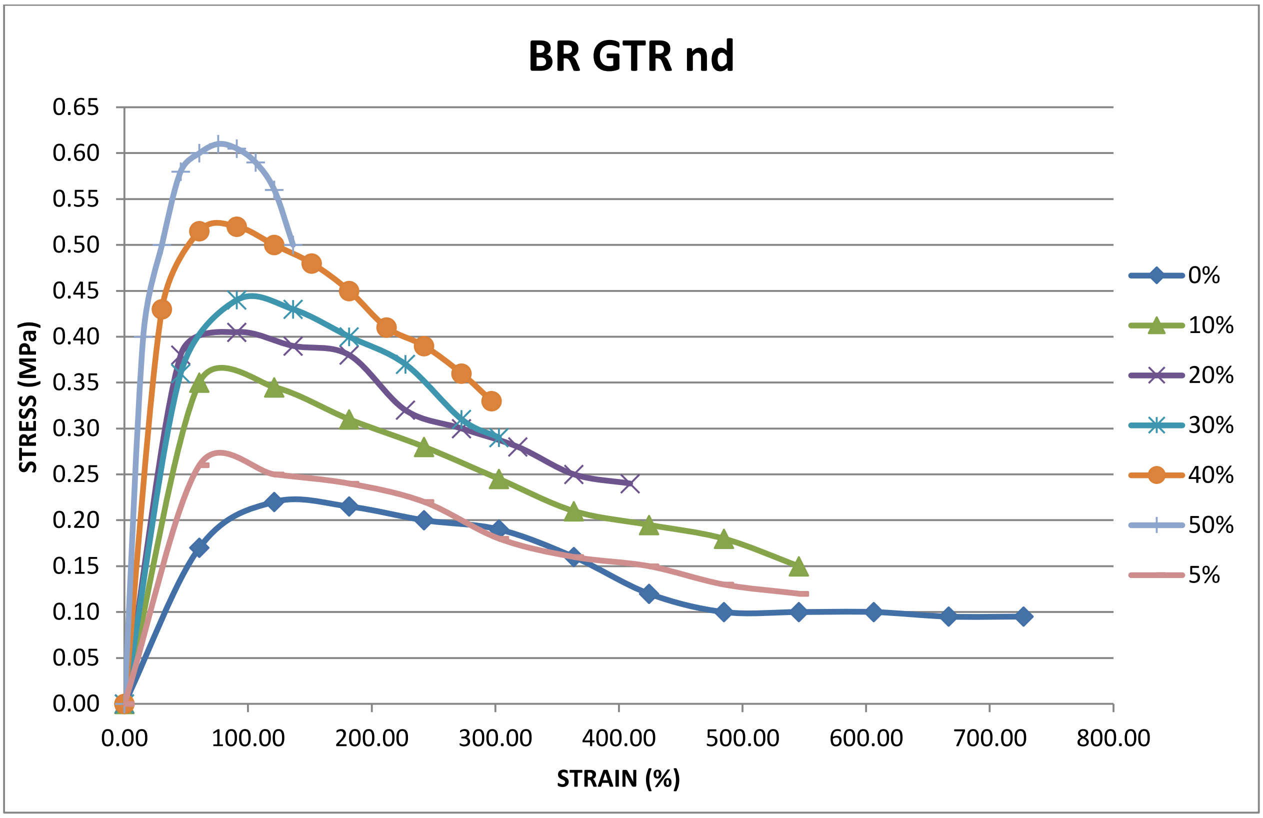


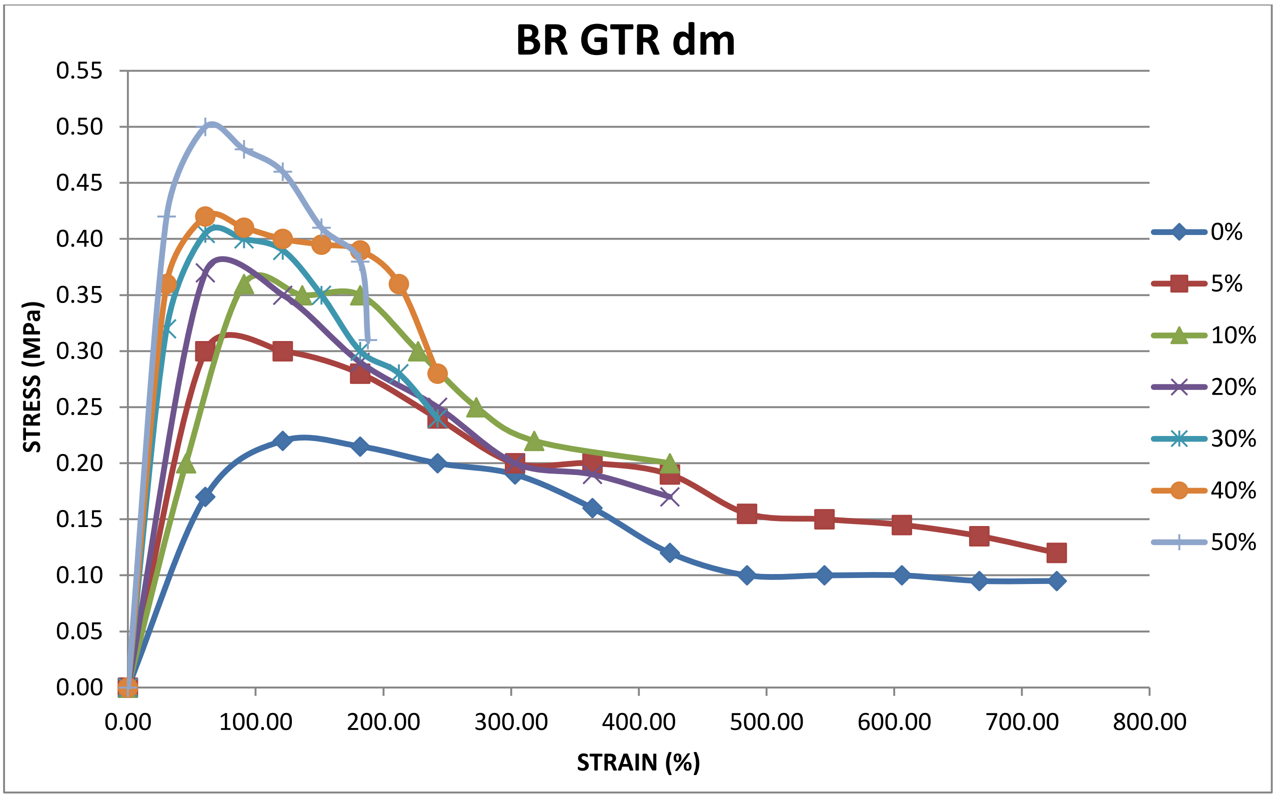
Figure 9 : Hardness values for BR/GTR of different GTR treatments

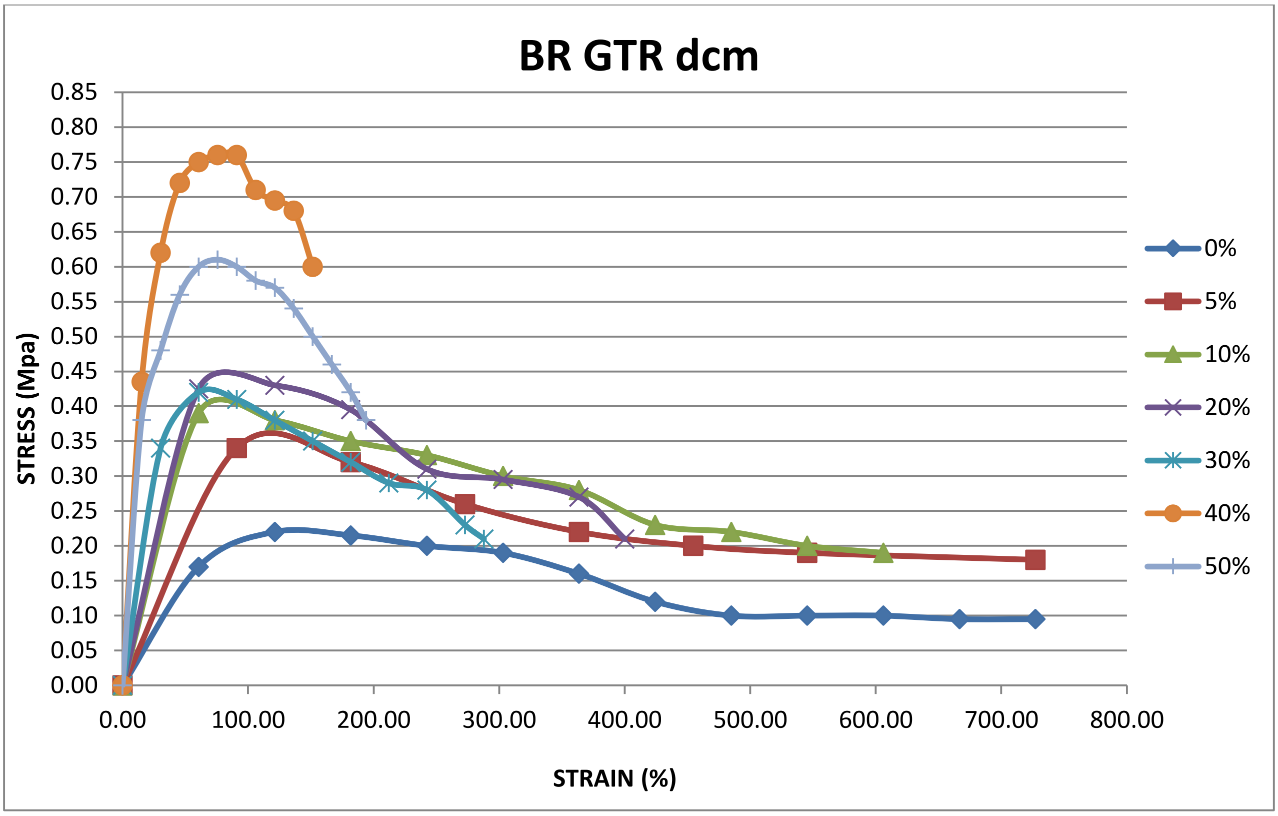
ii. Relation between the elongation at break and toughness

