Production and Characterization of Thermoplastic Elastomers based on Recycled Rubber

Thèse

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Résumé

Ce travail de doctorat est consacré à la production et à la caractérisation de composés polymères à base de matrices thermoplastiques en mélange avec des particules de caoutchoucs recyclés. Les principales applications visées sont: (A) la production d'élastomères thermoplastiques (TPE) à haute teneur (50% et plus) en poudrette de caoutchouc de pneus usés (GTR); et (B) l'amélioration de la résistance à l'impact des composites thermoplastiques avec de faibles concentrations en GTR.

Dans la première partie de ce travail, du polyéthylène maléaté (MAPE) a été utilisé comme matrice pour produire des mélanges MAPE/GTR présentant d'excellentes caractéristiques en tant qu'élastomère thermoplastique. Puis, les effets de différents mécanismes de dégradation (humidité, chaleur et recyclage) sur les propriétés des composites MAPE/GTR ont été largement examinés afin d'évaluer le potentiel de ces matériaux après plusieurs cycles d'utilisation. Enfin, le renforcement des TPE/GTR par différentes particules solides (poudre de bois et talc) a été étudié pour des applications plus exigeantes (caractéristiques mécaniques).

Dans la seconde partie de ce travail, une nouvelle approche est proposée pour la modification de la résistance aux chocs des composites à base de polypropylène renforcé par des charges organique (chanvre) et inorganiques (talc, verre). L'amélioration des propriétés à l'impact de ces composites a été réalisée par l'addition d'un mélange à base de polypropylène maléaté (MAPP) et de poudrette de caoutchouc (GTR et déchets d'EPDM) contenant des concentrations élevées (jusqu'à 70% en poids) de déchets caoutchoutiques.

Abstract

This Ph.D. work is devoted to the production and characterization of polymer compounds based on thermoplastic matrix filled with waste rubber powder. The main applications include: (A) the production of thermoplastic elastomer (TPE) resins containing high ground tire rubber (GTR) contents (50% and higher), and (B) impact modification of thermoplastic composites using low concentrations of GTR.

In the first part of the work, maleated polyethylene (MAPE) is proposed as a matrix to produce MAPE/GTR blends having excellent characteristics as thermoplastic elastomers. Then, the effects of different degradation mechanisms (weathering, thermal degradation and reprocessing) on the properties of MAPE/GTR compounds were extensively investigated to determine their potential for further recycling. Finally, the reinforcement of GTR filled TPE was investigated using different types of solid particles (wood flour and talc) for more demanding applications (mechanical characteristics).

In the second part of the work, a new approach is proposed for impact modification of polypropylene based composites based on organic (hemp) and inorganic (talc and glass) reinforcements. The effective improvement of the impact properties of these composites is performed through the addition of a masterbatch based on maleated polypropylene (MAPP)/waste rubber powder (GTR or waste EPDM) containing high concentrations (70% by weight) of waste rubber.

Foreword

This Ph.D. dissertation is mainly based on a series of journal papers and consists of seven chapters:

In chapter one, a brief introduction on the importance and challenges of recycling discarded tires is presented. Ground tire rubber is introduced as a promising approach for reprocessing of waste rubber. Inclusion of ground tire rubber into thermoplastics is discussed to produce compounds for a variety of applications: (i) thermoplastic elastomers with high waste rubber content (higher than 40-50%), and (ii) impact modified thermoplastic composites with low concentrations (lower than 20-30%) of waste rubber.

In chapter two, ground tire rubber filled thermoplastic elastomers are extensively discussed. The main challenges and commonly suggested modification methods regarding mechanical properties of such compounds, along with selected literature review, are presented. The objectives of this research work are also specified at the end of this chapter.

The following four chapters present experimental results in the form of journal articles, published or submitted. My contributions in these research works included performing the experimental works, collecting and analyzing the data and writing the manuscripts.

In chapter three, an effective approach is proposed to develop thermoplastic elastomers by blending ground tire rubber with maleic anhydride grafted polyethylene. It is shown that highly compatible and highly filled compounds can be produced using MAPE as the matrix. The results are also compared with high density polyethylene/ground tire rubber compounds containing maleated polyethylene as a coupling agent. The paper was published as:

Ramezani Kakroodi, A. and Rodrigue, D., Highly filled thermoplastic elastomers from ground tire rubber, maleated polyethylene and high density polyethylene, Plast. Rubber Compos., 42, 115-122 (2013).

Chapter four is devoted to investigate the effects of different degradation processes (namely thermal ageing, weathering and re-extrusion) on the properties of neat maleated polyethylene and maleated polyethylene/ground tire rubber thermoplastic elastomers. Different concentrations of waste rubber (40, 60 and 80 wt.%) are used to determine the effect of waste rubber content on compound stability. The effects of three types of stabilizers (thermal stabilizer, UV absorber and hindered amine light stabilizer) on the degradation behavior of the compounds are also investigated. The reported data provide a comprehensive insight regarding properties of MAPE/GTR compounds during their life cycle. The paper is currently submitted as:

Ramezani Kakroodi, A. and Rodrigue, D., Degradation behavior of maleated polyethylene/ground tire rubber thermoplastic elastomers with and without stabilizers, Polym. Degrad. Stabil., (submitted).

In chapter five, reinforcement of ground tire rubber filled thermoplastic elastomers is performed through inclusion of rigid (organic and inorganic) particles. The morphological, mechanical and physical properties of these ternary composites are then studied to evaluate the effect of each particle. Modeling of the elastic modulus of MAPE/GTR compounds and hybrid MAPE/GTR/particle composites is also performed using Kerner and Halpin-Tsai models, respectively. This study shows that GTR filled thermoplastic elastomers can be used for more diverse and more demanding applications using the right reinforcements. The paper is currently submitted as:

Ramezani Kakroodi, A. and Rodrigue, D., Reinforcement of maleated polyethylene/ground tire rubber thermoplastic elastomers using talc and wood flour, J. Appl. Polym. Sci., (submitted).

In chapter six, a new approach is proposed for impact modification of brittle polypropylene based composites with both organic (hemp) and inorganic (talc and glass) reinforcements. The proposed protocol includes production of maleated polypropylene/waste rubber powder (ground tire rubber and also waste ethylene propylene diene monomer) master-batch, and then to add this compound to polypropylene based composites to increase impact strength. Effective modification of PP based composites using waste rubber is performed. This paper is currently under revision as:

Ramezani Kakroodi, A. and Rodrigue, D., Impact modification of polypropylene based composites using surface coated waste rubber crumbs, Polym. Compos., (submitted).

In chapter seven, a general conclusion for the aforementioned works and recommendations for future works are presented.

Nevertheless, more results obtained from these research works were also presented in the following articles or conference presentations:

Ramezani Kakroodi, A., Kazemi, Y. and Rodrigue, D., Mechanical, rheological, morphological and water absorption properties of maleated polyethylene/hemp composites: effect of ground tire rubber addition, Composites Part B, 51, 337-344 (2013).

Ramezani Kakroodi, A., Leduc, S. and Rodrigue, D., Effect of hybridization and compatibilization on the mechanical properties of recycled polypropylene-hemp composites, J. Appl. Polym. Sci., 124, 2494-2500 (2012).

Ramezani Kakroodi, A., Bainier, J. and Rodrigue, D., Mechanical and morphological properties of flax fiber reinforced high density polyethylene/recycled rubber composites, Int. Polym. Proc. 27, 196-204 (2012).

Ramezani Kakroodi, A., Leduc, S., Gonzalez-Nunez, R. and Rodrigue, D., Mechanical properties of recycled polypropylene/SBR rubber crumbs blends reinforced by birch wood flour, Polymers & Polymer Composites 20, 439-444 (2012).

Ramezani Kakroodi A, Kazemi Y, Rodrigue D. Impact modification of waste plastic/wood flour composites via structural modification. *The 19th International Conference on Composite Materials*, Montreal, QC, Canada, July 28-August 2 (2013).

Ramezani Kakroodi A, Rodrigue D. Mechanical and morphological properties of TPE composites based on recycled PP, waste rubber crumb and wood flour. *PPS Americas Conference 2012*, Niagara Falls, ON, Canada, May 21-24 (2012).

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"You cannot be buried in obscurity:

you are exposed upon a grand theater to the view of the world.

If your actions are upright and benevolent,

be assured they will augment your power and happiness."

Cyrus the Great

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Abbreviations

d	Thickness of particles
DTG	Derivative thermogravimetry
E	Tensile modulus
E_c	Tensile modulus of composite
EDS	Energy dispersive spectroscopy
E_{GTR}	Tensile modulus of GTR
E_m	Tensile modulus of matrix
E_p	Tensile modulus of particle
EPDM	Ethylene propylene diene monomer
E_{TPE}	Tensile modulus of thermoplastic elastomer
EVA	Ethylene vinyl acetate
F_m	Flexural modulus
GTR	Ground tire rubber
HALS	Hindered amine light stabilizer
HDPE	High density polyethylene
I_s	Impact strength
kGy	Kilogray
l	Length of particle
LDPE	Low density polyethylene
L_i	Individual particle size
LLDPE	Linear low density polyethylene
$\overline{L}_w$	Weighted average particle size
MA-EPDM	Maleated ethylene propylene diene monomer
MAPE	Maleated polyethylene
MAPP	Maleated polypropylene
M_w	Average molecular weight
NR	Natural rubber
PE	Polyethylene
POE	Ethylene-octene copolymer
PP	Polypropylene

SBR	Styrene butadiene rubber
SBS	Styrene butadiene styrene copolymer
SEBS	Styrene ethylene butylene styrene triblock copolymer
SEM	Scanning electron microscopy
SRP	Scrap rubber powder
T_{10}	Temperature for 10% weight loss
T_{50}	Temperature for 50% weight loss
TCF	Tire cord fabric
TDF	Tire derived fuel
TDM	Tire derived material
TGA	Thermogravimetric analysis
T_m	Torsion modulus
$T_{max.dec.}$	Temperature for highest weight loss rate
TPE	Thermoplastic elastomer
UVA	Ultraviolet absorber
V_i	Individual particle volume
WF	Wood flour
W_i	Individual particle weight
ε_b	Elongation at break
ν_m	Poisson ratio
ξ	Shape factor
ρ	Density
σ_y	Stress at yield
Φ_f	Volume fraction of particle
Φ_{GTR}	Volume fraction of GTR

Chapter 1. Introduction

1.1 Tire recycling

Today, vulcanized rubber poses one of the most noticeable threats regarding waste disposal management. The crosslinked structure of such materials, combined with presence of different types of stabilizers in their formulation, makes their natural degradation a very challenging and time consuming process. Vulcanized rubber is also impossible to melt or dissolve which causes serious challenges regarding their reprocessing. Therefore, rubber products belong to the category of non-environmentally friendly materials [1]. Among all rubber based materials, tire is the most important and most commonly used product (around 70% of rubber is used to produce tires). In 2011, 160.32 million tires were produced in Japan which represents almost 1,180,000 tons of rubber. This amount accounts for over 80% of their domestic rubber production [2]. Globally, an estimated one billion tires reach the end of their service life every year [3]. On average, one passenger tire per person is discarded each year in developed countries [3]. Such statistics clearly show the importance of dealing with discarded tires.

