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MASTER THESIS

Master's degree in Advanced Materials Science and Engineering

**PROCESSING AND OPTIMIZATION OF PLA/RUBBER BLENDS
BASED ON WASTE TIRE RUBBER AND NATURAL RUBBER**



Report and annexes

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Resumen

Para hacer frente al problema de los residuos de plástico y participar en el desarrollo de una economía circular en la industria de caucho, la creación de materiales que contienen residuos de neumáticos, llamados ground tire rubber (GTR), para reforzar el ácido poliláctico (PLA), un termoplástico frágil y de base biológica, fue propuesta. La compatibilidad entre estos dos polímeros fue optimizada con el uso de caucho natural (NR) como tercer componente, con el objetivo de encapsular las partículas de GTR. Las mezclas fueron vulcanizadas dinámicamente con dicumyl peroxide (DCP) durante el proceso de mezcla por fundición. Los efectos de los parámetros de proceso (tiempo de residencia, temperatura de proceso) así como los parámetros de los materiales (tamaño de las partículas de GTR, proporción y origen del PLA y del caucho) sobre las propiedades mecánicas de las mezclas fueron investigados. El uso de un tamaño de partículas más fino (diámetro $<63 \mu\text{m}$) dio las mejores propiedades de tensión para cada tipo de mezcla con una base de PLA-GTR, con o sin NR. Además, remplazar 1/3 del NR por GTR en las mezclas ternarias PLA/NR/GTR permitió aumentar el módulo elástico, el límite elástico, la tenacidad y la resistencia al impacto hasta una incorporación de 15 wt.% de caucho reciclado. Los resultados fueron atribuidos a (i) una encapsulación eficaz que permite una distribución homogénea de las partículas de GTR, (ii) una buena compatibilidad entre el NR y ambos PLA y GTR (iii) un refuerzo mecánico debido al fenómeno de cristalización inducida por deformación del NR.

Resum

Per tal de fer front al problema dels residus de plàstic i participar al desenvolupament d'una economia circular en la indústria del cautxú, s'ha proposat la creació de materials amb residus de pneumàtics, anomenats "ground tyre rubber" (GTR), per reforçar el polímer àcid polilàctic (PLA), un termoplàstic fràgil i de base biològica. La compatibilitat entre aquests dos polímers s'ha optimitzat amb l'ús de cautxú natural (NR) com a tercer component, amb l'objectiu d'encapsular les partícules de GTR. Les mescles han sigut vulcanitzades dinàmicament amb "dicumyl peroxide" (DCP). S'han investigat els efectes dels paràmetres de procés (temps de residència, temperatura de procés) així com els efectes dels paràmetres dels materials (mida de les partícules de GTR, proporció i origen de l'PLA i de el cautxú) sobre les propietats mecàniques de les mescles. Les millors propietats mecàniques s'han obtingut amb l'ús d'una mida de partícules més fines (diàmetre <63 micres) per a cada tipus de mescla amb una base de PLA-GTR, amb o sense NR. A més, el fet de reemplaçar 1/3 de NR per GTR en les mescles ternàries PLA / NR / GTR ha permès augmentar el mòdul elàstic, el límit elàstic, la tenacitat i la resistència a l'impacte fins a una incorporació de 15 wt.% de cautxú reciclat. Els resultats han sigut atribuïts a (i) una encapsulació eficaç que permet una distribució homogènia de les partícules de GTR, (ii) una bona compatibilitat entre el NR i ambdós PLA i GTR (iii) un reforç mecànic a causa del fenomen de cristal·lització induït per deformació de l'NR.

Abstract

To face the problem of plastic wastes generation and to participate in the development of a circular economy of the rubber industry, the design of materials incorporating waste ground tire rubber (GTR) to toughen the Polylactic Acid (PLA), a brittle biobased thermoplastic, has been proposed. The compatibility between these two polymers was optimized by using natural rubber (NR) as a third component, aiming to encapsulate the GTR particles. The blends were dynamically vulcanized with dicumyl peroxide (DCP) during melt-blending. The effects of the processing parameters (residence time, processing temperature) as well as the material parameters (GTR particles size, PLA and rubber content and origin) on the mechanical properties of the blends were investigated. The finest GTR particles size (diameter $<63 \mu\text{m}$) was found to render the best tensile properties for all type of PLA-GTR based blend, with or without NR. In addition, the replacement of 1/3 of the NR by GTR in ternary PLA/NR/GTR blends resulted in the improvement of the elastic modulus, the yield strength, the toughness and the impact strength using up to 15 wt.% of wastes rubber. The results were ascribed to (i) an efficient encapsulation allowing a homogeneous distribution of the GTR particles, (ii) a good compatibility of NR with both PLA and GTR and (iii) a mechanical reinforcement due to strain induced crystallization of the NR.

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Hector Jeannot

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Table of abbreviations

PLA	Polylactic Acid
NR	Natural Rubber
GTR	Ground Tire Rubber
DCP	Dicumyl Peroxide
E_T	Tensile modulus
σ_y	Yield strength
ε_b	Strain at break
U_T	Energy at break
SIC	Strain Induced Crystallization
TPE	Thermoplastic elastomer
TPV	Thermoplastic vulcanizate
T_g	Glass transition

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1. Preface

1.1. Origin of work

The student is involved in the research group Eco-friendly Plastics and Composites (e-PLASCOM, 2017-SGR 1141) that belongs to the Centre Català del Plàstic (CCP). The main objective of the group is the reduction of the environmental impact of plastic products, using recycled or renewable raw materials, as well as sustainable manufacturing technologies. In this context, the strategic objectives are articulated around three axes:

- Axis 1 - Materials: research on natural, bio-based, and biodegradable polymers; natural fillers and fibers (at a micro- and nanoscale); and the thermal, mechanical, and rheological characterization of these materials.
- Axis 2 - Design, processing, and service performance: application of eco-design concepts and novel thermoplastic processing techniques, with a focus on component weight reduction.
- Axis 3 - Plastic Waste: study on recycling and valorization of plastic waste.

In order to strengthen the axis 3 of the research activities of the PLASCOM group, a project named “Towards a Circular Economy of Rubber” (CEcoR), funded by the European Union in the frame of the H2020 Marie Skłodowska-Curie actions, has been initiated in November 2019. The CecoR project aims to develop a circular economy of rubber for the automotive industry. It addresses key research areas such as sustainable mobility, advanced materials and advanced manufacturing. The objective will be achieved by:

- Understanding and optimization of mechanical devulcanization of rubber by developing a multiscale approach of the process (WP1) and a bio-mechanical devulcanization process (WP2).
- Implementing a dynamic re-vulcanization process to manufacture advanced PLA based green materials by the recycled rubber wastes (WP3).
- Scale-up of both developed manufacturing techniques and materials (WP1, WP2, WP3) to industrial processes economically sustainable for the automotive industry (WP4).

In this context, this Master thesis is aimed to contribute to the CEcoR project, by continuing the works done on the WP3 axis with the production and optimization of new PLA/rubber blends based on natural rubber and waste rubber.

1.2. Motivation

Due to its high elasticity and resistance, rubber is an extensively used polymer in the industry, especially in the automotive field for the production of tires. That production causes mega-tons of rubber wastes to be treated every year. However, unlike the thermoplastics, vulcanized rubber cannot be melted to be reprocessed, making its recycling more complicated. Nowadays, rubber waste is frequently burned or landfilled, in spite of its non-biodegradable nature and the pollution of the oceans it generates, or transformed into granulates to be re-used as components in floors, cements or walls. This linear model is not sustainable and solutions have to be found to include rubber in a circular economy, upcycling the wastes.

After a devulcanization process consisting in the breakage of the sulfur bonds linking the rubber chains, rubber wastes can be regenerated into new industrial components. A recycling solution consists in blending them via dynamic re-vulcanization with other polymers, like fresh rubber having a close structure or conventional thermoplastics (PE, PS, PVC), as shown in Figure 1-1. The waste is thus valorized and considered as a raw material, starting a new product’s life cycle and saving natural resources while being financially advantageous. Blending waste rubber with conventional thermoplastics remains, however, non-ecological due to the synthetic nature of these polymers. For that reason, this project proposes the recycling of Ground Tire Rubber (GTR), blending them via dynamic vulcanization with the bio-sourced thermoplastic Polylactic acid (PLA) and Natural Rubber (NR), with the aim of toughening PLA and opening applications in the non-tire automotive industry.

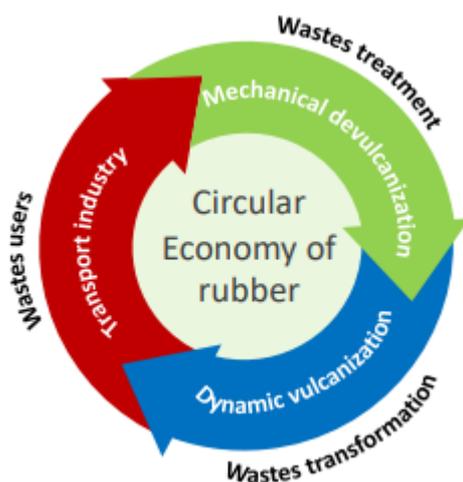


Figure 1-1 : Schematic view of the proposed circular economy of rubber showing the three main steps: (i) waste treatment by mechanical devulcanization, (ii) waste transformation by dynamic vulcanization and (iii) utilization of rubber waste-based product.

2. Introduction

Polymeric based materials, namely plastics and rubber, are widely used as a cheap and easy to process material. Through the years, it has become omnipresent in the objects surrounding us, from clothing to crisp packets, and electronic equipment to car parts (tires, bumpers, O-Rings, airbags, seals, mats...). Indeed, they can be of different nature and can be made into all sorts of shapes, colors and sizes. However, their abundant use is not compatible with the scope of sustainable development for several reasons. Firstly, the vast majority of plastics are made of fossil sources, which are facing depletion and scarcity issues, especially petroleum [1]. Secondly, the massive production of polymers leads to huge amounts of plastic wastes. For instance, the rubber industry generates mega-tons of rubber wastes each year in Europe (3,6 mega-tons in 2018 [2]), ending up mostly in landfills and oceans, which represents an important ecological risk.

Hence, the development of biobased and biodegradable polymers is needed and currently studied. Furthermore, recycling solutions must also be investigated to limit the waste amount. In the field of elastomers, researchers focused on various alternative solutions which would limit the materials environmental impact. Indeed, rubber products such as tires are not recyclable and the rubber industry generates mega-tons of rubber wastes each year in Europe [3]. These solutions include the creation of thermoplastic vulcanizates (TPVs) mixing fresh rubbers with bio-based thermoplastics such as polylactide (PLA), or conventional thermoplastics with waste tire rubber particles. The challenge remains to achieve relevant properties and a cost-effective process for these materials, making them competitive against conventional polymers. To this end, several parameters can be taken in account, for instance the use of additives and compatibilization agents, the rubber content and nature, the process parameters and the large-scale processability.

To give an oversight of this chapter, at first, an overall description of the two raw materials involved in the blends of interest, namely polylactide (PLA) and rubber, will be given. Especially, their manufacturing processes, thermomechanical properties, aging behavior and recyclability will be discussed. Then, literature investigating several types of binary blends made of these materials, including the incorporation of waste rubber or fresh rubber in petroleum- or bio-based thermoplastics are presented. Thereafter, the properties and limits of ternary blends of waste rubber, fresh rubber and thermoplastic are introduced, and lastly the objectives and scope of this work will be explained.

2.1. PLA: a promising biobased thermoplastic

Within the frame of the sustainable development, alternatives to petroleum based polymeric materials as well as solutions to waste disposal are to be considered. For this purpose, biodegradable and biobased polymers, that is to say polymers that can break down by bacterial decomposition process or abiotic factors (light, temperature, moisture...) to result in natural byproducts and that are derived from natural resources, have recently gained much interest. Indeed, their use to replace conventional polymers such as PS, PE and PP would lead to reducing the environmental impact of plastic production and waste.

One of these biomaterials is the polylactide (PLA). PLA is a biodegradable linear aliphatic thermoplastic polyester derived from biomass such as sugar cane, corn or beet. More precisely, the starch extracted from this biomass can be fermented by bacteria to synthesize the monomers D- and L-lactic acid, which will then be polymerized by polycondensation to obtain PLA. Thanks to its excellent physical and mechanical properties, it could be used to replace conventional polymers for some applications. It is also known for its good biodegradability, since it is able to break down by hydrolytic scission to its monomeric form, lactic acid [4]. Moreover, its production is energy saving, as PLA requires 25–55% less energy to produce than petroleum-based polymers [5].

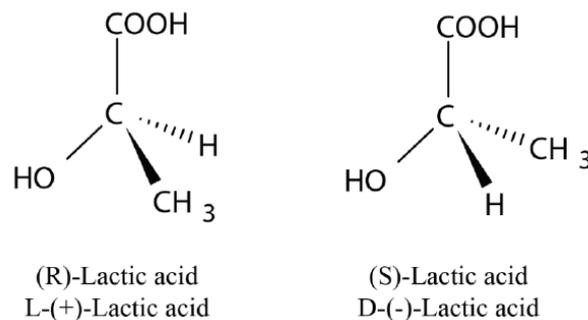


Figure 2-1 : D- and L-lactic acid, two enantiomeric monomers [6]

Due to its initial important production costs, the starting applications of PLA have been focused on high value products such as medical devices, since it has an excellent biocompatibility. This included drug delivery systems and tissue engineering, among others. But from 1990 and the discovery of the lactide ring opening reaction, a commercially viable production has been considered. Due to its transparency and relatively good mechanical properties, PLA has a high potential for food packaging for short life applications [7].

Nevertheless, some drawbacks are remaining regarding the properties of PLA, such as its high brittleness and poor crystallization behavior, that makes its large scale commercialization challenging [8].

2.1.1. Thermal stability of the melt

PLA has the advantage of being suitable for various processing technologies, such as drying, extrusion, injection molding, injection stretch blow molding, film and sheet casting, extrusion blown film, thermoforming and foaming, among others. However, processing effects on PLA is an important issue. The polymer must possess adequate thermal stability to prevent degradation of its molecular weight (Mw) and physical properties. PLA is known to undergo thermal degradation at temperatures above 200 °C by various mechanisms, including hydrolysis, lactide reformation, oxidative main chain scission, and inter- or intramolecular transesterification reactions. PLA degradation is dependent on time, temperature, low-Mw impurities, and catalyst concentration [5].

Thus, when extruding and injection molding PLA, the process parameters have to be thought to optimize the properties of the polymer, like its crystallinity but also its molecular weight. In the study of R. Pantani et al. [9], it was found that extrusion did not induce significant changes in low shear rate viscosity of the polymer, whereas injection molding caused a noticeable lowering in viscosity, which is a clear indication of a lower molecular weight due to mechanical and thermal degradation. Indeed, in injection molding, polymers are processed at high temperatures, pressures and shear rates before to be cooled to the ejection temperature [10]. In addition to the induced degradation, these processing conditions significantly affect the crystals nucleation and growth and consequently the spherulites number and size.

2.1.2. Thermomechanical properties in the solid state

2.1.2.1. Properties of amorphous PLA

Some of the mechanical properties of PLA, such as the Elastic modulus and the tensile strength, are usually comparable to those of PS or PET, even though it can be tailored by material parameters such as the molecular weight, the stereoregularity, the crystallinity and the degree of orientation of the crystallites, most of which depend on the processing conditions. Amorphous PLA is defined as a stiff and brittle polymer with low strain at break (from 2 to 8%) which fractures through crazing mechanism under uniaxial tensile loading. Numerous authors reported a Young's modulus ranged from 1 to 4 GPa and a tensile strength between 50 and 90 MPa [6]. The impact resistance values were reported using

Izod impact tests for amorphous and annealed PLA samples [11], and the notched strength ranged from 17 to 26 J/m for amorphous samples and from 32 to 70 J/m for annealed samples.

2.1.2.2. Effect of PLA crystallization on thermomechanical properties

PLA is known to have a slow crystallization rate, and thus a high crystallization half time. That is why obtaining an injection molded PLA article with high crystallinity remains a challenge [12]. Several properties of polymers depend on their crystallinity, such as the impact resistance and the mechanical resistance at high temperatures, two crucial factors to account for the PLA commercialization. Indeed, the Heat Deflection Temperature (HDT) of an amorphous polymer is mostly determined by its glass transition (T_g), and thus related to the mobility of the polymer segments. Hence, a high crystallinity would limit the segments motion in the amorphous phase and therefore increase the HDT [13].

However, a high crystallinity in PLA can also lower other mechanical properties, like the biodegradability or the impact strength. It has been found that the impact strength of PLA varies inversely with the percent crystallinity [12]. Crystallites can, indeed, act as stress concentrators, which means that in some small volumes of the material, the stress will be much greater than the average stress applied to the whole sample. Thus, failure can occur at the lamellae boundaries [10]. Another explanation of this impact strength reduction is that crystallites also reduce multiple crazing and shear yielding, which are both energy-dissipative mechanisms of polymer matrices playing a role in the impact strength.

Nevertheless, the impact resistance also depends on the number and the size of the crystallites, as it is inversely related to spherulite size. Blends with lower crystallinity and with smaller and less perfect spherulites usually have an improved impact behavior [10]. These parameters can be tuned by controlling the cooling rate and the nucleation time [14], and a compromise between impact strength and HDT must be found by tuning the crystallinity of PLA [12].

On the other hand, the influence of annealing on PLA/PC blends has been studied [15]. Annealing at a temperature higher than T_g may be used to increase the crystallinity. As expected, it has been found that annealing, by increasing the crystallinity, raised the HDT under 1.82 MPa of neat PLA from 48°C to 65°C. But surprisingly, the impact resistance also increased with the crystallinity of PLA for every PC content, even for neat PLA. The change in impact strength caused by annealing could be explained by yielding mechanism as proposed by Nimmer [16], [17]. According to this principle, the ability to sustain the high local stress during the impact was significantly improved due to the dramatic increase of crystallinity of PLA, so the plastic deformation was initiated and developed to the entire material,

resulting in the ductile fracture. The same trend, that is to say an increase of impact strength with high crystallinity, has been obtained by G. Perego et al. in their work [18].

Besides the processing conditions, the crystallization of PLA can be tailored by additives such as nucleating agents. For instance, the efficiency of talc and clay, two mineral nucleating agents, has been emphasized [19]. Another parameter having an influence on the crystallization ability of PLA is the crosslinking density. PLA/PBS blends were manufactured in presence of DCP and the crystallinity of PLA was revealed to be enhanced by the addition of DCP [20]. Indeed, some crosslinked or grafted structures were generated in the matrix, acting as nucleating points.

2.1.2.3. Effect of PLA physical aging on thermomechanical properties

One of the drawbacks of PLA is its performance in terms of durability, that are limited by multiple chemical aging mechanisms such as thermal decomposition, hydrolysis, photo-oxidation, natural weathering and thermo oxidation at high temperature [5]. Moreover, the high physical aging kinetics in amorphous PLA has drastic effect on its mechanical properties. Physical aging on PLA results in the increase of the stiffness and the tensile strength, while the elongation at break is strongly reduced, leading to a ductile to brittle transition [6].

The influence of accelerated weather aging on the mechanical and physical properties of neat PLA has been reported [21]. For that purpose, the neat PLA samples underwent accelerated aging using UV irradiation and water spray at 50 °C for four different time intervals (250, 500, 750 and 1000 h). A reduction in tensile strength, flexural strength, Young's modulus, and flexural modulus from their mean values for neat PLA with increased aging duration was observed. Impact strength (IS) of neat PLA was also found to decrease with increased accelerated aging time.

Recently, D. Rasselet et al. [22] have reported PLA aging in atmospheric conditions with the absence of water and UV light. In this study, the oxidative degradation of PLA induced at moderate temperatures (i.e. below the melting temperature of PLA) and for more than 500 h has been investigated. The authors concluded, firstly, that the hydrolysis aging can be neglected in air, and secondly, that the thermal oxidation mechanism of PLA at low temperatures ($T < 160$ °C) leads to a random chain scission process, responsible for the decrease of the PLA molecular weight (Mw) and thus a degradation of the physical and mechanical properties of the polymer.

2.1.2.4. Effect of crosslinking agent on thermomechanical properties

The crosslinking can also play a role on the mechanical performances of PLA. The effects of crosslinking of PLA induced by adding small amounts of crosslinking agent triallyl isocyanurate (TAIC) and dicumyl peroxide (DCP) has been investigated [23], and the results showed that a low content of TAIC and DCP (0,15wt% and 0.2wt% respectively) was responsible for the initiation of PLA crosslinking. The consequences of crosslinking of PLA are an enhanced tensile modulus and tensile strength. On the other hand, it also leads to the material embrittlement, with a decrease of the elongation at break.

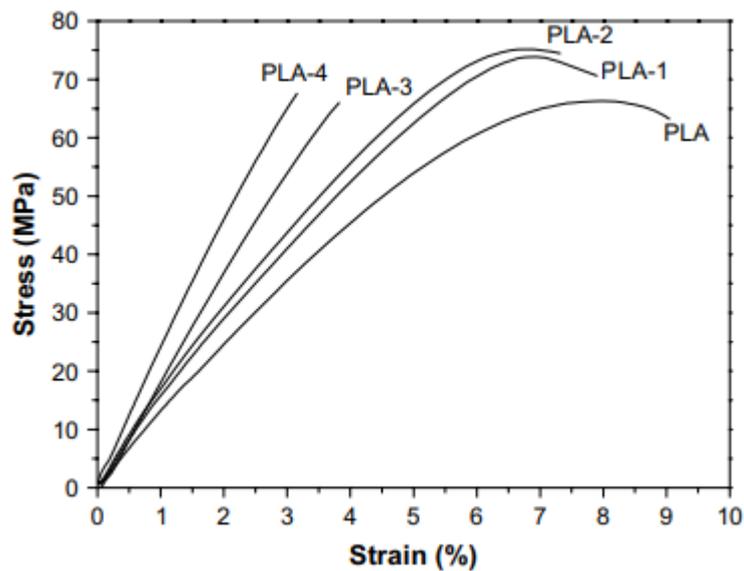


Figure 2-2 : Stress-strain curves of neat PLA 3001D and crosslinked PLAs containing 0.15 wt% TAIC and 0.5 wt% DCP (PLA-1), 0.5 wt% TAIC and 0.5 wt% DCP (PLA-2), 1.0 wt% TAIC and 1.0 wt% DCP (PLA-3), 3.0 wt% TAIC and 1.0 wt% DCP (PLA-4) [23]

As a conclusion, PLA is an interesting and promising biobased and biodegradable thermoplastic, and some of its properties are similar to that of conventional engineering thermoplastics. However, some challenges remain to overcome, in order to use this material at a larger scale. It includes PLA's brittleness, its poor crystallization ability and HDT, and its sensitivity to aging. To do so, its properties could be tailored by blending with other polymers, among which rubbers, either fresh or recycled.

2.2. Rubber: from vulcanization to recycling

Rubber is undoubtedly an important branch of polymers, and it is widely used in several fields, especially in the automotive industry. It can be originated from natural resources, such as the latex of the Hevea tree, or synthesized from fossil sources. In both cases, before being used in the objects surrounding us, the raw material must be transformed through more or less complex processes. But rubbers have a limited lifespan and solutions must be found to recycle the material and overcome the waste issues.

2.2.1. Rubber as main component of the pneumatic tire

An important part of the rubber production goes into vehicle tires. As an example, the composition of tire manufactured in Japan in 2014 was: approximately half rubber, reinforcing agent such as carbon black and silica 25%, and tire cord such as steel cord and organic fiber cord 14%.

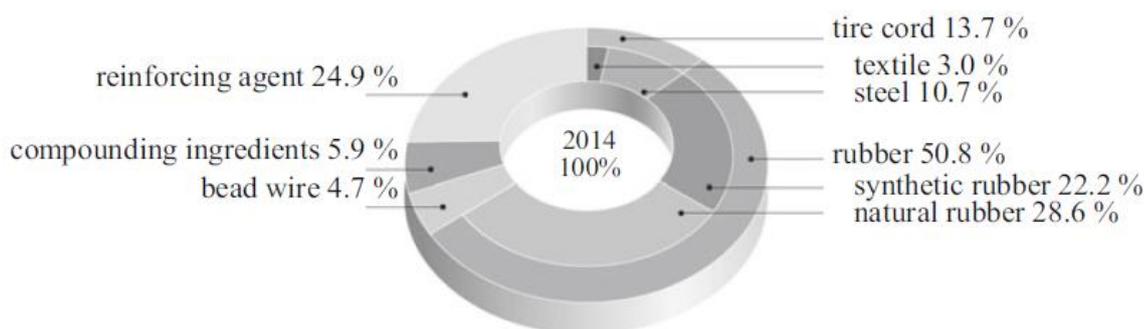


Figure 2-3: Weight composition of raw materials in tires in Japan in 2014 [3].

The rubber blend used in tires is essentially made of natural rubber (NR), styrene-butadiene rubber (SBR) and butadiene rubber (BR). Although natural rubber (NR) is known to exhibit numerous outstanding properties, reinforcing fillers are necessarily added into NR for purposes of reinforcement, reduction in material costs and improvements in processing. Indeed, the incorporation of fillers enhances the strength and strength-related properties, abrasion resistance, hardness and modulus. Carbon black (CB) and silica are commonly used reinforcing fillers that increase the usefulness of rubbers [24]. Thus, the use of carbon black in tires, known from 1904, enabled to improve by 10 times the durability of a tire [3].

2.2.2. Cross-linking reaction

Industrial rubber possesses a three-dimensionally structured network, which give them a stable elasticity. To do so, they have to undergo cross-linking reaction that creates transverse bonds which connect the rubber chains to form the cross-linked 3-dimensional structure [3]. Two main types of crosslinking methods can be found: sulfur crosslinking, also called vulcanization, and peroxide crosslinking.

Vulcanization is a type of cross-linking which is, by definition, the process of rubber crosslinking utilizing sulfur or sulfur containing compound. This process, discovered by Charles Goodyear in 1839, is irreversible. Therefore, rubber is an insoluble and infusible thermoset material that cannot be re-processed like thermoplastics. However, by using only sulfur to crosslink the polymer chains, the reaction time of vulcanization would be too long, ranging from several hours to a few days in order to get vulcanizates. Hence, activators combined with accelerators must be used. The combination effect of metal oxide with sulfur and organic accelerator system has been established as a standard through the years, and zinc oxide (ZnO) is frequently used as a metal oxide because of his excellent activator properties [25]. It is usually used in combination with stearic acid, having an acceleration effect on the vulcanization reaction due to the increasing solubility of zinc ion into the hydrophobic rubber matrix after zinc stearate has been generated. The organic accelerators added are from several types, including thiuram-type, guanidine-type, thiazole-type, and sulfenamide-type accelerators. They aim to improve the antiscorch properties and high reaction rate of cross-linking, and lower the reversion tendency [3].

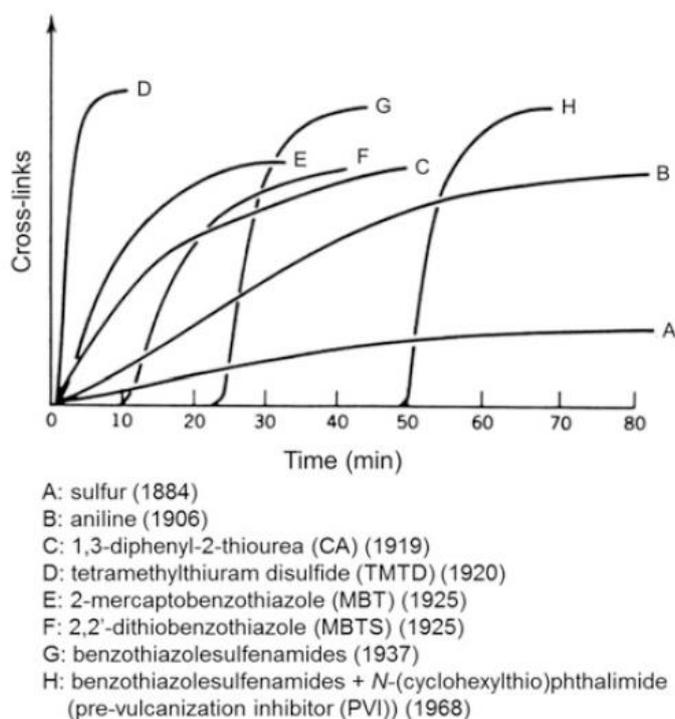


Figure 2-4: Comparison of cross-linking ability of various accelerators for sulfur vulcanization of natural rubber at 140°C. [3]

Nevertheless, the use of sulfur vulcanization is not the only way to crosslink rubber. Another process is based on peroxide cross-linking. In this reaction mechanism, free radicals are generated by the homolysis of peroxide and extract hydrogen atoms at the allyl position and/or tertiary hydrogen atoms in rubber molecules. This is followed by radical coupling and/or addition reaction to form a cross-linked structure. Here, the bonds created are C–C linkages. Peroxide cross-linking has the advantage of being simpler in formulation and processing steps and has a smaller number of added reagents and steps than the sulfur cross-linking reaction (vulcanization) [3].