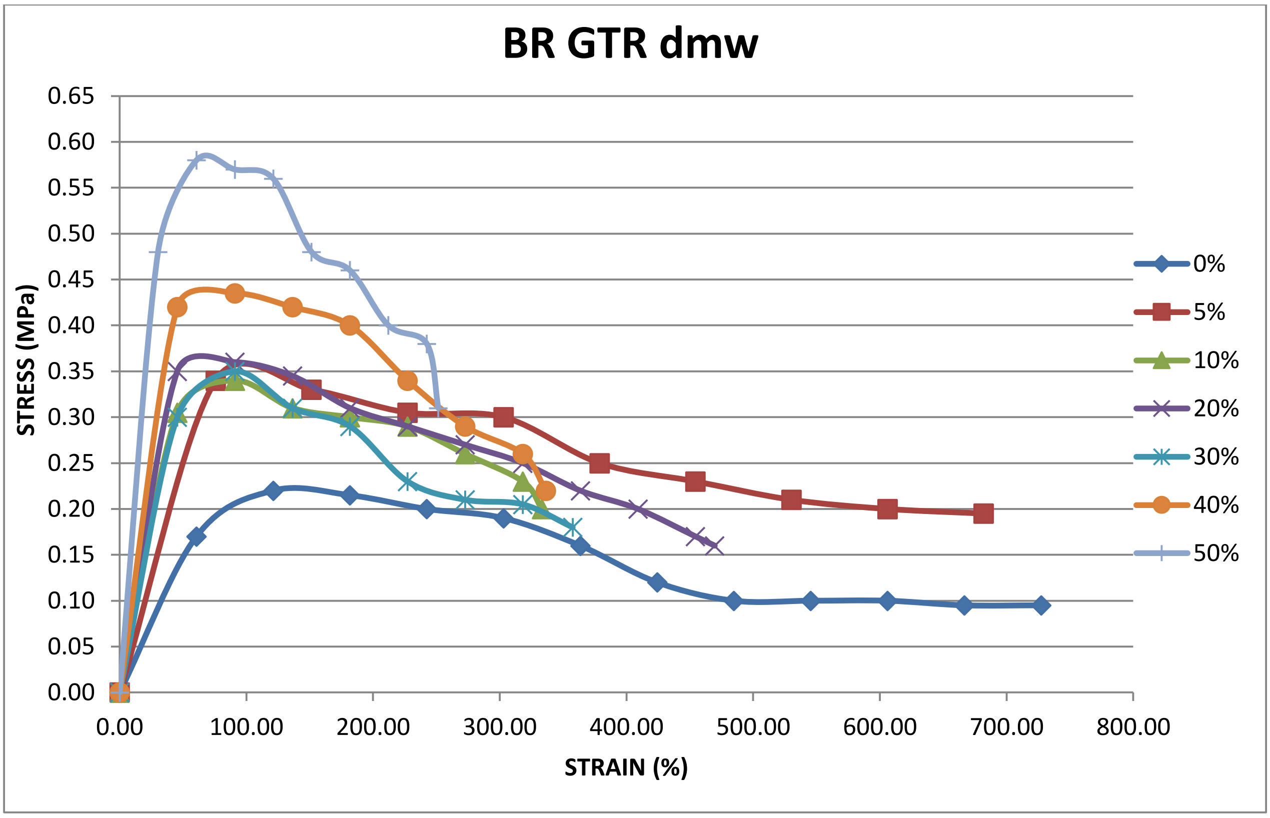
Given from figure 10b, as the %GTR increases, the elongation at which the samples break decreases. From this trend, we could say that the sample cannot elongate more and more as the amount of GTR increases. In addition, the ductility and toughness were reduced with the higher incorporation of the GTR inside the matrix as the tensile test graph(Figure 10a) showed a reduction of area under the graph which by that we could then determined the toughness of that sample. Besides that, the increasing proportions and the aggregations of those GTR probably cause the stress concentration at certain point inside the matrix to occur and resulted in the breaking of the samples to be faster and incapable to return to its original shape as well as undergo plastic deformation just at a very short time. Other than that, the increasing amount of GTR caused the vulcanizate to demand high loads in order to elongate during the elastic deformation resulted in the high TS and YM values as explained before. So, the presence of GTR helped to increase the stiffness and strongness of the material but reduced their elongation and ductility properties compared to the reference sample of 0 GTR that showed a good amount of elongation.

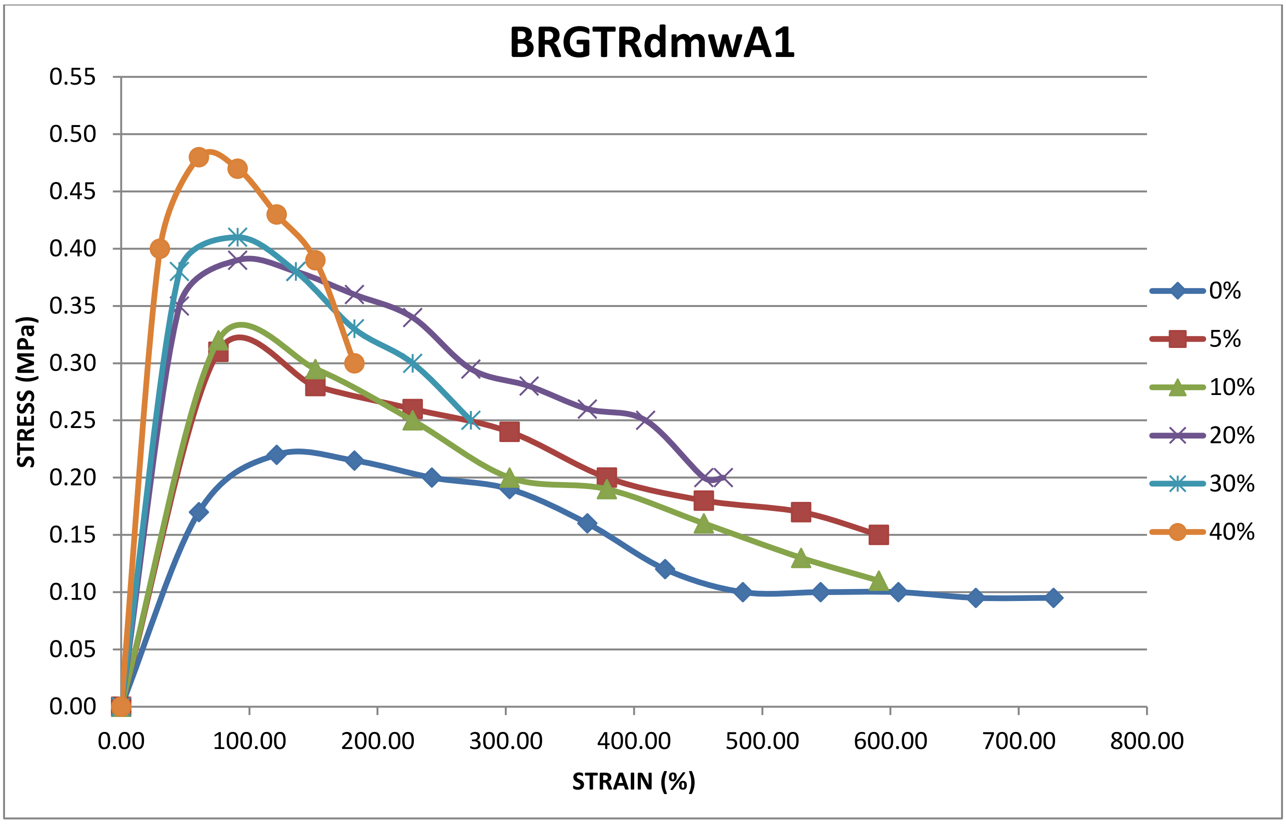
Figure 10a : TENSILE TEST GRAPH FOR EACH VULCANIZATE

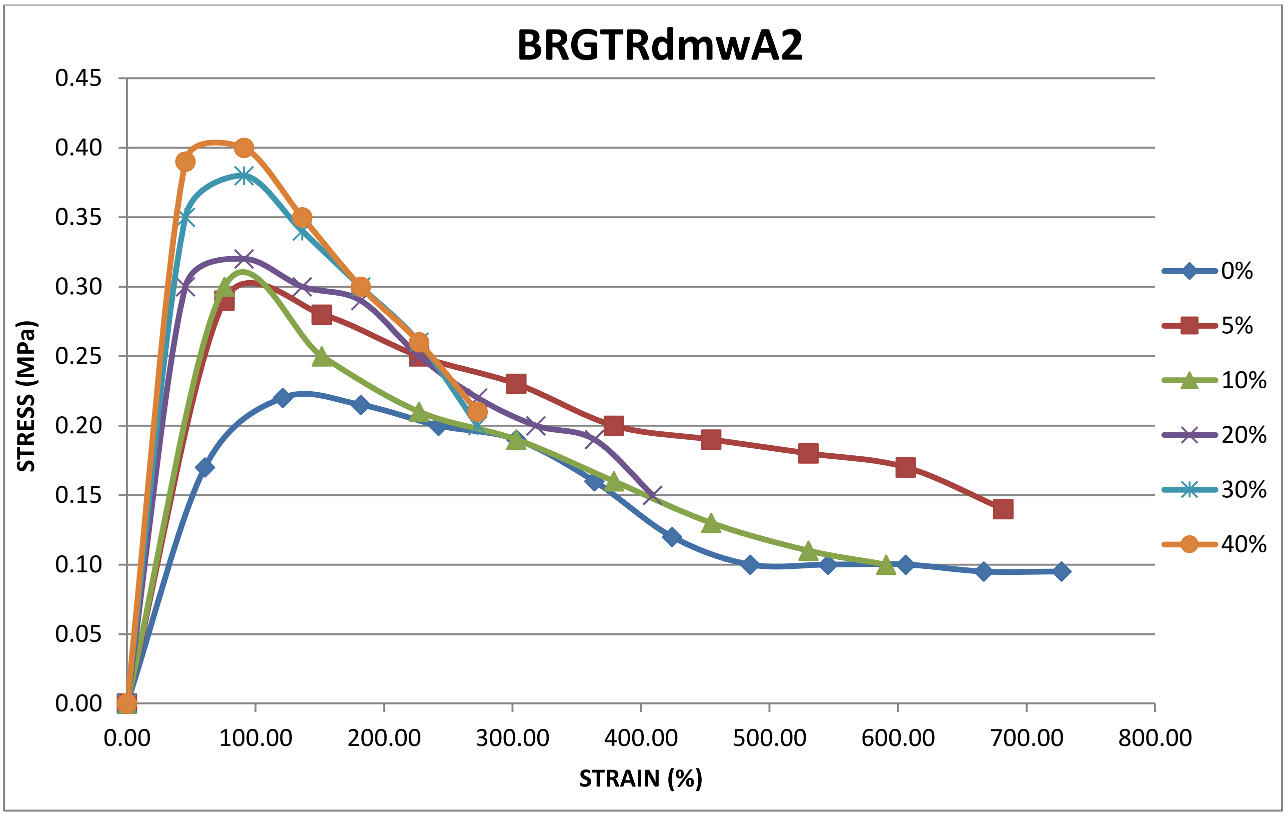





BR GTR dcm
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
STRESS (Mpa)
0.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
STRAIN (%)
0%
5%
10%
20%
30%
40%
50%