Tires are oil based products and their composition makes them very important and valuable materials to reprocess. But if discarded as waste, they are very prone to make environmental, health and safety hazards. For instance, disposing of tires in landfills can lead to leakage of pollutants (small molecule components such as stabilizers, plasticizers, etc.) which are not ecofriendly and kill advantageous bacteria in soil [4]. Creation of vicious fires which are very difficult to extinguish have also been reported. In February 1990, a huge pile of discarded tires in Hagersville, Ontario, caught fire and burned for 17 days. The Environmental Emergencies Program of Environment Canada estimated that 12.6 million tires burned in this case alone [5]. Accumulation of discarded tires can also take considerable space and cause health problems due to breeding of mosquitoes and bacteria. Today several methods have been developed to deal with worn tires, some are used to make tire derived material (TDM), some are used in civil engineering, but still a considerable portion of waste tires are land disposed [6,7]. Figure 1.1 presents a diagram showing the life cycle of produced tires.

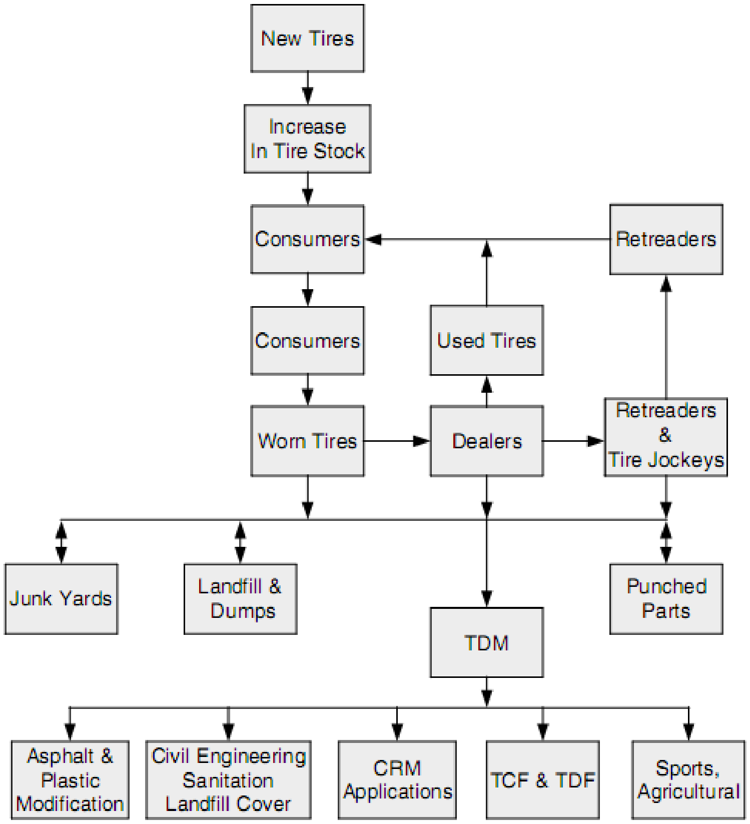

Figure 1.1 Life cycle of produced tires [7].

A significant part of recycled tires is used to make tire derived fuels (TDF). To produce these materials, tires are first ground to tire derived chips containing wires, mostly bead wire. After separation of 95% of the wires the product is now TDF. This product is useful for reduction of sulfur emission from power plants. TDF is also being considered to be used as fuel in alcohol production plants. Utilization of discarded tires as fuel, however, is not actually a real recycling process. It creates new problems (such as air pollution) and is a low value recovery for rubber. It is usually preferable to develop more effective recycling methods to fabricate more valuable products from discarded tires [8]. Used tires can also be sold as worn tires or even be recapped, but developing an effective method to fully recycle the worn tires in a practical manner is eventually compulsory. This matter has attracted a lot of attention. Tire particles are used in polymer and construction industries [9,10].

1.2 Ground tire rubber (GTR)

Since reprocessing of tire rubber is not possible via melting or dissolving, fabrication of ground tire rubber is proposed as a promising method to make use of scrap rubber products. Ground tire rubber usually refers to ultrafine fractions of rubber powder with a diameter of less than 1 mm. It should be noted that ground tire rubber is also known in the literature by other terms such as particulate tire rubber, scrap tire powder, crumb tire rubber etc. Tires are made of different parts and components. Effective recycling methods should be taken to handle these components to produce recycled materials out of discarded tires. Table 1.1 presents the approximate composition of tires for passenger cars (7.5-9 kg) and trucks/buses (50-80 kg) [4]. Ground tire rubber virtually includes all components of tires except for metal reinforcements and fabrics. Metal reinforcement was not recovered in the past, but today tire wire is considered as a highly valuable by-product [4].

Table 1.1 Composition of tires for passenger cars and trucks/buses in Europe (wt.%) [4].

Component	Passenger cars	Trucks/Buses
Rubber	48	43
Carbon black	22	21
Metal reinforcements	15	27
Fabric	5	-
Zinc oxide	1	2
Sulfur	1	1
Additives (oils, wax, stabilizers...)	8	6

Several methods have been proposed to prepare rubber powder. The conditions used in each method affect average particle size, particle size distribution, and particle shape greatly. Some common methods to prepare rubber powder are presented here [7].

1.2.1 Ambient grinding method

In this method, vulcanized rubber parts are passed through the nip gap of a shear mill or a two roll mill. This process is performed at room temperature and the particle size is controlled by the number of passes. To have finer rubber powder, higher number of passes are needed which leads to increased production costs.

1.2.2 Cryogenic grinding method

In this method, ambient conditions are used to perform the initial grinding. Then, liquid nitrogen is used to cool the rubber chips to temperatures below their glass transition temperature (between -30°C and -80°C depending rubber type) at which rubber particles become brittle. Rubber particles are then ground by a hammer mill to produce finer products. Smaller particles are separated by sieving. Particle size is controlled by the temperature of the process and by mesh size of the sieve.

1.2.3 Wet grinding method

In this method, small rubber chips are passed through circular grinding plates moving concurrently, and the process is lubricated by water. Particle size is controlled by the residence time of rubber particles in the grinding process.

1.2.4 Extrusion method

Rubber powder is produced in a twin-screw extruder which creates compressive shear on the polymeric material at determined temperatures. The channel depth of the screw decreases from the feeding zone to the extruder outlet. The number of passes controls the particle size and particle size distribution, while increased number of passes leads to narrower particle size distribution.

1.2.5 Abrasion method

In this method, the rubber particles are removed from the tire treads using an abrasion process.

Among all the grinding methods presented above, the cryogenic method is the most economically suitable one to produce rubber powder with very small particle size (around 100 microns). Since rubber particles are easier to grind under cryogenic conditions, this method also reduces the tear and wear of the machinery, leading to lowered maintenance cost. Using a cryogenic method also decreases ignition hazard during the process, due to less gas liberation compared to ambient methods. During ambient methods, the temperatures can rise up to 130°C during milling. Using cryogenic grinding, it is also easier to separate impurities from rubber particles. Compared to cryogenic and ambient methods, lower productivity is achieved through wet methods. The highest purity and finest ground rubber, 400-500 mesh size, on the other hand, can be produced with this method.

1.3 GTR as filler in thermoplastics

1.3.1 GTR filled thermoplastic elastomers

Fabrication of thermoplastic elastomers (TPE) is one of the most promising applications of ground tire rubber. In this case, the ground tire powder is introduced in a thermoplastic matrix as filler [11-13]. Thermoplastic elastomers benefit from mechanical properties of elastomers at ambient temperature while presence of thermoplastic phase, as matrix, makes them possible to be reprocessed and recycled. It is also possible to fabricate products with a wide range of mechanical properties by changing their formulations. In this work, the environmental aspects have been the main driving force so far, but no successful future can be imagined if the job is not economically feasible. Improving mechanical, morphological and physical characteristics of TPE blends, via phase compatibilization, enables economical recycling of ground tire rubber.

Low compatibility between GTR and thermoplastic, mostly polyolefins molecules is a major problem in production of high quality TPE. Once again, the vulcanized structure of tire macromolecules is responsible in this case. Crosslinked rubber molecules do not have enough freedom to entangle with the macromolecules of the matrix [14]. Poor compatibility causes significant loss in characteristics of the blends such as elongation at break and elastic recovery [14].

Several modification methods have been developed to increase the compatibility between both phases in thermoplastic elastomers. Surface coating of GTR particles is one of the most frequently used approaches. In this case, rubber particles are covered with a material which is compatible with both rubber particle and thermoplastic matrix. The material is mostly virgin rubber of the same origin as recycled rubber. Another method to increase the compatibility is to devulcanize rubber particles, at least partially [14,15]. Devulcanization processes can be performed with thermo-mechanical and thermo-chemical techniques or even using ultrasonic [16,17] and microwave [18] methods. The objective is to devulcanize the GTR particles (or at least their surface) to increase the entanglement between rubber and matrix molecules. Surface treatment methods, such as acid treatment or polymer grafting, are also taken into consideration to increase the activity on the surface of rubber particles.

To obtain a well homogenized compound of waste rubber powder in thermoplastics, a good distribution and dispersion is also needed. Choosing suitable processing conditions, i.e. temperature and rotor speed, plays a very important role here. The temperature of the blend should be high enough, but it is very important that the mix does not get too hot since it will lead to degradation in the materials. Thermogravimetric analysis (TGA) of GTR, in air atmosphere, was performed by the author [19]. It was proven that the degradation of GTR powder started at around 200°C implying that processing temperatures should not exceed this value. Increase in processing temperature will also decrease the viscosity of the blend resulting in a lack of effective dispersion.

1.3.1.1 Rubber devulcanization methods

During an ideal devulcanization process of tire rubber, crosslinks between the rubber molecules (carbon-sulfur and sulfur-sulfur bonds) are expected to break without damaging the backbone of the rubber molecules [8]. However, it is almost inevitable to break the crosslinks without considerable scission of rubber molecules. Therefore, the process is often referred to as reclamation of waste rubber (instead of devulcanization). Several methods have been developed to lower the crosslink density in rubber products. The differences between the methods arise from the techniques used to apply stresses on the crosslinks. It is possible to break crosslinks using a combination of harsh mechanical, thermal and chemical conditions. Microwave, ultrasound, and biological treatments are other possible methods. The most common methods regarding GTR devulcanization are listed in Table 1.2.

Table 1.2 Rubber devulcanization processes.

Technology	Basis of Processing	Zone of Reaction
Chemical	Chemicals/Chemical reactions	Surface of particles
Ultrasonic	Ultrasonic waves	Throughout particles
Microwave	Microwaves	Throughout particles
Biological	Microorganisms	Surface of particles
Thermo-mechanical	Thermal and mechanical stresses	Throughout particles

1.3.1.2 Applications of TPE

As demonstrated earlier, waste tire in the form of GTR can be blended with thermoplastic materials, virgin or recycled, in absence or presence of other polymeric materials to form environmental and cost friendly products. Such materials can be used to produce porous hoses, automotive parts, flooring, security elements, motorway sound barrier and most importantly sealing and seal extension. It is reported that thermoplastic elastomers exceed paper based cushioning products in shock absorption, fatigue endurance and compression set. Blalock and Nelson [20] patented a product from ground tire rubber and thermoplastics to be used as roofing shingles. The products are lightweight and have very good strength, durability, temperature stability and weathering resistance. They used branched polyolefins containing hexene and octene co-monomer, combined with fillers and processing oil. The products are inexpensive, efficiently manufactured and they also passed usual pull test and tear test required for roofing purposes.