These two methods both aim to create crosslinks between the polymer chains but result in different mechanical properties of the rubber. In their work, A.A. Basfar et al. [26] compared the consequences of different crosslinking systems, among others sulfur and peroxide systems, on the mechanical and thermal properties of natural rubber (NR) and styrene-butadiene rubber (SBR). It has been shown that the tensile strength and ultimate elongation for both peroxide-cured SBR and NR were lower than for the sulfur-cured formulations. In addition, independently of the curing system used, NR exhibits a higher tensile strength and modulus stress at 300% than SBR, but also a lower elongation at break.

2.2.3. Devulcanization

Even though rubber products are thermosets and therefore cannot be melted to be processed again, reversing the chemical structure of the rubber material to get back to an unvulcanized state is one of the strategies on rubber recycling [27]. It implies the conversion of a three dimensionally interlinked thermoset polymer to a two dimensional, soft, plastic, more tacky, low modulus, processable and vulcanizable product whose properties are close to those of virgin rubber [28]. This kind of product can then be incorporated in a polymeric matrix. To achieve this, two mechanisms are to distinguish: reclamation and devulcanization. The main difference is the target of the chemical attack involved.

Indeed, Reclaiming is defined as scission of carbon–carbon bond on the rubber back bone. As a consequence, the molecular weight of the polymer is reduced to attain plasticity [29], [30]. On the contrary, devulcanization targets the sulfuric crosslinks in the vulcanized rubber and thus C–S and S–S bonds are selectively cleaved.

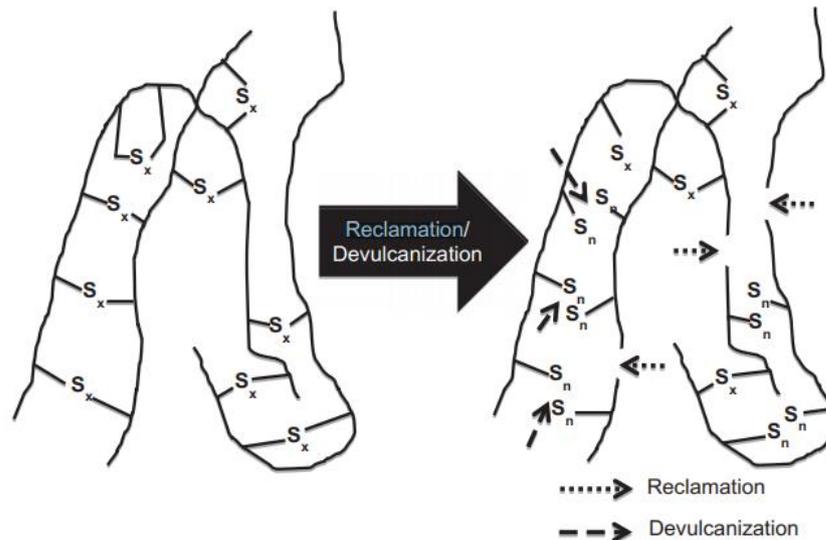


Figure 2-5 : Schematic representation of devulcanization and reclaiming [3]

Both processes aim to obtain a rubber compound which can be processed and vulcanized similar to fresh/virgin rubber. With the aim of recycling rubber, Devulcanization would be preferred to reclamation in order to keep an acceptable molecular weight. However, there is still no process able to entirely target chemical bond breakage. Hence, it is still impossible to obtain a rubber that has been entirely devulcanized without any reclamation. For this reason, the name “devulcanized rubber” or “reclaimed rubber” can be used independently.

2.2.4. Aging of rubber

Vulcanized, reclaimed and devulcanized rubbers are known to be sensitive to high temperatures because of the reversion phenomenon. Thus, the maximal service temperature of natural rubber is 70°C. Reversion is a thermally driven process by which vulcanized natural rubber (NR) reverts back to the gum state. This process involves three types of crosslinks in the vulcanizate: polysulfidic, disulfidic and monosulfidic. It can happen while both anaerobic and oxidative thermal aging of the material [31]

The effect of thermal degradation upon the mechanical properties of a natural rubber compound has been investigated [32], and it was pointed out that as thermal aging proceeded, reversion occurred, decreasing the percentage of polysulfidic crosslinks and increasing the percentage of monosulfidic crosslinks. Yet, the higher levels of polysulfidic crosslinks usually gives the higher mechanical property values.

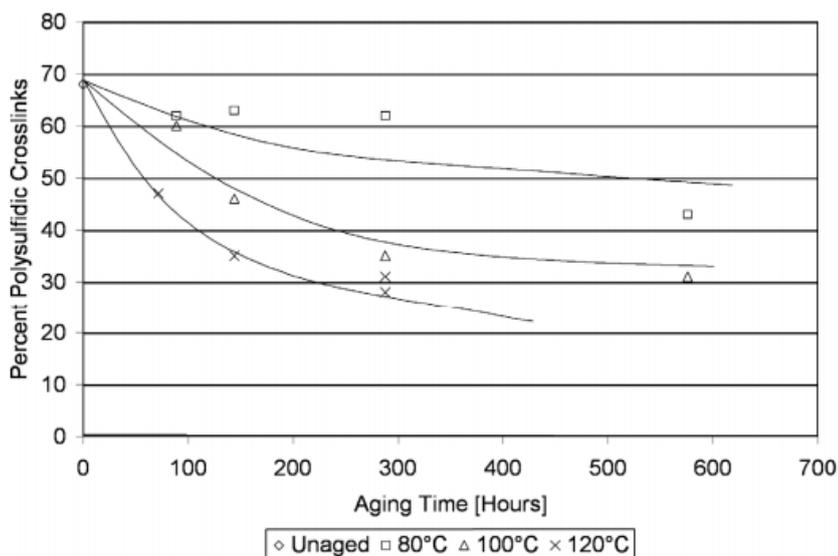


Figure 2-6: Dependence of the percentage of polysulfidic crosslinks with time at elevated temperatures for a natural rubber compound [32]

The effects of the time on thermal aging were also investigated on samples of a tire tread compound originally cured to 90% crosslink [33]. In this study, the rubber compounds were aged at 80°C during 4 weeks and the results show that the crosslink density increases rapidly within the first week, the crosslinking possibly occurring at the free rubber chains. This phenomenon is named “residual curative”.

The aging characteristics of devulcanized GTR (GTR^D) should be specifically taken in account, as devulcanized GTR itself is a degraded product. To do so, the aging behavior of dynamically vulcanized

blends of GTR^D/virgin rubber has been investigated [34]. The tensile strength of the blends has been found to be slightly reduced after 24h aging at 70°C for the high GTR^D content blends. However, the reduction of the elongation at break has been reported to be considerable for all the blends compositions, due to a thermooxidative degradation and post-revulcanization of GTR^D. A loss of tensile strength has also been reported for GTR^D/natural rubber blends after 22h aging at 100°C, with a tensile retention of around 80% for sulfur vulcanized systems [35].

In spite of its interesting properties, rubber has to face a problem of recycling since the crosslinking reaction, necessary during the manufacturing, is irreversible and makes the material impossible to melt and reshape. Blending waste rubber or fresh rubber with thermoplastics can, however, offer a recycling possibility, the material obtained being meltable and re-processable.

2.3. Thermoplastic vulcanizates (TPVs) binary blends

Several possibilities have been investigated to mix a rubber with a thermoplastic, and thus obtain a thermoplastic elastomer. Under certain conditions, a good compatibility between the phases can be achieved, leading to good physico-mechanical properties, elasticity, processability, recyclability, and resistance to heat, chemicals, and ultraviolet radiation.

2.3.1. Thermoplastic / Fresh rubber TPVs

One of the well known possibility to obtain these kind of blends is to mix a rubber in its fresh, unvulcanized state, which means that the molecules of the rubber are not crosslinked, with a thermoplastic.

2.3.1.1. General examples

Thermoplastic vulcanizates (TPVs) are defined as a type of thermoplastic elastomers (TPEs) that are not based on block-copolymers but on polymer blends. They are produced via dynamic vulcanisation of a rubber/thermoplastic blend, i.e. the selective cross-linking of the rubber while melt mixing with the thermoplastic. Hence, TPVs have the advantage of having both the elastic and mechanical properties of thermoset cross-linked rubbers and the melt processability of thermoplastics [36]. The first examples of TPV were ethylene-propylene-diene terpolymer (EPDM)/plastic systems in 1981, with

a considerable amount of work reported on the blends with PP as a thermoplastic due to their commercial importance [37]. Natural rubber was also extensively used for these types of blends, owing to low cost and availability as a natural product extracted from rubber tree (Hevea). It has also been widely mixed with PP, the microstructure of the blends being co-continuous phases [38], [39]. HDPE was also blended with natural rubber at various ratios and using a phenolic compatibilizer [40].

2.3.1.2. PLA / natural rubber (NR) TPVs

NR has been found to be a suitable candidate to be used as an impact modifier for PLA and to improve its brittleness issues, the blends thus created being 100% biobased. Y. Chen et al. [4] prepared a significantly toughened biobased dynamically vulcanized PLA/NR blends in presence of the cross-linking agent DCP and obtained a continuous honeycomb-like network structure of cross-linked NR phase, and thus a co-continuous morphology of the blend, in opposition to the “sea-island” morphology usually obtained for this kind of blends. They also reported an impact strength of 58.3 kJ/m² for 35wt% NR, corresponding to approximately 21 times that of the neat PLA [4].

Similarly, a dynamically vulcanized PLA/NR blend (60/40 wt. %) using DCP as a crosslinking agent showed the highest mechanical performance (impact strength, elongation at break and tensile strength) and thermal stability, among all the NR contents and curing agents investigated, such as sulfur or phenolic resin [41].

The same kind of compounds have been processed without dynamic vulcanization [8] and the morphology obtained was no more co-continuous but the rubber phase was dispersed as droplets in the thermoplastic matrix. The ductility of PLA has been significantly improved by blending with NR. The elongation at break improved from 5% for neat PLA to 200% by adding 10 wt.% NR, which has been found to be the optimal NR content. In addition, the incorporation of NR increased the crystallization rate and enhanced the crystallization ability of PLA, the small molecules contained in the elastomeric phase being believed to be acting as nucleating agent. A similar observation has been made by K. Pongtanayut, et al.[42]. They blended PLA with natural rubber (NR) and epoxidized natural rubber (ENR) and suggested that the incorporation of NR and ENR would enhance the crystallization PLA. This is proved by the cold-crystallization exothermic peaks observed in DSC. The enhanced crystallinity of the blends was linked to higher tensile strength and modulus, as it is the case in most polymers. Yet, a high crystallinity is also often responsible of a lower ductility. That is why it is important to control the annealing conditions, having an influence on the spherulites number and size.

However, the thermal stability of PLA/NR blends was found to be decreased with addition of NR and due to the migration of small molecules to surface of NR that can lead to chain scission of PLA while mixing, and thus decrease the molecular weight of PLA [42].

These studies tend to show that blends of PLA and natural rubber can be successfully prepared as toughened biobased TPVs for industrial applications. Despite this potential, the re-use of waste rubber through recycling instead of the use of virgin NR would present a step further in the reduction of the environmental impact, being in addition more economic.

2.3.2. Thermoplastic / waste tire rubber blends

To face the problem of the increasing amount of tire wastes, several recycling solutions have been developed [30]. Firstly, vehicles tires can be retreaded, which consists in replacing only the tread on worn tires while keeping 90% of the old tire. Secondly, tires can be re-used as a whole, for example in artificial rafts or cover foilweights, or in parts, like in building blocks. The waste tires can also be submitted to pyrolysis to extract compounds like oils, monomers or carbon black. Finally, this section will focus on the solution of grinding, reclaiming or devulcanization of the waste tire rubbers to incorporate them into fresh thermoplastics.

2.3.2.1. Thermoplastic / Ground Tire Rubber (GTR) blends

- **General properties and limitation**

One of the solutions researchers recently focused on is mixing particles of Ground Tire Rubber (GTR) with a thermoplastic polymer. GTR is an industrial waste from tires and contains rubbers, plasticizers, curatives and reinforcing fillers like carbon black. This solution has several advantages. Indeed, even if a small percentage of GTR is incorporated in thermoplastics (usually around 10 wt%), it would correspond to a significant consumption of GTR if the blend is produced at an industrial scale. It would then allow to recycle a considerable proportion of the tire wastes. Besides, GTR incorporation may yield enhanced properties compared to the neat thermoplastics, in particular toughness and elongation at break. Finally, blending waste tire rubber with polymers would permit for lowering the cost of the products created [29].

Several parameters may tune the properties of thermoplastic/GTR blends. First, particle size of GTR was found to influence the mechanical properties. The general tendency is that smaller particles render better mechanical properties than the bigger ones, due to higher probability of failure cracks induced

by big particles. Colom et al. [43] observed the drop in tensile strength of 20 wt% GTR containing HDPE blend with $<200\mu\text{m}$ particles was 25%, whereas it was 51% when $>500\mu\text{m}$ particle size was used.

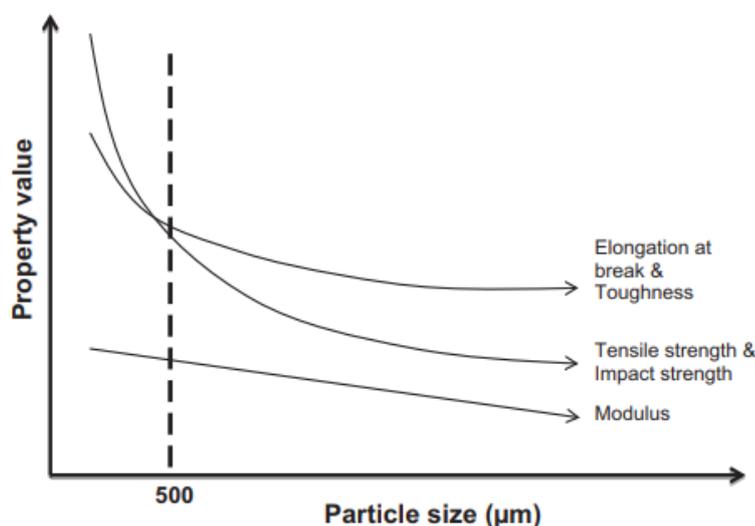


Figure 2-7: Influence of the particle size of GTR on mechanical properties of thermoplastic blends [29]

Also, the GTR loading obviously plays a role on the properties of the blends. Tensile and impact properties are generally deteriorated with increasing GTR content, due to their poor adhesion with the matrix [44]. A compromise is thus to be found, between the amount of recycled material and the properties of the blends.

The crystallinity of the thermoplastic matrix is another parameter affected by the presence of GTR as a filler. GTR addition tend to increase the crystallinity, as it has been shown by P. S. Lima et al [10]. In their work, they analyzed the crystallization process of a TPE based on GTR, and confirmed that GTR has a strong nucleating effect on the PP matrix and that its presence leads to higher crystallization rates. As a consequence, the crystallization of the polymer is accelerated, which is shown by the reduction of the crystallization half time. Similarly, it was found that GTR could have a nucleating effect on non-compatible PP/GTR blends [45]. The crystallinity rate of a polymer is, besides, an important factor since it has an influence on the heat deflection temperature (HDT). Indeed, in order to increase the HDT, the polymer should be as crystalline as possible. A high HDT is required for an engineering thermoplastic, which must be adapted for a continuous use at elevated temperatures.

The thermal aging properties of a polymer may also be affected by the addition of GTR. Different degradation processes, including thermal aging, on maleated polyethylene(MAPE)/GTR blends have been studied [46], revealing that GTR addition reduced compounds stability against thermal ageing at both 80 and 90°C. Indeed, even though thermal aging had no effect on MAPE, Tensile modulus of sample MAPE₄₀/GTR₆₀ increased by almost 90% after one week of ageing at 80°C, while its elongation

at break decreased by around 50%, because of chain scissions, creating macro radicals, bringing about crosslinking that decreases the GTR particles deformability.

Hence, the addition of GTR in polymers can be an efficient solution to recycle the increasing amount of tire wastes. However, it is limited by the properties of these materials, since adding GTR often tends to decrease some mechanical properties as compared to the neat polymers. Nevertheless, to limit this negative impact, two solutions have been proved to be efficient: the interface compatibilization and the dynamic crosslinking at the interface.

- **Interface compatibilization**

To prevent the problem of insufficient bonding between GTR and the virgin matrix which limits the stress transfer from the matrix to the rubber particles [29], the surface of GTR can be modified. This modification, named compatibilization, provides specific interaction sites between the phases, thus strengthening the interface between GTR and the thermoplastic. During the processing, a dynamic reaction will happen between the polymer, GTR particles and a compatibilizer acting as a bridge. Not only compatibilization enables to improve adhesion between faces by reducing interfacial tension, but it also enhances the dispersion of GTR in the matrix during blending and stabilizes the morphology during the processing and the service life.

In order to improve the interfacial adhesion, researches on surface functionalization of GTR are currently carried out. The surface of these particles can be modified using several ways, such as chemical modification, graft polymerization, radiation induced modification and gas modification. These methods aim to oxidize the GTR surface to form polar groups, enhancing the interaction with polar polymers [29].

The chemical compatibilization consists in reducing the interfacial tension by enhanced wetting, thereby forming a stronger interphase. It can be achieved by reactive and non-reactive methods.

In the non-reactive method, compatibilizers are incorporated into the polymer blends in order to improve the blend compatibility with the recycled rubber particles. Commonly used compatibilizing agents are Maleic anhydride grafted polymers like SEBS, ethylene propylene diene monomer (EPDM) and PP. For instance, Sung et al. [27] prepared polypropylene/GTR blends and used allylamine to modify the surface of GTR. The grafting reaction has been induced by UV radiation. Maleic anhydride polypropylene has been used as a compatibilizer.

On the other hand, another compatibilization solution is the reactive method, where reactive additives are added during blending and react to bind the GTR with the thermoplastic.

- **Dynamic crosslinking**

Dynamic crosslinking is a reactive method, in which the two phases react with each other during the process, thereby forming chemically linked interphase. Thermoplastic blends comprising GTR or devulcanized GTR often employ peroxide crosslinking or sulfur crosslinking on that purpose. A commonly used peroxide crosslinking agent is dicumyl peroxide (DCP). Above a certain temperature, a reaction of decomposition of peroxide occurs, which forms radicals that extract hydrogen atoms from the polymer chain. Macromolecular radicals are thus created. Then, they combine to form crosslinking between chains (C–C bonds) [29].

The number of free radicals of peroxide depends on the temperature, as shown in *Figure 2-8*. The minimum temperature needed to reach a significant amount of free radicals generated by DCP is around 150°C, which is achieved during the mixing of GTR with most of thermoplastics [47].

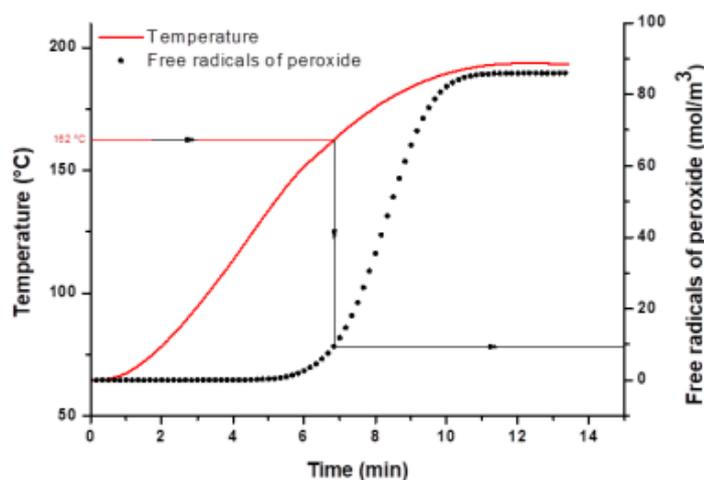


Figure 2-8 : Prediction of the free radical concentration generated during mixing in EPDM from thermal DCP decomposition [47].

The reaction with DCP can be qualified as co-crosslinking and occurs in two steps. First, the crosslinking agent goes to the interphase. A block or graft co-polymer is generated during vulcanization. Then, the interface is thickened and the components are compatibilized. The co-crosslinked system can be described as interpenetrating network (IPN) [29].

Sonnier et al. [48] treated recycled HDPE/GTR blends with peroxide. They found improved elongation at break and impact properties compared to the non-dynamically vulcanized samples and suggested that it could be due to co-crosslinking of HDPE and GTR phase.

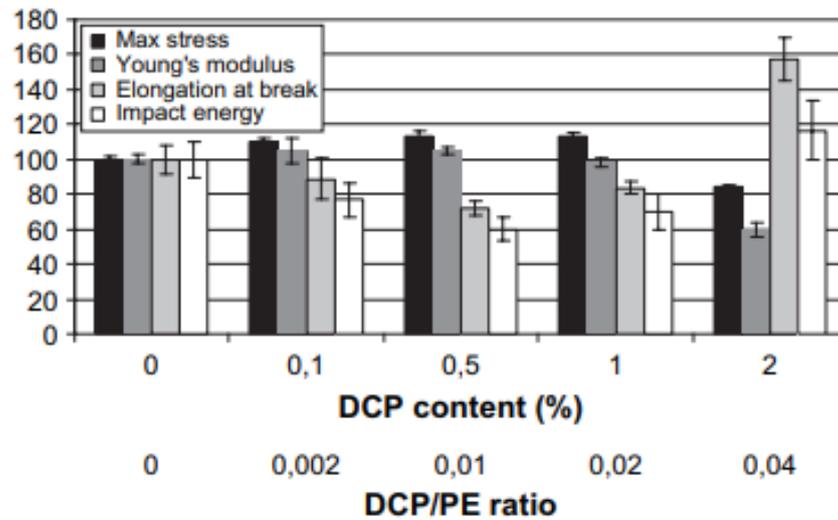


Figure 2-9: Mechanical properties of 50/50 HDPE/GTR blends treated with DCP [48].

In a similar way, Compounds of ground tire rubber (GTR) and polypropylene (PP) were prepared using organic peroxides as radical donators [49], showing that the dynamic vulcanization induced by DCP makes the stress–strain behavior of the GTR/PP blends similar to that of TPE-V or TPV, whereas only physical compounding led to materials with poor mechanical properties. The impact properties were also significantly improved with the use of peroxide.

However, organic peroxides can also have a negative effect on a thermoplastic. It has been reported on GTR/PP blends [49], where the impact strength of the 30 wt.% GTR blends containing DCP were lower than without DCP, which may be explained by the pronounced degradation of the PP matrix during reactive mixing owing to the peroxide radicals. This result is confirmed by the lower melting peak temperature of DCP-compatibilized blends.

• PLA/GTR blends

An interesting solution from an environmental point of view would be the production of PLA/GTR blends. Indeed, As PLA is a biodegradable material, the GTR particles could be re-used after degradation of the matrix, thus resulting in a fully recyclable material. PLA being a brittle polymer, fresh rubber has been used as a second phase polymer to toughen it, but only few investigations focused on the addition of GTR in PLA. The GTR particles, are supposed to behave as stress concentrators, enhancing the fracture energy absorption of brittle polymers and ultimately results in a material with improved toughness [42]. This kind of blend has been processed in a “Brabender” internal mixer [50]. An improvement in toughness compared to the neat PLA was measured by Izod test only for tire

volume contents higher than 60 %. Moreover, Tensile strength and E-modulus decreased and ductility rose with increasing rubber content. Similarly, Yang et al. [51] improved the impact strength and elongation at break of PLA incorporating micro-sized waste rubber powder (WRP). The optimal volume fraction of waste rubber powder has been found to be 15%, for which the impact strength and elongation at break improved from 14,47 kJ/m² and 0.83% for neat PLA to 37,39 kJ/m² and 2,03% for PLA₈₅/WRP₁₅, respectively.

Hence, several solutions exist to reach enhanced properties of Thermoplastic/GTR blends, including various types of compatibilization, reducing the size of the rubber particles and finding the optimal GTR content. Yet, another possibility is to change the chemical nature of GTR by devulcanizing it.

2.3.2.2. Thermoplastic / Devulcanized Ground Tire Rubber (GTR^D) blends

The use of devulcanized Ground Tire Rubber (GTR^D), having an uncrosslinked rubber structure, as filler should be more efficient to improve the ductility and the impact properties of thermoplastics. This can be achieved thanks to the dynamic cross-linking of the devulcanized GTR free chains, which will create new bonds with the thermoplastic matrix and thus improve the adhesion between the two phases [29]. This is made possible by the molecular entanglement with thermoplastics and curable devulcanized rubbers. A thick interphase is supposed to be formed between the recycled rubber and the thermoplastic when the resin swells the partially decrosslinked GTR particle [29]. The interfacial adhesion can then be enhanced by various surface activations, which have been mentioned above.

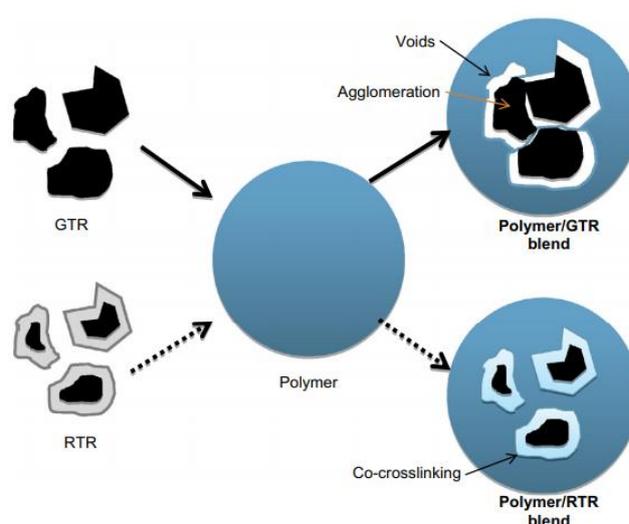


Figure 2-10 : Schematic diagram showing the difference in microstructure of polymer blends with GTR and reclaimed tire rubber (RTR) [29].

Although several studies focused on the preparation of these kind of thermoplastic/GTR^D blends [52]–[54], none of them deals with PLA as a thermoplastic. However, PP and HDPE based blends have been investigated.

As for the above-mentioned thermoplastic/GTR blends, various crosslinking agents may be used to induce dynamic vulcanization in order to improve the interfacial compatibility and properties of the blends. Reclaimed Tire Rubber (RTR)/PP blends have been dynamically vulcanized using either a sulfur crosslinking agent, maleic anhydride (MA), dicumyl peroxide (DCP), or the combination of MA and DCP [52]. Firstly, the RTR/PP blends with sulfur crosslinking has been compared to GTR/PP blends prepared with the same crosslinking system. The authors found that the RTR/PP blends showed an appreciable improvement in the Notch-Izod impact strength, which is about 2 times higher than that of neat PP. However, GTR/PP blends showed low impact strength, nearly the same as that of PP. Indeed, RTR is supposed to have more free chains (due to the devulcanized state) to participate in the crosslinking process, as opposed to GTR which is a vulcanized rubber.

Then, the crosslinking systems have been compared and the best impact strengths are found to be those of 30/70 RTR/PP blends with MA + DCP, which gave an impact strength 160% higher than neat PP. To explain this, MA was believed to be grafted onto both PP and GTR phases, which induces compatibilization thanks to the dipolar interaction between the MA grafted PP and MA grafted RTR. In addition, all kind of crosslinked PP/RTR blends show higher impact strength than that of the non-crosslinked blends. This significant increase in impact strength was believed to be the result of the impact energy absorption of RTR, but also of the crosslinking between RTR particles.

The influence of sulfur, peroxide and mixed crosslinking system on properties HDPE/RTR blends has also been studied by Punarak et al. [53]. As opposed to the previously mentioned study, it revealed that sulfur crosslinking system rendered the best properties enhancement, with improved impact strength and tensile properties, whereas peroxide cured blends were showing inferior impact strength compared to unvulcanized blends. The explanation is that the macroradicals produced by peroxide can either combine to generate cross-linking or accelerate chain scission of HDPE and rubber.

In another study [54], gamma irradiation has been used to crosslink devulcanized waste rubber and HDPE phase, enhancing the hardness and the tensile strength of the blend compared to the ones that have not been irradiated, but decreasing the elongation at break. Indeed, the crosslinking induced by radiations is believed to hamper the mobility of molecules.

In spite of the various compatibilization methods above-mentioned, some compatibility issues must still be resolved. Most of the time, vulcanized GTR acts as semirigid filler, and the adhesion with the thermoplastic matrix is poor. Thus, ternary blends of thermoplastic, GTR and fresh rubber could be

another solution to face the insufficient mechanical properties of thermoplastic/GTR blends, especially the elongation at break and impact resistance.

2.4. Ternary blends

The dynamically crosslinked binary blends of thermoplastics with rubber, so called thermoplastic vulcanizates (TPVs), are well known. EPDM rubber blended with a thermoplastic PP matrix, dynamically vulcanized in presence of sulfur, organic vulcanization accelerators, stearic acid, and zinc oxide, is one of the first TPV processed [3]. Still in the purpose of recycling waste tire rubber incorporating it in polymers, investigations have been carried out to partially replace the elastomer phase by GTR in these kinds of TPVs.

2.4.1. Fresh rubber / waste tire rubber blends

The aim here is to create ternary blends made of an elastomeric phase, made of a GTR/fresh rubber compound, and a thermoplastic phase. The principle of ternary blends is based on an encapsulation strategy of the GTR by an elastomeric phase. Indeed, the compatibility of GTR with virgin rubbers is usually better than with thermoplastics.