BR GTR dmw
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
STRESS (MPa)
0.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
STRAIN (%)
0%
5%
10%
20%
30%
40%
50%


BRGTRdmwA1
STRESS (MPa)
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
STRAIN (%)
0%
5%
10%
20%
30%
40%


BRGTRdmwA2
STRESS (MPa)
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
STRAIN (%)
0%
5%
10%
20%
30%
40%

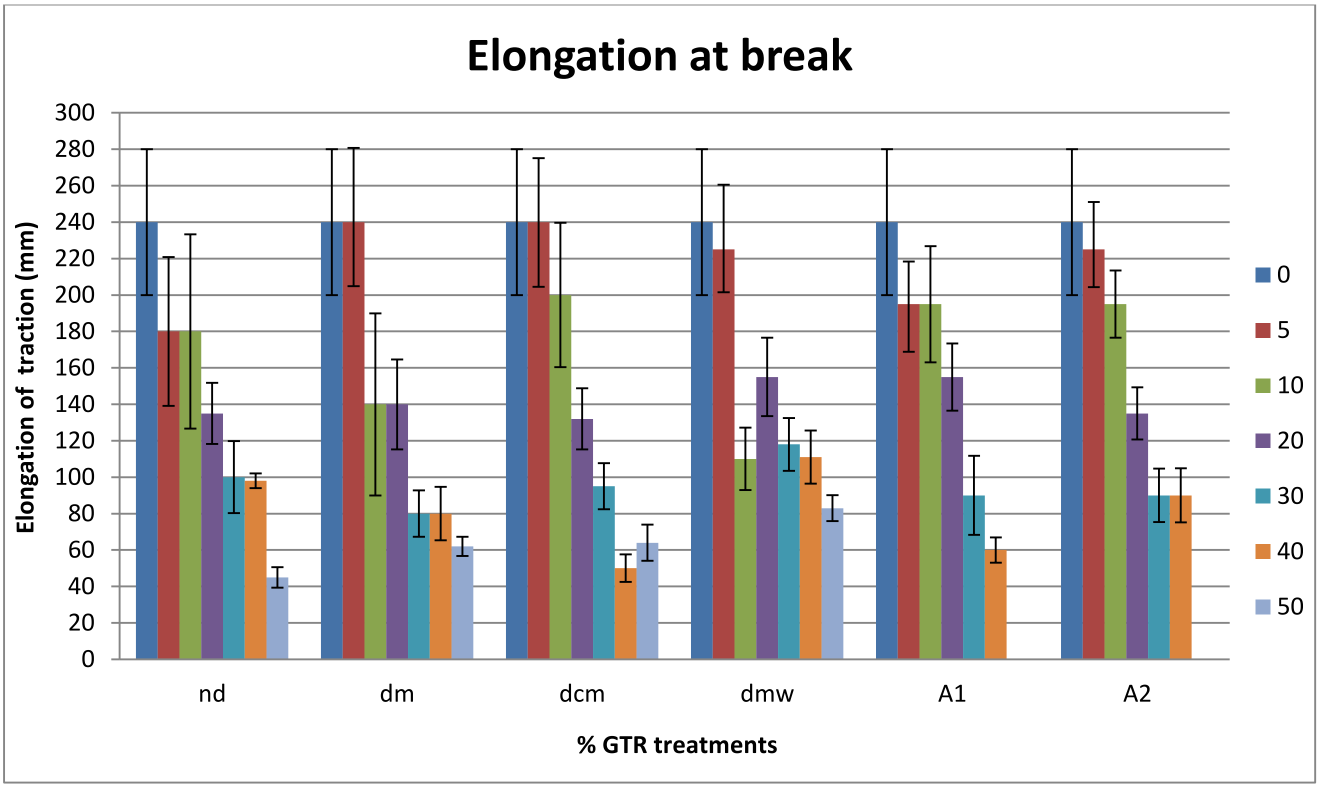


Figure 10b : Elogation at break values for BR/GTR of different GTR treatments

iii. Co-related gel fraction with crosslinking-density

The rubber gel fraction and crosslinking density of the vulcanizate were correlated between each other. So, based on the result that we obtained during the extraction of the sample using the soxhlet apparatus we were able to relate the degree of insolubility which was the gel fraction with the density of crosslinking that formed during the vulcanization process. Other than that, we also might relate the crosslinking density with the degree of swelling owned by these vulcanizates. Higher gel fractions means that the sample was less soluble with the acetone and the vulcanizate has low degree of swelling as the presence of those linkages restricted the movement of molecules. Moreover, these bonds linkage prohibited the penetration of the acetone which then reduced the solubility of the materials. Likewise, the high gel fraction values determined a great number of crosslinking bonds were being created. As shown in the following figure 11, we saw that the gel fraction of the vulcanizates increase or in other words the decrease of the sol fraction (i.e soluble fraction) with the %GTR means that high density of crosslinking were formed which supported our previous explainations on the increment of TS and YM values as well as the hardness of the vulcanizates due to the presence of these bonds.

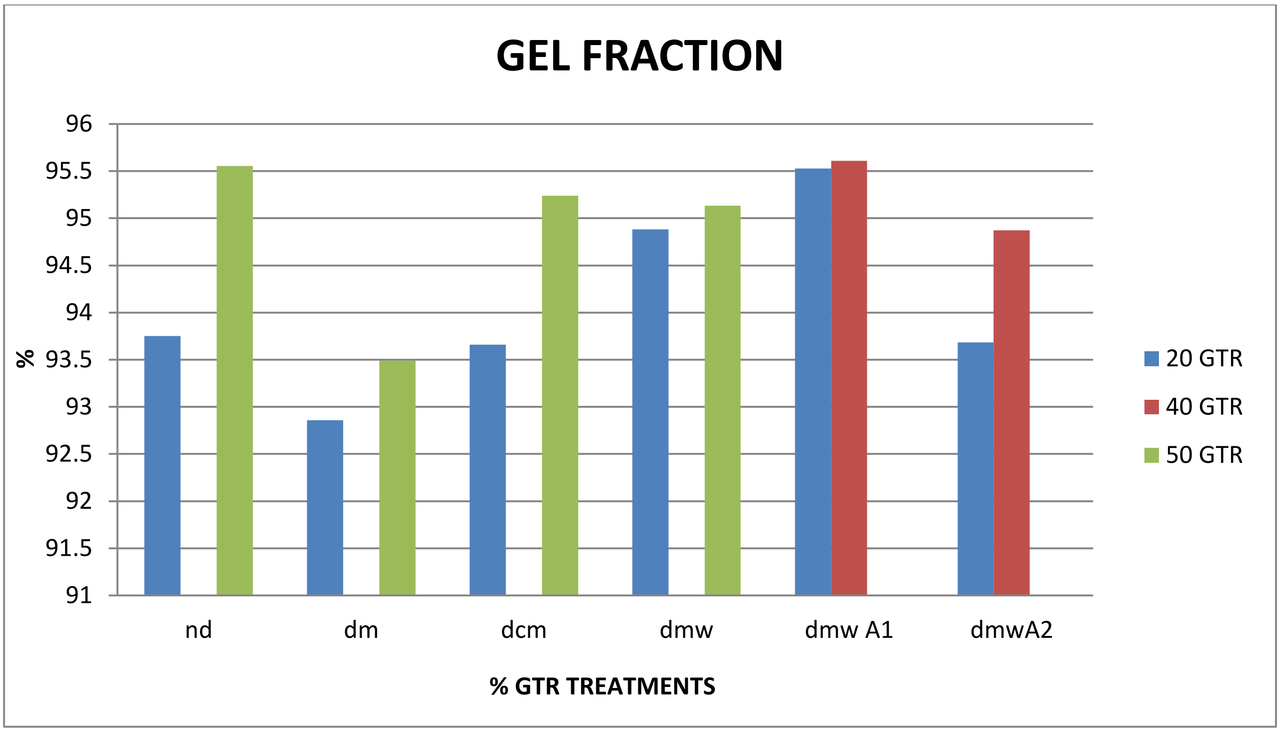


Figure 11 : Sol fraction values for BR/GTR of different GTR treatments

iv. Thermogravimetric analysis (TGA)

Thermal degradation of the vulcanizate could be investigated and analysed from the TGA curves as shown in the following figures. This process had been done in the nitrogen atmosphere without the presence of oxygen. As we could see from the figure 12a and figure 12b, there were two degradation peaks formed along the process for 50%GTR and 20%GTR respectively, same goes with the reference sample of 0GTR. The first peak was due to the volatilitzation of oil or any other low boling point components (27) of the vulcanizate while the second peak was corresponding to the thermal degradation of the polymer itself. Unfortunately, we cannot exactly obtained the amount of weight loss due to the volatile components and the weight loss due to the degradation of the polymers as the relative slowness of the oil evolution cause the polymer degradation to start before the low boiling point components totally evaporated. So, in this result, we assume that we had almost differentiate both of this occurrence and the results were tabulated in Table 3 (the obtention of these values were based on what being shown in figure 13a and figure 13b).