1.3.2 GTR in thermoplastic based composites

In order to expand the applications of polymeric materials and to cope with their limitations, such as low stiffness, reinforcements in different shapes (particles, short and long fibers etc.) and different sizes (micro/nano scale) are usually incorporated to polymers. Such reinforcements can also be found in form of manmade and naturally occurring materials. Despite superior mechanical properties of synthetic reinforcements, natural fiber reinforced composites (especially thermoplastic matrix) have found a growing interest during the past decades. The main advantages of natural fibers over manmade reinforcements include environmental friendliness (due to their natural and renewable source), low cost, lightweight, low abrasiveness and lower equipment wear compared to manmade reinforcements. Although natural fibers have lower mechanical performance compared to manmade reinforcements, some natural fiber composites were shown to have similar specific properties (on weight basis) due to their lower densities, especially compared to glass fiber composites [21]. Mechanical properties like elongation at break (ε_b), tensile strength (σ) and elastic modulus (E), as well as densities (ρ) of some natural fibers are shown in Table 1.3 in comparison with some commonly used reinforcements [22].

Table 1.3 Characteristics of natural fibers compared to conventional fibers [22].

Fiber	ρ (g/cm^3)	ε_b (%)	σ (MPa)	E (GPa)
Cotton	1.5-1.6	7.0-8.0	287-597	5.5-12.6
Jute	1.3	1.5-1.8	393-773	26.5
Flax	1.5	2.7-3.2	345-1035	27.6
Hemp	-	1.6	690	-
Sisal	1.5	2.0-2.5	511-635	9.4-22.0
Coir	1.2	30.0	175	4.0-6.0
Soft wood	1.5	-	1000	40.0
E-glass	2.5	2.5	2000-3500	70.0
S-glass	2.5	2.8	4570	86.0
Aramide (normal)	2.4	3.3-3.7	3000-3150	63.0-67.0
Carbon (standard)	1.4	1.4-1.8	4000	230.2-240.6

Cellulose and hemicellulose content on the surface of natural fibers contain plenty of hydroxyl groups (-OH) whose polar nature leads to a number of inappropriate characteristics. Mixing of natural fibers with hydrophobic polymers results in low interfacial bonding and leads to reduced stress transfer at the fiber-matrix interface under mechanical loadings. Another limitation to the use of natural fibers in composites is their ability to absorb water. The water content can cause defects such as swelling, lowered mechanical properties (due to loss of adhesion and plasticizing effect of water), and higher degradation rate of fibers. It may also be noted that the hydroxyl groups of cellulose can form hydrogen bonds between cellulose chains. This causes fiber aggregation which could cause poor fiber dispersion in a composite [22].

To work out such problems, numerous modification methods have been applied to increase bonding at the fiber-matrix interface. Inclusion of maleic anhydride grafted polyolefins, also called maleated polyolefins, has been most widely considered in this field. Noticeable improvements in mechanical properties of natural fiber composites were observed due to incorporation of such materials [22].

Adding natural and manmade particles and fibers as reinforcing phase usually leads to decreased ductility of composites due to stress concentration. For example, PP itself has low impact strength, especially at low temperatures, and PP based composites are usually very brittle. To increase the impact properties of such composites, elastomer phases such as copolymers of polyethylene or polypropylene such as ethylene propylene diene monomer, styrene ethylene butylene styrene tri-block copolymer etc. can be incorporated into the composites through melt-mixing [23]. Rubber particles with uniform distribution and small size, smaller than 1 micron in diameter, are expected to increase impact strength of the composites effectively. Elastomer phase can act in natural fiber composites in three ways: (i) it can act as a third phase in the blend, (ii) it can encapsulate the particles and act as an interface, and (iii) it can have a mixed behavior between (i) and (ii).

Clemons [24] studied the effect of introduction of elastomer into polyethylene (PE)/polypropylene (PP)/wood flour (WF) composites. He used ethylene propylene diene monomer (EPDM) and maleated EPDM (MA-EPDM) as impact modifier and reported that incorporation of 10% MA-EPDM led to a significant increase (63%) in impact strength of composite with PE/PP:75/25 and with 30% WF, while the same amount of EPDM proved to be less effective (46% increase). Decrease in tensile modulus of the composites was also reported (32% reduction for MA-EPDM compared to 26% for EPDM).

GTR can also be considered as a very interesting candidate in impact modification of reinforced thermoplastics. Such approach is beneficial from both environmental and economical aspects. But two main drawbacks in this work are low compatibility between GTR and polyolefins and large size of GTR particles. If the compatibility between GTR and matrix is low, (i) effective load transfer from the matrix to the rubber phase cannot be expected, and (ii) creation of gaps and voids at the rubber-matrix interface causes even higher stress concentration leading to premature compound failure. For the moment, no research work was successful in performing this task.

Chapter 2. GTR filled thermoplastic elastomers

The most direct method to recycle rubber based products seems to be devulcanizing and reprocessing them to produce new rubbery products. Several methods have been proposed to reclaim and reuse scrap rubbers so far [25-27]. The level of tire rubber degradation caused by these methods, however, makes it impossible to produce highly engineered products such as tires from recycled rubbers. On the other hand, almost 70 percent of the virgin rubber produced in the world is consumed in tire production [7]. Therefore fabrication of non-tire rubbery materials from recycled rubbers is narrowed to a very limited range of products.

The alternative method to consume considerable amounts of waste rubber is inclusion of GTR particles into polymer matrices (especially thermoplastics). It is believed that successful inclusion of even small contents of ground tire rubber to thermoplastics can significantly contribute to recycling of waste rubbers due to large market share of thermoplastics [4]. Thermoplastic/ground tire rubber compounds have the ability to flow at determined temperature and pressure conditions using common machines such as extruders and injection molding devices. This characteristic makes it possible to rapidly process (and reprocess) several products having a variety of shapes and sizes, and at reasonable cost. It is also possible to add different contents of waste rubber powder to thermoplastics to produce products for different applications. Depending on GTR concentration, these products can be classified as either thermoplastic elastomers with high GTR contents (higher than 40-50%) or simply impact modified thermoplastics or thermoplastic based composites with lower GTR contents.

In the past decades, several conventional rubbers have been replaced with compounds containing thermoplastics and elastomers. Such products are commonly used for several applications such as automotive, construction, medical purposes, etc. Vulcanization of rubber particles in TPE is usually performed during the mixing process in order to improve the physical and chemical properties of the blends. An important drawback regarding TPE, which are produced using virgin materials, is the fact that they are expensive products [4].

Incorporation of large amounts of already vulcanized rubber (i.e. GTR) to thermoplastics also leads to thermoplastic elastomers. As mentioned earlier, the most important concern in the fabrication of such materials is low surface interaction between the rubber phase and the matrix due to low surface activity of rubber particles. In the past, many research works have been conducted to improve compatibility between a thermoplastic matrix and ground tire rubber. Karger-Kocsis and coworkers [4] recently published a useful review on this subject. However, they concluded that fabrication of TPE from GTR and thermoplastics has not been a rewarding task so far. After performing an extensive literature survey, they suggested that it is only in the presence of considerable amounts of expensive/virgin rubbers that GTR filled TPE may have acceptable characteristics. The most common compatibilization techniques are presented here [8].

2.1 Physical compatibilization

Physical compatibilization of thermoplastics and ground tire rubber is performed using external energy. In this approach, the three-dimensional network of vulcanized rubber molecules is broken using different sources of energy. The main idea of these methods is to increase the interaction between the thermoplastic and rubber molecules through increased physical entanglements. The rubber phase can then be re-vulcanized in order to increase the physical and chemical properties of the blend. The most important physical compatibilization processes are:

2.1.1 Thermo-mechanical compatibilization

In this method, reduction of crosslink density in the rubber phase is performed by mechanical and/or thermo-mechanical stresses [8]. This process results in higher surface activity of rubber particles and improved interaction between both phases (reclaimed rubber and thermoplastic matrix). Thermo-mechanical process can be assisted by incorporation of regeneration aids such as different kinds of oils. In this case, the swelling of waste rubber particles is performed using regeneration aids which stretch the bonds between rubber macromolecules and thereby decrease the required energy for breaking the crosslinks.

Macsiniuc et al. [28] studied the effect of different regenerating aids on reclaiming scrap ethylene/propylene/diene-monomer rubber. They used both batch (internal mixer) and continuous (twin-screw extrusion) processes to treat rubber particles. They concluded that, although rubber regeneration occurs in absence of any kind of chemical agent, choosing the best regenerating aid coupled with good processing conditions will lead to higher regeneration degrees. Grigoryeva et al. [14] characterized the thermoplastic elastomers from high density polyethylene/regenerated ground tire rubber and ethylene propylene rubber. They used bitumen as a regenerating aid and concluded that pre-treatment of GTR powder with bitumen resulted in significant increase in compatibility between each phase in the blends. Bitumen was reported to work as both regenerating aid and vulcanizing agent (during re-vulcanization of GTR) in the process.

2.1.2 High energy radiation

Using this technique, and in theory, a specific dose of high energy radiation (such as microwave or γ radiation) is used in order to increase the compatibility between the thermoplastic phase and rubber particles via two mechanisms: (i) devulcanization of GTR through breaking of crosslinks without causing any scission in the rubber macromolecules [8], and (ii) chain scission of thermoplastic and rubber macromolecules leading to crosslinking between both phases, as well as possible co-crosslinking between the matrix and rubber phase at the interface [29]. In case (i), suitable chemicals should be used to consume the radicals that are produced after breaking the crosslinks.

Hirayama and Saron [30] studied the effects of devulcanization of styrene-butadiene rubber using microwave treatments. They reported that treatment of waste rubber with microwave resulted in some devulcanization only in case of rubbers containing high carbon black contents (60 and 100 phr). For instance, gel content of compound containing 100 phr of carbon black decreased from 87 to 77% after the devulcanization process. For compounds containing lower carbon black contents (0 and 40 phr), a slight increase in crosslinking degree of the rubber molecules was observed. In case of compounds containing 40 phr of carbon black, gel content increased from 79 to 80%. They suggested that more significant compounds heating due to higher carbon black contents led to such observations. Low level of devulcanization (even in samples with high carbon black contents) is also linked to formation of new crosslinks after devulcanization. They also reported that for samples with devulcanization, crosslink breaks were mostly observed for polysulfidic bonds, while monosufidic bonds (with higher energy) were preserved.

Sonnier et al. [29] used γ irradiation to compatibilize thermoplastic elastomer blends of recycled HDPE and GTR. They reported that inclusion of GTR to the matrix reduced its elongation at break significantly (40% reduction after inclusion of only 30% GTR). γ irradiation of the compounds containing 50% GTR (with an irradiation dose of 50 kGy) resulted in increase in both elongation at break (almost 40%) and yield stress (almost 15%), while elastic modulus decreased (almost 20%). They suggested that enhanced adhesion between the rubber and thermoplastic matrix was a result of mechanism (ii).

2.1.3 Ultrasonic method

Compatibilization of GTR and thermoplastics can also be conducted using ultrasonic waves. Two theories exist to explain the changes caused by ultrasonic waves [4]: (i) hot spot theory and (ii) electrical theory. According to the hot spot theory, when a polymer is subjected to high frequency ultrasound waves, cavitation takes place which results in a significant increase in local temperature and stress. It is suggested that localized bubbles may have a temperature of 5000 K and a pressure of 500 bars [4]. Polymeric molecules rupture under severe conditions of cavitation and macro-radicals are produced. Electrical theory, on the other hand, suggests that an electrical field gradient (formed on the surface of the bubble) is enough to break the crosslinks.