The dynamically cured blends of various types of rubber mixed with GTR is well known in the literature. These blends are usually prepared with a first step of mastication, where the GTR and the fresh rubber are mixed together. In a second step, the curing agents are added to initiate the crosslinking. GTR has been used as a filler for Butyl Rubber within the range of 10–90 phr [55], 30 phr revealing the highest tensile strength and elongation at break, exceeding the values of the neat rubber. Strong interactions between the butyl rubber matrix and GTR have been observed by microstructural analysis. The interface between the two phases can even be improved using GTR^D, as it has been done with NR/GTR^D blends [56], [57], creating a co-crosslinked interphase. The results showed that the tensile properties of the GTR^D/NR vulcanizates were much better than those of the undevulcanized GTR/NR vulcanizates, with a tensile strength and an elongation at break of the GTR^D/NR blends increased by 69% and 47%, respectively, compared to the blends containing the undevulcanized GTR [57].

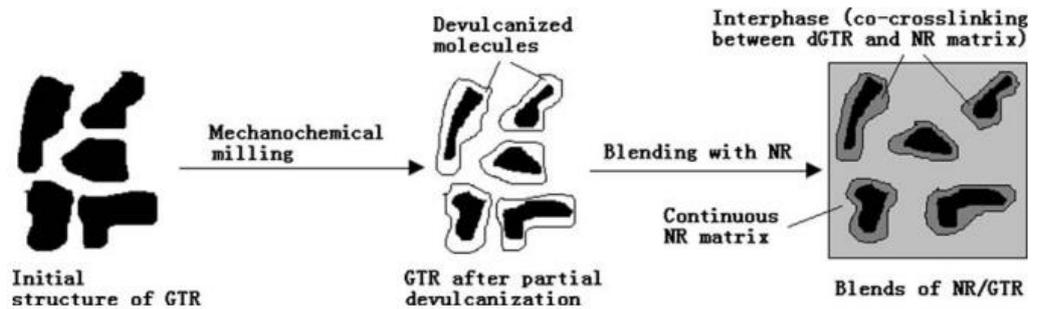


Figure 2-11: Schematic diagrams of the partial devulcanization and further re-vulcanization process [57].

Thus, the good compatibility between the two elastomeric phases is likely to allow a good encapsulation of GTR in the rubber phase, making it possible to add a third thermoplastic phase, which would reduce the problem of the bad compatibility between GTR and thermoplastics.

2.4.2. GTR / fresh rubber / thermoplastic blends

Even though only few studies focused on the development of ternary blends of GTR, fresh rubber and thermoplastics, these materials show promising properties. Ternary blends, composed of a highly flowable polypropylene homopolymer, an ethylene propylene diene monomer (EPDM) and GTR were formulated [27]. The blending process was carried out in two stages. First, EPDM was mixed with GTR in a brabender type internal mixer to promote a better encapsulation of the GTR particles by EPDM. This mixture was then milled to obtain the granules, and then added to PP for the second blending stage for the next blending stage. Under 70wt% rubber phase, the ternary blends show a continuous-disperse morphology, with a homogeneous dispersion of GTR particles and EPDM domains. However, for the $PP_{30}/(EPDM_{0.7}-GTR_{0.3})_{70}$ and $PP_{30}/(EPDM_{0.5}-GTR_{0.5})_{70}$ blends, a co-continuous morphology has been observed, due to a higher content of EPDM, with embed GTR particles.

It has been reported that the partial replacement of EPDM by GTR leads to a decrease of elongation at break and impact strength for all elastomeric phase contents. The reduction of the impact strength with increasing GTR content can be explained by the nature of the GTR particles, by the reduction of EPDM content and also by an inferior encapsulation effect of the GTR particles. However, compared to the GTR/PP blends, the use of EPDM as a third phase allowed a significant improvement on the toughness of the material, making it an adequate choice to compatibilize GTR with polyolefin materials. To be noted, the strategy of GTR encapsulation by EPDM seems to be more effective on the blends that gather two parameters: a small GTR particles size and a high EPDM/GTR content ratio. The increase on PP crystallinity with the GTR content has also be pointed out, due to the GTR nucleation effect which leads to higher crystallization rates. This effect has also been observed by the same

authors in another work focusing on the crystallization kinetics of thermoplastic elastomeric blends based on GTR [10].

The same kind of blends have been processed with acrylic modified HDPE as a thermoplastic [58] and DCP as a cross-linking agent, and it has been found that 1 phr of DCP was the optimum for dynamic crosslinking of 60/40 composition of rubber (1:1 GTR/EPDM) / thermoplastic (A-HDPE). It was also pointed out that 50% of EPDM could be replaced by GTR without adverse effects on the processability and physical properties of the blend.

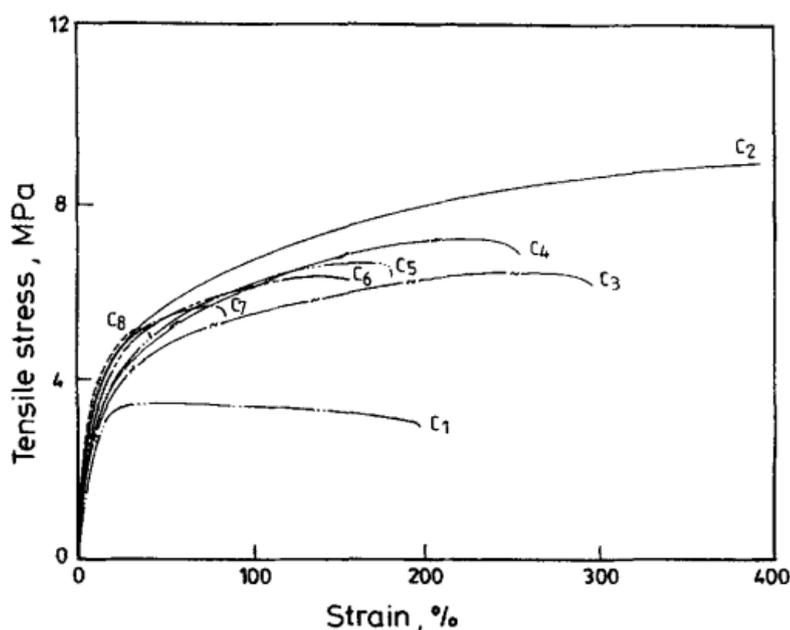


Figure 2-12: Stress-strain curves of 60/40 rubber/thermoplastic blends at different EPDM/GTR ratios: 60/0, no DCP (C₁); 60/0, DCP 1phr (C₂); 50/10, DCP 1phr (C₃); 40/20, DCP 1phr (C₄); 30/30, DCP 1phr (C₅); 20/40, DCP 1phr (C₆); 10/50, DCP 1phr (C₇); 0/60, DCP 1phr (C₈) [58].

2.4.3. Devulcanized GTR / fresh rubber / thermoplastic blends

As it has been done for binary blends, a few studies have focused on the use of GTR^D in ternary blends. C. Radheshkumar et al. [59] used thermochemically devulcanised GTR added to fresh rubber compositions (either NR, Styrene/butadiene rubber or EPDM). This was then melt blended with low density polyethylene (LDPE). In contrast to most of the above-mentioned study, during blending, dynamic curing was achieved using various curing agents. The tensile strength and elongation at break of blends containing devulcanized GTR have been reported to be higher than those containing normal GTR, showing an effective interfacial stress transfer between the GTR^D particles and the surrounding matrix thanks to the entanglement of the GTR rubber chains with the fresh rubber matrix's chains

during the dynamic revulcanization. Furthermore, all the TDV compositions were remarkably stable to aging at 70°C during 24h. Nevertheless, among all the fresh rubber tested in the blends, NR gives the worst properties while EPDM was reported to be the most efficient rubber, due to a dual mechanism of compatibility, namely molecular entanglement with LDPE and interfacial crosslinking with the GTR⁹.

Similarly, in their work, S. Al-Malaika et E. J. Amir [60] studied the effect of a partial replacement of NR by thermo-chemically reclaimed rubber from waste tires on NR/PP blends (60:40 weight ratio). It has been observed, first, that the mechanical properties are almost unaffected by replacing up to 50% of NR by RTR. Secondly, the effect of DCP as a crosslinking agent has been investigated on such blends, and the partial replacement of NR by RTR has been shown to prevent the loss of tensile strength usually observed on NR/PP blends at concentrations of DCP higher than 0,3 phr. This is believed to be due to the presence of additives (mainly antioxidants) in RTR. These antioxidants were assumed to decrease the extent of degradation in the PP phase, leading to a continuous increase in tensile strength even for high DCP amounts.

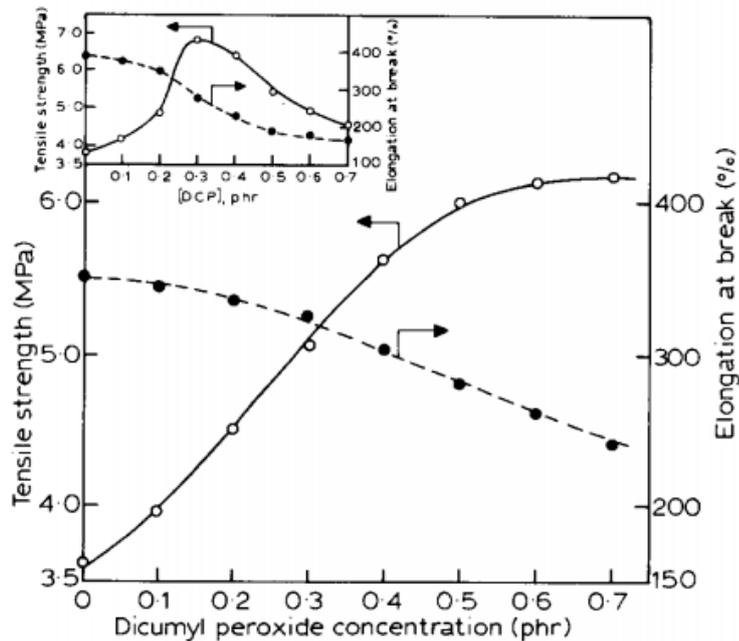


Figure 2-13: Effect of DCP on the tensile strength and elongation at break of RTR/NR/PP (30:30:40) blends. Inset shows the same effect on NR/PP (60:40) containing no RTR and processed under the same conditions [60].

To conclude, due to the potential of waste tire rubber as a toughener of thermoplastics and to the interest of PLA as a biobased and biodegradable polymer, the number of publications regarding the above-mentioned blends considerably raised in the last decades (Figure 2-14). The PLA/NR blends would be a 100% biobased alternative to conventional TPVs, and GTR has been extensively used in

combination with thermoplastics as a way to reuse the huge amount of waste tires that is hardly recyclable. Nevertheless, there is still a lack of investigation regarding the use of waste tire rubber in PLA and the previously discussed ternary blends.

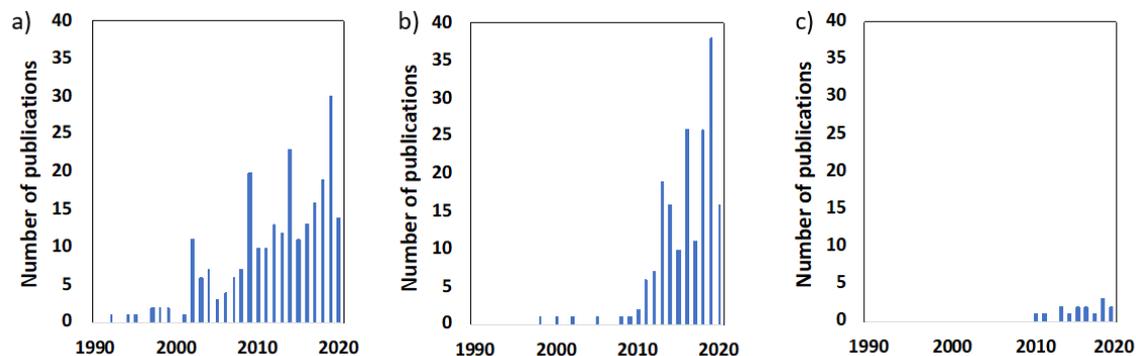


Figure 2-14: Number of publications in the last 30 years about a) Waste rubber in thermoplastics, b) NR in PLA, and c) Waste rubber in PLA

2.5. Objectives of this work

From the literature review, thermoplastic elastomers made of waste tire rubber and conventional engineering thermoplastics such as PP or EPDM are well known as a recycling solution of waste tires and show interesting mechanical properties.

However, in spite of the opportunity of including rubber in a circular economy that they propose, the environmental impact of these TPE could be further reduced by replacing the thermoplastic by an eco-friendlier component. This is why this work will focus on the production of Polylactic acid (PLA) based blends, a bio-sourced and biodegradable polymer whose production results in a low carbon footprint. The addition of micronized waste tire rubber particles in PLA would, in addition, toughen this intrinsically brittle polymer, as it has been shown in previous works of the CEcoR project in which an increase of 70 % of the tensile energy at break of PLA was obtained [66].

To continue these works and further improve the mechanical properties of the PLA based blends, especially the ductility, energy at break and impact strength, this work aimed to process PLA/Ground Tire Rubber (GTR) blends at a laboratory scale, via melt-blending dynamic vulcanization. The addition of natural rubber as a third component has been studied, expected to bring more ductility and improve the interfacial adhesion of GTR with PLA. To characterize the produced materials, their mechanical properties at low and high deformation speed were determined by quasi-static tensile and tensile-impact testing. To have more information on the phenomena implied during dynamic vulcanization, the GTR powder and the vulcanized NR/GTR blends were also characterized by swelling to determine their average crosslink density.

2.6. Scope of the master thesis

The scope of this Master Thesis, namely the preparation and physico-chemical and mechanical characterization of PLA/waste rubber and PLA/Natural Rubber/waste rubber blends at a laboratory scale, is the revalorization of waste material to be reused as an economic material to toughen bio-based thermoplastics for industry applications. In the frame of a circular economy of rubber, this solution aims to lead to environmental and economic benefits, especially in the automotive industry. Various potential components were identified in this sector to be applicable: rubber pads, interior trim parts, air filter box, etc. Included in the laboratory scale and pilot scale investigations combining devulcanization and dynamic revulcanization of thermoplastic/rubber blends based on waste rubber, this work will serve to characterize the material and improve its properties.

3. Materials

3.1. Polylactic Acid (PLA)

PLA is a biobased and biodegradable thermoplastic derived from annually renewable resources, which makes it environmentally friendly and sustainable. Indeed, PLA takes only 6 months to 2 years to degrade, compared to conventional thermoplastics which degrade after 500 to 1000 years [6].

The monomer from which is produced PLA is lactic acid, which exists in two enantiomeric forms (Figure 2-1). It is mostly synthesized by a method of microbial fermentation, performed by the bacteria *Lactobacillus*. From this monomer, the high molecular weight PLA is preferably manufactured by ring opening polymerization (ROP).

The material selected in this work is PLA2002D[®] extrusion grade from NatureWorks[®] (Arendonk, Belgium). It is a transparent high molecular weight PLA designed for extrusion/thermoforming applications and can be used in dairy containers, food serviceware, transparent food containers, blister packaging and cold drink cups [61]. The pellets are of white to pale yellow color and have a diameter of around 3 mm (see Figure 3-1).



Figure 3-1 : Unprocessed PLA2002D[®] pellets

As the rest of the PLA grades, PLA2002D[®] behaves brittle and stiff, with a low strain at break (6,0%), a strain at break of 60 MPa and an elastic modulus of 3,45 GPa. It has a density of 1,24 g.cm⁻³ [61].

More information provided by NatureWorks for the physical, mechanical, optical and processing properties of PLA2002D[®] is presented in the appendix (cf. Table A0-1).

3.2. Ground Tire Rubber (GTR)

The Ground Tire Rubbers that we selected for this work were obtained as byproducts of different parts of truck tires and were micronized by various processes. The tire crumb was also received with different range of sizes. The characteristics of the three different types of GTR studied in this report are listed in Table 3-1.

Table 3-1 : Characteristics of the three different GTR types.

GTR's number	Particle's maximum size (μm)	Available mass (kg)	Process	Tire part
1	420	25	Ambient grinding	Tire tread
2	200	10	Cryogenic process	Whole tire
3	420	25	Ambient grinding + Physico-chemical devulcanization	Tire tread

The used materials were micronized by the company J. Allcock & Sons Ltd by either process of ambient grinding or a cryogenic process, and is aimed to be subsequently recycled in compounding applications, including tire formulations, general mechanicals, mastics and as a dusting agent [62].

The tire tread crumbs coming from ambient grinding have been obtained from tire buffing, produced when used tire carcasses are prepared for remolding. The tread is removed by combination of grinding and shredding, without damaging the carcass. This, in addition to a subsequent magnetic separation, guarantees a GTR free of fibers and metal. Moreover, the controlled dry ambient grinding allows to select a specific particle size, excluding larger parts and dusts. However, the most frequently used rubber in this study was micronized by a cryogenic method, in which vulcanized rubber is processed at low temperature (below its embrittlement temperature) and then converted to a powder under high shearing conditions [63]. This process enables to further reduce the size of the rubber particles. Finally, the rubber type n°3 has been devulcanized after ambient grinding by applying a combination of heat, pressure and chemical softening or plasticizing agents.

The micronized GTR crumbs are made of around 85% of natural rubber and 15% of SBR but can contain small amounts of other components as stated by the company. The GTR crumbs should also be free of contaminants such as textile, metal and road dirt, but can contain particles of talc, used during the process of grinding. The crumbs have a black color and a density of $1,14 \pm 0,02 \text{ g.cm}^{-3}$ (Figure 3-2).

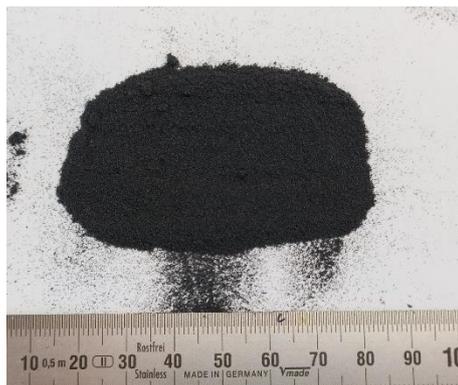


Figure 3-2 : GTR crumbs of type n°2, particle size <math><200 \mu\text{m}</math>

3.3. Natural Rubber (NR)

Natural rubber (NR) is an elastomer biosynthesized by Hevea trees, as the polymer is contained in the latex they produce. It is a linear polymer chain of cis-1,4-polyisoprene with a high stereoregularity. This high regularity as well as the presence of a naturally occurring network due to the presence of phospholipids and proteins at chains ends give to NR its unique properties, especially its strain-induced crystallization (SIC) behavior [3]. Usually, natural rubber is extracted of the latex thanks to coagulation in which the polyisoprene is thickened into a mass, which is made possible by the addition of an acid into the latex, such as methanoic acid. The NR bulk is obtained after drying to remove the excess water.

The material chosen for this study is an SMR (Standard Malaysian Rubber) CV60 supplied by the company Akrochem (Akron, Ohio, USA). This is a viscosity-controlled natural rubber, with 0,15% of hydroxylamine added to the latex stage to prevent the raw rubber stiffening while storing [64]. The bulk material is a 25 kg block of orange-brown rubber (Figure 3-3), and was stored under -18°C in our laboratory (CCP,UPC).



Figure 3-3 : Unprocessed Natural Rubber SMR CV60

The properties and specifications of the NR grade SMR CV60 are listed in Table 3-2:

Table 3-2 : properties and specifications of the used NR grade (SMR CV60, Akrochem, Akron, Ohio, USA) [64].

Dirt Content, less than	0,02
Ash Content, less than	0,50
Nitrogen Content, less than	0,60
Volatile matter, less than	0,80
Plasticity Retention Index, %	60,0
Mooney Viscosity: ML 1+4, 100°C	55-65
Color of Plastic Strip	Orange

3.4. Additives

3.4.1. Irganox® 1010

To prevent the thermo-oxidative degradation of PLA during processing, Irganox® 1010 was used as a sterically hindered phenolic antioxidant. It is frequently added to the compositions of polyolefins, olefin co-polymers, polyesters and elastomers such as BSS, EPDM, synthetic rubber, natural resins and other substrates [65], an can be used in combination with other additives. Irganox® 1010 has a low volatility, a high resistance to extraction and is odorless.

3.4.2. Dicumyl Peroxide (DCP)

In this study, Dicumyl peroxide was used as a reactive for revulcanization of the rubber phase in the PLA blends. It is a strong free radical source which is usually used as a polymerization initiator, catalyst and vulcanizing agent in the plastic and rubber industry. Indeed, the molecule of DCP thermally decomposes under high temperatures to form alkoxy radicals, likely to abstract hydrogen atoms from the polymer main chain. Two radicals can then combine to form a crosslink between two polymer chains. Dicumyl peroxide was stored between 2°C and 8°C. It has a white powder appearance, and it is flammable and cand cause health and environmental damages. For these reasons the product was handled with protective equipment. Its molecular formula is represented in Figure 3-4.

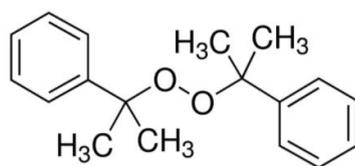


Figure 3-4 : formula of dicumyl peroxide (DCP)

3.5. Solvents

3.5.1. Cyclohexane

Cyclohexane is a low molecular weight cyclic alkane used for the swelling tests of rubber. It is a colorless liquid and is classified as flammable, irritant and health and environmentally damaging. The solvent has a high volatility and had to be manipulated in a ventilated environment to avoid inhalation and wearing protective equipment. It was disposed separately as hazardous waste.

3.5.2. Dichloromethane

Dichloromethane is an anhydrous chlorinated organic solvent used for dissolution tests on rubber blends, and which chemical formula is CH_2Cl_2 . This colorless liquid had to be handled with protective equipment due to its health hazardous nature.

4. Methods

4.1. Material preparation

4.1.1. Sieving of GTR

Every type of GTR particles, listed in Table 3-1, were sieved by a vibratory sieve shaker (Analysette 3, Fritsch, Idar-Oberstein, Germany), Figure 4-1.



Figure 4-1 : Vibratory sieve shaker used.

The sieve shaker was used with an amplitude of 1,5 mm. One sieving cycle consisted in 5 minutes of sieving with vibration, followed by 3 sievings of 2 minutes each, the powder being stirred between each step to obtain a homogeneous particle size distribution. This cycle was repeated with a new batch of rubber powder until the needed weight of sorted particles was reached.

Three different sieve meshes were available: 80's, 120's and 230's mesh, corresponding to an opening of 180 μm , 125 μm and 63 μm respectively. This enabled to retrieve particles with the desired maximum size for the following studies.

4.1.2. Drying

PLA is known to have an affinity to absorb humidity, which could have an influence while further processing. Therefore, the PLA was dried for 16 hours before the melt-blending in a vacuum oven (Vaciotem-TV, J.P. SELECTA[®], Barcelona, Spain), Figure 4-2. The drying temperature was 70°C. The oven is equipped with a vacuum pump, and silica gel. The GTR particles were dried under the same conditions.



Figure 4-2 : Vacuum oven used to dry PLA and GTR at 70°C.

4.2. Processing

4.2.1. Internal mixer

An internal mixer (Brabender Plastic-Corder W50EHT, Brabender GmbH & Co., Duisburg, Germany) was used both to process the materials by melt-blending and to carry out the mastication of natural rubber. The software WinMix Brabender Mixer was used to acquire the torque and the temperature during the process. The torque was calibrated before the introduction of the materials and continuously measured during the whole blending. The targeted temperature inside the mixing chamber was reached thanks to three electrical heating elements and compressed air as a cooling system. The temperature of the melt was given by a thermocouple inside the chamber. A good mixing was ensured by two counter-rotating screws (roller blade type “W”). A fumes extraction system was used when adding DCP to avoid toxic gases (Figure 4-3).



Figure 4-3 : Internal mixer Brabender Plastic-Corder and fumes extraction system (CCP, UPC)

4.2.1.1. Mastication parameters

Prior to its addition PLA during the melt-blending, the natural rubber was masticated inside the mixing chamber of the internal mixer. The NR was taken from a bulk material and cut in pieces before being introduced into the internal mixer. A temperature of 80°C and a residence time of 15 minutes were chosen after the study performed in section 5.3.1, and the rotation speed of the screws was 40 RPM. The feeding mass of rubber to introduce to fulfill the mixing chamber was experimentally found to be 40g.

Regarding the production of ternary blends, GTR and DCP are added during the mastication, forming a masterbatch of elastomer containing 2/3 of NR and 1/3 of GTR. Two steps are needed to perform the mastication while always maintaining a full mixing chamber:

- (1) Pre-mastication of 40g of NR during 5 minutes
- (2) • **Minutes 0-5:** Mastication of 26g of NR with 13g of GTR (NR:GTR at a ratio 2/3:1/3)
 - **Minutes 5-10:** addition of 1,5 wt.% DCP (600 mg) and mixing with the elastomer for other 5 minutes.

For binary PLA/NR blends, natural rubber is simply masticated during 10 minutes before adding DCP for five additional minutes.

The processing parameters are summarized in Table 4-1:

Table 4-1 : mastication parameters of the rubber masterbatch

Temperature	80°C
Screws' rotation speed	40 RPM
Feeding mass	40 g
Reactive	1,5 wt.% DCP (of total elastomer mass)
NR residence time	15 minutes

4.2.1.2. Melt-blending parameters

All the produced blends containing PLA were melt-blended in the internal mixer Brabender. A temperature of 170°C and a rotation speed of 60 RPM was chosen according to a parameter study carried out in a previous works [66]. Not only this temperature allows a complete melting of PLA2002D®, since its end melting peak temperature peak, determined by DSC, is 158±1°C [6], but also

it is high enough to initiate the decomposition of the peroxide reactive used for dynamic vulcanization of the blends containing rubber (Figure 2-8). A higher temperature could have brought more degradation of both PLA and GTR.

The peroxide crosslinking agent Dicumyl Peroxide (DCP) was added during the melt blending for the PLA/GTR blends and during the mastication for the blends containing natural rubber, with a quantity of 1,5 wt.% of the total mass of elastomer (GTR and/or NR). To avoid the thermal degradation of PLA during blending, an antioxidant, Irganox® 1010 was also added (0.2 wt. % of the total blend mass).

For the preparation of PLA/GTR blends, a residence time of 14 minutes has been determined after a subsequent study. The melt-blending is carried out as follows:

- (1) **Minutes 0-4:** Introduction and melting of dried pellets of PLA2002D® and addition of Irganox® 1010 shortly after PLA.
- (2) **Minutes 5-9:** Addition of dried GTR powder and blending with PLA.
- (3) **Minutes 9-14:** Addition of DCP and further blending.

As for the blends containing natural rubber, the residence time was 9 minutes and the melt-blending followed these steps:

- (1) **Minutes 0-4:** Introduction and melting of dried pellets of PLA2002D® and addition of 88g of Irganox® 1010 shortly after PLA.
- (2) **Minutes 5-9:** Addition of masticated natural rubber or masticated NR/GTR blend containing DCP, and dynamic vulcanization.

The melt-blended parameters are summarized in *Table 4-2*:

Table 4-2 : Melt-blending parameters of the blends containing PLA

Temperature	170°C
Screws' rotation speed	60 RPM
Feeding mass	44 g
Reactive	1,5 wt.% DCP (of total elastomer mass)
Additive	88 mg Irganox® 1010
Residence time	<ul style="list-style-type: none"> • PLA/GTR blends: 14 min • Blends containing NR: 9 min

4.3. Compression Molding

After the melt-blending of the materials, they were compression molded in an IQAP LAP PL-15 hot plate press (IQAP Masterbatch SL, Barcelona, Spain), Figure 4-4. Two 170°C pre-heated steel plates were prepared, and right in the end of the blending in the internal mixer, the melt was taken out and introduced in between these two hot plates covered by a Teflon layer, inside a square aluminum frame of 150 mm wide and 1 mm thick. The whole was placed in the heated molds of the hot press. At first, a low pressure of 1 MPa was applied for 1 minute to pre-melt the material. Thereafter, the pressure was raised to 4 MPa for 5 minutes to get a homogeneous plate. Finally, the whole was removed of the hot mold and placed into the cold molds, enabling a fast cooling (-50°C/min) to room temperature. After 4 minutes of cooling down at low pressure, the material was taken out of the press. The molding parameters are presented in Table 4-3:

Table 4-3 : Hot press parameters

Pre-melting	1 MPa, 1 min
High pressure	4 MPa, 5 min
Cooling	1 MPa, 4 min, cooling rate -50°C/min



Figure 4-4 : Hot press molding machine (CCP, UPC)

4.4. Rubber characterization

4.4.1. Swelling in cyclohexane

Several types of GTR powder and DCP-crosslinked NR based samples were submitted to a swelling test in order to determine their network chains density, according to the network theory of Flory-Rehner [67]. This method allows to approximate the number of elastically effective chains per unit volume,

taking into account both the crosslinks and the physical entanglements. Three samples of each elastomer type were analyzed.

For the measurements of GTR, around 1g of waste tire powder was placed in a beaker containing the solvent cyclohexane, and the sample was left for 3 days. After that period, the swelling equilibrium was reached, and the swollen mass was measured with a micro-balance. The mass was taken directly after taking out the powder of the beaker, since cyclohexane is highly volatile. Then, regular mass measurements were carried out up to 3 hours after the first one, allowing an analyze of the swelling kinetics. Ultimately, the GTR was dried for 4 hours at 70°C, and a dry mass was measured.