	Blends	Weight (mg)		First degradation peak		Second degradation peak		Total weight loss	
		Initial	Final	Weight loss (mg)	%	Weight loss	%	weight loss	%
0%	BR pure matrix	15.17	0.028	1.9122	12.6058	13.2298	87.2103	15.142	99.8161
	BR	15.77	0.8921	2.5146	15.9452	12.3633	78.3977	14.8779	94.3429
20%	nd	15.71	1.4685	2.7642	17.5951	11.4773	73.0587	14.2415	90.6538
	dm	15.76	1.4533	2.7941	17.729	11.5126	73.0492	14.3067	90.7782
	dcm	15.75	1.3362	3.0023	19.062	11.4115	72.4538	14.4138	91.5158
	dmw	15.73	1.5644	2.9599	18.8171	11.2057	71.238	14.1656	90.0551
50%	nd	15.72	2.2843	2.9302	18.64	10.5055	66.8291	13.4357	85.4691
	dm	15.86	2.2699	2.8274	17.8273	10.7627	67.8608	13.5901	85.6881
	dcm	15.89	2.2677	3.2489	20.446	10.3734	65.2824	13.6223	85.7284
	dmw	15.86	2.2422	3.3258	20.9696	10.292	64.8928	13.6178	85.8624

Table 3 : Amount of weight loss at each of the degradation peak

Based on the increasing percentage of the weight loss at the first peak for the 0%, 20% and 50% GTR as shown in table 3, we colud say that 50% GTR vulcanizate has higher amount of volatile and low boiling point components as the incorporated GTR contained a higher amount of additives that were originated from the tires production. But the second degradation peak showed the contrary. The percentage weight loss decrease as the amount of GTR introduced increases. This might due to the high weight loss that occured during the first degradation and high carbon black content inside the vulcanizate. The higher weight loss at the first resulted in the reduction of weight loss at the second one.

In comparison with the pure BR matrix and BR (0% GTR) vulcanizates, the weight loss at the first degradation peak for pure BR was low. So, here the presenced of the additives (zinc oxide, sulphur, strearic acid and redozon) during the making of vulcanizates increase the amount of volatile components results in the increase of the weight loss percentage. Besides that, the amount of total weight loss for these two were quiet significant. Almost 100% from the initial weight of pure BR matrix was decomposed while for BR vulcanizate, about 94% from its initial weight was lost and few percent was remained that may derived from the silicon oxide and other inorganic materials.

We also might comment on the time for both degradations to start. The first peak for 50% GTR started earlier than 0% GTR which corresponds to occur at lower temperature. This also means that the second degradation peak for 50% GTR to start earlier and ended faster than the 0% GTR.

As we compared generally between our reference of 0% GTR and 50% GTR irrespect to the type of treatments used, the total percentage of weight loss decreases as the amount of GTR increases. Significant reduction of the total weight loss from 94% to 85% means that there was an increase in the percentage of weight remained at the end of process. These showed that the amount of residues left were high as the amount of GTR increases. The residues left were mainly made up of silicion oxide and carbon black as well as inert fillers originated from the tire formulations. As the process was done in nitrogen gas, we cannot completely decomposed the carbon black that left to carbon dioxide as the oxidation process cannot occurred due to the absent of oxygen or air. Higher GTR added to the vulcanizate correspond to the increase in the carbon black content. The total weight loss at any of the treatments were about the same. So, this means that, the amount of residues left do not depend on the type of the treatments that the GTR went through.

Generally, we could determine the stability of the vulcanizates by observing the first derivative graphs that we obtained as in Figure 14. As all the curves moved and displaced slightly to the right from the reference sample of 0 GTR, the themal stability of the vulcanizates for all treatments are then positive.

In addition, as we compared the BR vulcanizate with the natural rubber (NR)/BR vulcanizate obtained from the test done by another student, we analysed that the BR used was not totally pure. It contained a certain amount of NR that can be seen from figure 15 at which the range for the first degradation of NR/BR vulcanizate occurred in the range of the first degradation for BR vulcanizate. This means that, the decomposition of NR was also conducted during the first decomposition process of BR vulcanizate together with the decomposition of volatile components. This could be proved by the Figure 16 that showed the first derivative curves for both of these vulcanizates. From this figure, two peaks were formed more or less at the same time. So, it was true that the first peak of BR vulcanizate was corresponding to the decomposition for both NR as well as the volatile components during this period of time. Hence, the existence of some of this NR improved the properties of the vulcanizates.

Figure 12a: Degradation curves of reference sample and 50%GTR of all treatments.

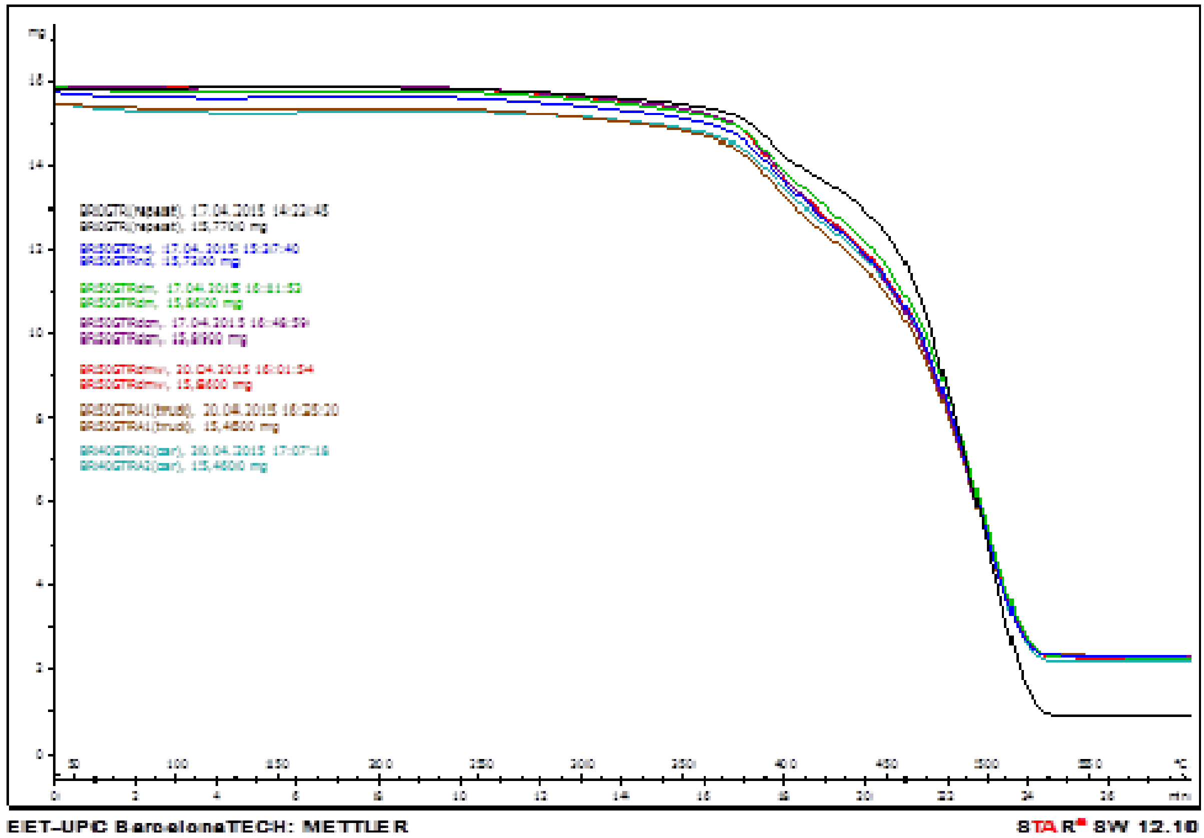


Figure 12b: Degradation curves of reference sample and 20%GTR of all treatments.

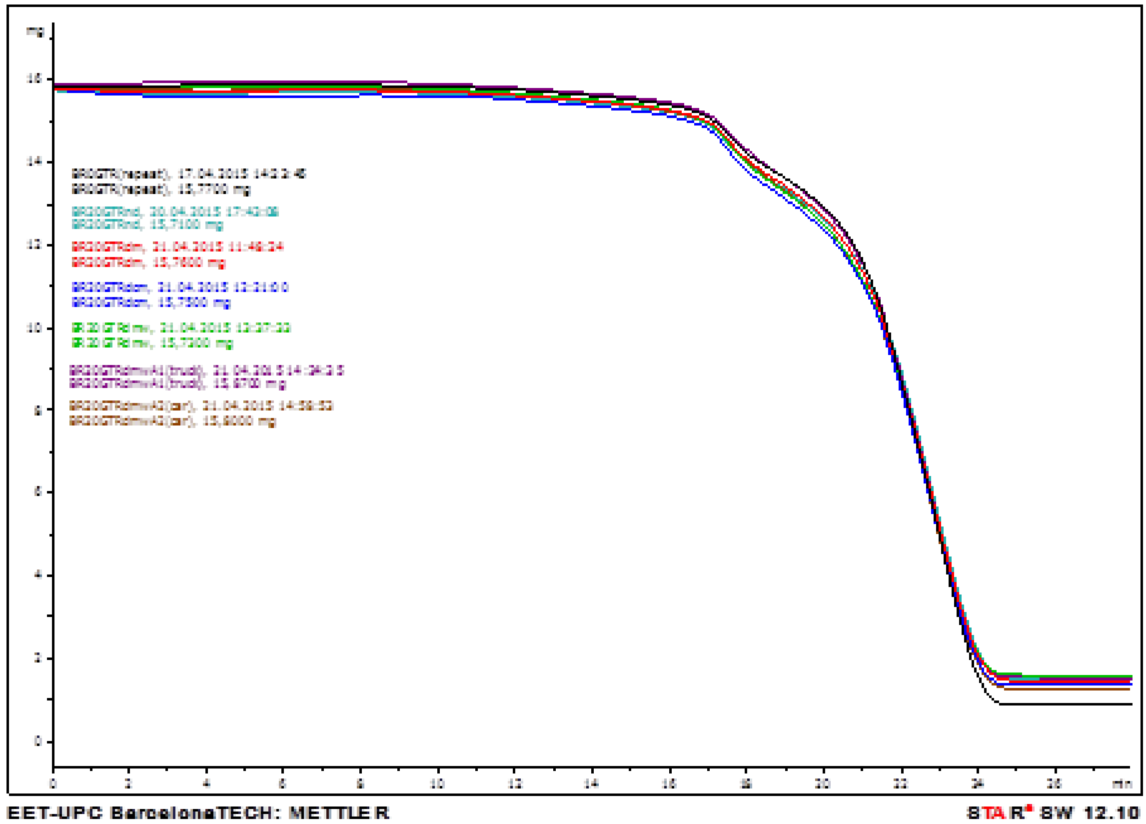


Figure 13a: Mass difference obtention from degradation curves of 50%GTR (with pure BR matrix)