Luo and Isayev [31] investigated the effect of GTR devulcanization on the compatibility of polypropylene/GTR compounds. Devulcanization of GTR was performed using ultrasonic devulcanization in an extruder, while GTR particles were preheated to 178°C. They reported that tensile elongation at break of the compounds increased slightly after GTR devulcanization using ultrasonic waves. Elongation at break of compound containing 40% of devulcanized GTR was around 17% compared to around 12% for sample containing the same amount of un-treated GTR. It should be noted that even after compatibilization of GTR and PP, elongations at break were well below 100% which is the minimum requirement for a good thermoplastic elastomer [4].

2.2 Chemical compatibilization

In this method the interfacial adhesion between rubber particles and the thermoplastic matrix is improved by inclusion of a chemical agent. This work can be done using the following methods [8]:

2.2.1 Non-reactive compatibilization

In non-reactive methods, the compatibility between the phases is increased through incorporation of a block or graft copolymer, which has chain units similar to both phases of the blend. The compatibilizer might be commercially available or be prepared before mixing. Kumar et al. [15] fabricated thermoplastic elastomers based on low density polyethylene (LDPE), GTR and virgin rubbers. They used three kinds of virgin rubbers to increase the compatibility between GTR and thermoplastic matrix: styrene butadiene rubber (SBR), natural rubber (NR) and EPDM. Formulation of the samples was LDPE/rubber/GTR : 50/25/25. They concluded that the highest level of improvement in mechanical properties of the blends was achieved with samples having EPDM as the virgin rubber. This can be due to structural similarity between EPDM and LDPE.

Wang and coworkers [32] also studied the effects of HDPE/GTR compatibilization using styrene-butadiene-styrene (SBS) block copolymers. They reported that tensile strength (around 15 MPa) and elongation at break (around 370%) showed maximum values at a compatibilizer content of 12 phr. Fayt et al. [33] studied the compatibilization effect of different copolymers on polymer-polymer blends and concluded that the molecular weight and structure of the copolymers have a significant impact on compatibilization efficiency.

They claimed that tapered block copolymers are more effective than linear block copolymers to increase the compatibility between two polymer phases.

The main drawback in using such block compatibilizers is the fact that they are expensive additives [4]. It should be noted that every recycling process must be cost-effective for market penetration and acceptance.

2.2.2 Reactive compatibilization

2.2.2.1 Reactive compatibilization via inclusion of compatibilizers

In this method, a reactive material is added during the mixing process as a blend component in order to increase the compatibility between both phases in thermoplastic elastomers. Blending of nylon with functionalized rubbers, especially maleic anhydride grafted EPDM, is one of the most frequently used processes in this field [34]. In this process the maleic anhydride groups of the maleated rubber react with the amine end groups of nylon, leading to increased interfacial adhesion between both phases.

Another common example for this method is the incorporation of maleated thermoplastics as compatibilizers to TPE blends. Maleic anhydride groups of the thermoplastics react with double bonds in the rubber molecules, while the thermoplastic part of the molecule is supposed to have good entanglement with the matrix. Tolstov et al. [35] studied the effect of reactive compatibilization of TPE blends from recycled LDPE and high density poly ethylene with ground tire rubber. They functionalized polyethylene with maleic anhydride, while the rubber part was functionalized with maleic anhydride or acrylamide using chemically (peroxide initiator) or irradiation (γ ray) induced grafting techniques. They concluded that the interactions between anhydride and amide functional groups of reactive polymers or between anhydride functional groups of polymers and coupling agents with amine/amide groups led to higher interfacial adhesion between the phases.

Rajalingam and Baker [36] improved the compatibility of PE/GTR blends using pre-coating of GTR with functional polymers such as ethylene acrylic acid copolymer, styrene ethylene butylene styrene tri-block terpolymer (SEBS), ethylene vinyl acetate (EVA) and maleic anhydride-grafted PE as coupling agents. The rubber particles were coated with the polymers in the chamber of a batch mixer, the coated GTR was then blended with PE. Addition of small amounts of functional polymers increases the impact energy of the polyethylene/GTR compound as much as 60%. Almost all blends showed a maximum impact strength at 6.7 wt% of reactive polymer.

2.2.2.2 Reactive compatibilization via chemical devulcanization of GTR

In this technique, reclamation of GTR is performed through inclusion of chemical reclaiming agents. Both organic and inorganic chemicals can be used at elevated temperatures for such purposes [8]. It should be noted that use of chemicals and also solvents in such techniques can cause new environmental pollution hazards.

2.2.2.3 Reactive compatibilization via surface activation of GTR

Ground tire rubber can be surface treated with reactive chemicals such as ozone, chlorine or sulfur dioxide to make the surface of the particles polar or reactive. Using such methods, increase in GTR compatibility with polymer matrices is achieved through: (i) reduction in interfacial tension or even (ii) creation of chemical bonds between GTR and matrix. For instance, exposure of GTR to chlorine is suggested as an effective method to make the surface of rubber particles polar. Kim and Burford [37] studied the effect of GTR particles treatment, as well as incorporation of different types of compatibilizers on the morphology and interfacial adhesion of compounds from GTR and natural rubber or nitrile rubber. In order to facilitate the morphological studies, carbon black was not incorporated to the virgin rubbers. GTR was surface chlorinated and the effect of a compatibilizer, polyoctenemer from Struktol, was also investigated. They concluded that addition of a chlorination agent and a compatibilizer to nitrile rubber/GTR blends led to increased compatibility between the phases, while no significant improvement was reported for NR/GTR blends. Surface of nitrile rubber is more polar than that of GTR, thus, chlorination of GTR led to higher polarity and improved compatibility of the blend.

Another important surface activation technique is grafting of unsaturated monomers and oligomers on the surface of GTR. Increase in compatibility is expected to occur due to either creation of chemical bonds or at least physical entanglement between the matrix and monomers (or oligomers). Presence of reactive double bonds on the surface of ground tire rubber particles is reported to act as anchoring site for grafting.

2.3 Effect of surface characteristics and size of rubber powder on thermoplastic/ GTR compounds

Surface characteristics of the GTR powder are mainly controlled by the grinding process from which the GTR is produced. Temperature, surrounding atmosphere and shear intensity control the morphological and even chemical characteristics of the powder [7]. Using a cryogenic process leads to smooth and angular surface of rubber particles, like crushed stone, while ambient wet grinding and ambient dry grinding methods produce rubber powder with porous and rough surface. The morphological characteristics of the rubber powders significantly affect the surface area of the particles.

Size distribution of rubber particles is also shown to play an important role on homogeneity and impact strength of thermoplastic elastomers. Rajalingam and coworkers [38] investigated the effect of size distribution of rubber powder and grinding method on impact properties of GTR/linear low density polyethylene (LLDPE) compounds. They concluded that rubber powder produced by wet ambient grinding increased the impact strength of the blend more effectively compared to cryogenic grinding. A decrease in rubber powder size also led to a slight increase in impact strength of the composites.

2.4 Thesis objectives and organization

Many techniques have been proposed in the past regarding fabrication of high quality thermoplastic/waste rubber (especially ground tire rubber) compounds. However, none of such techniques was proven to be effective, especially when high GTR concentrations are used (over 50% wt.). Therefore, the main objective of this thesis is to enhance the quality of the interface between the thermoplastic matrix and waste rubber particles and even alter the role of waste rubbers from a burden to an actual modifier in the compounds.

Chapter one was devoted to present a brief introduction regarding the magnitude and sources of concerns about waste rubber (discarded tire in particular). Ground tire rubber was introduced as a promising approach for reprocessing discarded tires. Potential applications of compounds containing ground tire rubber in thermoplastic matrices (with different rubber contents) and even thermoplastic based composites were presented.

In chapter two, ground tire rubber filled thermoplastic elastomers (with high waste rubber content) were extensively discussed. The main challenges and commonly suggested modification methods regarding the mechanical properties of such compounds were presented. A literature review was also performed on the aforementioned topics.

This dissertation was devoted to pursue the following objectives:

1) Developing a ground breaking approach to fabricate high quality thermoplastic/ground tire rubber compounds with a wide range of waste rubber contents to enable economically feasible recycling of waste rubber with the least possible environmental impact.
2) Determining the potential of the aforementioned compounds for further recycling via investigation of the effects of different environmental stresses and also degradation caused by reprocessing.
3) Further enhancement of the thermoplastic/ground tire rubber compounds characteristics through inclusion of natural/manmade particulate reinforcements, as well as prediction of the elastic modulus of ternary composites using appropriate models.
4) Utilization of waste rubber powder as an impact modifier for brittle polypropylene based composites using masterbatches of maleated polypropylene and waste rubber powder.

Chapter 3. Highly filled thermoplastic elastomers from ground tire rubber, maleated polyethylene and high density polyethylene

Résumé

Dans ce travail, le polyéthylène maléaté (MAPE) a été utilisé comme matrice pour la fabrication d'élastomères thermoplastiques en mélange avec de la poudrette de caoutchouc provenant de pneus usés (GTR). Des concentrations élevées de GTR, entre 50 et 90% en poids, ont été utilisées. Les composés ont également été comparés avec des élastomères thermoplastiques en utilisant le polyéthylène de haute densité (HDPE) comme matrice. Des photos au microscope électronique à balayage ont révélé une compatibilité élevée et une très bonne adhérence interfaciale entre la matrice MAPE et les particules de caoutchouc. Les échantillons dans la gamme de 50 à 70% de GTR dans le MAPE ont montré de bonnes élongations à la rupture et de bonnes résistances à la traction, tandis que les propriétés de ces échantillons diminuent en présence d'une concentration plus élevée de GTR. L'élasticité des élastomères thermoplastiques a également été étudiée par des mesures en compression. Tous les composés GTR/MAPE ont montré un comportement très élastique et une élasticité croissante avec l'augmentation du GTR. De plus, l'élasticité des composés HDPE/GTR, avec et sans agent de couplage MAPE, étaient significativement plus faibles que celles à base de MAPE. Par ailleurs, une grande stabilité a été observée pour les deux composés à base de MAPE et HDPE après un vieillissement thermique à 70°C. La dégradation thermique a également été caractérisée par rapport à l'évolution des viscosités à l'état fondu.

Abstract

In this work, maleated polyethylene (MAPE) is proposed as matrix for fabrication of thermoplastic elastomers filled with ground tire rubber (GTR) with a focus on high GTR concentration (50-90% by weight). The compounds were also compared with thermoplastic elastomers with high density polyethylene (HDPE) as matrix. SEM micrographs revealed high compatibility and very good interfacial adhesion between the MAPE matrix and rubber particles. Samples in the range of 50-70% of GTR in MAPE showed very good tensile elongation at break and tensile strength, while the properties decreased for samples at higher GTR content. The elasticity of the thermoplastic elastomers was also investigated via compression set measurements. All GTR/MAPE compounds showed highly elastic behaviour with elasticity increasing with GTR content. Tensile and elastic recovery values of HDPE/GTR compounds, with and without MAPE coupling agent, were significantly lower than those based on MAPE. High stability was observed for both MAPE and HDPE based compounds after thermal ageing at 70°C. Thermal degradation was also characterized with respect to changes in melt viscosities.

Keywords: Ground Tire Rubber (GTR), Thermoplastic Elastomer (TPE), Recycling, Polyethylene (PE), Maleic Anhydride (MA), Thermal Stability.