In the same way, three samples of each NR-based elastomer were swollen in cyclohexane for 3 days, before measuring the swollen mass. The dry mass was taken after 3 days of drying at room temperature.

4.4.2. Dissolution in dichloromethane

The phase morphology of binary PLA/NR blends and ternary PLA/NR/GTR blends was analyzed by dissolution test. The samples were placed in beakers containing the solvent dichloromethane and left for an hour. The beakers were regularly stirred to facilitate the dissolution of the blends. To follow the evolution of the dissolution, photographs were taken before the immersion, after 15 minutes and after 1 hour of contact with the solvent.

4.5. Mechanical testing

4.5.1. Tensile testing

The mechanical behavior of the studied blends was mostly determined by uniaxial tensile tests performed according to the ISO 527 standard. The dumbbell shaped samples of type 1BA (Figure 4-5) were extracted from the molded sheets after compression molding. Die-cutting was performed to shape the specimens thanks to a specimen preparation punching machine (CEAST, Torino, Italy).

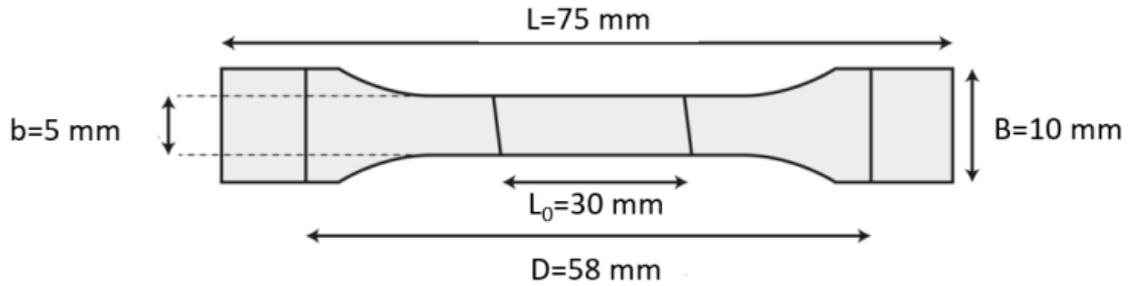


Figure 4-5 : 1BA Tensile sample with dimensions. L : total specimen length, L_0 : gauge length, B : overall width, b : width of narrow section, D : distance between grips.

The tensile tests were performed after 1 week aging of the samples at room temperature. The aim of this aging is to simulate the industrial storage of the material, inducing a ductile-brittle transition of the PLA. A universal tensile testing machine (SUN 2500, GALDABINI, Cardano al Campo, Italy), Figure 4-6, was used to carry out the tensile tests at room temperature with a load cell of 1 kN and the crosshead speed was constant and set to 10 mm/min. The displacement ΔL_x was recorded by a video extensometer (OS-65D CCD, Minstron, Taipei, Taiwan), measuring the distance between the gauge marks in the linear zone of the sample, and the data were processed by a Windows based software (Messphysik, Fürstenfeld, Austria).



Figure 4-6 : Tensile testing machine (CCP,UPC)

From the load-deformation curves given by the software, the engineering stress-strain curves can be calculated.

The engineering stress σ_i was obtained by dividing the tensile force F_i by the initial cross-section in the linear region A_0 :

$$\sigma_i = \frac{F_i}{A_0} \quad (1)$$

Where A_0 is defined by $A_0 = t * b$, with t the thickness and b the width of the sample. These values are an average of three measures, among which one is made at each gauge mark and one is taken in the center.

The engineering strain ε_i is the ratio of the displacement ΔL_x and the initial gauge length L_0 :

$$\varepsilon_i = \frac{\Delta L_x}{L_0} = \frac{L_x - L_0}{L_0} \quad (2)$$

To compare the mechanical behaviors of the studied materials, four tensile properties were calculated as follows:

- E_T : Tensile modulus. It is defined as the slope of the engineering stress-strain curve in the linear elastic regime. Even though the ISO 527 standard indicates a linear region in the strain ranges 0,05% - 0,25%, this interval has been shifted to different values depending on the type of blend studied to have a more accurate representativity, since the studied blends showed very dispersed behaviors. The strain ranges used are listed in Table 4-4:

Table 4-4 : Strain ranges used for the determination of the elastic modulus for different types of blends

Blend type	Strain range (%)
PLA/GTR	0,2 – 0,55
PLA/NR – PLA/NR/GTR	0,4-1

While studying elastomer blends, the tensile modulus cannot be calculated with the slope of the stress-stress curve and has been approximated by modelling the stress-deformation relation of the molecular chains following the Gaussian approximation, as subsequently explained in section 5.2.2.

- σ_y : Yield strength. It is defined as the maximum stress reached after the elastic region ends. The yield strength was directly read from the engineering strain-stress curve.

- ε_b : Strain at break. It is the engineering strain when the failure occurs, directly read from the engineering strain-stress curve.

- U_T : Energy at break. Energy absorbed by the sample from the start of the test to the failure. For its calculation, the area under the engineering stress-strain curve until failure was determined by integrating the stress over all measuring points:

$$U_T = \sum_{i=1}^n \frac{\sigma_{i+1} + \sigma_i}{2} * \varepsilon_{i+1} - \varepsilon_i \quad (3)$$

With n the total number of measuring points per sample.

Finally, a strain hardening slope was calculated for PLA/NR-based blends, defined as the slope of the engineering stress-strain curve during strain hardening. The slope has been calculated from $\varepsilon = 15\%$ to $\varepsilon = 20\%$.

4.5.2. Tensile-impact testing

The tensile-impact strength a_{tU} , defined as the energy absorbed by the specimen until the fracture divided by the initial cross section, has been determined through tensile-impact testing according to the standard ISO 8256. The same type of specimens as for tensile testing has been used (type 1BA), and the tests have been performed two weeks after the processing of the sheets.

A swinging pendulum (CEAST 6545, Torino, Italy), Figure 4-7, having a length $L = 374$ mm, assembled with a hammer having a mass of 3,655 kg and a potential energy of 25J, is released from an angle of 45° and hits the specimen at its lower position with an impact energy of 3,93 J and an impact velocity of 1,47 m/s. The specimen, clamped with a crosshead of 60g, is submitted to a high-speed tensile load.



Figure 4-7 : Swinging pendulum CEAST 6545 (CCP, UPC)

The energy E needed to break a specimen is calculated by the software DAS8WIN from CEAST, and the tensile-impact strength a_{tU} is calculated by dividing E by the cross section $A_0 = t * b$, with t the thickness and b the width of the sample, measured in the same way as explained in section 4.5.1.

The parameters used for the tensile-impact tests are summarized in Table 4-5:

Table 4-5 : tensile-impact test parameters

Specimen type	1BA
Pendulum length	374 mm
Hammer mass	3,655 kg
Hammer energy	25J
Initial angle	45°
Impact energy	3,93 J
Impact velocity	1,47 m/s
Crosshead weight	60g

4.6. Scanning electron microscope (SEM)

The fracture surfaces of the specimens were observed after tensile testing with a field emission scanning electron microscope (JSL-7001F, JEOL, Barcelona, Spain), Figure 4-8 (a). To do so, the specimens were cut 5 mm under the fracture surface and placed on a support (Figure 4-8 (b)). Due to the non-conductive nature of polymers, the samples had to be metallized before any SEM observation to avoid the accumulation of electrons on the surface. Thus, a few nanometers thick conductive layer of a Pt80/Pd20 alloy was sputtered on the fracture surface using a high-resolution sputter coater (Cressington 208HR). Afterwards, the support with the samples was placed in the vacuum chamber of the SEM to carry out the observations.



Figure 4-8 : (a) Field emission scanning electron microscope (CCP, UPC) and (b) Support holding the specimens

First, the surface topography was observed with a voltage of 1 kV. Micrographs were taken with a magnification of x20, x100, x300 and x1000. A chemical analysis was then performed by EDX with a voltage of 20 kV, to identify the GTR particles. A chemical spectrum and a mapping of the elements O, Si, S and C were obtained for each material at magnifications of x100 and x300.

4.7. Sample nomenclature

The studied blends are referenced in this document with a specific code. The name of the blends describes its characteristics, and is usually following this pattern:

$$\text{PLA/NR}_a/\text{GTR}_b^{c} (<S)$$

With:

- X, Y and Z the name of the components: PLA, NR and GTR
- a and b the weight fraction of the corresponding component
- c = \emptyset for cryogenically micronized GTR or c=D for devulcanized GTR
- S the maximum size of the particles in μm , for the blends containing GTR.

A few examples are given in Table 4-6:

Table 4-6: Examples of nomenclatures for the prepared blends

sample code	Blend characteristics accounting for code				
	PLA wt.%	NR wt.%	GTR wt.%	GTR type	Maximum particles size, μm
PLA	100	0	0	/	/
PLA/ GTR _b (<S)	100-b	b	0	cryo.	S
NR/GTR ^D _b (<S)	0	100-b	b	dev.	S
PLA/NR _a	100-a	a	0	/	/
PLA/NR _a /GTR _b (<S)	100-a-b	a	b	cryo.	S

5. Results and discussion

5.1. PLA/GTR blends

In spite of the biodegradability and biobased nature of PLA, the uses of this thermoplastic are still limited because of its brittle nature resulting in poor ductility and impact properties. In this project, several solutions to face this problem have been experimented. One of them is the incorporation of GTR, originated from waste tires, in a PLA matrix. Not only this is expected to improve the toughness of the material thanks to the addition of a deformable rubber phase, but it would offer a new opportunity to recycle tire wastes by at the same time lower the PLA based material's cost.

Several parameters have been studied to improve the properties of PLA/GTR blends. The effect of the type of used GTR, including the pre-treatment process of the particles and the tire part they are originated from, has been firstly discussed, before focusing on the influence of various processing parameters and finally the effects of the GTR particle size.

5.1.1. Effect of the GTR treatment

With the aim of introducing GTR into PLA, we aim to answer one main challenge of this project, namely the use of recycled materials. Its properties are difficult to control because of the large diversity of material's origin (type of tire, part of the tire) and its quality (variable life-times of the pneumatic). Moreover, several processes can be used to obtain GTR crumbs, playing a role on its physico-chemical and mechanical properties. For this project, three types of GTR powders with different origins were used. The material's characteristics are presented in Table 3-1.

In order to produce blends with good properties, different GTR have been selected. Three GTR powders having a maximum size of 125 μm have been mixed with PLA with a weight fraction of 15% (PLA/GTR₁₅) using Dicumyl Peroxyde (DCP) as a cross-linking agent, supposed to enhance the compatibility between the particles and the matrix via the dynamic vulcanization process. The use of certain amount of DCP in PLA has been reported in the literature to likely lead to the embrittlement of the material, due to an over crosslinking induced by the peroxide agent [23]. In order to ensure that the DCP does not deteriorate the mechanical behavior of the neat PLA, the tensile properties of the latter has been compared to DCP-crosslinked PLA, using the same DCP content than the one in PLA/GTR₁₅ blends. No significant deterioration of the polymer has been observed (cf. appendix 1A2).

Tensile tests have been carried out on the three different PLA/GTR₁₅ blends in presence of crosslinking agent (Figure 5-1). The tensile properties, namely the elastic modulus E , the yield strength σ_y , the strain at break ϵ_b and the energy at break U_T , have been measured and compared in Figure 5-2.

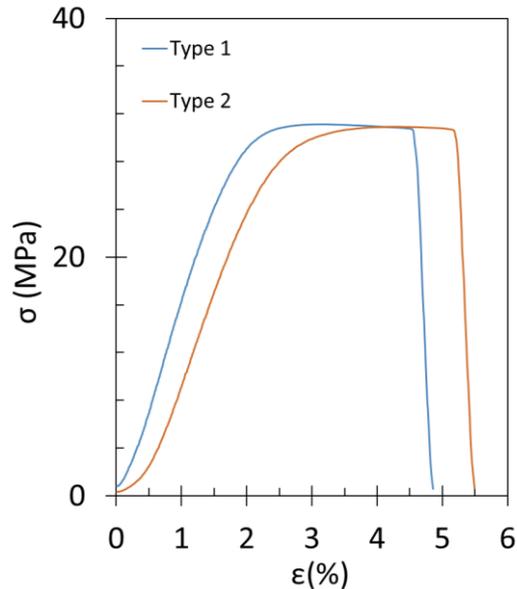


Figure 5-1 : GTR origin: tensile test engineering stress-strain curves for peroxide crosslinked PLA/GTR₁₅ blends from (i) lot n°1, (ii) lot n°2; for all particle size <125 μm

The mechanical properties of the PLA/GTR blend containing devulcanized GTR (n°3) is too brittle to make tensile test feasible as it broke during clamping. The material degradation during processing has been revealed by the decreasing torque after the introduction of GTR in the internal mixer (cf. appendix 1A4). This degradation can possibly be caused by the remaining chemical agents used during the process of devulcanization of the GTR, degrading the PLA matrix at high temperature. Indeed, even though devulcanized GTR has already been used in thermoplastic blends [52]–[54], it has not been reported to be used with PLA so far, due to easy degradation of the ester group.

The blends originating from GTR n°1 and n°2 show similar tensile properties, in spite of their distinct grinding process and the different tire parts they are originated from. A slightly more ductile behavior is noted for the blend containing GTR n°2 as compared to the n°1. Moreover, the highest proportion of fine particles contained in the GTR n°2 allows to retrieve particles with a diameter inferior to 63 μm, which will be needed thereafter. For this reason, the rest of the blends studied subsequently have been prepared from the GTR n°2.

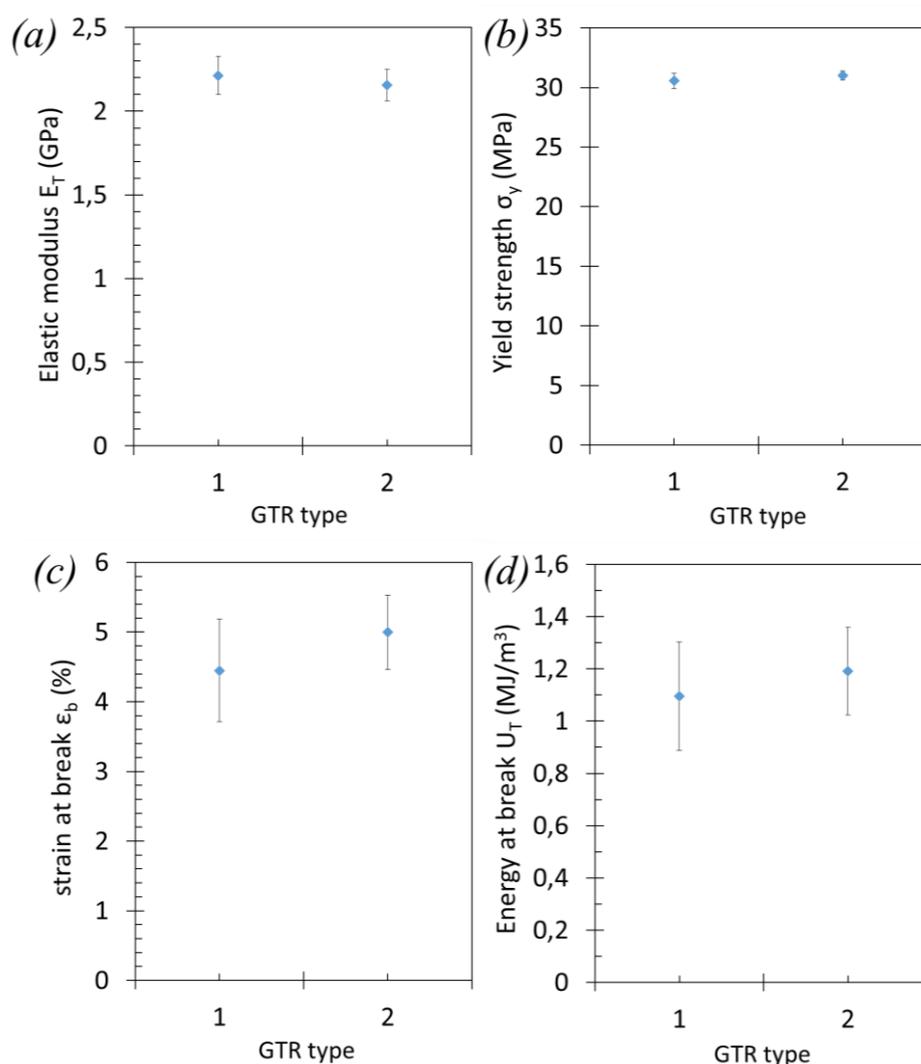


Figure 5-2: GTR origin: tensile properties (a) elastic modulus E_T (b) yield strength σ_y (c) strain at break ϵ_b and (d) energy at break U_T for peroxide crosslinked PLA/GTR₁₅ blends from (i) GTR n°1, (ii) GTR n°2; for all particle size <125 μm

5.1.2. Effect of the processing conditions

The processing conditions of the GTR-PLA blends have been investigated in order to get the optimum mechanical properties of the produced blends and thus making them comparable to the results found in the literature for PLA/GTR blends obtained with other methods than the one using crosslinking agent [50], [51]. The effects on mechanical properties of the residence time of the materials in the internal mixer and of the drying time of GTR before processing are presented thereafter.

5.1.2.1. Residence time

Residence time (the time that the material spends in the mixing chamber of the internal mixer) is a key parameter influencing the mechanical behavior of the produced materials through various mechanisms:

Firstly, both the PLA and the GTR are sensitive to high temperatures and can be deteriorated by a too long time exposed at processing temperature, being 170 °C in the frame of this project. In particular, PLA can suffer hydrolysis, lactide reformation or oxidative main chain scission. Moreover, GTR, as a vulcanized rubber, could be affected by the reversion phenomenon, reverting back to a material with properties close to gum state because of the transition from polysulfidic bonds to monosulfidic bonds [31], [32], and by the phenomenon of residual curative, leading to an over crosslinking as discussed in section 2.2.4.

Secondly, a sufficient residence time is needed to reach a homogeneous dispersion of the GTR particles into the PLA matrix. Besides, the DCP crosslinking agent, allowing an enhancement of the interface PLA/GTR via reactive blending, requires sufficient time in the mixing chamber to react, as shown in Figure 2-8. Hence, a compromise is to be found in the residence time of the materials to fulfill these criteria.

To investigate the effect of the residence time on the properties, 3 blends of PLA/GTR₁₅ with a particle size of 125 µm have been processed during the time t_1 , with an addition of DCP, 5 minutes before the end of the mixing. Three residence times t_1 , defined as the time between the introduction of the PLA in the chamber and the extraction of the melt, have been selected equal to 9 minutes, 14 minutes and 24 minutes. Tensile tests have been performed on each blend and Figure 5-3 shows the obtained stress-strain curves.

From this figure, the properties of the three blends at small deformations seem to be very similar. Only a slight increase of the modulus with increased residence time is to be reported in Figure 5-4 (a), probably due to the over crosslinking of PLA induced by DCP and an enhanced residual curative of GTR. On the other hand, the yield strength stays almost unchanged by the residence time. Then, a more brittle behavior is observed for the materials having been submitted to longer residence times.

Figure 5-4 (d) represents the energy at break U_T of the blend as a function of the residence time, and a clear U_T decrease is to be noted for longer residence times, with a drop of 12% and 33% for, respectively, $t_1 = 14$ min and $t_1 = 24$ min, compared to $t_1 = 9$ min. This is the result of a lower strain at break for these materials (Figure 5-4 (c)), probably because of the thermal degradation of PLA and GTR.

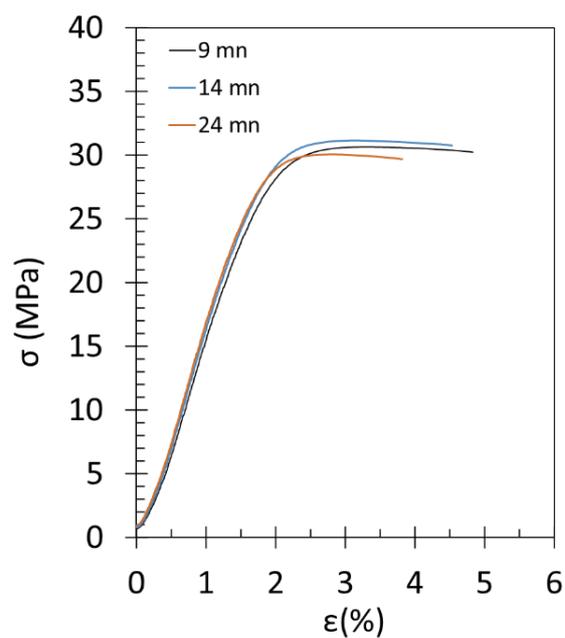


Figure 5-3: Residence time: Tensile test engineering stress-strain curves for peroxide crosslinked PLA/GTR blends with residence times t_1 of (i) 9 minutes, (ii) 14 minutes and (iii) 24 minutes; for all particle size $<125 \mu\text{m}$ and 15 wt.% GTR

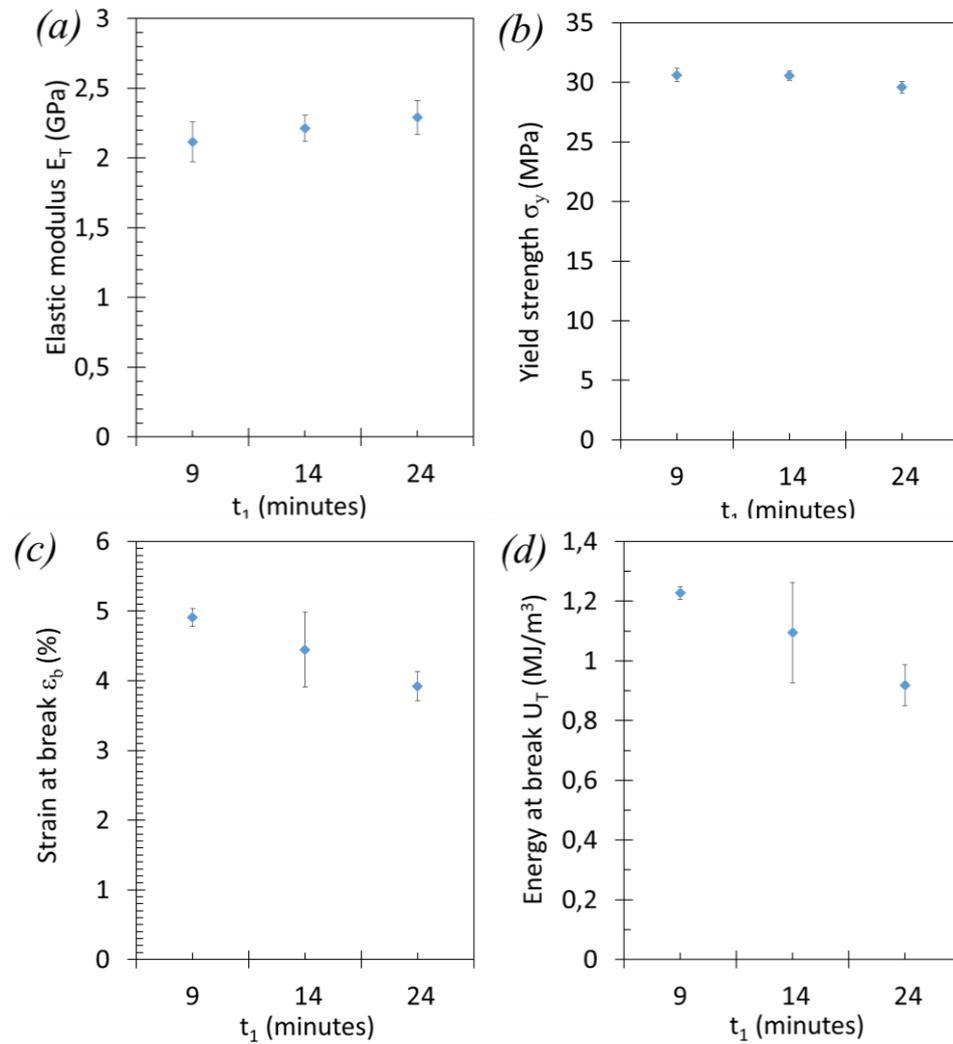


Figure 5-4 : Residence time : tensile properties (a) elastic modulus E_T (b) yield strength σ_y (c) strain at break ϵ_b and (d) energy at break U_T for PLA/GTR₁₅ blends with particles <125 μm and residence times t_1 = (i) 9 minutes, (ii) 14 minutes and (iii) 24 minutes; for all dynamically DCP-crosslinked

As a conclusion, the shortest residence time of 9 minutes for the processing of the blends is chosen, resulting in better mechanical properties by limiting the degradation of the material. Moreover, the particles' dispersion is believed to be sufficiently homogeneous at this residence time.

5.1.2.2. GTR drying time

Before mixing the GTR particles with PLA, it is necessary to dry them and reach a low moisture content to avoid the evaporation of residual water during the process, degrading the mechanical properties. To do so, the particles are dried in a vacuum oven at 70 °C during a time t_2 . It has been reported in the literature that a long exposition at this temperature could lead to reversion [32] and residual curative [33], increasing the crosslink density and possibly reducing the reactivity of the rubber with DCP. For this reason, in addition to the optimization of the residence time in the internal mixer during the blending, a study about the influence of the drying time of GTR has been performed.

Thus, DCP-vulcanized PLA/GTR₁₅ blends, with a maximum GTR size of 125 µm, have been prepared with a GTR drying time t_2 of 1 hour, 4 hours and 16 hours. The resulting samples have been submitted to tensile tests and the tensile properties are presented in Figure 5-5. No difference of modulus and yield strength was observed between the 3 materials, but the drying time seems to have an effect on the strain at break and the energy at failure:

- Firstly, a drying time of 1 hour gives a significantly more brittle behavior of the material, with a lower strain and energy at break. This could be explained by an insufficient drying of the powder, with remaining moisture in the material.
- The 4 h and 16 h drying allow to have better properties, especially a better ductility, proving the efficiency of the drying. 4 h drying is however reported to render a slightly higher strain and energy at break compared to 16 h drying, possibly because of a slight degradation of the GTR after 16 h at 70 °C.

In the following, the GTR particles have been dried for 16 hours before their introduction in the blends, firstly because of the very few properties degradation observed after this time, and secondly due to its conveniency, since the particles can be dried overnight.

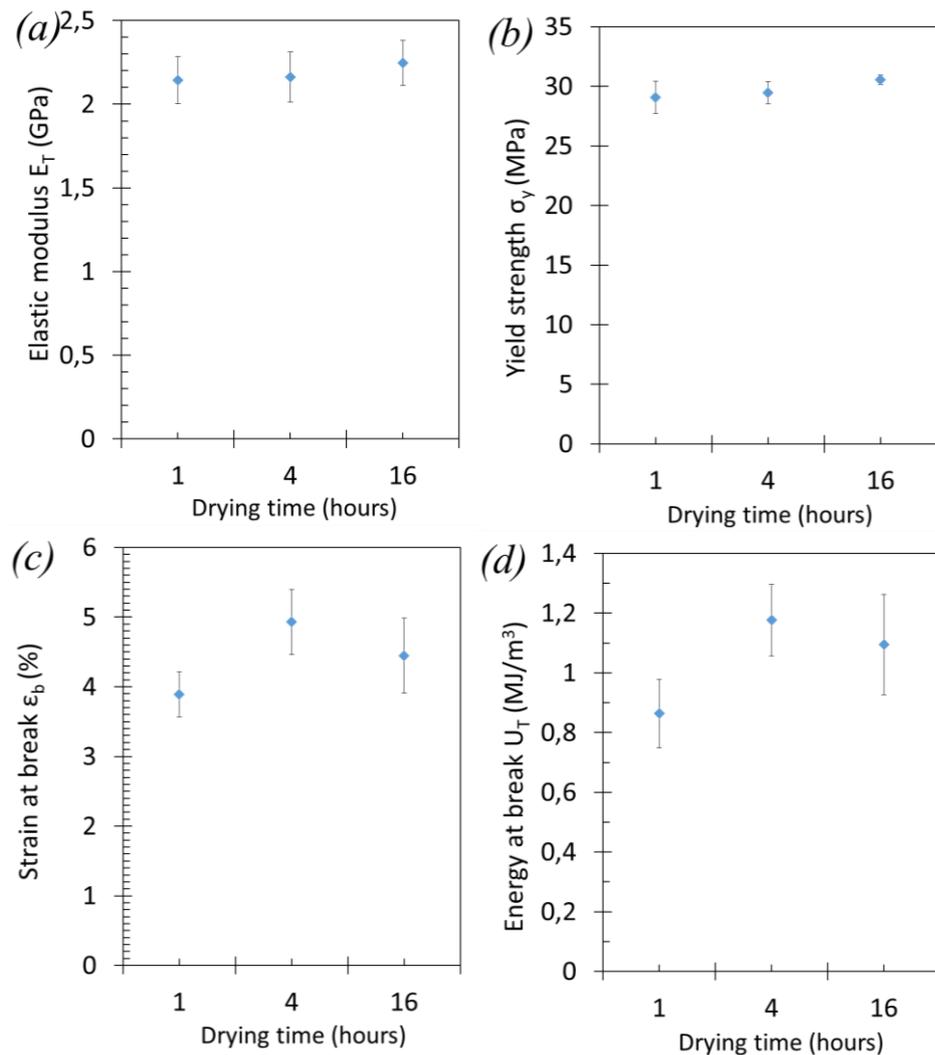


Figure 5-5 : Drying time: tensile properties (a) elastic modulus E_T (b) yield strength σ_y (c) strain at break ϵ_b and (d) energy at break U_T for PLA/GTR₁₅ blends with particles <125 μm and drying times t_2 = (i) 1 hour, (ii) 4 hours and (iii) 16 hours; for all dynamically DCP-crosslinked

5.1.3. Effect of particle size

in the previous sections, it has been shown that the size of the rubber particles has a significant effect on the tensile properties. Smaller particles provide better properties as compared to larger ones [29], [66]. However, the finest mesh used so far was 120's, allowing to retrieve particles with a size lower than 125 μm . For that reason, blends of PLA/GTR with particle size inferior to 63 μm , obtained with 230's mesh, are studied in this part and compared to the blends with <125 μm particles and neat PLA. The GTR containing blends have been dynamically vulcanized in presence of DCP. Tensile tests have been carried out (Figure 5-6). Stress-strain curves show that the smallest particles seem to enhance

the stiffness, the yield strength, and the strain at break compared to the bigger size, even though the yield strength stays lower than the one of PLA.