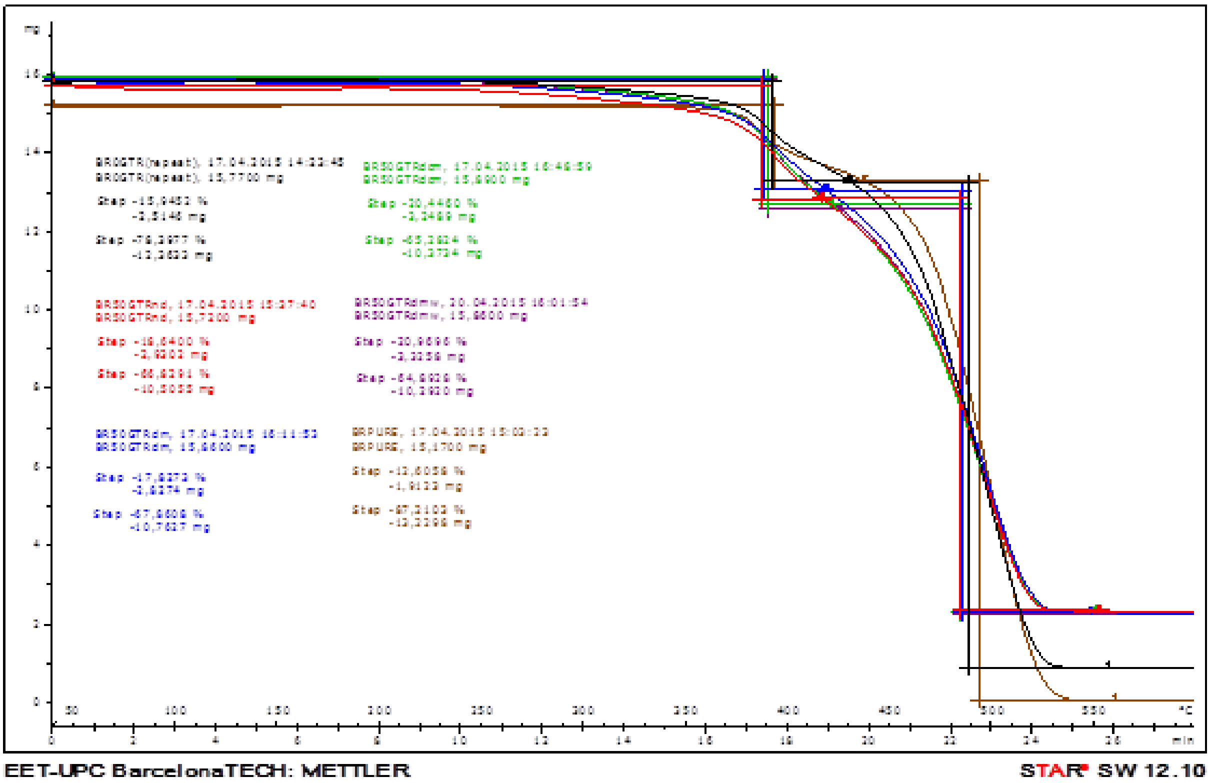


Figure 13b: Mass difference obtention from degradation curves of 20%GTR (without pure BR matrix)

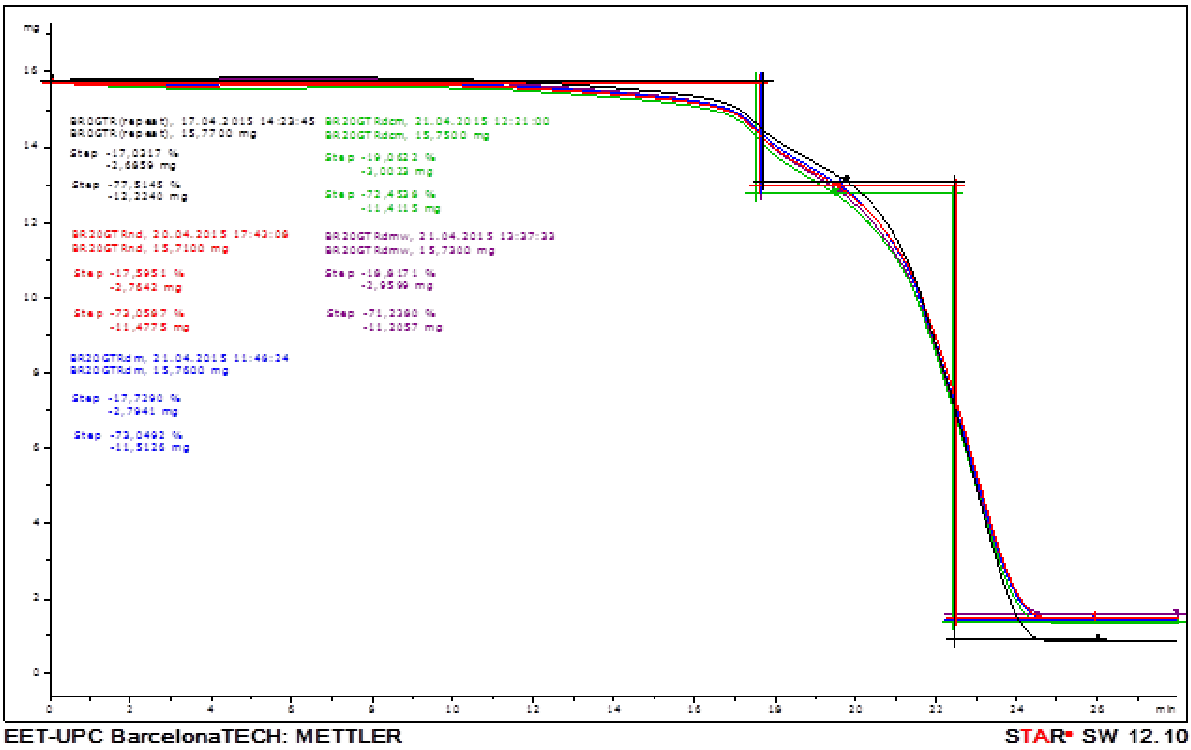
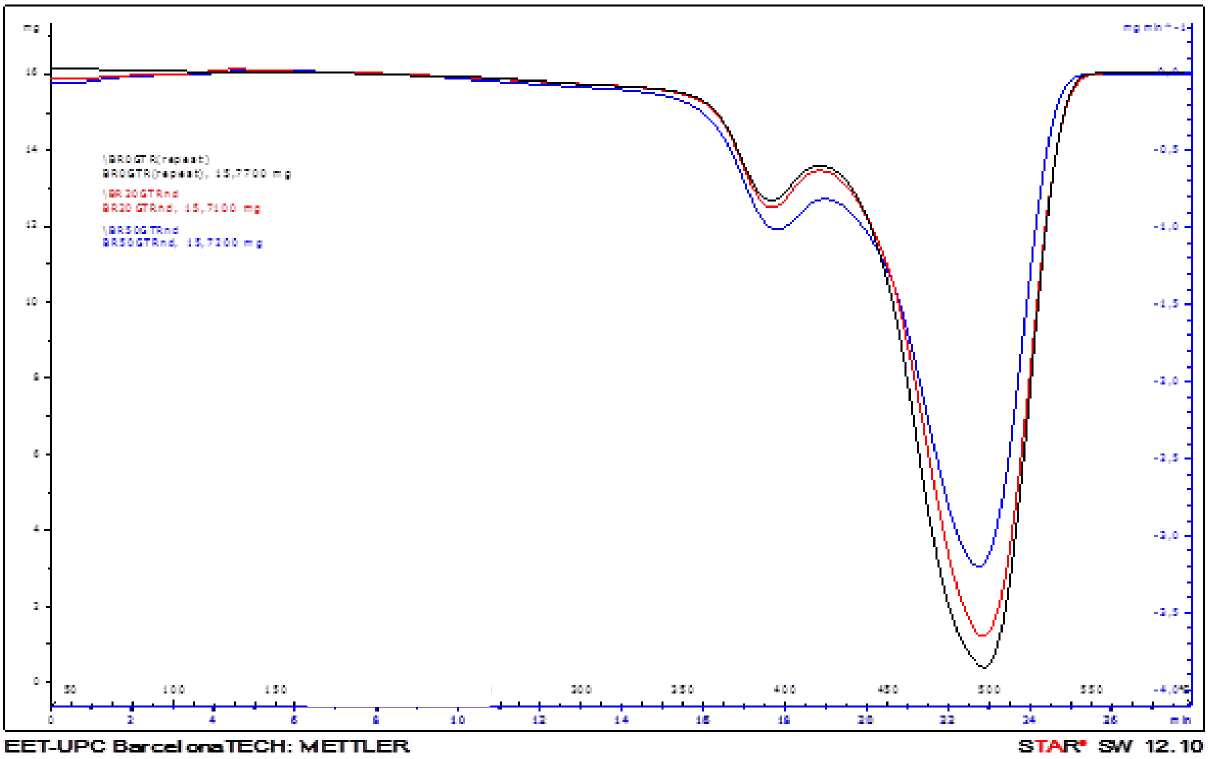
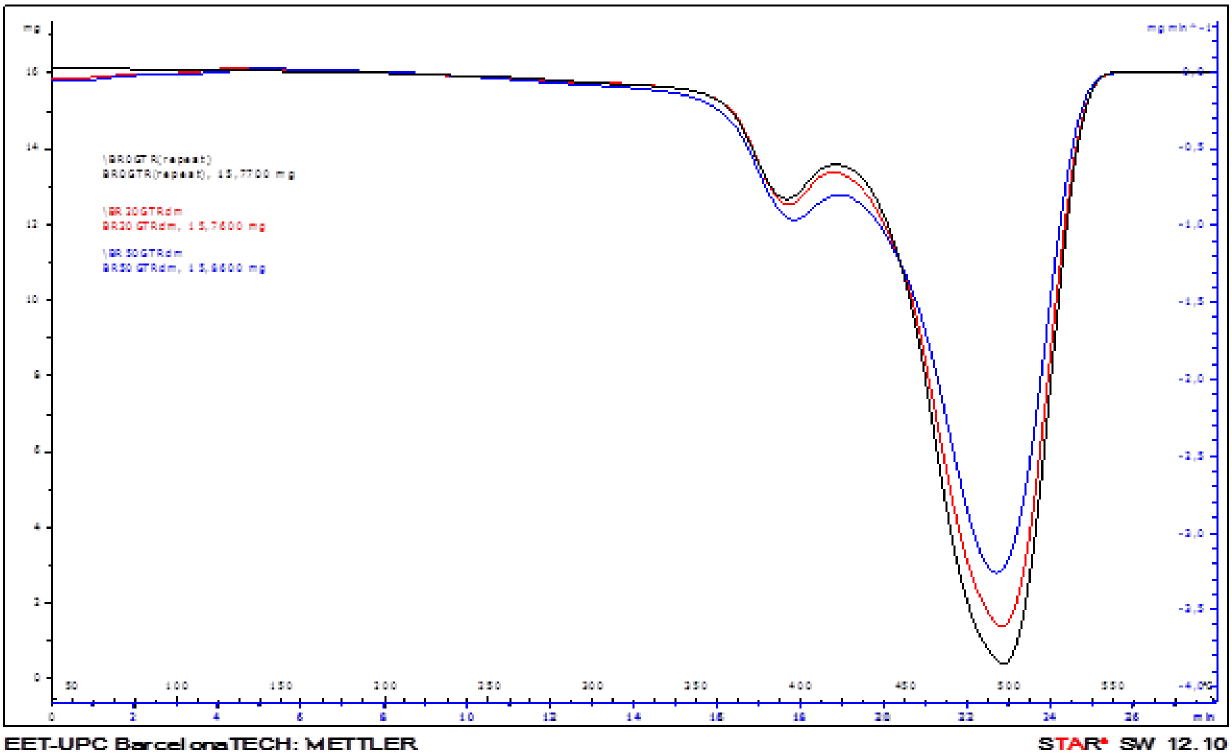