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3.1 Introduction

The cross-linked structure of rubber products has turned them into a significant environmental concern ever since the first vulcanization process was developed by Charles Goodyear. The presence of cross-links in the molecular structure of rubber parts, such as tires, makes them impossible to melt or dissolve [25,39,40]. For this reason, ground tire rubber (GTR) production is proposed as a promising method to make use of scrap rubber parts [29,36,41-43]. Ground tire can be blended with new materials, e.g. thermoplastics, thermosets and even virgin elastomers, to produce a wide range of products. Among these, thermoplastic elastomers (TPE) are one of the most promising applications of ground tires [44,45] because the presence of a thermoplastic phase in the final product makes it possible to reprocess and recycle the compounds. Nevertheless, GTR/thermoplastic blends have shown poor mechanical characteristics compared to virgin materials and are usually destined to less demanding products. Environmental aspects have always been the main driving force in the fabrication of these compounds so far, but improving the mechanical and thermal characteristics is now very important to make these blends more attractive for the polymer industry.

The main drawback in the production of GTR based thermoplastic elastomers is the low compatibility between both components [46,47]. For the moment, almost no methods have been proposed to effectively produce suitable GTR filled compounds at high GTR powder concentration (higher than 40-50%). The cross-linked structure of GTR is again responsible for low compatibility because the rubber molecules do not have enough freedom to entangle with the thermoplastic matrix molecules which results in poor interaction between the phases [11,15].

So far, almost all the studies have concluded that a suitable interfacial adhesion between the phases can only be expected through effective treatment methods. Several treatments have been proposed to improve interface quality and mechanical properties [4,8,14,48]. Addition of compatibilizing aids (coupling agents) or surface covering materials, as well as a variety of devulcanization methods are of the most commonly used techniques [49-51]. While some of these methods have been relatively effective, none have been successful to make well compatibilized blends at GTR concentrations higher than 50%.

As mentioned above, several treatment methods include rubber devulcanization and revulcanization. These methods not only reduce the mechanical properties of final product, through degradation of the rubber powder, but create substantial rise in costs due to increased consumption of energy, time and material (vulcanization formulation, sulphur, peroxides, initiators, etc.). It is also very important to develop a method to produce compounds over a large range of concentrations to cover a wide spectrum of mechanical properties for different possible applications of thermoplastic elastomers.

Kumar et al. [15], worked on the production of thermoplastic elastomers of low-density polyethylene (LDPE), virgin rubber and recycled ground tire rubber (GTR) with and without dynamic curing. All the samples had the same composition of LDPE/rubber/GTR (50/25/25). They concluded that the best performance was observed after dynamic vulcanization of the samples containing virgin EPDM and thermo-mechanically devulcanized GTR. But for their samples, the maximum elongation at break was only 52%, while suitable elongation at break for such materials is expected to be at least 100% [14].

Grigoryeva et al. [14] investigated the effect of bitumen as a devulcanizing agent in the production of recycled HDPE, virgin EPDM rubber and GTR thermoplastic elastomers. Thermoplastic elastomers with 35% GTR, without bitumen and 25% virgin EPDM showed an elongation at break of 46%. On the other hand, samples with 17.5% GTR, 25% virgin EPDM and 17.5% bitumen had elongation at break up to 377% after GTR devulcanization.

Thermal degradation and oxidation are common disadvantages among polymers and polymer blends at high temperatures. Thermal degradation leads to significant loss in mechanical properties such as tensile strength and elongation at break due to chain scission over time. Effects of thermal stresses are mainly controlled by the chemical structure of the polymeric compounds. The resistance of virgin rubbers to thermal degradation is poorer due to high concentrations of double bonds in their chain [52]. Incorporation of ground tire rubber, therefore, is expected to give good thermal stability of TPE because of lower concentration of double bonds and also the presence of stabilizers in GTR.

Although the compatibilizing effect of maleic anhydride has been investigated before [53,54], maleated polyethylene has never been used as the matrix to produce TPE with ultra high GTR content. In this work, an effective method is proposed to develop highly compatible and highly filled thermoplastic elastomers by blending recycled GTR powder with maleic anhydride grafted polyethylene (MAPE). The main advantages of this method are simplicity combined with high effectiveness. Very high concentrations of GTR, up to 90%, in the thermoplastic elastomers are achieved. The results are also compared with compounds based on high density polyethylene (HDPE) as the matrix and MAPE as the coupling agent.

3.2 Material and methods

3.2.1 Materials

Recycled rubber powder (manufactured through ambient mechanical grinding of tire rubber) was obtained from Recyc RPM inc. Canada and used as received. It had a particle size distribution between 50 and 850 μm (weighted average particle size of around 300 μm) and its acetone extract was 8%. The maleic anhydride grafted polyethylene, Epolene C-26, with an average molecular weight of M_w = 65000 g/mol, acid number of 8 (mg KOH g^{-1}) and flow index of 8 g/10 min (190°C and 2.16 kg), was supplied by Westlake Chemical Corporation. The high density polyethylene (HDPE) matrix was HD 6605 from ExxonMobil Chemicals. This polymer has a melt flow index of 5 g/10 min (190°C and 2.16 kg) according to ASTM D1238. Density and melting point of the HDPE were 948 kg m^{-3} and 130°C, respectively.

3.2.2 Compounding

To investigate the effectiveness of the process at industrial scale, GTR and thermoplastic matrix were compounded continuously in a twin-screw extruder. Samples with 50, 60, 70, 80 and 90%wt. of GTR were prepared in a Leistritz ZSE-27 with a L/D ratio of 40 and 10 heating zones. The screw speed was set at 150 rpm and the temperature was kept at 170°C in all zones to prevent degradation. Using higher temperatures during mixing may lead to negative effects on final product due to thermal degradation and decrease in viscosity leading to lower stresses (good dispersion cannot be expected in this case). MAPE and rubber powder were fed to the extruder in the first zone (main feed). Flow rates varied from 4 kg h^{-1} for blends with 50, 60 and 70% of GTR to 3 kg h^{-1} for samples with 80 and 90% of the recycled rubber because of increased viscosity (high motor torque and die pressure). The compounds were cooled in a water bath and then pelletized at the die (5.9 mm in diameter) exit. The compositions tested are presented in Table 3.1. To extend the study, two samples with 70 and 90% of recycled rubber powder in HDPE were also prepared to determine the effect of using HDPE as the matrix and MAPE as a coupling agent (5% on a GTR basis) for HDPE/GTR compounds.

Table 3.1 Formulation and coding of the compounds.

Sample code	GTR (wt.%)	MAPE (wt.%)	HDPE (wt.%)
GTR(90)	90	10	-
GTR(80)	80	20	-
GTR(70)	70	30	-
GTR(60)	60	40	-
GTR(50)	50	50	-
HDPE/GTR(90)	90	-	10
HDPE/GTR(70)	70	-	30
HDPE/GTR(90)+	90	5*	10
HDPE/GTR(70)+	70	5*	30

* The amounts are on a weight basis of GTR content.

Finally, the compounds were pelletized to be compression moulded at 200°C in a laboratory Carver press to make sheets of 3 and 6 mm in thickness for different characterisations. The compounds were preheated for 5 minutes and pressed for 6 minutes in moulds with dimensions of 115×115 mm^2 and a load of 3 tons.

3.2.3 Morphological observation

Scanning electron microscopy (SEM) was used to study the morphology of the blends and to observe the quality of interfacial adhesion. A JEOL model JSM-840A was used to take micrographs at different magnifications. The samples were first fractured cryogenically in liquid nitrogen and the exposed surface was coated with gold/palladium to be observed using a voltage of 15 kV.

3.2.4 Mechanical testing

Dog bone samples were cut according to ASTM D638 type V from the compression moulded plates to perform tensile tests. The tests were done at a crosshead speed of 100 mm min^{-1} on an Instron model 5565 with a 500 N load cell at room temperature (23°C). The data reported are Young's modulus (E), tensile strength (σ_Y) and most importantly tensile elongation at break (ε_b). A minimum of five samples were tested to report the average and standard deviation.

3.2.5 Compression set and hardness

The compression set of the thermoplastic elastomers was determined according to ASTM D395. Specimens, 13 mm in diameter and 6 mm in thickness, were cut from the compression moulded plates. The samples were first compressed to 85% of their original thickness (specimens were placed between two metal sheets and the gap was controlled using screws) and then heated at 70°C for 24 hours in an oven. The thickness of the specimens was measured after recovering at standard conditions for 30 min. Hardness (shore A) data were also determined by a PTC Instruments Model 307L.

3.2.6 Thermogravimetric analysis (TGA)

The thermal stability of the compounds was investigated with a TGA Q5000 IR (TA Instruments) at a heating rate of 10°C min^{-1} from 30 to 600°C. The tests were performed in nitrogen and air atmospheres to evaluate both thermal and oxidative resistance of the blends.

3.2.7 Thermal ageing

Dog bone samples of the compounds were kept at two different temperatures (70 and 90°C) in an oven. Tensile tests were conducted, at room temperature, after 24, 48 and 168 hours of ageing to determine the effect of thermal degradation on the chemical structure of the compounds.

3.2.8 Rheological analysis

Rheological properties were measured on an ARES Rheometer with a parallel-plate geometry (25 mm diameter). Frequency sweeps were performed in a range of 0.05-315 rad s^{-1} at 170°C to determine the behaviour of the melts under processing conditions. A strain sweep test was previously performed to determine the linear viscoelastic range for each compound (0.5-5%).

3.3 Results and discussion

3.3.1 Morphological observations

SEM micrographs of GTR powder are presented in Figure 3.1. From Figure 3.1a, it is clear that the recycled rubber powder contains a considerable amount of impurities due to its recycled origin. GTR particles are found in a variety of shapes and sizes, the surfaces of some rubber particles are porous while for others, like in Figure 3.1b, smooth angular surfaces can be seen. This observation implies that the particles are either from different types of tires or different grinding methods.

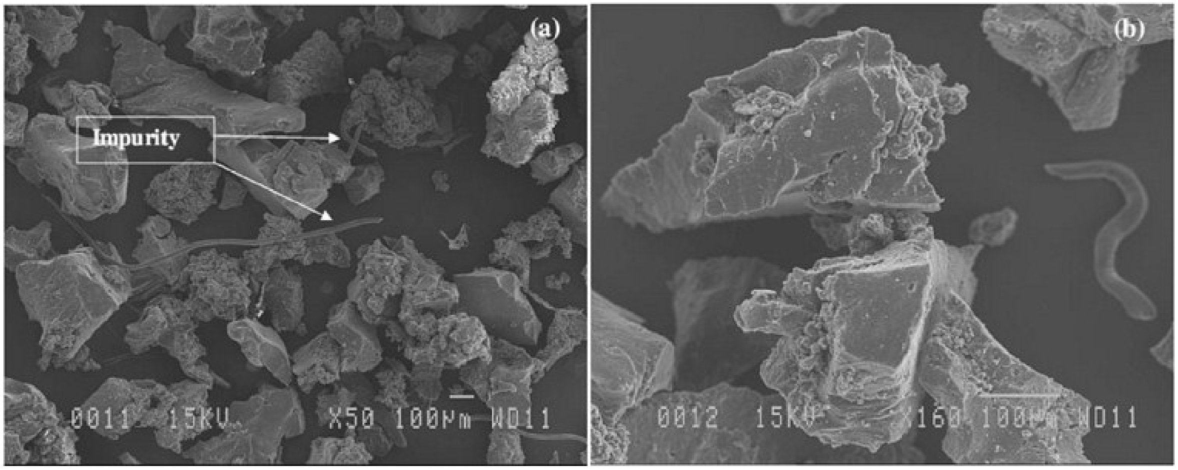

Figure 3.1 SEM micrographs of GTR particles at different magnifications.