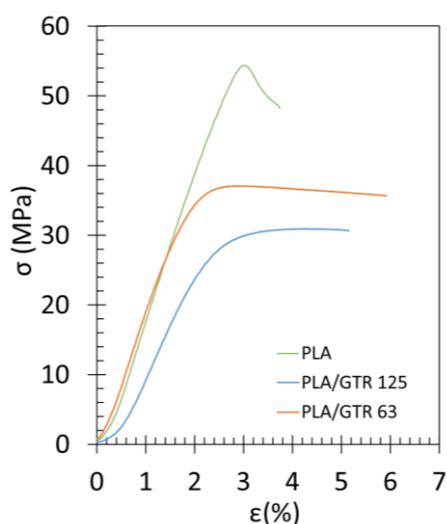


Figure 5-6: GTR particle size: tensile test engineering stress-strain curves for (i) PLA and peroxide crosslinked PLA/GTR₁₅ blends with particle size (ii) <125 μm and (iii) <63 μm

The Elastic modulus, yield strength, strain at break and energy at break have been calculated and compared for each material in Figure 5-7.

Firstly, in accordance with the trends observed with the stress-strain curves, the use of finer particles provide higher elastic modulus. The modulus drop of PLA/GTR 63 is found to be of only 7% compared to PLA, whereas PLA/GTR 125 shows a 35% elastic modulus drop. This could be the consequence of a better distribution of the GTR in the PLA matrix. Similar modulus enhancement for small particles has been reported in literature [68].

Moreover, the yield strength and strain at break of PLA/GTR 63 are, respectively, 19% and 21% higher than the ones of PLA/GTR 125. On the one hand, the yield strength enhancement could be the consequence of a better particle distribution for the smallest size, promoting the distribution of the plastic deformation of the matrix upon loading and thus avoiding localized yielding into the PLA matrix [69]. On the other hand, this homogeneous distribution enabled by small sizes, in addition to a higher particles number, resulting in distributed small microcracks, then preventing premature failure [29]. As a result, while the blend with <125 μm particles shows no significant difference with PLA for the energy at break, the use of fine particles under 63 μm allow a 52% enhancement.

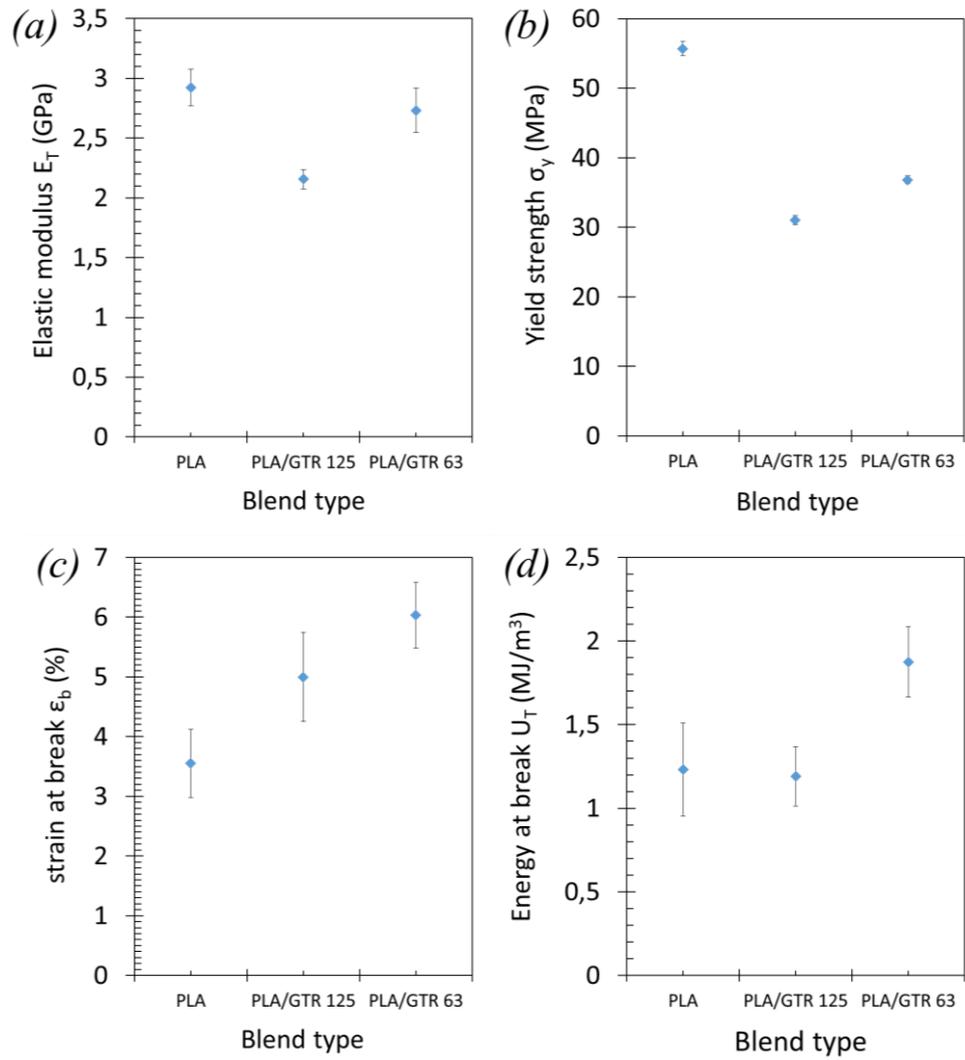


Figure 5-7: GTR particle size : tensile properties (a) elastic modulus E_T (b) yield strength σ_y (c) strain at break ϵ_b and (d) energy at break U_T for (i) PLA and peroxide crosslinked PLA/GTR₁₅ blends with particle size (ii) <125 μm and (iii) <63 μm

5.2. NR/GTR Elastomeric blends

In spite of the promising properties of PLA/GTR blends, it still shows some limitations regarding the improvement of toughness and deformation energy as compared to neat PLA. In the following, the possibility to encapsulate the GTR particles into a rubber matrix to further improve the mechanical properties of the studied blends and at the same meet the need of waste tire recycling incorporating higher quantity of GTR has been envisaged.

Natural rubber has been chosen as the rubber matrix due to its proximity in nature with the GTR. Indeed, GTR crumbs are reported to be mostly composed of a rubber phase (73 wt. %), including 85 wt. % natural rubber and 15 wt. % Styrene Butadiene rubber, and carbon black particles (27 wt. %).

Moreover, natural rubber, in addition to its bio-based nature, once vulcanized, is known to possess good mechanical properties. This material is able to crystallize under strain, which is known to be at the origin of its enhanced mechanical properties such as crack growth resistance and fatigue behavior [70].

In this section, the physico-chemical and mechanical properties of the vulcanized NR/GTR blends have been investigated. The crosslink density of the GTR powder and the NR/GTR blends will be firstly characterized. Then, the effect of the nature of the particles will be presented by comparing the devulcanized GTR and the grinded GTR. Lastly, the effect of the particle size and the influence of the GTR content on the mechanical behavior of the blends will be presented.

5.2.1. Average crosslink density of the GTR powder and the elastomeric blends

The average crosslink density in the material before (GTR) and after processing (NR/GTR blends) gives important information about the efficiency of the vulcanization process. It also allows to explain some of the mechanical properties of the elastomer blends, which are partly ruled by the crosslink density.

The average crosslink density has been calculated for the GTR powder as received, that is to say before the process of blending, and for the NR/GTR blends after having been vulcanized with the peroxide crosslinking agent. The polymers network chains' density, or crosslink density, has been determined from swelling ratio Q_{pol} in cyclohexane, defined as $Q_{pol} = V/V_0$, where V and V_0 are the volumes of the polymer, respectively, at swelling equilibrium and after drying. The crosslink density ν_c is calculated through the Flory-Rehner equation [67]:

$$- [\ln(1 - \nu_2) + \nu_2 + \chi_1 \nu_2^2] = V_1 \nu_c \left(\nu_2^{\frac{1}{3}} - \frac{\nu_2}{2} \right) \quad (4)$$

Where $v_2 = \frac{1}{Q_{pol}}$ is the volume fraction of the polymer in the swollen mass, V_1 (108,7 cm³/mol) is the molar volume of the solvent (cyclohexane), ν_c represents the number of active network chains per unit volume and χ_1 is Flory-Huggins polymer-solvent dimensionless interaction term (χ_1 is equal to 0,399 for the NR-cyclohexane system [71]).

5.2.1.1. Average crosslink density of the GTR powder

The main types of particles used along the project, originated from cryogenic process and devulcanization process, have been characterized before their incorporation into the blends by a crosslink density measurement. The network chains density as a function of the particles size has also been investigated. The characterized GTR powders are represented in Table 5-1 .

Table 5-1 : characteristics of the analyzed GTR powders

Material's name	Pre-treatment of the GTR powder	Particles maximum size (µm)
GTR 63	Cryogenic process	63
GTR 125	Cryogenic process	125
GTRD 125	Ambient grinding + Physico-chemical devulcanization	125

GTR, as a material originated from tires, can be considered as a composite made of a rubber matrix, mostly composed of natural rubber, and carbon black particles, considered as not deformable and not affected by swelling. For this reason, the swelling ratio of the composite Q , found by measuring the volume ratio between the swollen and the dry state, is underestimating the real swelling ratio of the polymer matrix itself Q_{pol} . Hence, assuming that there is a perfect interface filler-rubber, the relation linking them is:

$$Q_{pol} = \frac{Q - \varphi_f}{1 - \varphi_f} \quad (5)$$

Where φ_f is the volume fraction of carbon black in the composite, equal to 0,13 in GTR crumbs.

Figure 5-8 shows the calculated crosslink densities of the polymer matrices of each studied GTR crumbs. Expectedly, the devulcanized GTR powder has a 2 times lower crosslink density than the cryogenically processed powder, testifying of the efficiency of the physico-mechanical devulcanization process to break the crosslinks.

The crosslink density of GTR 125 originated from cryogenic process, equal to $1,4 \cdot 10^{-4} \text{ mol.cm}^{-3}$ is, furthermore, found to be the same as the one of the ambient grinded GTR of the same size, as reported in the previous works of this project [66], showing that these two processes give similar rubber properties. However, an important increase of calculated crosslink density is to be noted for the smallest particles, whereas no size effect was reported on crosslink density in the previous works. These results are to be taken carefully, since the overestimation of the crosslink density could be due to:

- **Measurement uncertainty:** when the powder is weighed in the swollen state, some solvent could be trapped in between the particles due to capillarity forces. Thus, the measured mass is not only the one of the swollen rubber, but also the free solvent mass, leading to an overestimation of the swelling ratio.
- **Presence of non-rubber components:** Due to the pre-treatments of the powders, a few quantities of talc particles are mixed to the GTR powder. This is believed not to affect the mechanical properties of the blends, but these particles do not swell in the solvent and could, thus, lead to the overestimation of the crosslink density. Moreover, due to their micrometric size, these talc particles are believed to be in higher proportions in the 63 μm GTR, having been finely sieved.
- **Gravity effect during sieving:** The particles of GTR with higher carbon black content are heavier due to the higher density of carbon black compared to rubber. Thus, they could preferentially go through the sieves, leading to a highest carbon black content in the finest particles. This would explain the observed lower swelling ratio.

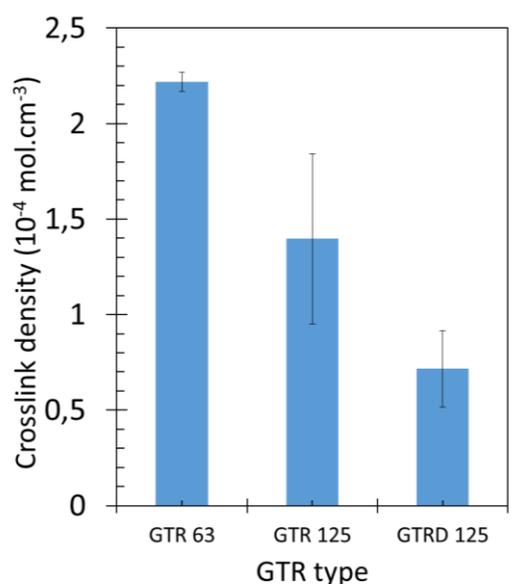


Figure 5-8 : Average crosslink densities of the rubber in GTR particles measured by swelling, for (i) cryogenically grinded GTR with particle size < 63 μm , (ii) cryogenically grinded GTR with particle size < 125 μm and (iii) devulcanized GTR with particle size < 125 μm

5.2.1.2. Average crosslink density of the elastomeric blends

Several types of NR/GTR blends have been processed by DCP-induced dynamic vulcanization, varying the type of GTR powder, as well as its size and content. The characteristics of the blends are shown in Table 5-2.

Table 5-2 : Characteristics of the produced DCP-crosslinked NR/GTR blends

Blend's name	GTR weight content (%)	Pre-treatment of the GTR powder	Particles maximum size (µm)
NR	0	/	/
NR/GTRD 125	33	Ambient griding + Physico-chemical devulcanization	125
NR/GTR 125	33	Cryogenic process	125
NR/GTR 200	33	Cryogenic process	200
NR/GTR 63	33	Cryogenic process	63
NR/GTR ₁₀ 125	10	Cryogenic process	125
NR/GTR ₂₀ 125	20	Cryogenic process	125

The cross-linking reaction induced by DCP is supposed to increase the crosslinking density of the NR matrix and, on the other hand, partially re-vulcanize the GTR particles, improving the interfacial adhesion with the NR. To characterize these phenomena, the crosslink density has been calculated on the NR and the blends, applying the swelling ratio correction for the blends due to the presence of carbon black. The influence of the GTR pre-treatment, the particle size and weight fraction on the crosslink density of the blends are represented in Figure 5-9 (a), (b) and (c), respectively.

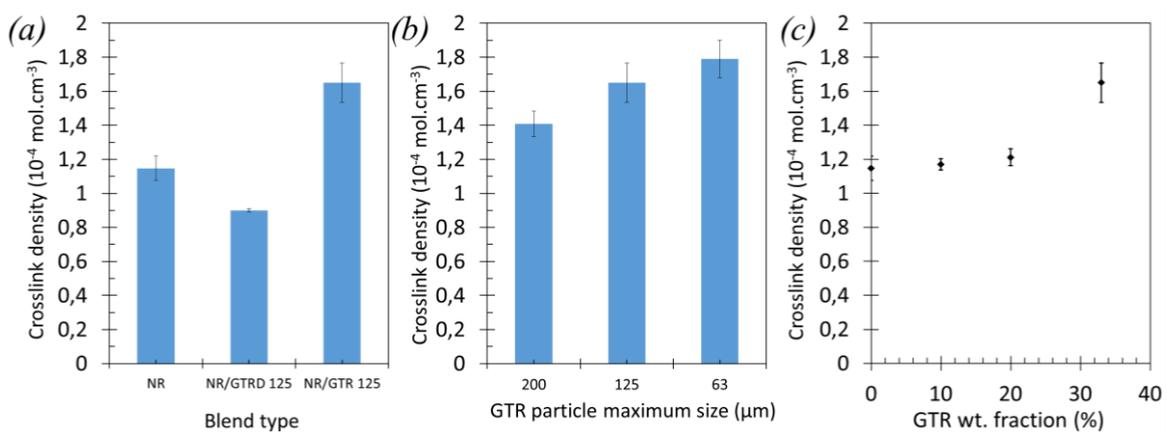


Figure 5-9 : Average crosslink densities calculated by swelling in cyclohexane of (a) NR, NR/devulcanized GTR and NR/GTR with particle size of 125 µm, (b) NR/GTR blends with particle size of (i) 200 µm, (ii) 125 µm and (iii) 63 µm, and (c) NR/GTR blends with particle size <125 µm as a function of the GTR weight content; for all dynamically DCP-crosslinked.

Firstly, the average chains' density of the vulcanized natural rubber is found to be equal to $1,1 \cdot 10^{-4} \text{ mol} \cdot \text{cm}^{-3}$. This value is in between the one of devulcanized GTR powder and the one of cryogenically processed GTR powder (Figure 5-9 (a)). After the blending of the GTR with NR, the same tendency is observed: the addition of devulcanized GTR leads to a lower crosslink density compared to vulcanized NR, while the incorporation of GTR from cryogenic process renders a higher crosslink density. With this result, no clear re-vulcanization of GTR during the process can be concluded, since the crosslink densities of the blends are not significantly higher than the one of NR. However, the particles might partially vulcanize on their surface and create crosslinks with the NR, the effect on the global crosslink density in the blends being not visible.

Nevertheless, some effects related to other parameters are to be pointed out:

- **Particle size (Figure 5-9 (b)):** As observed for the GTR powders, the decrease of the GTR size goes along with a slight enhancement of the crosslink density. It could be explained by the phenomena discussed in 5.2.1.1, as well as by a higher surface area of the smallest particles for the same GTR weight content, enabling an enhanced crosslinking at the surface of the particles.
- **GTR content (Figure 5-9 (c)):** The crosslink density of the blends containing GTR from cryogenic process and with a size of $125 \mu\text{m}$ seems to raise with the GTR content. It may be explained by the slightly highest crosslink density of GTR particles compared to the NR matrix, so according to the rule of mixtures, increasing its amount would increase the global crosslink density of the blends. Moreover, increasing the GTR content would also mean more potential particles crosslinking during the process, supporting the phenomenon.

5.2.2. Mechanical properties

5.2.2.1. Effect of the nature of the GTR particles

This section focuses on the use of two different types of GTR in the elastomeric blends, having been subjected to distinct pre-treatment. The first one, referred as GTR n°2 in Table 3-1, has only been ambient grinded and is supposed to not having been extensively devulcanized, whereas the second one, GTR n°3, has also undergone a physico-chemical devulcanization. The use of devulcanized GTR is reported to enhance the compatibility between the particles and the matrix in NR/GTR blends in the literature [56], [57]. Thus, the mechanical properties of peroxide crosslinked NR/GTR and NR/GTR^D blends containing 33% of waste rubber (1/3 GTR, 2/3 NR) with a maximum particle size of $125 \mu\text{m}$ have been compared, namely the elastic modulus and the strain induced crystallization characteristics. To do so, uniaxial tensile tests have been performed on the two blends and the results were compared to the pure NR (Figure 5-10). It can be seen on the stress-strain curves that all of the elastomer blends

have an hyperelastic behavior, characteristic of vulcanized rubbers. This is characterized by a nonlinear stress-strain relationship, with a first phase in which the material is relatively stiff at small deformations, followed by a softening and finally a hardening at high deformations.

The stress-strain curves show that the blends with devulcanized GTR seem to have an intermediate behavior between the soft NR and the stiffer NR/GTR blends. The failure properties (elongation at break, ultimate tensile strength) of the different blends has not been investigated because the fracture of the sample was usually not reached. The samples usually slipped out of the clamps before the failure. For this reason, the stress-strain curves have only been represented up to $\epsilon=350\%$.

The nonlinear elasticity of vulcanized rubbers implies that the elastic modulus E_T cannot be calculated directly from the tensile curve. Yet, the modulus can be approximated by modelling the stress-deformation relation of the molecular chains following the Gaussian approximation [72]. This model is applicable in deformation regime where hyperelastic behaviour is expected and dissipative mechanisms are not expected (e.g. viscoelasticity, strain induced crystallization). Following the Gaussian model, the stress can be predicted as a function of the strain according to:

$$\sigma_G = \frac{E_G}{3} * \frac{\lambda-1}{\lambda^2} \quad (6)$$

Where σ_G and E_G are the stress and elastic modulus given by the Gaussian chains model, and the stretching ratio λ is equal to $1+\epsilon$.

Thus, a Gaussian model stress-strain curve can be plotted and compared to the tensile curve, and by using the least square method at small deformations (until $\epsilon = 100\%$) between these two curves, the best-fitting gaussian curve can be found. This curve will enable to calculate the elastic modulus using the Gaussian chains theory and equation (6).

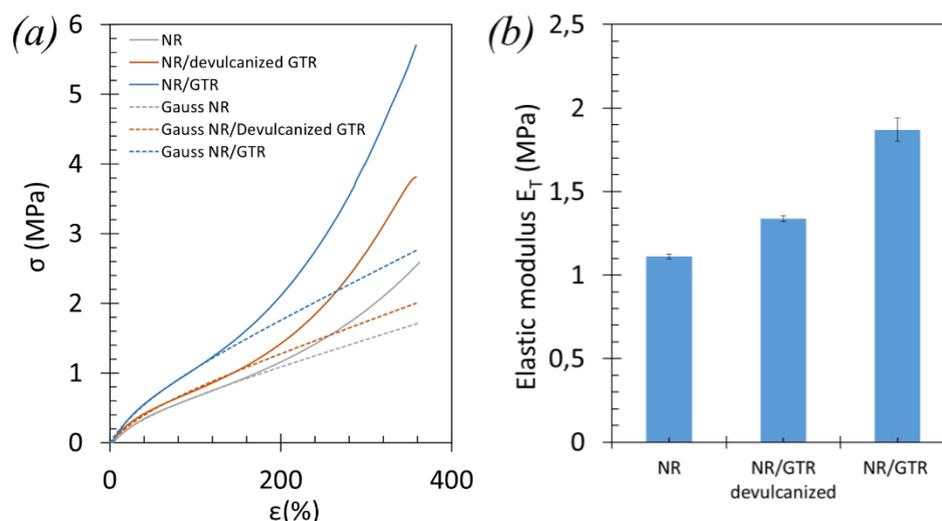


Figure 5-10 : GTR particles nature. (a) Tensile test engineering stress-strain curves and Gaussian approximation and (b) Elastic modulus for peroxide crosslinked elastomer blends of NR, NR/devulcanized GTR₃₃ and NR/GTR₃₃; for all particle size <125 μm .

Figure 5-11 (a) reveals that NR/GTR^D blends modulus is 40% lower than the one of NR/GTR blends, and closer to the modulus of pure natural rubber with an enhancement of only 20,2%. It is known that the carbon black contained in the waste rubbers with a volume fraction of 0.27 wt.% is considered as a not deformable particle responsible of the increase of the modulus, which may explain part of the reinforcement in both blends as compared to the NR. However, due to the expected same amount of carbon black particles in both GTR^D and the GTR blends, the difference of modulus between these two materials is not related to the presence of carbon black. Rather, it is likely due to a difference of crosslinking density of the waste rubbers. The grinded GTR has already been vulcanized before the processing of the blends and thus has a relatively high crosslink density before processing the rubber blends. The processing of NR/GTR blends involves a high temperature maintained for 9 minutes and the use of a peroxide crosslinking agent, enabling the rubber of GTR particles to undergo an over crosslinking, making them stiffer. On the other hand, GTR^D is supposed not to be crosslinked before the processing and is probably still less crosslinked after the processing of the blends than grinded GTR.

For small strains, it can be seen on Figure 5-10 (a) that the Gaussian curve and the tensile curve fit. Indeed, the Gaussian chains method is realistic. From a certain strain, the two curves deviate. This gap is due to a strain hardening of the material, which for natural rubber can possibly be explained by strain induced crystallization.

The strain induced crystallization (SIC) onset has been calculated by plotting the difference of energy between the gaussian approximation and the experimental tensile curve (Figure 5-11 (b)). The crystallization has been considered as initiated from an energy gap of $0.01 \text{ MJ}\cdot\text{m}^{-3}$. With this method, only the energy dissipation due to crystallization can be revealed. First, it is show that the SIC onset for

the GTR^D blends is very close to the one of NR (Figure 5-11 (b)). Theoretically, the introduction of filler in NR changes the stress field and increases the local strain of the rubber chains. This phenomenon is also called strain amplification [67]. Yet, the carbon black content in the studied blends (9 wt%) is very small, which would have its minor effect on the crystallization onset.

Nevertheless, the SIC onset occurs at 30% lower strain for the GTR blends compared to GTR^D blends and NR (Figure 5-11 (b)). This suggests that the onset of crystallization, in this case, is not ruled by the strain amplification induced by the filler presence, but mostly by the crosslink density of the blends. These results are in line with Flory's type models, in which SIC is triggered by the density of the cross-linking nodes of the vulcanized NR [70]. Thus, the higher crosslink density in regular GTR particles is believed to allow a faster crystallization of natural rubber.

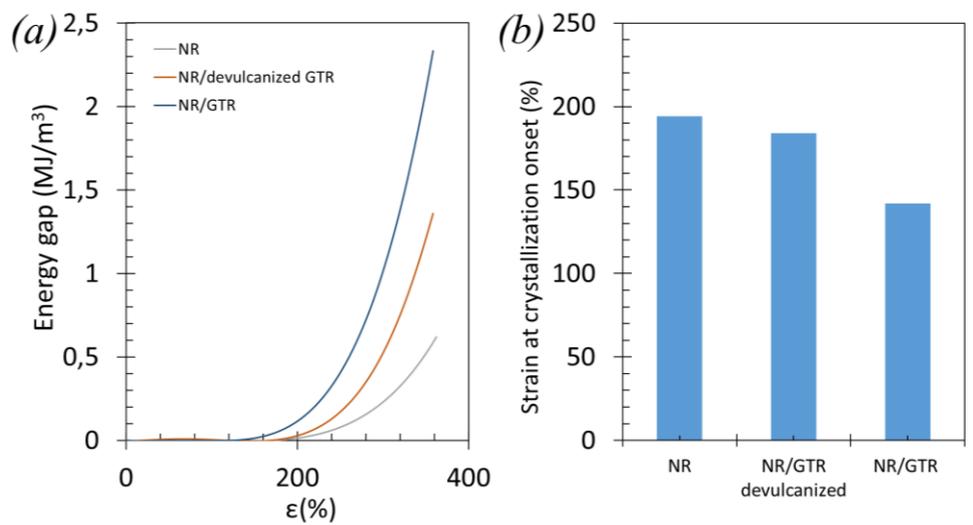


Figure 5-11 : GTR particles nature : (a) Energy gap between the tensile and Gaussian curves, and (b) strain at crystallization onset for peroxide crosslinked elastomer blends of (i) NR, (ii) NR/devulcanized GTR₃₃ and (iii) NR/GTR₃₃; for all particle size <125 μm

In order to characterize the dissipative energy associated with strain induced crystallization in the two types of blends, incremental tensile cycles have been carried out, increasing the displacement between the grips of 20 mm for every cycle. The cycle consists in a loading phase up to the required displacement and an unloading phase up to a null force. The corresponding stress-strain curves are reported in Figure 5-12 and compared to the single tensile curves of the same materials.

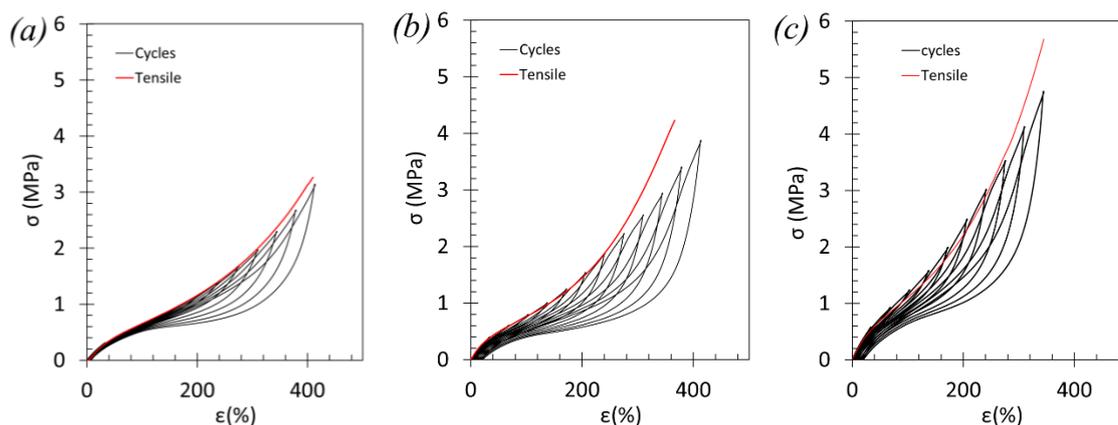


Figure 5-12 : GTR particles nature: engineering stress-strain curves of peroxide crosslinked elastomer blends of (a) NR, (b) NR/devulcanized GTR₃₃ and (c) NR/GTR₃₃ for (i) loading-unloading incremental cycles and (ii) tensile test; for all particle size <125 μm

Assuming that the behavior of the elastomers is hyperelastic, the loading phase of the cycles should be consistent with the tensile curve. However, a difference is observed, which is believed to be due to the slipping of the samples out of the grips. Moreover, some minor contributions from viscoelastic effects (chains friction, chains slippage) may also contribute to slightly relax the stress in incremental cycles as compared to single tensile test.