Figure 14: First derivative curves for each treatment

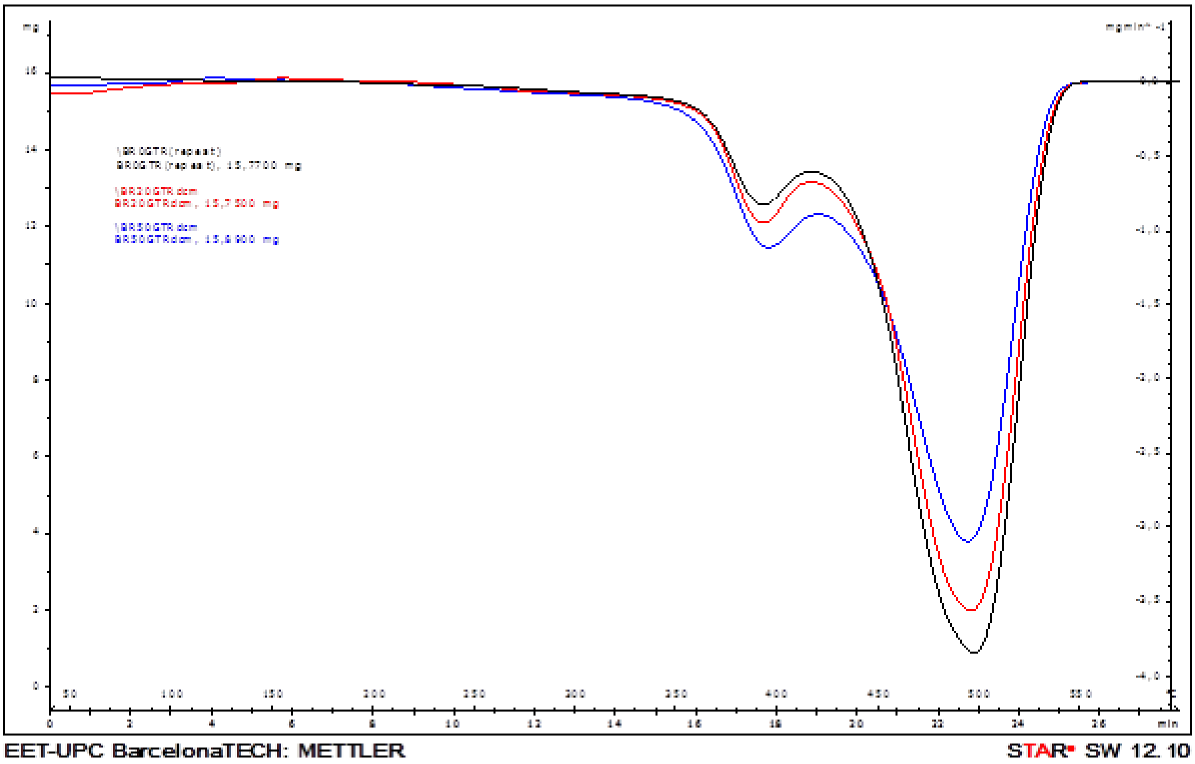
BR nd



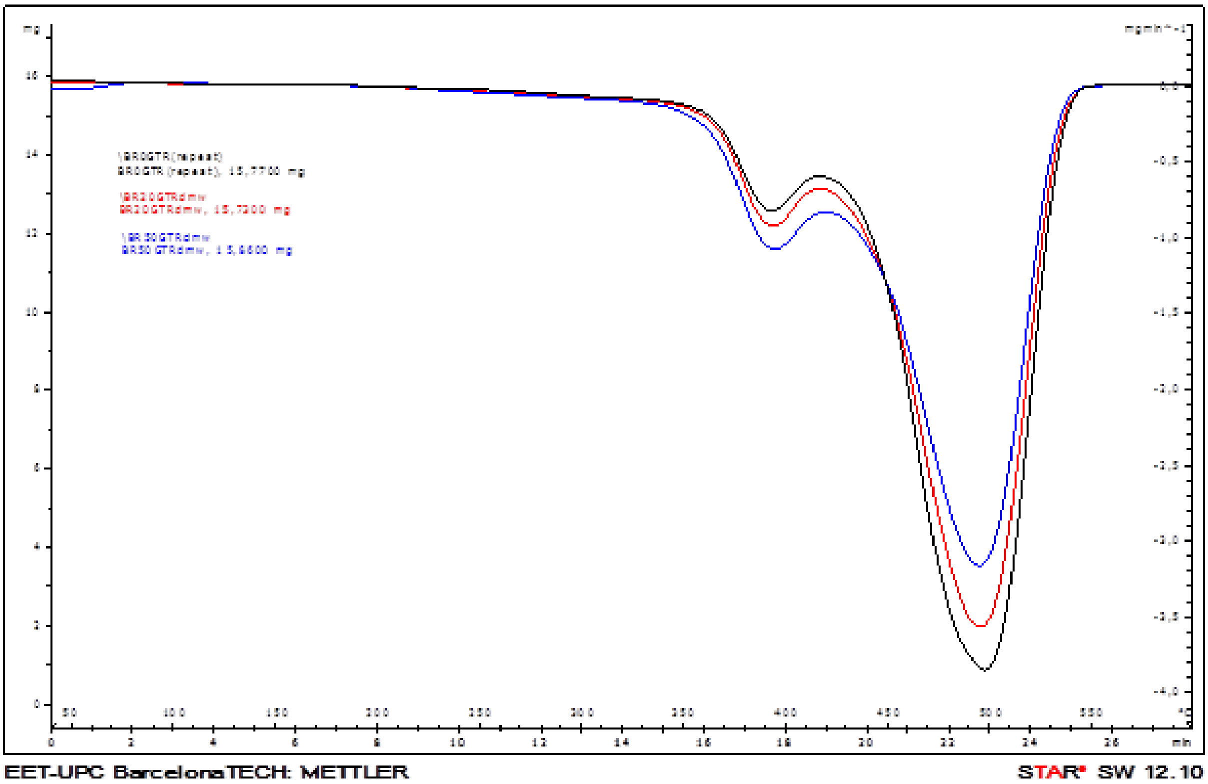
BR dm



BR dcm


mg
mgmin^-1
16
14
12
10
8
6
4
2
0
0,0
-0,5
-1,0
-1,5
-2,0
-2,5
-3,0
-3,5
-4,0
\BR0GTR(repeat)
BR0GTR(repeat), 15,7700 mg
\BR20GTRdcm
BR20GTRdcm, 15,7500 mg
\BR50GTRdcm
BR50GTRdcm, 15,6900 mg
50
100
150
200
250
300
350
400
450
500
550
0
2
4
6
8
10
12
14
16
18
20
22
24
26
min
EET-UPC BarcelonaTECH: METTLER
STAR SW 12.10

BR dmw


mg
mgmin^-1
16
14
12
10
8
6
4
2
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0,0
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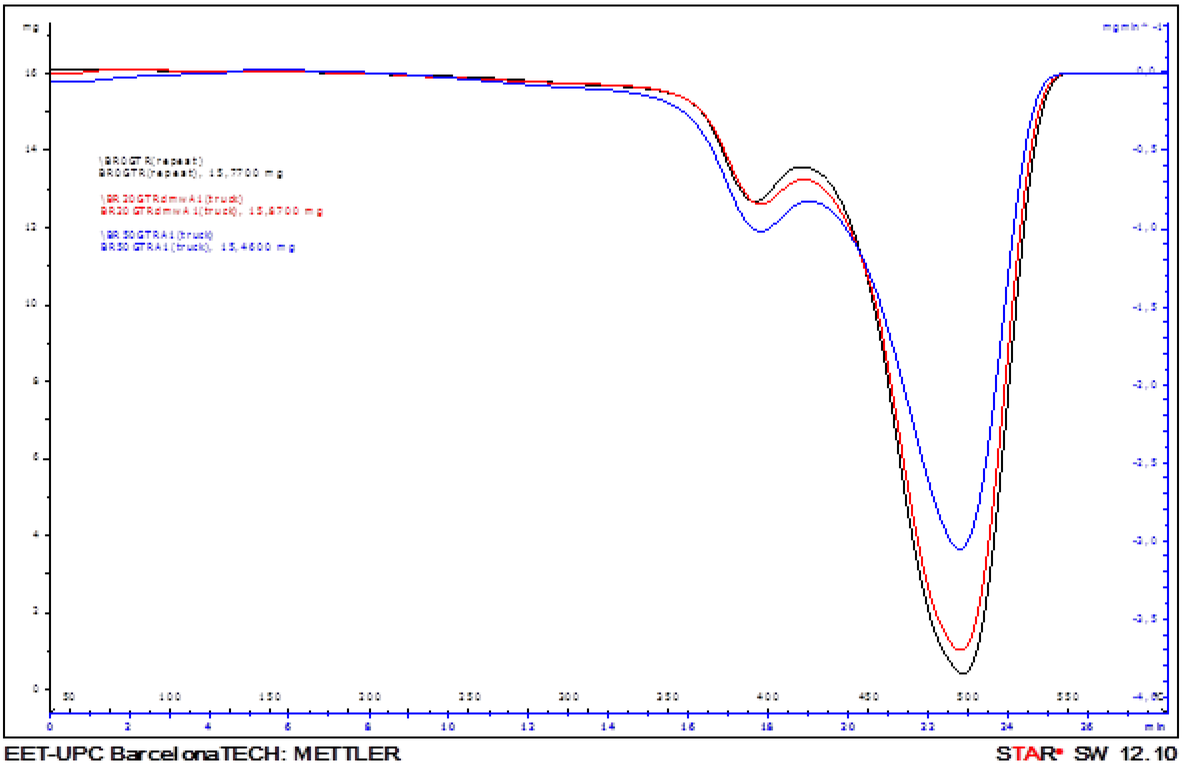
-1,0
-1,5
-2,0
-2,5
-3,0
-3,5
-4,0
\BR0GTR(repeat)
BR0GTR(repeat), 15,7700 mg
\BR20GTRdmw
BR20GTRdmw, 15,7200 mg
\BR50GTRdmw
BR50GTRdmw, 15,6600 mg
50
100
150
200
250
300
350
400
450
500
550
0
2
4
6
8
10
12
14
16
18
20
22
24
26
min
EET-UPC BarcelonaTECH: METTLER
STAR SW 12.10