SEM micrographs of samples with HDPE matrix are shown in Figure 3.2. The micrographs clearly show low compatibility between GTR rubber particles and HDPE matrix. In Figure 3.2a, a gap is seen between both phases and a closer view of the gap is presented in Figure 3.2b. On the other hand, the particle is totally clean, which is a result of low interfacial adhesion between the rubber and matrix. If the compatibility between both phases is not good enough, the interface will not be able to transfer the load from the matrix to the particles and failure will occur at the interface, leaving the particles clean. Presence of several holes on the fracture surface also confirms low compatibility. When good compatibility occurs, failure starts in the continuous phase instead of the interface and higher mechanical properties are expected. SEM micrographs of MAPE based samples clearly show this behaviour in Fig 3.3.

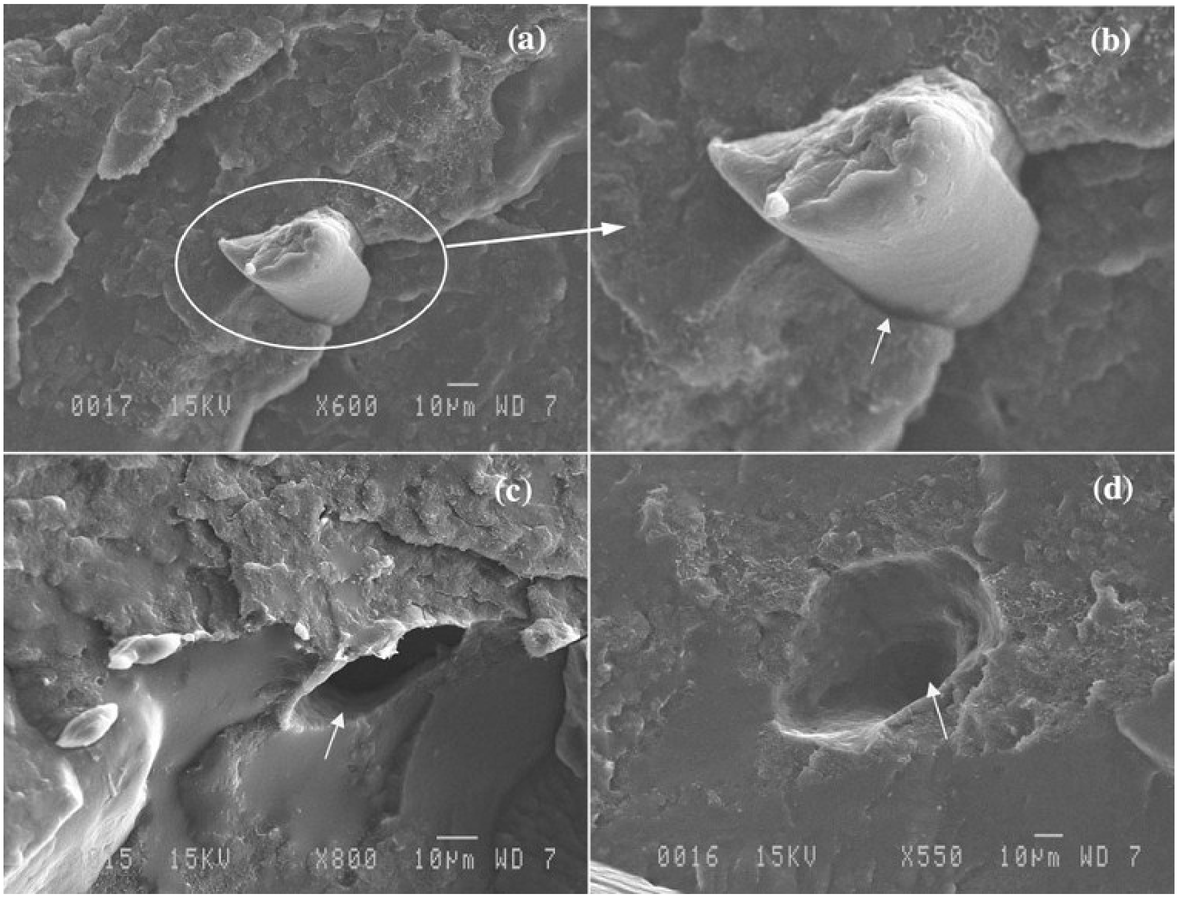

Figure 3.2 SEM micrographs of HDPE/GTR(70) at different magnifications.

As shown in Figure 3.3, the fractured surface of the specimen is totally smooth and clean. It is almost impossible to detect the rubber particles and no holes on the surface can be seen. A closer view of the rubber particles in this sample are presented in Figure 3.4. Once again, GTR rubber particles are very difficult to detect because no gap between each phase can be seen: the rubber particles are almost completely covered by the MAPE matrix.

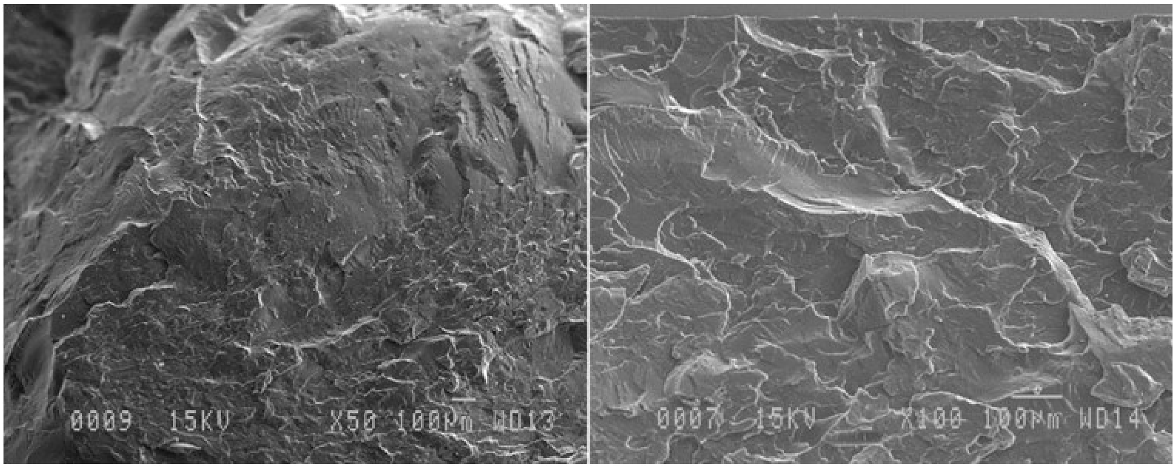

Figure 3.3 SEM micrographs of GTR(70) at two different magnifications.

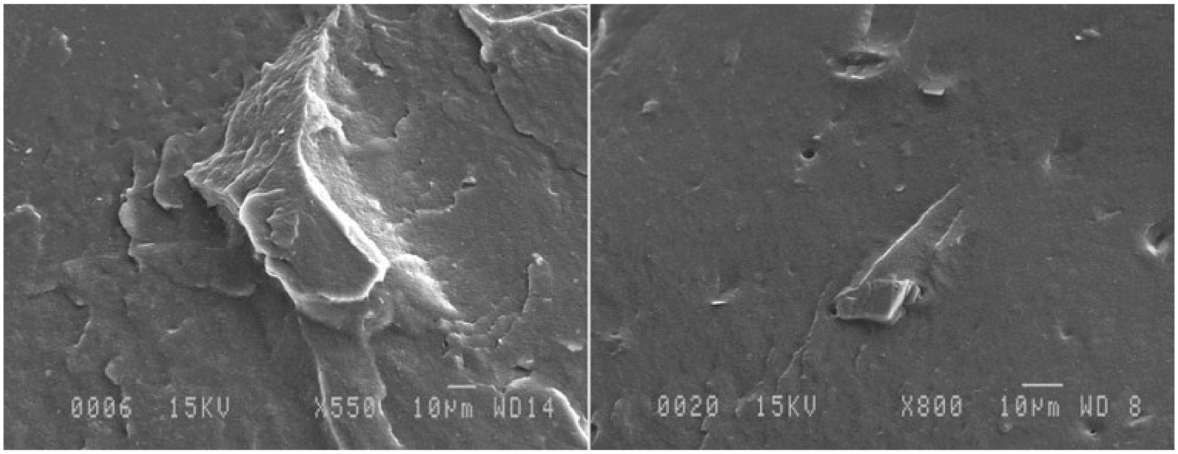

Figure 3.4 SEM micrographs of GTR(70) at higher magnifications.

3.3.2 Mechanical properties

The most important property to determine the compatibility between the phases and homogeneity of the compounds is the tensile elongation at break. Better bonding between the thermoplastic matrix and the small rubber particles should lead to higher elongation at break. A good thermoplastic elastomer is considered to have an elongation at break of at least 100% [14]. Table 3.2 presents the tensile properties of the samples produced compared to neat MAPE. It is clear that all the GTR/MAPE compounds have elongations at break above 200% (twice the amount required).

Table 3.2 Tensile properties of the TPE compared to neat matrix.

Sample code	**E (MPa)**	**σ_y (MPa)**	**ε_b (%)**
HDPE	376.6 (19.3)	25.8 (0.9)	1178 (194)
MAPE	104.3 (6.7)	9.1 (0.5)	1804 (236)
GTR(90)	4.6 (0.5)	3.0 (0.2)	219 (31)
GTR(80)	7.6 (0.9)	4.3 (0.5)	258 (53)
GTR(70)	11.9 (0.7)	7.0 (0.2)	431 (22)
GTR(60)	19.3 (0.5)	7.9 (0.5)	440 (71)
GTR(50)	32.7 (1.1)	8.7 (0.1)	465 (25)
HDPE/GTR(90)	6.0 (0.3)	1.8 (0.2)	44 (5)
HDPE/GTR(70)	26.7 (0.8)	4.2 (0.4)	64 (4)
HDPE/GTR(90)+	9.2 (0.8)	3.6 (0.2)	143 (20)
HDPE/GTR(70)+	36.1 (3.3)	6.1 (0.2)	109 (9)

*Numbers in parenthesis denote standard deviations.

It can be seen from Table 3.2 that incorporation of GTR powder inside HDPE led to very low homogeneity in the blend because the elongation at break of sample with 70% GTR in HDPE is only 64%, while adding more GTR reduces this value even more significantly. Adding MAPE as a coupling agent led to increased tensile properties of the blends, but elongation at break is still low. Tensile elongation at break of sample with 70% GTR in HDPE increased to 109% after adding 5% of coupling agent.

Li et al. [55] investigated the effect of incorporation of scrap rubber powder (SRP) to HDPE matrix. They also concluded that adding even small amounts of SRP decreased the characteristics of the compounds drastically. Elongation at break of HDPE decreased from 800% to 33% after adding just 40% SRP. They also added ethylene-vinyl acetate copolymer (EVA) and ethylene–octene copolymer (POE) to increase the compatibility but the results were not promising.

Introduction of maleic anhydride grafted polyethylene as matrix, on the other hand, is demonstrated to create remarkable blend compatibility. Sample GTR(90), with 90% ground tire rubber, has an elongation at break of 219%. Samples with lower GTR content show very high homogeneity with GTR(70) having an elongation at break as high as 431%, while this amount increases to 465% after increasing the MAPE content to 50%. The mechanical properties of TPE are always expected to be much lower than those of the thermoplastic matrix. But as presented in Table 3.2, tensile strength of compounds with 50 and 60% of recycled GTR rubber powder are very close to that of neat MAPE (between 8 and 9 MPa).