It is shown that the mechanical hysteresis, attesting for the energy dissipation, appear at lower strains for the GTR-filled natural rubber than for the NR. This observation is in line with the strains at crystallization onset given by Figure 5-11 (b). In contrast, this method shows that the SIC onset of NR/GTR^D is about the same as for NR/GTR, whereas the previous method showed an earlier SIC onset of NR/GTR blends. This difference of results may be explained by the fact that the two methods allowing to detect the crystallization onset, namely the energy gap between the tensile curve and the gaussian curve and the energy dissipation calculated through incremental cycles, do not take in account the same parameters. Indeed, the energy dissipation observed with the hysteresis could be explained by two causes, namely viscoelastic effects due to the successive cycles and strain induced crystallization, whereas the gaussian method only considers the strain hardening due to crystallization.

To quantify this energy dissipation, the area of the hysteresis, corresponding to the energy dissipation, has been plotted as a function of the maximum deformation reached during the cycle in Figure 5-13. This graph also shows that for a given strain, the energy dissipation is higher for the filled rubbers, especially the GTR-filled rubber, than for the NR (Table 5-3). This could be explained by the effect of the crosslink density on the crystallization onset, as a high crosslink density allows to crystallize at a lower strain due to faster chains alignment, thus shifting the crystallization process to lower strains.

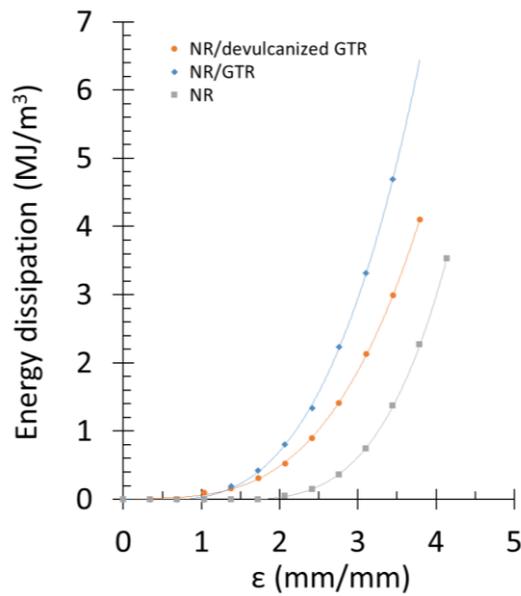


Figure 5-13: GTR particles nature: Energy dissipation as a function of the maximum strain reached during the cycle for peroxide crosslinked elastomer blends of (i) NR, (ii) NR/devulcanized GTR₃₃ and (iii) NR/GTR₃₃; for all particle size <125 μm

Table 5-3 : Energy dissipation for the 345% strain cycle for (i) NR, (ii) NR/devulcanized GTR₃₃ and (iii) NR/GTR₃₃; for all particle size <125 μm

Material	Energy dissipation at strain $\epsilon=345\%$ (MJ.m ⁻³)
NR	1.37
NR/devulcanized GTR ₃₃	2.99
NR/GTR ₃₃	4.69

5.2.2.2. Effect of the GTR particles size

In this section, the mechanical and strain induced crystallization properties of elastomer blends containing 33% of GTR (NR/GTR₃₃) containing different particle sizes have been investigated. To do so, 3 different NR/GTR₃₃ blends have been sieved with different mesh sizes: 70's mesh (<200 μm), 120's mesh (<125 μm) and 230's mesh (<63 μm).

Firstly, as for the comparative study of the GTR nature, monotonic tensile tests have been carried out to extract the values of the modulus and the SIC onset of all the blends. The experimental engineering stress-strain curves and theoretical gaussian stress-strain curves, used to calculate the modulus and the SIC onset, are represented in Figure 5-14. The 3 particles sizes gave very similar shapes of the stress-strain curves, especially at high deformation. Only a slightly higher stress in the small strain domain is

reported for the lowest size. Hence, the particles sizes seem to have few impacts on the mechanical behavior of the blends.

The modulus of the blends containing <200 μm and <125 μm particles are found to be about the same (Figure 5-14 (b)), but a small increase in modulus of 21.7% is to be noted for <63 μm particles compared to the <200 μm particles. Possibly, the size effect on elastic modulus may be explained by the partial rubber particles connectivity due to the good dispersion of the lowest particle sizes in the NR matrix, allowing the stiffer GTR particles to bear part of the load in the elastic regime, hence increasing the elastic modulus.

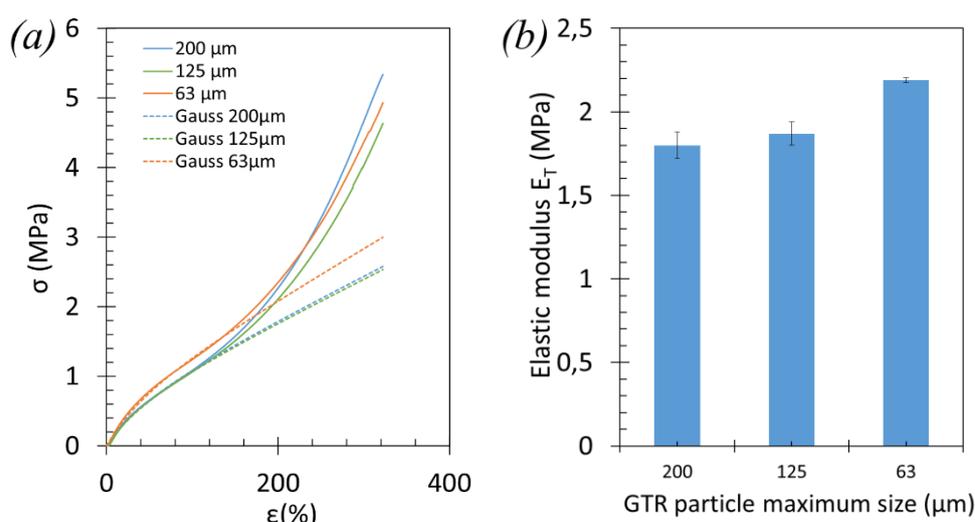


Figure 5-14 : GTR particles size : (a) Tensile test engineering stress-strain curves and Gaussian approximation and (b) Elastic modulus for peroxide crosslinked elastomer blends of (i) NR/GTR <200 μm , (ii) NR/GTR <125 μm and (iii) NR/GTR <63 μm ; for all 33 wt% GTR

The increased elastic modulus with the particles size is consistent with the increased network chains density (Figure 5-9 (b)). This would have resulted in a lower strain onset for crystallization. However, an opposite trend is observed here, with only slight variations from 132% to 148%. Indeed, it is shown in Figure 5-15 (a) and (b) that the strain at crystallization onset is slightly delayed with increased particle size. This tendency may be explained by the possible bias in the measure of the network chains density for the blend containing the smallest particles size (e.g. the presence of more carbon black and clay particles may result in an overestimate of the network chains density). Hence, the improved elastic modulus and network chains density by decreasing the GTR particle sizes, partly due to the presence of micron sized clay particles, conversely do not significantly modify the onset of the SIC process.

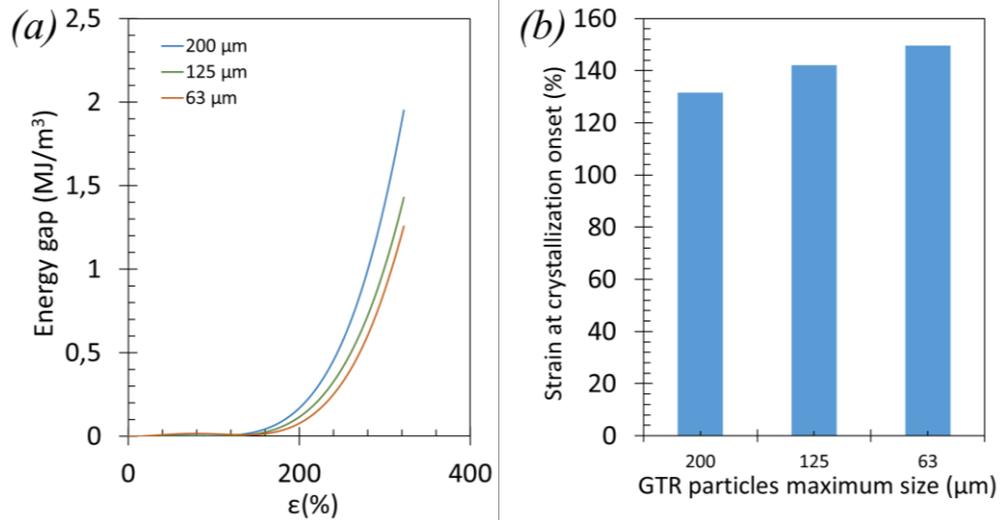


Figure 5-15 : GTR particles size: (a) Energy gap between the tensile and Gaussian curves, and (b) corresponding strain at crystallization onset for peroxide crosslinked elastomer blends of (i) NR/GTR <200 μm, (ii) NR/GTR <125 μm and (iii) NR/GTR <63 μm; for all 33 wt% GTR.

To quantify the energy dissipation and complement the results obtained about SIC onset, incremental cyclic loading have been performed. In accordance with the previous results, the amount of dissipated energy as a function of the strain reached during the cycles seems to be very similar for all of the 3 particles sizes. Furthermore, the energy dissipation onset, revealed by the appearance of a hysteresis in the cycles, seems to be about the same for the three materials (Figure 5-17).

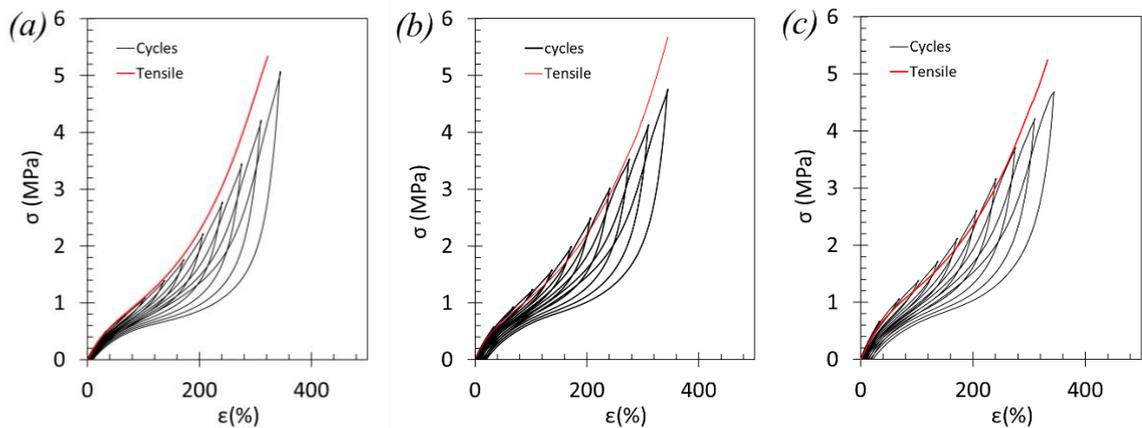


Figure 5-16 : GTR particles nature: engineering stress-strain curves for peroxide crosslinked elastomer blends of (a) NR/GTR <200 μm, (b) NR/GTR <125 μm and (c) NR/GTR <63 μm for (i) loading-unloading incremental cycles and (ii) tensile test; for all 33 wt% GTR

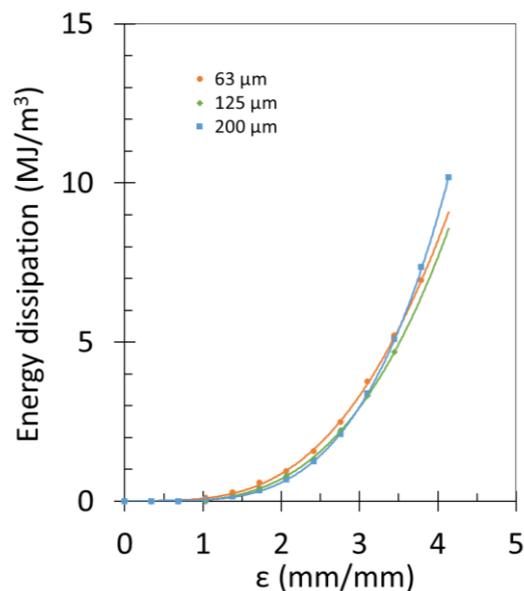


Figure 5-17 : GTR particles nature: Energy dissipation as a function of the maximum strain reached during the cycle for peroxide crosslinked elastomer blends of (i) NR/GTR <200 μm , (ii) NR/GTR <125 μm and (iii) NR/GTR <63 μm ; for all 33 wt% GTR

5.2.2.3. Effect of the GTR content

In this section, the mechanical properties of the elastomer blends with increasing GTR content is presented. To carry out this study, four blends of NR/GTR with a maximum particle size of 125 μm have been produced and subjected to tensile tests, with a weight fraction of GTR in the blends of 0%, 10%, 20% and 33%. The tensile curves are presented in Figure 5-18 (a), showing an increase of the stiffness of the blends with increasing GTR content.

The modulus, determined thanks to the gaussian approximation (Figure 5-18 (b)), and the crystallization onset, calculated through the energy gap between the experimental tensile curve and the gaussian curve (Figure 5-19), have been compared as a function of the weight fraction of GTR in the blends.

Expectedly, the modulus increases with increasing GTR content. As discussed in 5.2.2.1, this effect can be partially explained by the increasing carbon black amount. Taking in account only the influence of carbon black as a not deformable particle, the modulus can be predicted as a function of the volume fraction of CB. A strain amplification factor, corresponding to the ratio between the modulus of the unfilled and the filled rubber, is defined as a function of the filler volume fraction [73]:

$$A(c) = \frac{E_f}{E_0} = (1 + 0.67\alpha c + 1.62\alpha^2 c^2) \quad (7)$$

With $\alpha = 5.8$, $A(c)$ the strain amplification factor, E_f and E_0 the modulus of, respectively, the filled and unfilled rubber, and c the volume fraction of rubber, corresponding to the volume fraction of GTR in the blend multiplied by the volume fraction of CB in the GTR, equal to 0.126. This method enables to plot a theoretical trend for the modulus, taking in account the carbon black content. However, the experimental modulus of all the filled blends are significantly higher than the theoretical ones. This difference can be due to the higher crosslinking of the NR-GTR blends, through re-vulcanization of the GTR particles, as discussed in section 5.2.2.1, as well as a possible migration of the sulfur vulcanization components from the GTR to the NR matrix. Thus, the carbon black fillers effect is believed to be minor and the modulus increase is mostly ruled by the crosslink density of the GTR.

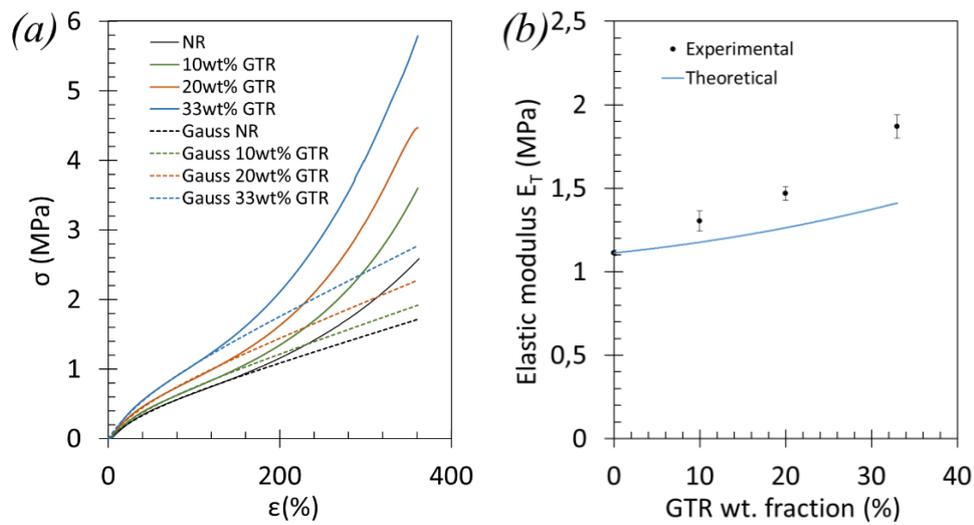


Figure 5-18 : GTR content: Tensile test engineering stress-strain curves and Gaussian approximation for peroxide crosslinked elastomer blends of (i) NR, (ii) NR/GTR₁₀, (iii) NR/GTR₂₀ and (iv) NR/GTR₃₃ and (b) corresponding elastic modulus calculated from (i) gaussian approximation and (ii) strain amplification factor method; for all particles size <125 μm

Regarding the strain induced crystallization behavior, the strain of initiation of energy dissipation is reported to decrease linearly with increasing GTR content, testifying of the fact that GTR shifts the crystallization onset in the blends to lower strain values.

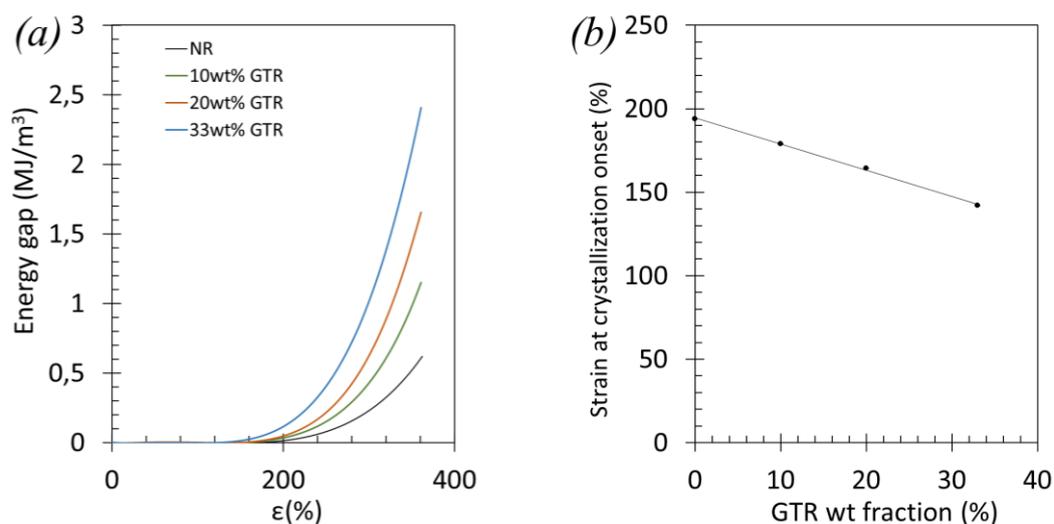


Figure 5-19 : GTR content (a) Energy gap between the tensile and Gaussian curves, and (b) corresponding strain at crystallization onset as a function of the GTR wt fraction for peroxide crosslinked elastomer blends of (i) NR, (ii) NR/GTR₁₀, (iii) NR/GTR₂₀ and (iv) NR/GTR₃₃; for all particles size <125 μm

The incremental loading-unloading cycles carried out for all of these blends and represented in Figure 5-20. They show that at a given strain, the hysteresis area increases with increasing GTR content, testifying of an enhanced dissipated energy and thus higher crystallinity (Table 5-4). This can be explained by a SIC onset shifted to lower strain values for GTR-filled blends. This can be explained by a higher ability of the GTR/NR blends to align the rubber chains due to higher network chains density (Figure 5-9) also traduced by a higher elastic modulus (Figure 5-18).

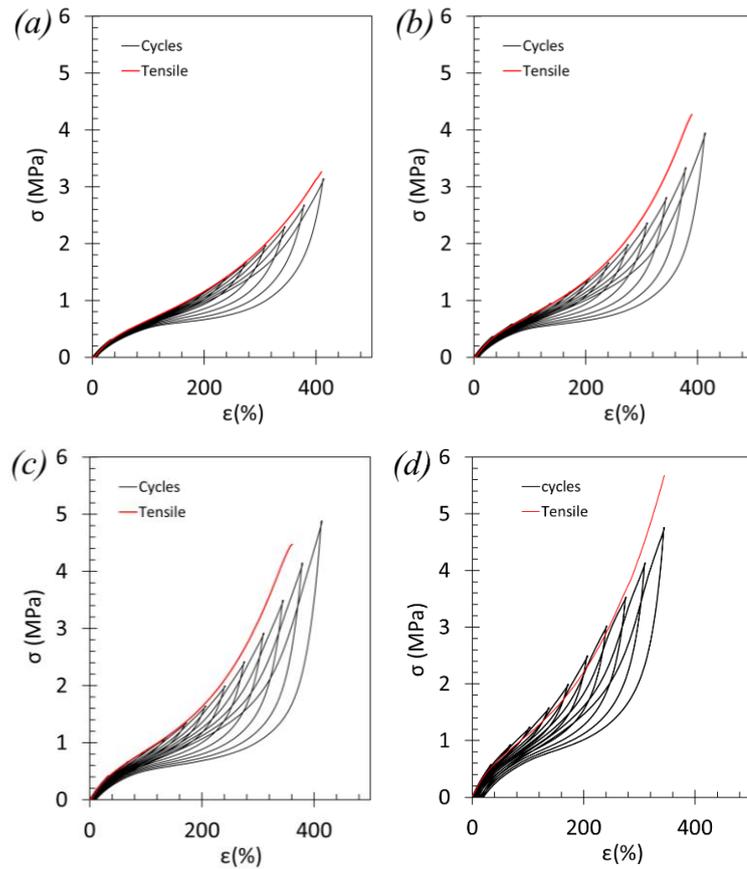


Figure 5-20 : GTR content: engineering stress-strain curves for peroxide crosslinked elastomer blends of (a) NR, (b) NR/GTR₁₀, (c) NR/GTR₂₀, and (d) NR/GTR₃₃ for (i) loading-unloading incremental cycles and (ii) tensile test; for all particles size <125 μm

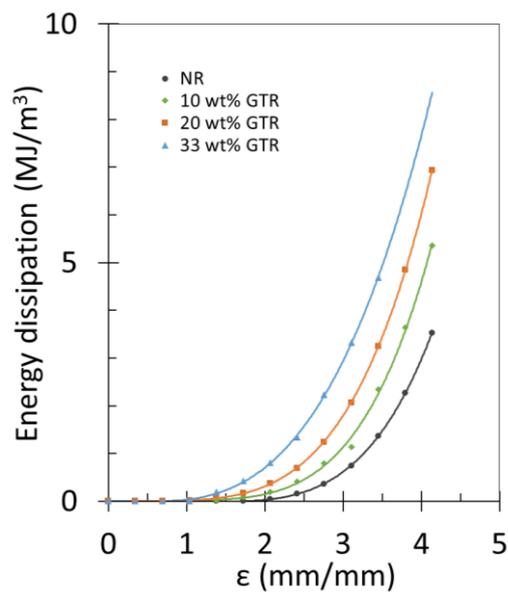


Figure 5-21 : GTR content: Energy dissipation as a function of the maximum strain reached during the cycle for peroxide crosslinked elastomer blends of (i) NR, (ii) NR/GTR₁₀, (iii) NR/GTR₂₀ and (iv) NR/GTR₃₃; for all particles size <125 μm

Table 5-4 : Energy dissipation for the 345% strain cycle for (i) NR, (ii) NR/GTR₁₀, (iii) NR/GTR₂₀ and (iv) NR/GTR₃₃; for all particles size <125 μm

GTR weight fraction (%)	Energy dissipation at strain $\epsilon=345\%$ (MJ.m ⁻³)
0	1.37
10	2.34
20	3.25
33	4.69

5.3. PLA/NR/GTR ternary blends

The elastomeric blends of natural rubber filled with ground tire rubber studied in the section 5.2 have been found to exhibit interesting mechanical reinforcement as compared to neat natural rubber. These results are of interest for the further use of GTR/NR to be blended with the brittle PLA. The objective here is to prepare ternary blends PLA/NR/GTR with comparable impact resistance and energy at break as compared to conventional PLA-GTR blends found in the literature, while replacing a fraction of the fresh NR by wastes rubber (GTR). To do so, ternary blends PLA/NR/GTR containing 1/3 of GTR and 2/3 of NR are studied and compared to the equivalent binary PLA-/NR blends, without GTR, i.e., containing the same ratio of rubber and PLA. The blends are dynamically vulcanized in presence of DCP.

5.3.1. Effect of the processing conditions

The processing of the ternary blends of PLA/NR/GTR was optimized to obtain the best mechanical performance. Several parameters have been studied on binary PLA/NR₄₅ blends (55 wt.% PLA, 45 wt.% NR). Especially, the addition of NR in PLA requires a prior step of mastication of the rubber to reduce its chains length distribution and hence avoid dispersion of its mechanical behavior. The efficiency of mastication is known to depend on the mixing temperature and its residence time [74]. Hence, the tensile properties of PLA/NR₄₅ blends with rubber mastication times of 10 and 20 minutes, as well as temperatures of 70 °C and 80 °C, have been compared. This range of mastication temperature was chosen as it is high enough to avoid high torques in the internal mixer, and low enough to avoid the activation of DCP when introduced during the mastication step.

Moreover, The PLA/NR blends must be dynamically vulcanized thanks to the addition of the peroxide crosslinking agent DCP. Two distinct methods of introduction of the DCP have been tested:

- Introduction during the melt-blending with PLA at 170°C: PLA is introduced in the mixing chamber, then rubber is added after 4 minutes, and DCP is added after 9 minutes, for a total residence time of 14 minutes.
- Introduction during the mastication of NR, at the mastication temperature (at which the DCP is not reactive), after 5 minutes of the mastication. DCP is added to the NR for 5 minutes. The DCP then, reacts when the masticated NR is added to PLA during the blending at 170 °C.

The characteristics of the prepared blends are summed up in Table 5-5.

Table 5-5: Mastication characteristics of the prepared PLA/NR₄₅ blends

Processing code	Mastication time M_t (minutes)	Mastication temperature M_T (°C)	Step at which DCP is introduced
NMb	0	/	Blending
70-10b	10	70	Blending
70-20b	20	70	Blending
80-10b	10	80	Blending
80-20b	20	80	Blending
80-10m	10	80	Mastication prior blending

The engineering stress-strain curves of the obtained PLA/NR₄₅ blends are represented in Figure 5-22. It can be noticed that the representative curves of all the materials exhibit a linear elastic region at small strains (until around 2%) followed by a yield point, a softening and a hardening at around 7%.

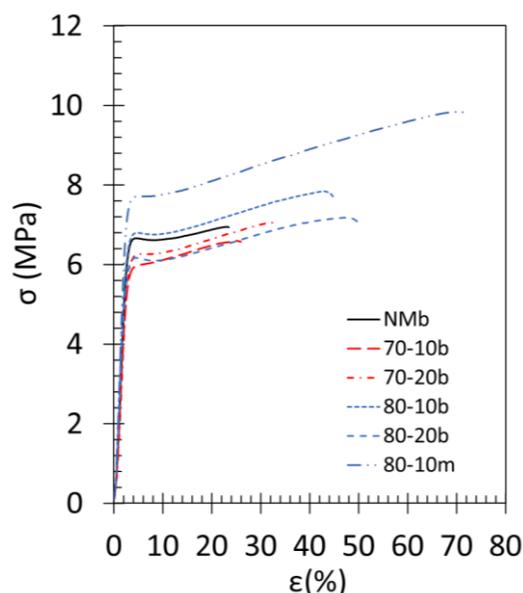


Figure 5-22: Processing conditions: tensile test engineering stress-strain curves for peroxide crosslinked PLA/NR₄₅ blends with the mastication parameters (i) no mastication, (ii) 70°C-10 minutes, (iii) 70°C-20 minutes, (iv) 80°C-10 minutes, (v) 80°C-20 minutes, (vi) 80°C-10 minutes with DCP introduction during mastication

Significant differences are noted between the different processing conditions. The elastic modulus, ultimate tensile strength, elongation at break and energy at failure have been determined (Figure 5-23) and the influence of the following parameters is discussed:

- **Mastication temperature M_T :** For the same mastication times, the choice of a mastication temperature of 80 °C rather than 70 °C enables a slight improvement of the modulus and σ_U , and an enhancement of the elongation at break of 46% for $M_T = 10$ minutes, resulting in a two times higher energy at break. The temperature of 80 °C for mastication seems to be efficient, which can be explained by a good compromise between mechanical mastication, more efficient at low temperatures, and the thermo-oxidative mastication, occurring at higher temperatures [74].
- **Mastication time M_T :** it can be seen on Figure 5-23 (c) that a long mastication time allows a weak increase of the elongation at break, especially for mastication occurring at 70 °C. However, it also implies a slight reduction of the stiffness of the blends. Besides, the mastication time seems to have no influence on the yield strength. It results that the energy at break of the blends containing NR masticated at 80° is the same for both mastication times. For this reason, the mastication parameters were chosen as $M_T = 10$ minutes and $M_T = 80$ °C.
- **Introduction of DCP:** peroxide crosslinking is convenient since only one reactive is needed, as contrarily to sulfur vulcanization. However, peroxide curing has been shown to yield in a heterogeneous distribution of crosslinks in the literature [75]. This results in very early failure for some

samples. The pre-mixing of DCP in the rubber during mastication is proposed to overcome this problem. As a result, this pre-introduction is found beneficial for the mechanical performance. In particular, this processing method allows a 63% increase of the energy at break and provides less disperse elongations at break and a lower associated standard deviation, as seen in Figure 5-23 (c). Hence, this processing method will be chosen in the following.