BR dmwA1 (truck)



BR dmwA2 (car)

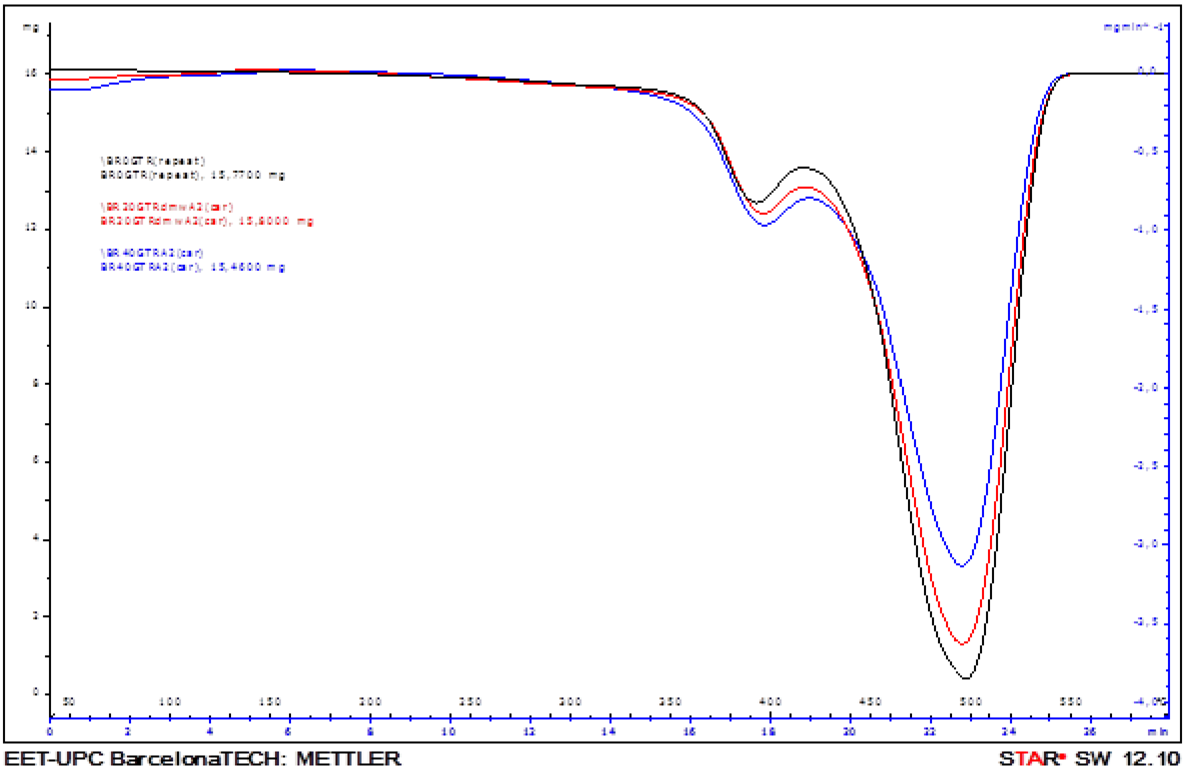


Figure 15: Determination of purity in BR

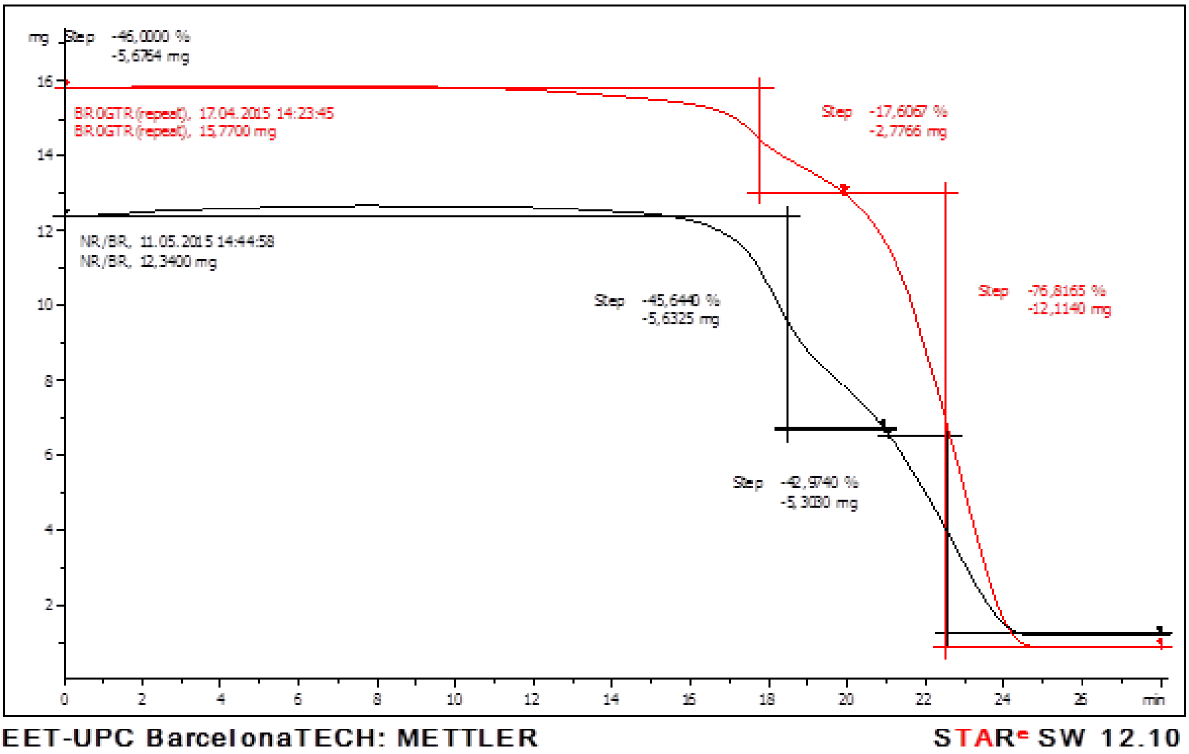
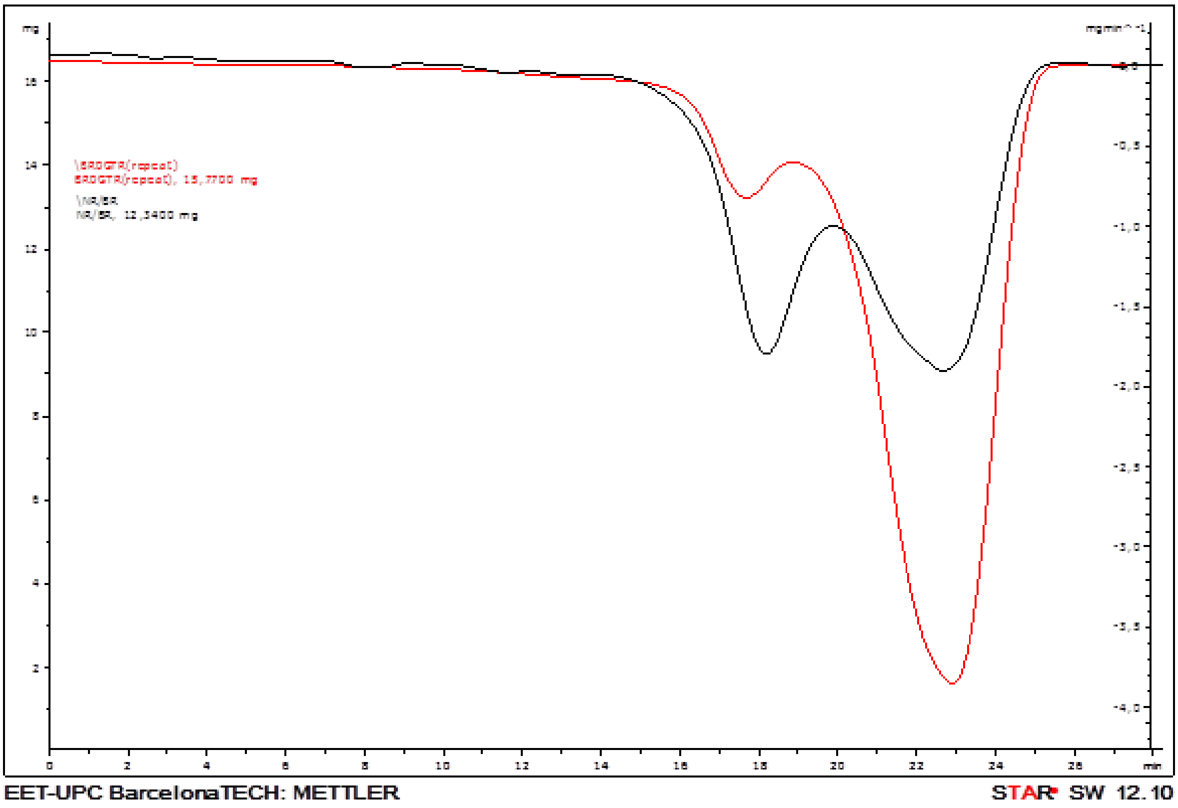