Sample HDPE/GTR(70) shows a tensile modulus of 26.7 MPa compared to 11.9 MPa for sample GTR(70). This behaviour can be related to two effects: 1- higher mechanical properties of HDPE compared to MAPE, and 2- higher effect of rubber particles on the mechanical properties of MAPE/GTR blends which is attributed to good compatibility between the phases.

As shown in Table 3.2, tensile properties of samples with 60 and 70% of GTR are slightly lower than those of sample GTR(50), while the properties decrease noticeably for GTR content higher than 70%. This indicates that a GTR concentration of 70% seems to be a critical point for these compounds.

Typical tensile stress-strain curves for GTR/MAPE and GTR/HDPE samples are presented in Figure 3.5 for comparison. When ductile thermoplastic materials such as polyethylene are subjected to tensile loads, necking usually occurs at the yield point and a plateau is expected hereafter. As clearly seen from Figure 3.5, there is no necking or plateau after the yield point for these samples. Although blends based on HDPE have higher tensile modulus compared to blends based on MAPE, they have significantly lower tensile elongation at break which indicates their lower quality.

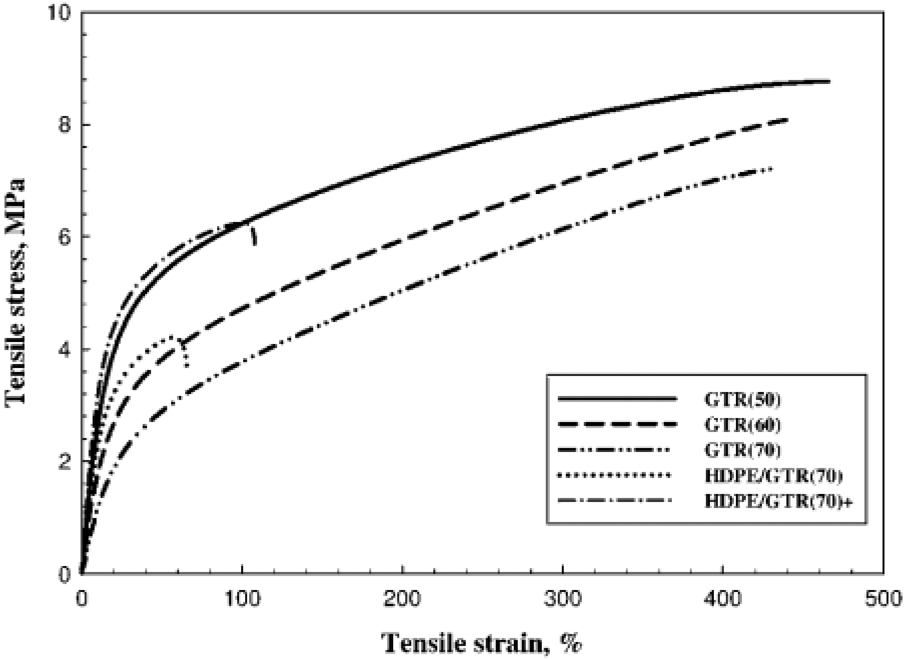

Figure 3.5 Tensile stress-strain curves for samples with different GTR concentrations.

3.3.3 Compression set and hardness

Compression set and hardness data of the compounds are shown in Table 3.3. From these data, it is clear that samples with MAPE as the matrix show very good elastic properties. Lower compression set indicates good elastic recovery of the thermoplastic elastomer. Sample GTR(50) shows a compression set of 51%, while an increase in rubber content led to even better elastic recovery of the materials. This behaviour can be related to the higher elasticity of vulcanised rubber compared to the thermoplastic phase. Results for samples with HDPE as the matrix on the other hand show poor elasticity with a compression set of sample HDPE/GTR(70) of 72%. Incorporation of MAPE as a coupling agent to these blends led to improved elasticity with the compression set of sample HDPE/GTR(70)+ being 60%.

Another important property of TPE is hardness, which is mainly controlled by the rubber content. Despite the presence of considerable amounts of carbon black in tire formulations, an increase in GTR content leads to lower hardness as shown in Table 3.3.

Table 3.3 Compression set and hardness of the different compounds.

Sample code	Compression set (%)	Hardness (Shore A)
GTR(50)	51.3 (1.2)	95.5 (0.7)
GTR(60)	49.1 (1.8)	92.0 (0.9)
GTR(70)	45.7 (1.4)	88.2 (0.9)
GTR(80)	42.3 (1.8)	85.6 (1.1)
GTR(90)	41.0 (0.9)	75.3 (0.6)
HDPE/GTR(90)	64.3 (2.4)	90.1 (0.3)
HDPE/GTR(70)	71.8 (3.1)	95.2 (0.5)
HDPE/GTR(90)+	45.9 (1.7)	88.6 (0.3)
HDPE/GTR(70)+	59.5 (2.2)	96.5 (0.7)

*Numbers in parenthesis denote standard deviations.

3.3.4 Thermogravimetric analysis (TGA)

Thermal degradation data of the thermoplastic elastomers compared to neat GTR, HDPE and MAPE are presented in Table 3.4. The results are presented for degradation in both nitrogen and air. T_{10} and T_{50} refer to temperatures for which the samples have lost 10 and 50% of their initial mass, respectively.

Table 3.4 Thermal degradation data for HDPE, MAPE, GTR and different blends.

Sample	**T_{10} (^oC)**		**T_{50} (^oC)**	
	in air	in N_2	in air	in N_2
GTR	301	322	471	438
HDPE	409	437	442	466
MAPE	394	418	442	463
GTR(90)	309	343	477	456
GTR(80)	324	350	477	462
GTR(70)	341	355	481	468
GTR(60)	354	359	479	472
GTR(50)	374	364	478	473
HDPE/GTR(90)	318	334	449	450
HDPE/GTR(70)	345	353	478	466
HDPE/GTR(90)+	322	342	451	453
HDPE/GTR(70)+	351	355	475	468

The results of Table 3.4 show that increasing GTR content led to lower T_{10} values for all thermoplastic elastomers. This observation is due to lower thermal stability of GTR compared to MAPE and HDPE. Generally, the samples have slightly lower thermal stability in air which is caused by oxidation. Thermogravimetric analysis (TGA) and derivative of the TGA curves (DTG) for HDPE, MAPE and GTR, in air, are shown in Figure 3.6. As shown in Figure 3.6, GTR degradation starts around 200°C, thus processing temperature for these blends should not exceed this value to avoid negative effects on final properties.

Figure 3.7 also presents some results for MAPE and HDPE based thermoplastic elastomers. It is clear in Figures 3.7a and 3.7b that thermal degradation of both GTR/MAPE and GTR/HDPE blends occurs in a two-step process: one low temperature peak related to GTR and one peak at higher temperature related to HDPE or MAPE.

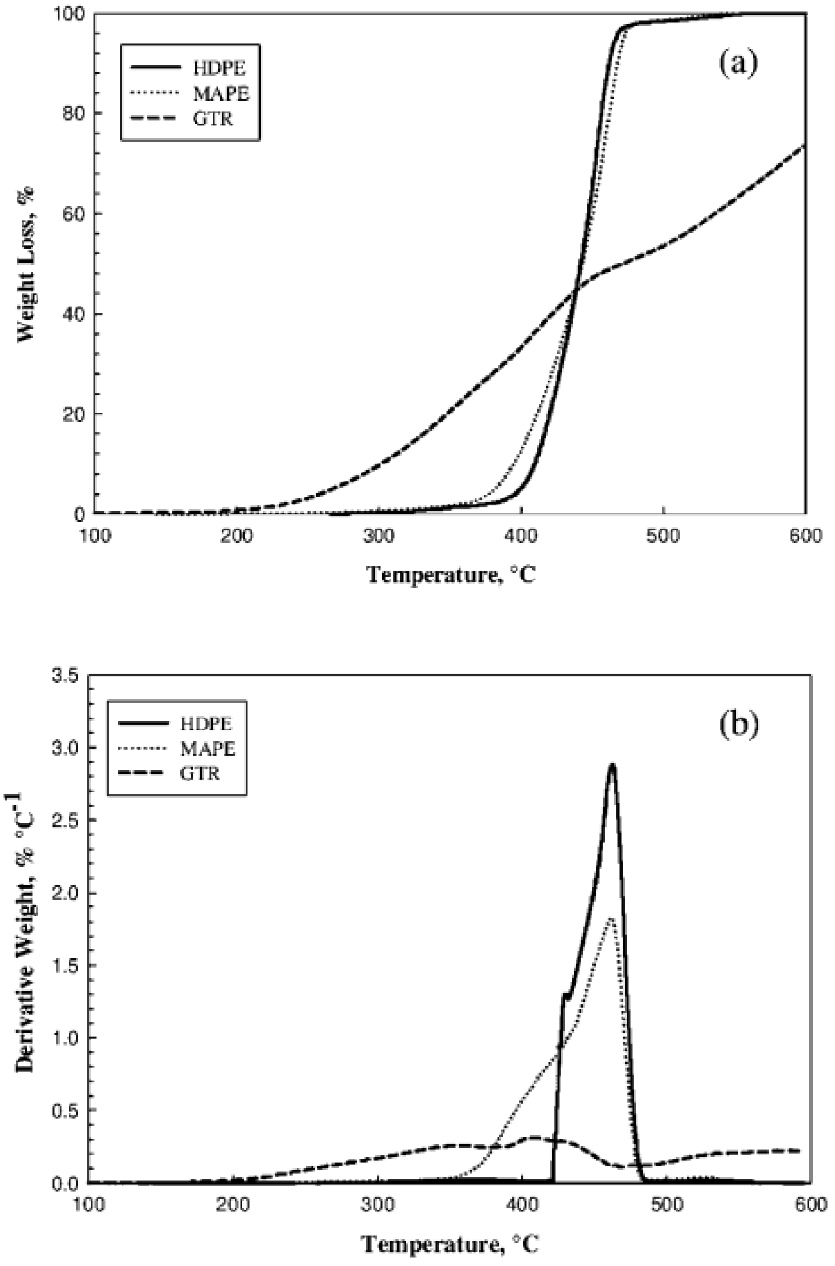

Figure 3.6 (a) Thermogravimetric analysis and (b) DTG results for HDPE, MAPE and GTR in air.