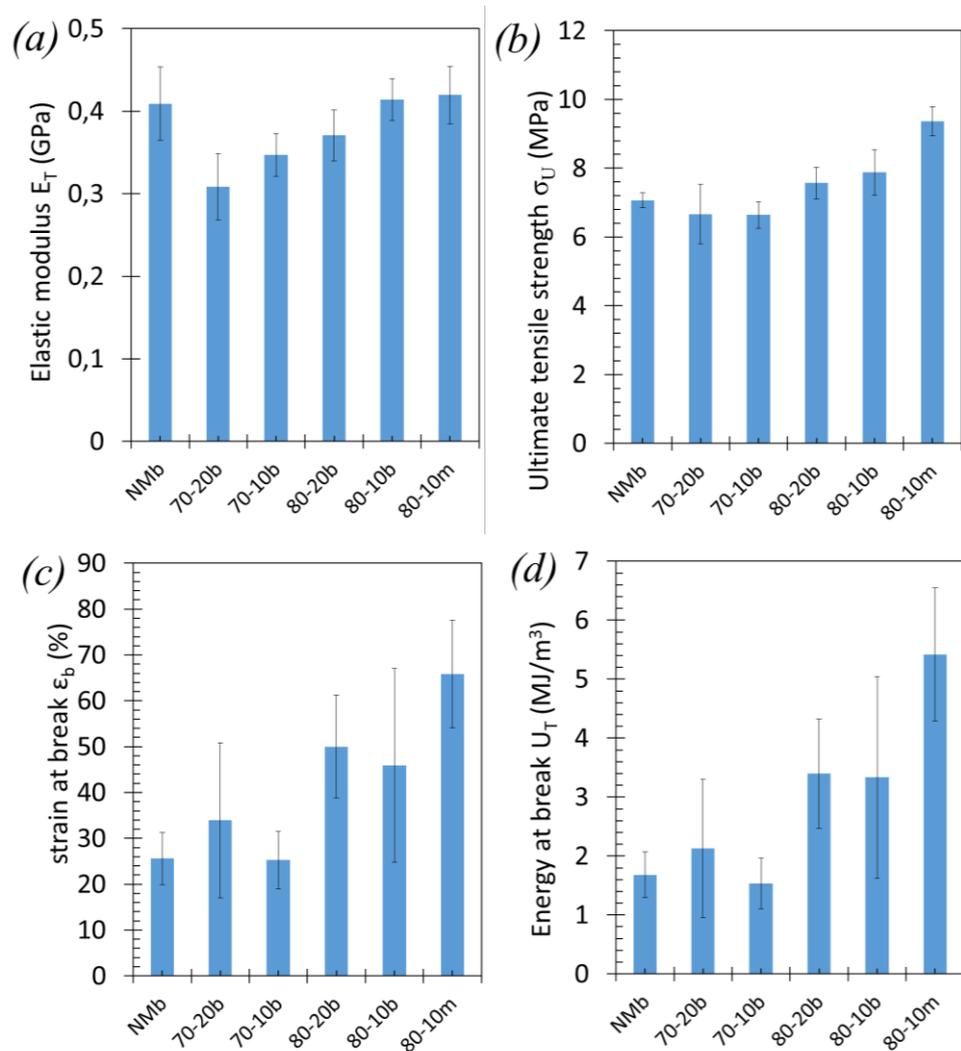


Figure 5-23 : Processing conditions: tensile properties (a) elastic modulus E_T (b) yield strength σ_y (c) strain at break ϵ_b and (d) energy at break U_T for peroxide crosslinked PLA/NR₄₅ blends with the mastication parameters (i) no mastication, (ii) 70°C-10 minutes, (iii) 70°C-20 minutes, (iv) 80°C-10 minutes, (v) 80°C-20 minutes, (vi) 80°C-10 minutes with DCP introduction during mastication

5.3.2. Effect of the particle size

It has been found in section 5.1.3 that the use of the smallest particle size, namely $<63 \mu\text{m}$, in PLA/GTR blends result in optimized elastic modulus, yield strength, elongation and energy at break. The effect of GTR particle size in the ternary blends PLA/NR₃₀/GTR₁₅ (PLA 45 wt.%, NR 30 wt/%, GTR 15 wt/%) are studied here. In particular, tensile properties of PLA/NR₃₀/GTR₁₅ on materials containing a maximum size of particles of $125 \mu\text{m}$ and $63 \mu\text{m}$ have been compared (in Figure 5-24).

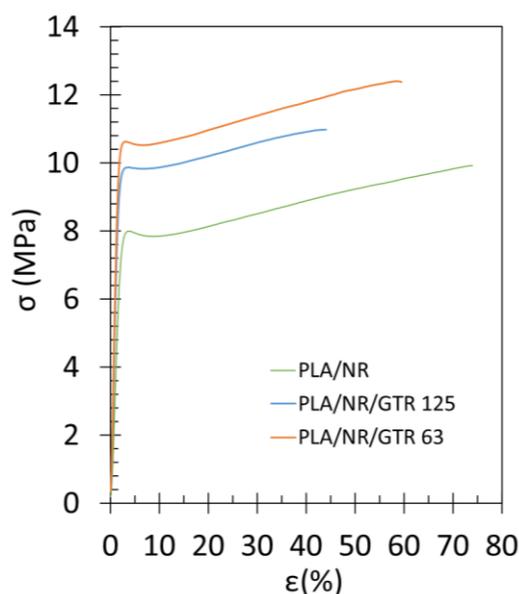


Figure 5-24 : Particle size: tensile test engineering stress-strain curves for (i) PLA/NR₄₅ blend and PLA/NR₃₀/GTR₁₅ blends with GTR particle size (ii) $<125 \mu\text{m}$ and (iii) $<63 \mu\text{m}$; for all dynamically DCP-crosslinked.

The tensile properties, namely the elastic modulus E_T , the yield strength σ_y , the strain at break ϵ_b and the energy at break U_T are represented in Figure 5-25 for the studied blends. The ternary blends obtained by replacing 1/3 of NR by wastes GTR show a higher elastic modulus and strength (Figure 5-25 (a) and (b)). However, independently on the GTR particle size, the binary PLA/NR blends show a higher elongation at break.

As for PLA/GTR blends (Figure 5-6), reducing the size of the particles to less than $63 \mu\text{m}$ in ternary blends leads to 44% and 60% increase of strain at break and energy at failure respectively as compared to the blends containing particles with a maximum size of $125 \mu\text{m}$. This could be explained by the initiation of smaller and more distributed microcracks under loading as well as a more distributed cavitation/decohesion of the GTR particles preventing premature failure. The further ternary blends processed and presented in the following will be processed by using smallest particle size ($<63 \mu\text{m}$).

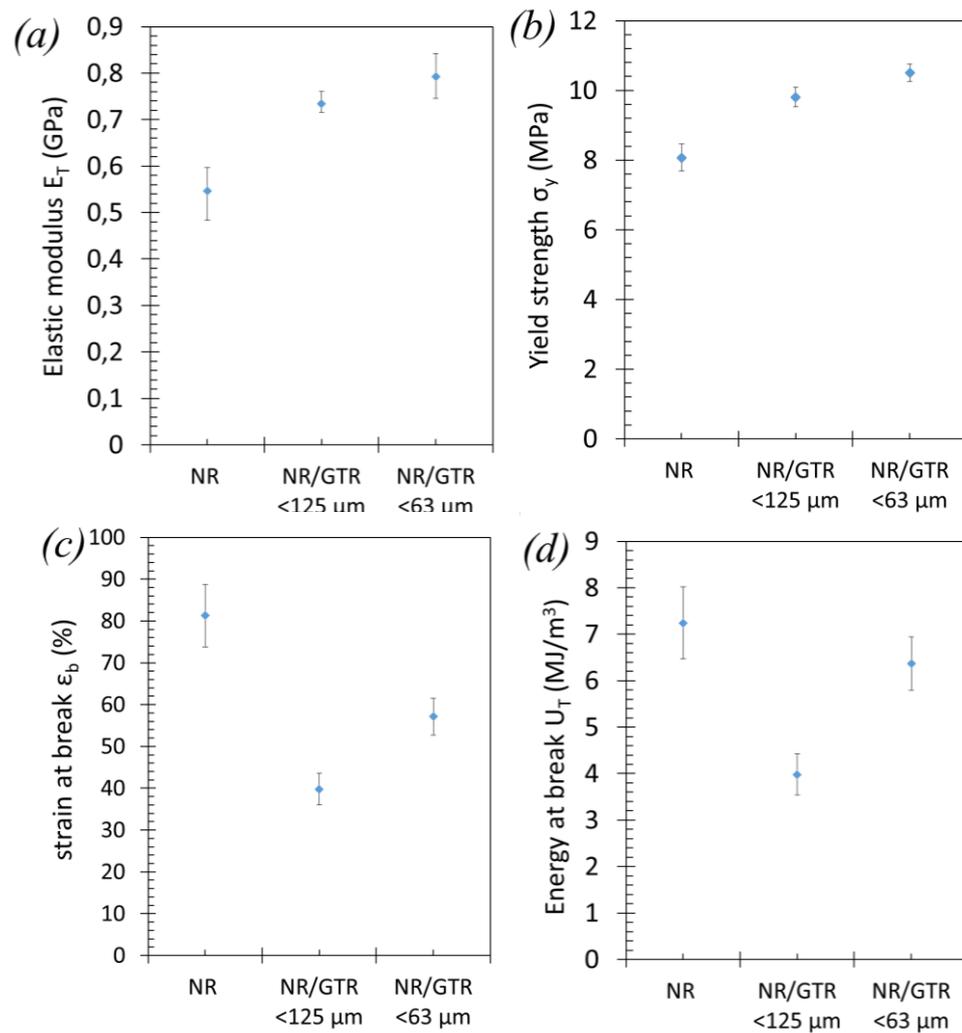


Figure 5-25 : particle size: tensile properties (a) elastic modulus E_T (b) yield strength σ_y (c) strain at break ϵ_b and (d) energy at break U_T for (i) PLA/NR₄₅ blend and PLA/NR₃₀/GTR₁₅ blends with GTR particle size (ii) <125 μm and (iii) <63 μm ; for all dynamically DCP-crosslinked.

5.3.3. Effect of the rubber content

With the aim of producing PLA/rubber blends by substituting 1/3 of natural rubber by GTR, the effects of the proportions of each components must be investigated. Especially, using the highest content of GTR would enable to achieve the highest fraction of recycled material, but the good mechanical properties of the blends have to be preserved. In particular, the changes of morphology with increasing rubber content (continuous PLA, co-continuous PLA/NR or continuous NR) and its influence on the mechanical properties at low deformation speed (quasi-static tensile) and high deformation speed (tensile impact) are investigated in this section. Three binary PLA/NR and three ternary PLA/NR/GTR DCP-crosslinked blends have been compared with a total rubber fractions from 15 wt.% to 45 wt.%

(Table 5-6). Prior to the mechanical characterization, the swelling behavior is studied to give insights on the materials morphology.

Table 5-6 : characteristics of the studied binary and ternary blends

Rubber weight fraction (wt.%)	Material's name
0	PLA
15	PLA/NR ₁₅ PLA/NR ₁₀ /GTR ₅
30	PLA/NR ₃₀ PLA/NR ₂₀ /GTR ₁₀
45	PLA/NR ₄₅ PLA/NR ₃₀ /GTR ₁₅

5.3.3.1. Swelling behavior in dichloromethane

The swelling of the blends as a function of the rubber content has been studied in this part for PLA/NR and PLA/NR/GTR blends. Various rubber contents, namely 15, 30 and 45 wt.%, have been investigated. As a reference material, the pure natural rubber (NR) is investigated.

The method consists in immersing the materials in dichloromethane. PLA is found to be dissolved in dichloromethane after 15 minutes (Figure 5-26 (b)). Contrarily, immersion of NR in dichloromethane results in swelling due to the presence of 3D chains network made of C-C bonds caused by DCP-vulcanization. This is also the case for binary and ternary blends containing at least 30 wt. of rubber suggesting these materials to be composed of a continuous rubber matrix. Contrarily, the binary and ternary blends with rubber content up to 15 wt.% are, like the pure PLA, dissolved in dichloromethane suggesting the continuous phase to be composed of PLA.

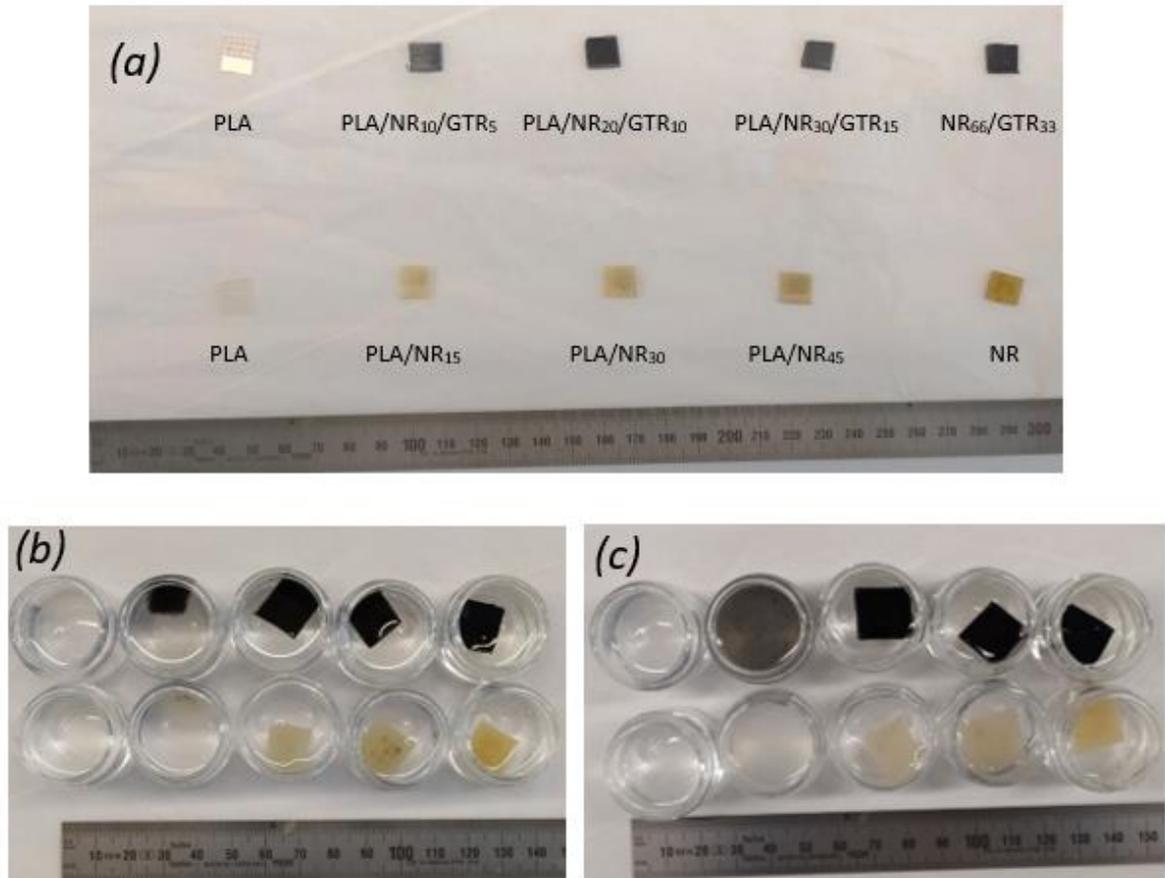


Figure 5-26: Digital photographs of swelling experiments in dichloromethane for PLA, ternary blends (PLA/NR₁₀/GTR₅, PLA/NR₂₀/GTR₁₀, PLA/NR₃₀/GTR₁₅ and NR₆₆/GTR₃₃) and binary blends (PLA/NR₁₅, PLA/NR₃₀, PLA/NR₄₅ and NR) (a) before swelling and after (b) 15 minutes and (c) 1 hour.

5.3.3.2. Mechanical properties

The mechanical properties of the blends (Table 5-6) have been characterized by tensile testing (UTS), and tensile-impact testing. Moreover, the fracture surfaces of the specimen tested by UTS have been observed by SEM.

5.3.3.2.1 Tensile properties

Here, we aim to discuss on the tensile properties of the PLA/NR binary blends obtained with various amounts of rubber component (0, 15, 30 and 45 wt.%). We also aim to compare these properties with those obtained on the PLA/NR/GTR ternary blends with 1/3 replacement of NR by GTR. The corresponding stress-strain curves show a transition from the brittle behavior of the neat PLA to a more ductile behavior by increasing the elastomer content, for both binary and ternary blends (Figure 5-27).

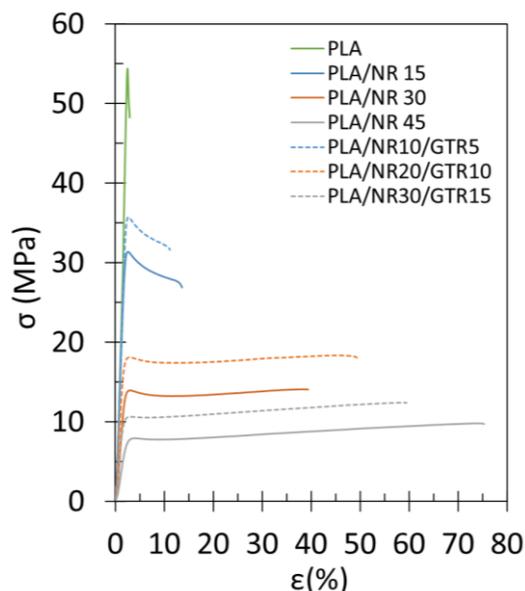


Figure 5-27 : Rubber content: tensile test engineering stress-strain curves for (i) PLA, 15 wt.% rubber (ii) binary PLA/NR and (iii) ternary PLA/NR/GTR blends, 30 wt.% rubber (iv) binary PLA/NR and (v) ternary PLA/NR/GTR blends and 45 wt.% rubber (vi) binary PLA/NR and (vii) ternary PLA/NR/GTR blends; for all dynamically DCP-crosslinked and GTR particles <math><63 \mu\text{m}</math>.

The binary PLA/NR and ternary PLA/NR/GTR blends' strain-stress curves are detailed for each total elastomer content in Figure 5-28. From this, a clear increase of the yield strength with the addition of GTR is visible for every rubber content. In addition, the curves of the binary and ternary blends have similar shapes for the same rubber content. For all the blends, a yield point followed by a softening is observed after the elastic linear domain. However, for 15 wt.% rubber blends, the failure occurs at the end of this softening, whereas a strain hardening is observed in the blends containing 30 wt.% of rubber or more. The strain hardening slope has been calculated between 15% and 20% strain (cf. appendix 1A3), and the values are similar for 30 wt.% and 45 wt.% blends. This hardening for high rubber contents is consistent with the mechanical reinforcement observed in NR-GTR blends, and is possibly ascribed to crystallization of the rubber phase under strain, as discussed in 5.2.2. Even though the SIC onset happens at more than 100% strain for all the rubber blends tested previously (Figure 5-19) and the hardening of the PLA/NR and PLA/NR/GTR blends starts around 10% strain, the rubber phase could be locally highly stretched under stress, possibly allowing a partial crystallization in these elongated zones.

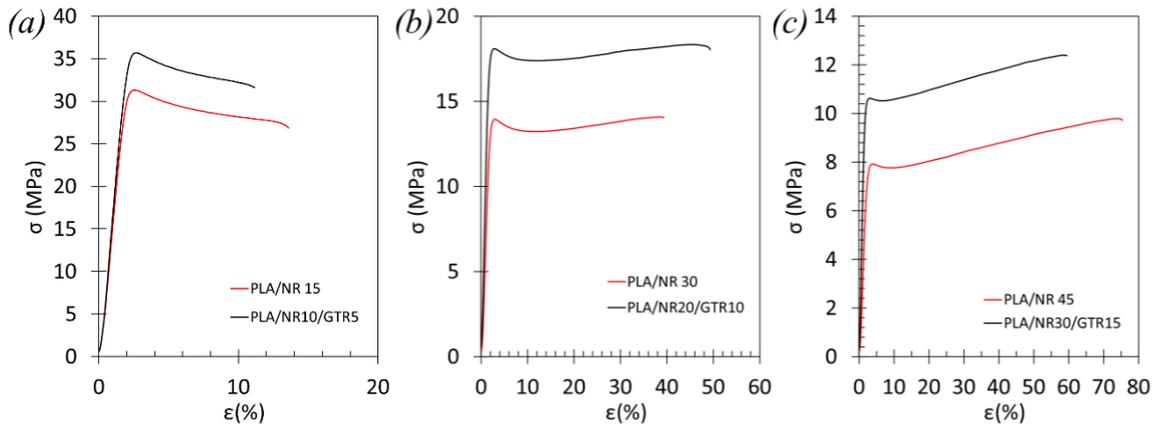


Figure 5-28: Rubber content: tensile test engineering stress-strain curves for (a) 15 wt.% rubber (i) binary PLA/NR and (ii) ternary PLA/NR/GTR blends, (b) 30 wt.% rubber (iii) binary PLA/NR and (iv) ternary PLA/NR/GTR blends and (c) 45 wt.% rubber (v) binary PLA/NR and (vi) ternary PLA/NR/GTR blends; for all dynamically DCP-crosslinked and GTR particles $<63 \mu\text{m}$.

From these tensile tests, the elastic modulus, yield strength, elongation at break and energy at break of the blends have been determined for each rubber content and the binary and ternary blends have been compared in Figure 5-30.

For the PLA/NR blends, the increase of the NR content is accompanied by a strong drop of modulus and yield strength, equal to 534% and 690% respectively for PLA/NR₄₅. This is due to the softer behavior of NR compared to PLA, since the modulus of NR has been found to be 1.1 MPa, that is to say around 3000 times lower than the one of PLA. On the other hand, the strain at break is multiplied by 23 by adding 45 wt.% of NR. As a result, the energy at break is increased with the NR content.

In addition to the above-mentioned increase of yield strength allowed by the partial replacement of NR by GTR, Figure 5-30 (a) shows that it also leads to an enhancement of the elastic modulus for all rubber contents. This is consistent with the above studied NR/GTR blends showing a higher modulus than vulcanized NR (Figure 5-29), probably because of the higher crosslink density of GTR particles as compared to vulcanized NR (Figure 5-8, Figure 5-9 (a)) and the partial additional crosslinking of GTR during the process. Moreover, remaining sulfur used for the vulcanization of the rubber contained in GTR could migrate from the GTR particles to the NR phase and contribute to a supplementary crosslinking.

Two tendencies are distinguished for the evolution of the strain at break of the ternary blends:

- Strikingly, from 0 wt.% to 30 wt.% of rubber in PLA, the partial replacement of NR by GTR does not affect the strain at break of the blends, since the evolution of the strain at break along with the total rubber content is about the same for binary and ternary blends.

- At higher rubber content (at and above 30 wt.%), the strain at break of PLA/NR/GTR blends keeps on increasing, but not as much as the one of PLA/NR blends, resulting in an earlier failure of the 45 wt.% ternary blends as compared to the binary blends.

This could be explained by the fact that until 30 wt.% of rubber in the ternary blends, the GTR content stays lower than 10 wt.%, so that the GTR proportion is too low to deteriorate the properties of the blends. Moreover, the interface between the GTR and the NR and PLA phases is thought to be improved by encapsulation, as will be shown in the SEM micrographs presented in the following. However, the introduction of 15 wt.% GTR implies more interfaces and more potential cracks, cavitation, decohesion sites upon loading, resulting in a difference of strain at break between binary and ternary blends.

Similar ternary blends, made of thermoplastic and a fresh elastomer partially replaced by GTR, have been studied in the literature [27], [58], [60]. The observed improvement of the elastic modulus and the decrease of the strain at break brought about by the introduction of 15 wt.% GTR is in line with the results given by these studies. On the contrary, the tensile strength is usually reported to be unchanged by the partial replacement of the elastomer by GTR, whereas in this study a clear tensile strength improvement is remarked with the introduction of GTR.

Finally, the partial replacement of NR by GTR surprisingly leads to an enhancement of the energy at break for a total rubber content of 30 wt.% due to a higher yield strength added to a similar strain at break. On the other hand, The PLA/NR₃₀/GTR₁₅ blends do not show enhancement of the energy at break as compared to PLA/NR₄₅. As a result, the maximum energy at break is obtained for PLA/NR₂₀/GTR₁₀ by substituting 1/3 of the fresh NR by wastes GTR.

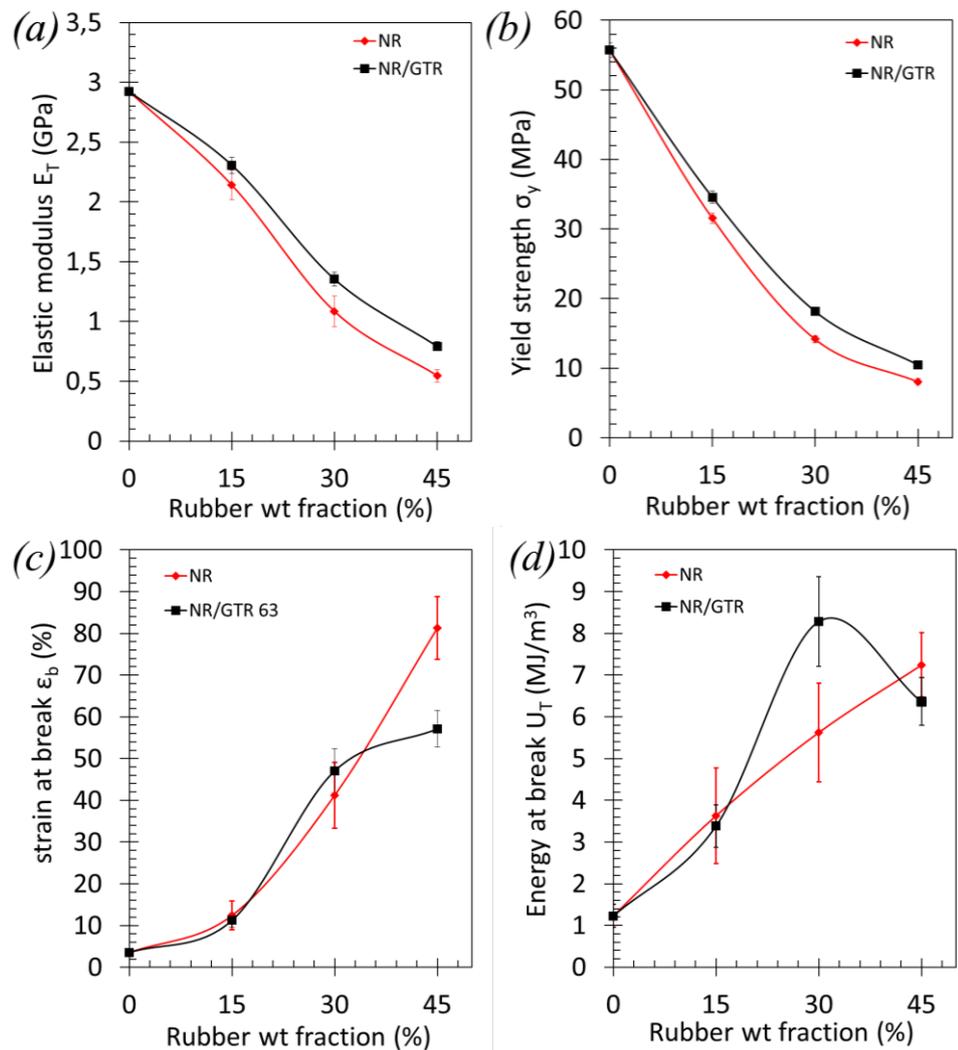


Figure 5-30 : Rubber content: tensile properties (a) elastic modulus E_T (b) yield strength σ_y (c) strain at break ϵ_b and (d) energy at break U_T as a function of the total rubber content for (i) binary PLA/NR and (ii) ternary PLA/NR/GTR blends; for all dynamically DCP-crosslinked and GTR particles <63 μm .

5.3.3.2.2 Fracture surfaces

Scanning electron microscope (SEM) observations have been performed on the fracture surface of the same binary and ternary blends, after tensile test. The micrographs of the binary PLA/NR blends with 0 wt.%, 15wt.%, 30wt.% and 45wt.% NR are shown in Figure 5-31. It can be seen on Figure 5-31 (a) that the fracture surface of neat PLA is representative of a brittle fracture. However, the addition of a small NR content, from 15%, allows a transition from a brittle to a more ductile failure, as shown by the elongated polymeric domains which are expected to be the plastically deformed PLA (Figure 5-31 (b)).

The PLA/NR₁₅ blend also seems to exhibit some cavitation mechanisms due to the decohesion of particles (expected to be NR in this material with the lowest NR content).

The crosslinked NR phase is hard to distinguish from the PLA phase because the SEM does not provide a sufficient electron contrast between the phases (further SEM observation after dichloromethane etching would be useful to characterize the morphology). This tends to show that both phases are embedded into each other, testifying of a good interfacial adhesion. Only for the PLA/NR₄₅, we can see in Figure 5-31 (d) that one phase domain shows a relatively smooth surface whereas the other one is rougher. The same observation has been reported in literature for PLA/NR₃₅ blends [4], the smooth phase having been associated to NR. The micrograph of Figure 5-31 (d) also reveals fibrils in the smooth phase domain, believed to be stretched NR, proving the large deformation of NR at a local scale.