Figure 16: First derivative curves for NR/BR vulcanizate and BR vulcanizate

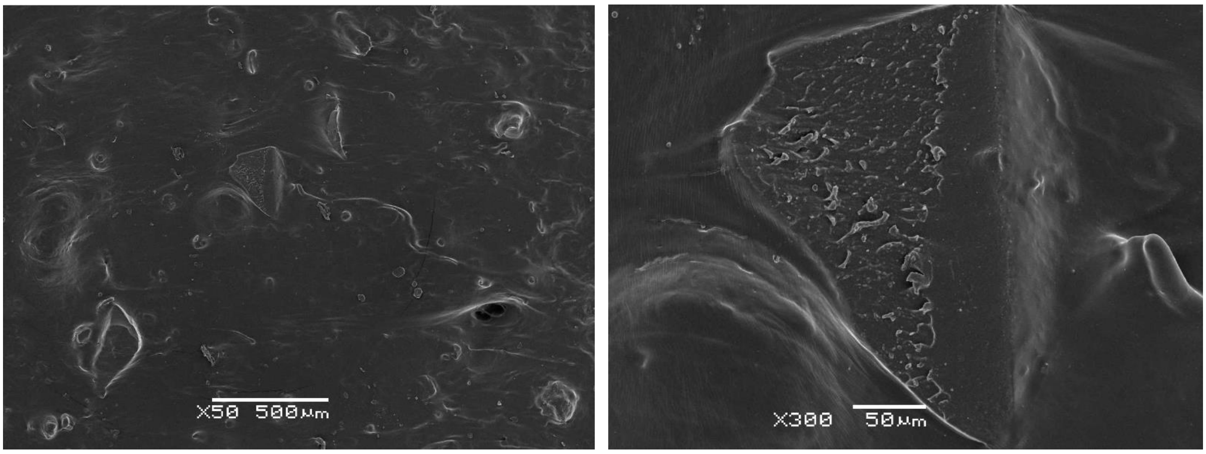


v. SEM study

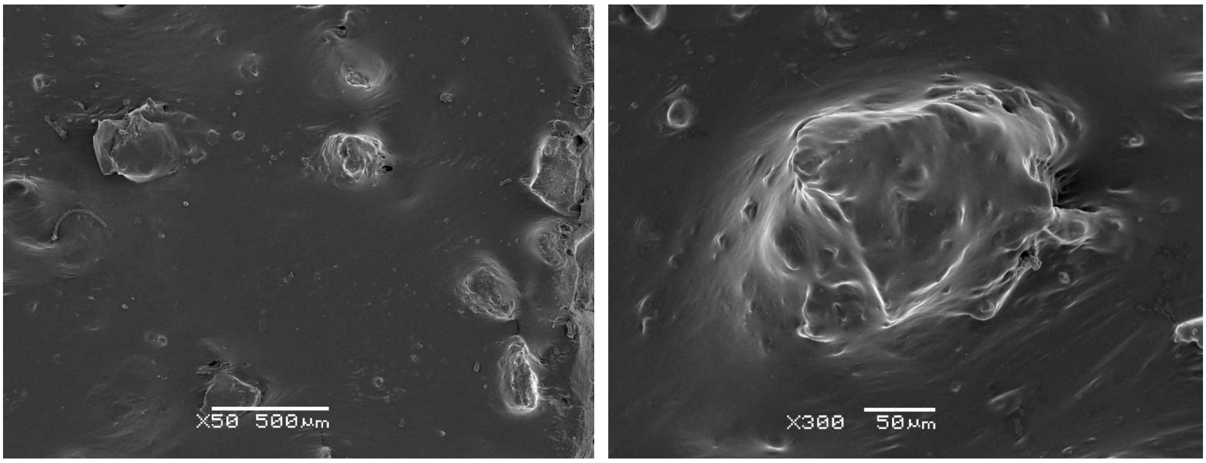
Generally, SEM gave us some information of the fractured structure that formed on the surface of the vulcanizates. As we could see, for the surface of the vulcanizate containing non-devulcanised GTR showed a morphology of homogeneity. Some cracks were formed and almost no aggregation by GTR were showed on the surface. An unsmooth surface can be seen as higher magnification was applied. This homogeneity helps in a smooth evolution and the distribution of the stress along the sample during tensile test.

In the case of BR/dmGTR and BR/dcmGTR, there were some aggregation of particles at certain points on the surface together with the holes surrounding at that points. These structures favored the breaking of the samples as the stress concentration might occurred as there were bad interactions between the particles. On the other hand, there were no cracks seemed to form on both surface of these vulcanizates.

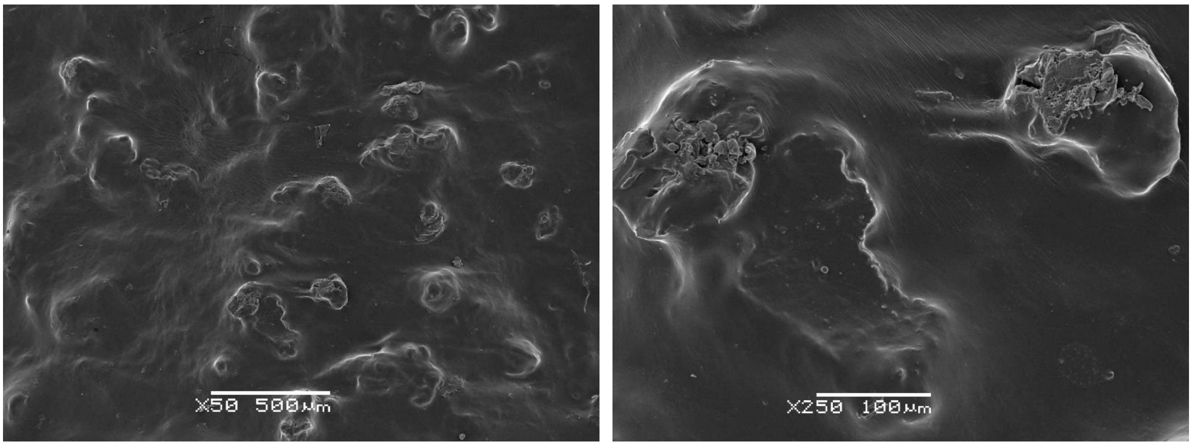
For the BR/dmwGTR, there were clearer image for the formation of cracks, holes and aggregation of particles that we could see. As higher magnification was applied, obvious cracks that concentrating at a point proved the stress concentration to be occurred at that point. The fracture that formed cause the vulcanizates to became less rubbery as they cannot elongate more due to the strong formation of crosslinking bonds that restrict the movements of the chains.



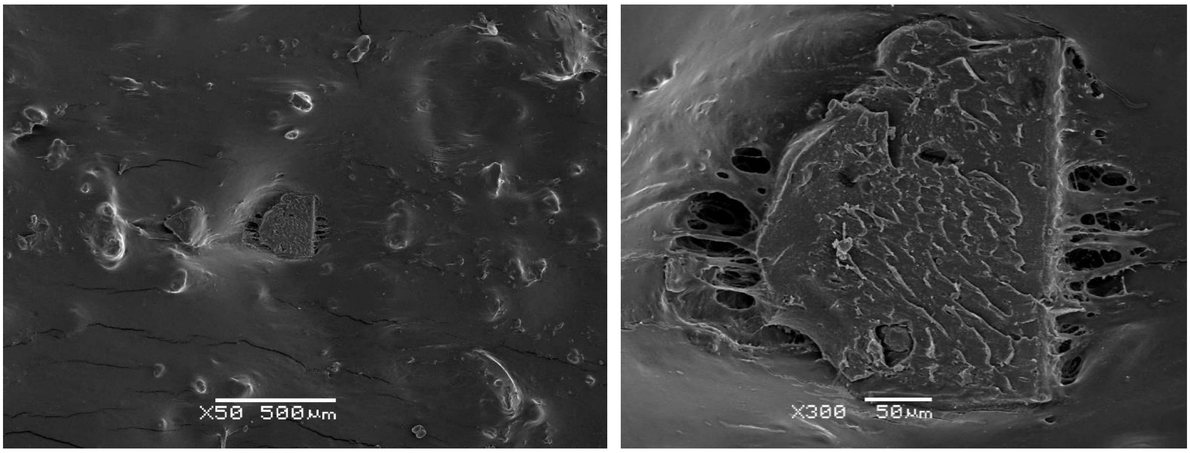
BR/20 ndGTR vulcanizate with x50 and x300 magnifications respectively.



BR/20 dmGTR vulcanizate with x50 and x300 magnifications respectively



BR/20 dcmGTR vulcanizate with x50 and x300 magnifications respectively.



BR/20 dmw GTR vulcanizate with x50 and x300 magnifications respectively.

5. Conclusions

The obtention of various behaviours on mechanical properties of the vulcanizates mainly determined by the amount of GTR that was incorporated with the BR virgin polymer matrix. Most of the treated GTR when incorporated with BR showed an increase in tensile strength and young modulus which also reduced their plastic deformation and the toughness. GTR treatment by devulcanized chemical mechanical process (dcm) gave higher value in both TS and YM make it the best process or treatment among the others although there was a limitation in the amount of GTR incorporated. The higher increase in the crosslinking density determined by the higher amount of insoluble gel fraction ensured an improved properties of the vulcanizates as they could withstand high stress when loads were applied during the tensile test due to the crosslinking bonds. The restricted movement of the chains caused the sample to exhibit strongness, rigidity and this was being verified by the values from the hardness test that had been obtained. Other than that, the positive stability of the vulcanizate was obtained in TGA test as the amount of GTR increases and also the residues that left after the process determined the presenced of carbon black which believed to aid in improved the tensile properties of the vulcanizates. Finally, the morphology resulted from SEM showed the surface structure of the vulcanizates that have some cracks, holes and aggregation of GTR that make the stress to be concentrated at certain points and reduced the amount of elongation that can be achieved as well as the toughness of the vulcanizates.

6. Recommendations

a. Investigate the effect of use different sizes of GTR in making the BR/GTR vulcanizates and analyse their behaviours.

b. Incorporation of accelerator together with the other components used in this project and compare the results obtained using the accelerator with the results obtained in this project.

c. Investigate the effect of two different time duration for vulcanization process using the same formulation of vulcanizates like in this project.

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