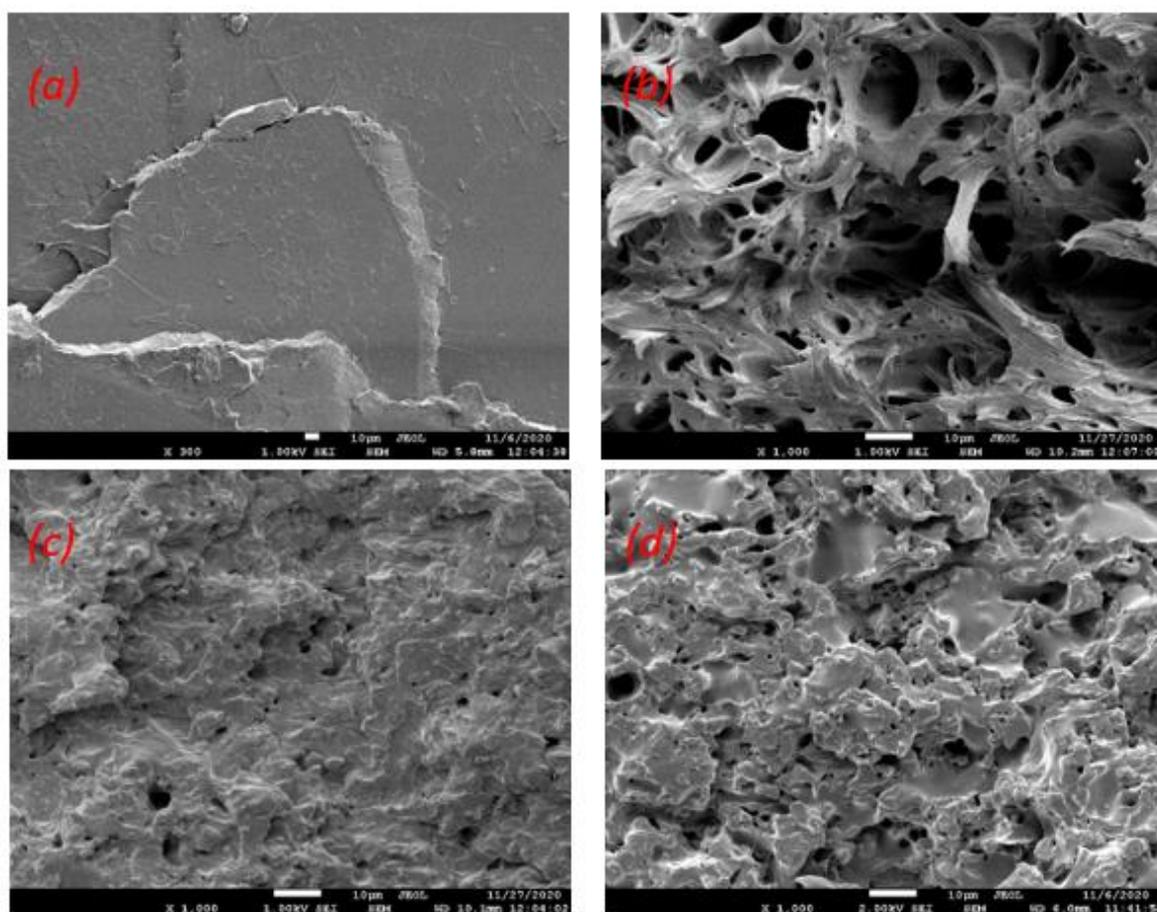


Figure 5-31: SEM images of the fracture surface of (a) PLA and dynamically DCP-crosslinked binary blends of (b) PLA/NR₁₅, (c) PLA/NR₃₀ and (d) PLA/NR₄₅.

As well as the PLA/NR blends, the fracture surface of ternary PLA/NR/GTR blends with GTR size <math> < 63 \mu\text{m}</math> has been observed by SEM for total rubber contents of 15 wt.%, 30 wt.% and 45 wt.%, and compared to PLA/GTR₁₅ with the same particle size (Figure 5-32).

The use of DCP to dynamically vulcanize PLA/GTR blends has been demonstrated to promote the compatibility between the PLA and the particles in previous works [66], resulting in enhanced mechanical properties. Nevertheless, it is clearly seen on Figure 5-32 (a) that for the PLA/GTR₁₅ blend, a decohesion occurred between the GTR particles and the PLA matrix. On the other hand, with the addition of natural rubber as a third component, the GTR particles seem more bonded to the matrix, the decohesion being less visible for the ternary blends. This suggests an improved compatibility between the disperse GTR and the polymer matrix, enabled by the partial encapsulation of GTR particles.

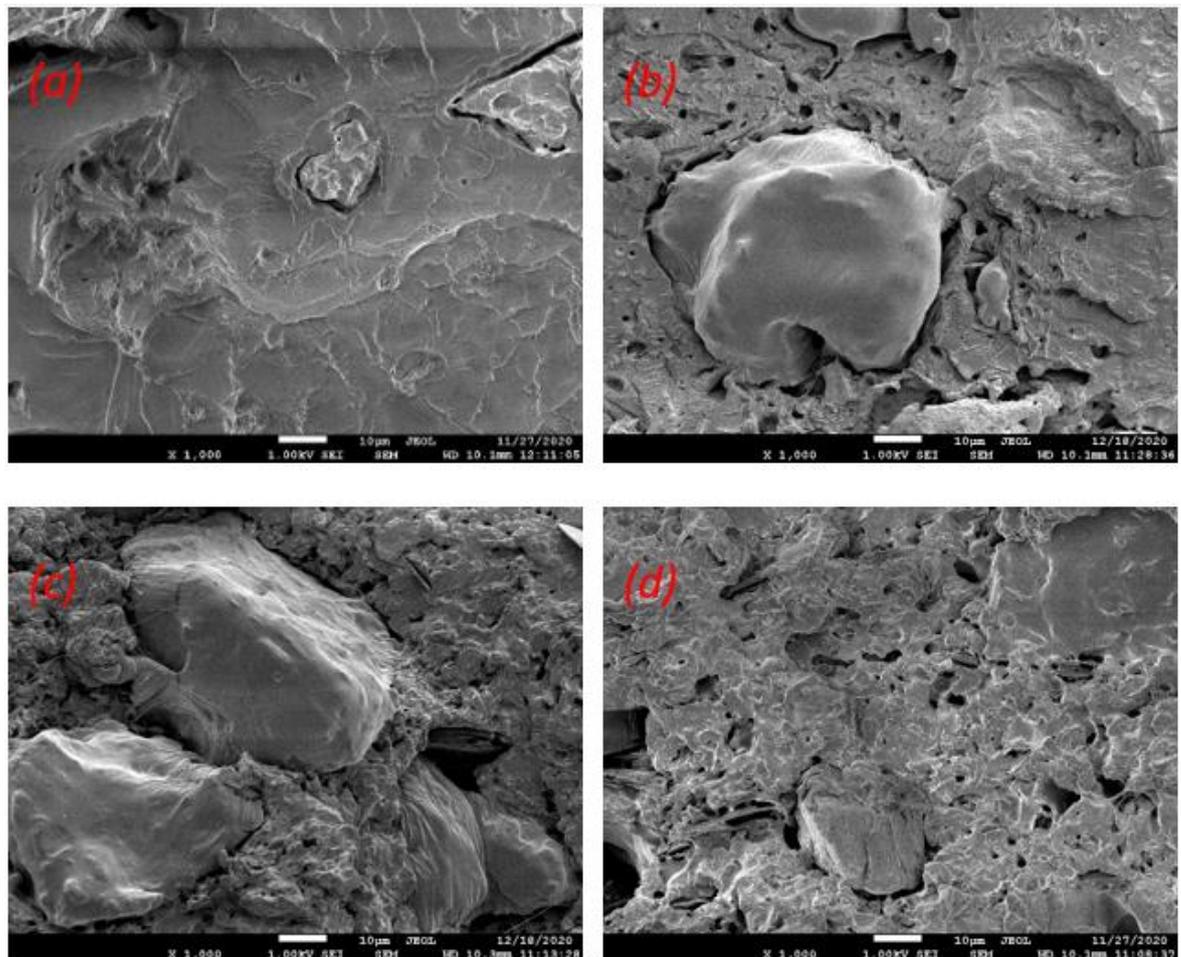


Figure 5-32: SEM images of the fracture surface of dynamically DCP-crosslinked (a) PLA/GTR₁₅ and ternary blends of (b) PLA/NR₁₀/GTR₅, (c) PLA/NR₂₀/GTR₁₀ and (d) PLA/NR₃₀/GTR₁₅.

5.3.3.2.3 Impact properties

One of the major drawbacks of PLA is its poor impact resistance. In order to characterize the toughness improvement induced by the addition of NR and GTR, the binary and ternary blends testing have also been submitted to tensile-impact tests. This way, the properties at high deformation speeds can be studied, and an impact strength can be calculated through the deformation energy. The tensile-impact strength α_{tU} is plotted as a function of the total rubber weight fraction for both the binary and ternary blends in Figure 5-33.

The tensile-impact strength of binary PLA/NR blends increases with the NR content, following the same tendency as the energy at break of the same blends found with tensile testing (Figure 5-30 (d)). Moreover, the partial replacement of NR by GTR is observed to enhance the tensile-impact strength for all rubber contents, showing a different behavior as compared to tensile (quasi-static) behavior, where the energy at break of PLA/NR₄₅ was reported to be higher than the one of PLA/NR₃₀/GTR₁₅.

This is in opposition with the general tendency shown in the literature where the partial replacement of rubber by GTR decreases the impact strength for all elastomeric phase contents [27]. The observed enhancement for PLA/NR/GTR blends could be due to the good compatibility between NR and GTR due to their similar chemical nature, resulting in stronger interfaces.

However, like for the energy at break calculated at smaller strain rates, the tensile impact strength improvement seems to be limited from a certain GTR content, since the impact strengths of PLA/NR₃₀/GTR₁₅ is reported to be very close to the one of PLA/NR₂₀/GTR₁₀. Nevertheless, the material with 15% GTR has the advantage of allowing more tire recycling.

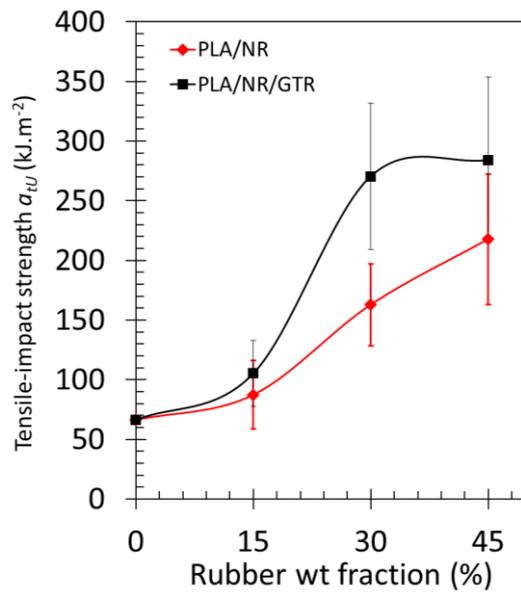


Figure 5-33: Rubber content: tensile-impact strength a_{tU} as a function of the total rubber content for (i) binary PLA/NR and (ii) ternary PLA/NR/GTR blends; for all dynamically DCP-crosslinked and GTR particles $<63 \mu\text{m}$.

Environmental impact analysis

In order to evaluate the global environmental impact of this master thesis, a maximum of impacting parameters were taken in account during all the 5 month period of the study, including the energy consumption due to the experimental phase, the production of the raw materials and their transportation.

The three main raw materials used during this project were PLA, natural rubber and ground tire rubber. PLA was taken from a batch ordered for previous projects, and a total of around 2 kg of PLA were consumed during the project. PLA is a low carbon footprint polymer which is nowadays allowing a 75% reduction of CO₂ emissions compared to conventional thermoplastics, having a global warming potential (GWP) of only 0,5 kg CO₂/kg of PLA [76]. Regarding natural rubber, two blocks of 25 kg have been ordered for this project. Even though only 900 g were used for the production of blends in this master thesis, the rest will be used for further investigations. The raw material was imported from the USA by shipping, representing 10 g of CO₂/ton.km, and the production of the material himself is estimated to release around 0,6 kg CO₂/kg of rubber [77]. The GTR being a recycled material, its carbon footprint has been neglected, in spite of the energy needed for its transformation. However, the supposed transportation by truck of the material from Manchester to Barcelona represents around 50 g of CO₂/ton.km.

Finally, the energy consumption of the machines used all along the project was estimated given their power consumption and their approximate time of use. As a result, the most energy consuming machine was the internal mixer with 756 kWh, due to the high processing temperatures and long time of use (63 h in total, including blending and pre-heating), followed by the vacuum oven, the hot press, the tensile test machine and the sieving machine. The total energy consumption was estimated to 1620 kWh or 5832 MJ, corresponding to 426 kg of CO₂ eq. considering the energy mix in Spain [78].

As a conclusion, the materials and energy used during this project have been approximated to represent a carbon footprint of 465 kg of CO₂ eq., with the experiments and use of the machines being the major part of it. Other criteria could have been considered, such as the eco-toxicity, the human toxicity or the waste disposal. Despite the non-neglectable environmental impact of this project, the perspectives of upscaling the process to industrialize the investigated material, containing only biobased and recycled components and resulting in a low carbon footprint, justifies the means used for its study.

Conclusion

The reduction of the environmental impact of the polymers production by using bio-based plastics and the development of new alternatives for rubber wastes valorization, are two essential ways of reversing the negative impact of the polymer industry on the environment. To contribute these two routes, this project focused on the toughening of Poly(lactic acid) (PLA), a bio-based but brittle material, impeding its wide industrial utilization, by blending it with wastes tire rubber. However, the simple blend of PLA and GTR blends developed in the literature did not show drastic enhancement of the PLA properties. To improve this, we blended, at the laboratory scale, PLA/ natural rubber (NR) / wastes tire rubber (GTR) blends via dynamic vulcanization by an encapsulation of the GTR particles into the rubber matrix. Assisted by dynamic vulcanization, the encapsulation allowed to obtain PLA/NR/GTR blends with a continuous rubber phase (NR/GTR) capable of drastically improve the PLA toughness and impact strength. To elaborate these materials, this project has been conducted following three phases.

Firstly, PLA/GTR blends were prepared using an internal mixer. The treatment of the GTR (type of grinding, particle size, drying conditions) and the processing parameters of the PLA/GTR blends (residence time) were optimized. The combination of (i) cryo-grinding treatment of the GTR, (ii) an overnight drying of the GTR and (iii) the selection of finest GTR size ($< 63 \mu\text{m}$) allowed the maintain of the elastic modulus, the smallest decrease of the tensile strength, a one fold increase of the elongation at break and a 70% increase of the energy at break as compared to neat PLA.

Secondly, the efficiency of the encapsulation of the GTR into the NR matrix has been tested by elaborating vulcanized NR/GTR blends and characterizing their swelling and tensile properties. As compared to vulcanized NR, vulcanized NR-GTR showed (i) higher crosslink density, (ii) higher elastic modulus and (iii) an early strain hardening ascribed to an acceleration of the strain induced crystallization (SIC), attributed to the strain amplification at the NR-GTR interface crosslinked by DCP.

Thirdly, accounting for the results obtained in the two previous phases, binary PLA/NR blends and ternary PLA/NR/GTR by substituting 1/3 of the NR by GTR were produced. In both binary and ternary blends, a mechanical hardening is observed and thought to be partly due to the strain localization in the rubber phase (NR or NR/GTR) owing its ability to show strain hardening. In addition, the ternary blends concomitantly exhibit (i) an increase of the elastic modulus, (ii) an increase of the yield strength, (iii) a maintain of the strain at fail. This results in an increase of the tensile strain energy and impact strength of the ternary blends as compared to binary blends.

Various blends were processed. A transition from the brittle behavior of the neat PLA to a more ductile behavior by increasing the rubber content was observed. Up to 30 wt.% rubber, the presence of GTR did not decrease the strain at break and energy at break of the PLA/NR blends. In addition, the partial

replacement of NR by GTR allows a promising enhancement of the impact strength for all the rubber contents, suggesting a good efficiency of the encapsulation method as proposed in this thesis. This is supported by the SEM observations, showing that ternary blends show good interfacial adhesion in all three components (PLA, NR and GTR).

In addition to the renewable nature of PLA and NR, the high tensile and impact properties of the prepared ternary blends PLA/NR/GTR via the encapsulation method, make them as promising materials for a sustainable development in the polymer industry. To this aim, an upscaling process of their processing from a laboratory to a pilot plant scale would be a step further for a future cost-effective and ecological production.

Further prospects

To better understand the phenomena leading to the observed properties of the studied blends at different scales and further improve their mechanical properties, more experiments could be carried out after this project.

Firstly, the materials produced at the laboratory scale show good mechanical properties and enable to toughen PLA. The next step of the development of these blends, before an eventual industrialization, would be the production at a larger scale (pilot plan) to reduce the costs and increase the quantity produced, while keeping the properties obtained at the laboratory scale.

Secondly, even though a phase of the work was dedicated to the optimization of the mastication and melt-blending process, the investigations could be continued. Especially, the problem of the defects observed in all the PLA/NR-based blends could be overcome by tailoring the mastication of NR. A longer mastication time at a lower temperature could be envisaged. Thermoporosimetry may also help to characterize the defects by verifying if they are due to a heterogeneous crosslinking.

Then, to understand better the observed reinforcement of the PLA/rubber blends, the hypothesis of a strain induced crystallization could be studied using in situ wide angle X-rays scattering (WAXS) measurements on stretched specimens. Also, a way to prove and characterize the crystallization of the NR and NR/GTR blends would be to analyze them under strain through infrared temperature measurements, giving a temperature field potentially revealing the exothermic crystallization, or by digital image correlation (DIC) to observe the expected volume decrease due to the crystallization.

In addition, the methods used in this work do not allow to precisely characterize the re-vulcanization of the GTR particles during the melt-blending. To determine whether the particles behave as an inert filler or if they react with DCP, a PLA/NR₃₀ blend could be processed with a DCP proportion higher than 1,5 wt.% with respect to NR. Thus, the DCP concentration in NR would be the same as the one in PLA/NR₃₀/GTR₁₅ considering that the GTR is inert. Then the crosslink density of this blend could be measured by swelling or thermoporosimetry to compare it with the one of a PLA/NR₃₀/GTR₁₅ blend containing the usual DCP content.

Finally, the good mechanical properties obtained by replacing 1/3 of the NR by GTR in PLA/NR/GTR blends encourages to go pursue the investigations and increase the replacing rate in order to incorporate as much GTR as possible in the blends, allowing to lower the price of the material and recycle more waste tire.

Economic analysis

The main costs of the project can be divided into 3 different parts:

- **Labour:**

During the training phase, the experimentation phase and the writing phase, the work of the student has been performed under the supervision of qualified researchers with PhD degree. With a salary of 20€/h and an estimation of 200 h dedicated to this project, the labour costs are estimated to 4000€.

- **Materials:**

All the materials used during this project, as well as their quantities and prices, are listed in *Table 0-1*.

Table 0-1 : Cost of the materials used during the project.

Material	Quantity	Price	Cost (€)
PLA	2 kg	3,5 €/kg	7
Natural Rubber	0,75 kg	13,7 €/kg	10,27
Ground tire rubber	<ul style="list-style-type: none"> • Devulcanized: 47g • Ambient grinded: 52g • Cryo-processed: 145g 	<ul style="list-style-type: none"> • Devulcanized: 1,45 €/kg • Ambient grinded: 4,5 €/kg • Cryo-processed: 1,87 €/kg 	0,6
Dicumyl peroxide	13g	244,2 €/kg	3,17
Irganox® 1010	4g	3,7 €/kg	0,02
Cyclohexane	0,45L	72€/L	32,4
Dichloromethane	0,15L	50€/L	7,5
Total			61€

- **Equipment:**

The price of the use of the equipment of the laboratory is taken in account in this part, depending on the machine used and its time of use. The costs are estimated according to the current tariffs in the *Centre Català del Plàstic* and detailed in *Table 0-2*.

Table 0-2 : Cost of the use of the equipment during the project.

Equipment	Use	Price	Cost (€)
Brabender internal mixer	31 h	200 €/h	6200
Hot press molding machine	51 sheets	<ul style="list-style-type: none"> • First sheet: 200€ • Additional sheet: 80€ 	5640
Universal tensile testing machine	50 series (7 samples/series)	<ul style="list-style-type: none"> • First series: 200€ • Additional series: 120€ 	7040
Tensile-impact testing machine	11 series (10 samples/series)	<ul style="list-style-type: none"> • First series: 200€ • Additional series: 120€ 	1480
SEM	6h	90 €/h	540
Total			20900 €

To sum up, considering the costs of the labor, the materials and the machines, the global cost of the project is estimated to 24960€, most of the cost being due to the use of the machines during the experimentation phase.

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Appendix

A1. Properties of PLA2002D®

Table A0-1 : Physical, mechanical, optical and processing properties of PLA2002D® supplied by Natureworks datasheet [61].

	Metric	Comment
Physical Properties		
Specific gravity	1.24 g/cc	ASTM D792
Melt Flow	5.0 - 7.0 g/10 min	ASTM D1238
Mechanical Properties		
Tensile Strength at Break	53.0 MPa	ASTM D882
Tensile Strength, Yield	60.0 MPa	ASTM D882
Elongation at Break	6.0 %	ASTM D882
Tensile Modulus	3.45 GPa	ASTM D882
Izod Impact, Notched	0.1281 J/cm	ASTM D256
Optical Properties		
Transmission, Visible	90 %	Thickness Unknown
Processing Properties		
Feed Temperature	180 °C	
Adapter Temperature	200 °C	
Die Temperature	190 °C	
Melt Temperature	210 °C	
Drying Temperature	90.0 °C (@Time 7200 sec)	
Moisture Content	<= 0.025 %	
Dew Point	-40.0 °C	
Drying Air Flow Rate	>= 14.2 l/min	
Screw Speed	20 - 100 rpm	

A2. Effect of the addition of DCP on PLA on the tensile stress-strain curve

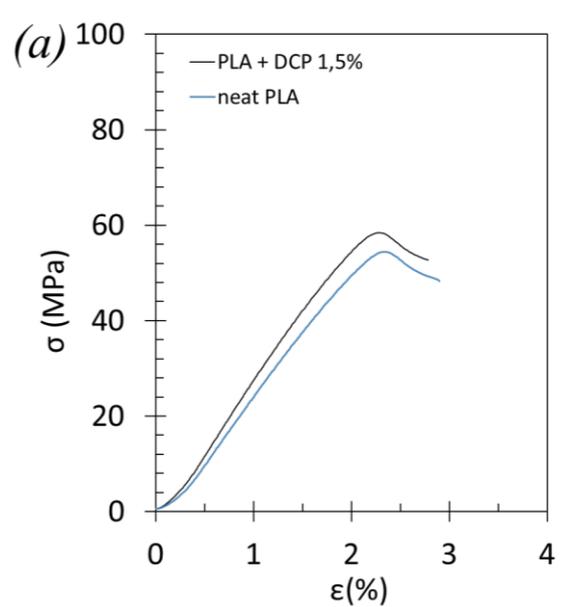


Figure A0-1 : DCP effect: tensile test engineering stress-strain curves for (i) neat PLA and (ii) PLA with addition of 1,5 wt.% DCP

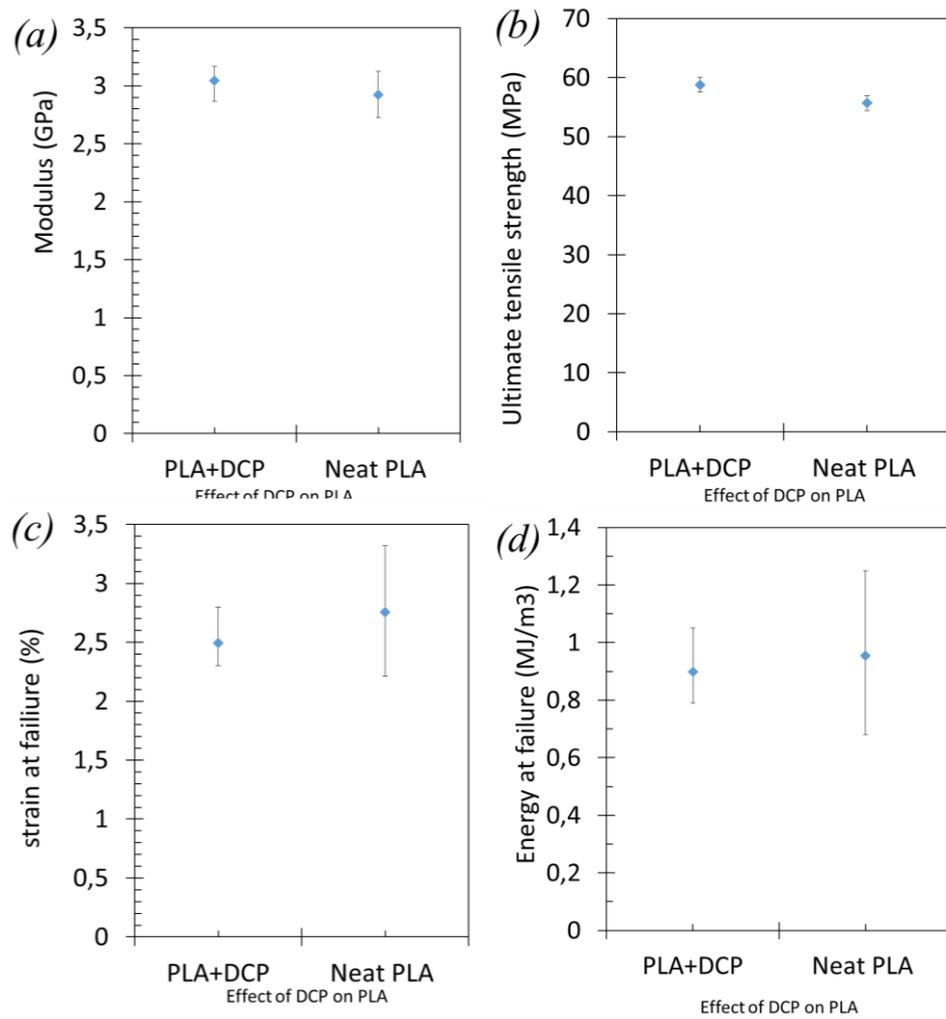


Figure A0-2 : DCP effect: tensile properties (a) elastic modulus E_T (b) yield strength σ_y (c) strain at break ϵ_b and (d) energy at break U_T for (i) neat PLA and (ii) PLA with addition of 1,5 wt.% DCP

A3. Strain hardening slope of binary PLA/NR and ternary PLA/NR/GTR blends

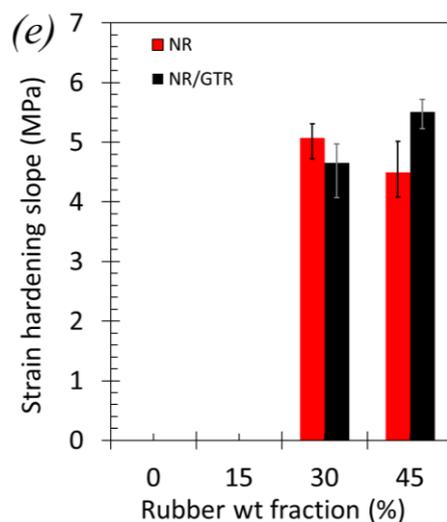


Figure A0-3 : Rubber content : tensile property - strain hardening slope as a function of the total rubber content for DCP crosslinked (i) binary PLA/NR and (ii) ternary PLA/NR/GTR blends with GTR particles <math><63 \mu\text{m}</math>

A4. Evolution of the torque during processing in internal mixer of PLA/devulcanized GTR blend

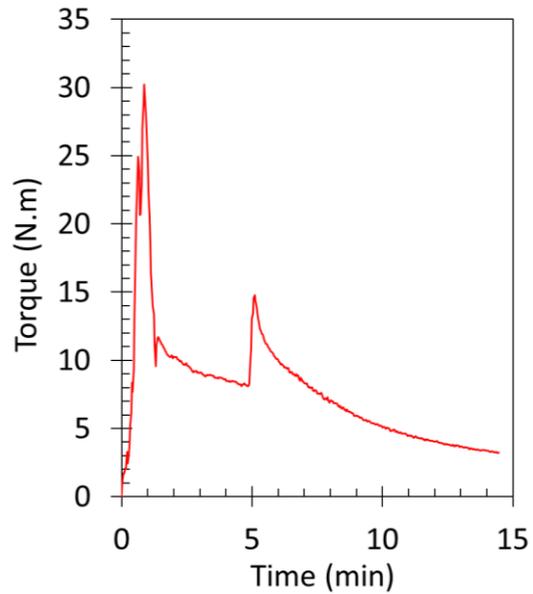


Figure A0-4 : GTR type : Torque as a function as time spent in the internal mixer for peroxide crosslinked PLA/devulcanized GTR blend; particle size <math><125 \mu\text{m}</math>