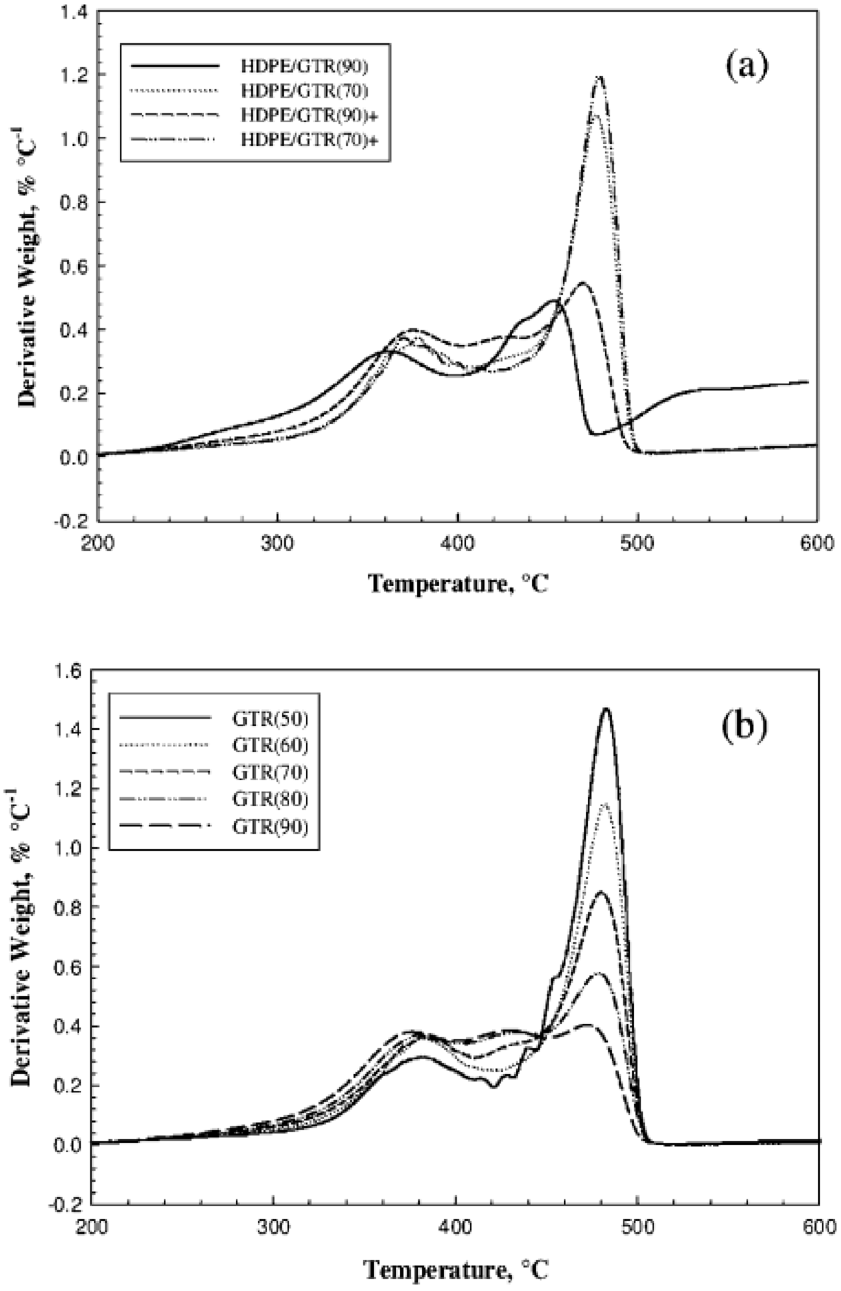

Figure 3.7 Derivative of the TGA curves results for (a) HDPE/GTR and (b) MAPE/GTR blends in air.

3.3.5 Effect of ageing

Tensile properties of the thermoplastic elastomers produced were characterized after thermal ageing at 70 and 90°C for 24, 48 and 168 h in an oven. The results obtained are presented in Tables 3.5 and 3.6.

Table 3.5 Tensile properties of thermoplastic elastomers after thermal ageing at 70°C.

	E(MPa)			**σ_Y(MPa)**			**ε_b (%)**		
	24 h	48 h	168 h	24 h	48 h	168 h	24 h	48 h	168 h
GTR(50)	30.8 (1.1)	29.8 (0.9)	29.4 (2.1)	9.1 (0.6)	8.8 (0.9)	8.9 (0.3)	443 (28)	447 (19)	439 (19)
GTR(60)	19.2 (0.4)	18.8 (0.5)	18.7 (0.5)	8.0 (0.2)	7.9 (0.2)	8.0 (0.2)	428 (19)	437 (24)	419 (33)
GTR(70)	11.0 (0.2)	10.7 (0.4)	10.8 (0.2)	6.9 (0.2)	7.1 (0.1)	6.9 (0.2)	432 (32)	424 (28)	420 (25)
GTR(80)	6.7 (0.1)	6.8 (0.2)	6.7 (0.3)	4.6 (0.1)	4.6 (0.2)	4.6 (0.1)	251 (28)	248 (19)	244 (15)
GTR(90)	4.2 (0.1)	4.3 (0.2)	4.3 (0.2)	3.0 (0.1)	3.1 (0.1)	3.1 (0.2)	187 (19)	191 (23)	179 (19)
HDPE/ GTR(90)	6.2 (0.5)	6.0 (0.4)	6.3 (0.5)	1.9 (0.2)	2.0 (0.1)	1.6 (0.3)	42 (3)	47 (5)	39 (3)
HDPE/ GTR(70)	26.1 (0.4)	26.3 (0.6)	27.2 (0.8)	3.8 (0.4)	4.1 (0.5)	3.9 (0.4)	64 (7)	60 (4)	60 (7)
HDPE/ GTR(90)+	9.0 (0.5)	9.3 (0.9)	9.0 (1.1)	3.7 (0.3)	3.6 (0.2)	3.4 (0.5)	135 (16)	141 (13)	136 (10)
HDPE/ GTR(70)+	37.4 (4.0)	36.7 (2.9)	35.5 (3.7)	6.3 (0.3)	6.0 (0.2)	6.1 (0.3)	107 (11)	100 (17)	104 (14)

*Numbers in parenthesis denote standard deviations.

Table 3.6 Tensile properties of the samples after thermal ageing at 90°C.

	E (MPa)			**σ_Y(MPa)**			**ε_b (%)**		
	24 h	48 h	168 h	24 h	48 h	168 h	24 h	48 h	168 h
GTR(50)	39.2 (0.8)	60.4 (2.0)	122.7 (6.5)	9.3 (0.4)	9.9 (0.2)	10.8 (0.6)	341 (20)	216 (11)	83 (6)
GTR(60)	30.1 (1.4)	47.8 (3.3)	118.4 (9.6)	7.1 (0.7)	8.0 (0.5)	10.1 (0.7)	314 (22)	194 (15)	71 (10)
GTR(70)	19.2 (1.1)	29.5 (2.7)	112.3 (8.4)	7.4 (0.6)	7.9 (0.5)	9.5 (0.7)	323 (35)	188 (14)	63 (8)
GTR(80)	14.8 (1.6)	20.5 (1.3)	109.8 (9.4)	5.0 (0.4)	5.3 (0.7)	6.8 (0.3)	183 (14)	152 (10)	31 (2)
GTR(90)	7.3 (0.4)	11.3 (1.4)	72.6 (5.9)	3.1 (0.2)	3.7 (0.1)	4.2 (0.5)	139 (12)	103 (8)	18 (2)
HDPE/ GTR(90)	8.5 (0.9)	32.0 (4.2)	107.3(14.7)	2.0 (0.2)	2.6 (0.2)	3.5 (0.3)	38 (4)	30 (2)	10 (1)
HDPE/ GTR(70)	31.0 (3.8)	42.6 (6.0)	86.0 (4.7)	4.5 (0.5)	4.9 (0.4)	5.7 (0.6)	55 (4)	36 (2)	19 (2)
HDPE/ GTR(90)+	11.8 (2.1)	30.5 (5.7)	120.8(23.2)	3.4 (0.3)	4.2 (0.6)	5.4 (0.3)	110 (18)	75 (14)	15 (3)
HDPE/ GTR(70)+	38.9 (4.0)	53.8 (6.3)	104.3 (7.9)	6.0 (0.4)	6.7 (0.7)	7.5 (0.3)	92 (8)	58 (11)	24 (2)

*Numbers in the parenthesis denote standard deviations.

As shown in Table 3.5 all samples have high thermal stability after one week of ageing at 70°C. Tensile properties of the compounds with both HDPE and MAPE as matrices did not change noticeably. For instance, elongation at break of GTR(50) decreased from 465% (for un-aged sample) to 439% (after 1 week at 70°C), about 5% decrease. The same trend was observed for all the other compounds.

On the other hand, ageing at 90°C induced significant decrease in tensile properties. Tensile elongation at break of HDPE/GTR(90)+ decreased from 121% to 15% after ageing one week and similar trends are observed for other HDPE and MAPE based blends. Increase in tensile modulus of these compounds is also observed after ageing at 90°C. For instance, tensile modulus of sample HDPE/GTR(90)+ increased from 12 MPa to 110 MPa. Increased tensile modulus and decreased elongation at break for the compounds is probably due to cross-linking of the matrices at ageing conditions.

3.3.6 Rheological analysis

Figure 3.8 presents rheological data for HDPE, MAPE and the thermoplastic elastomers with 70% of ground tire rubber. Based on Figure 3.8a, high density polyethylene shows much higher viscosity compared to maleated polyethylene. Thermoplastic elastomers based on MAPE, on the other hand, have higher viscosity compared to samples with HDPE matrix with the same content of GTR (Figure 3.8b). This observation is due to better interactions between the matrix and solid fillers in MAPE/GTR compounds. It is well established that incorporation of a solid phase to polymer melts leads to increased viscosity [56], but our results also suggest that blend viscosity strongly depends on compatibility between the polymer and filler phase.

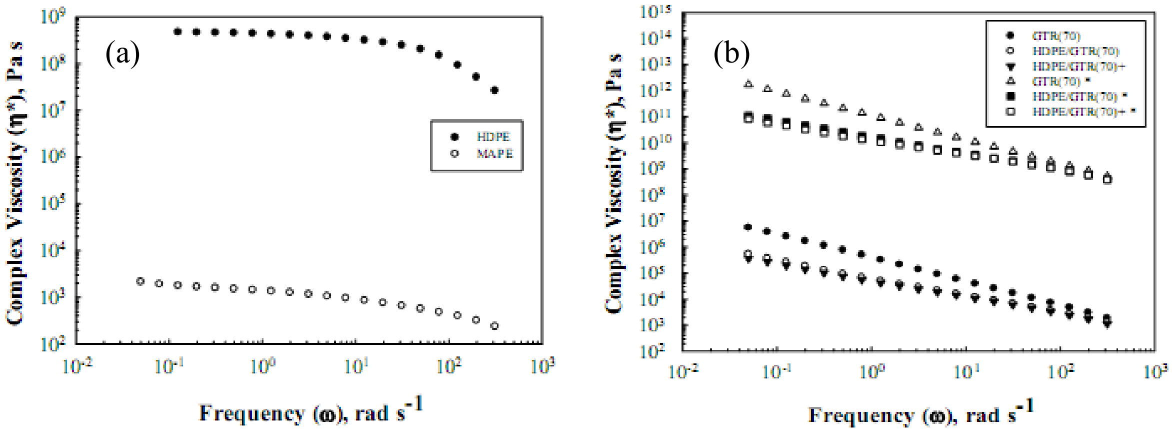

Figure 3.8 Viscosity data for (a) HDPE and MAPE and (b) TPEs, Samples with asterisk were subjected to ageing at 90°C for seven days.

Interesting results are also achieved through rheological analysis of the thermoplastic elastomers after ageing at 90°C for seven days. It is observed that ageing of all samples led to increase in viscosities of the blends, this behaviour suggests that cross-linking probably occurred through thermal ageing of the compounds. This conclusion is in good agreement with results obtained from Table 3.6.

3.4 Conclusions

Maleic anhydride grafted polyethylene was proposed as a promising candidate to produce GTR based thermoplastic elastomers with a very wide range of rubber content. Compounds with intermediate to high concentrations of ground tire rubber GTR (up to 90%) showed very good tensile properties. Increase in GTR concentration led to decrease in tensile elongation at break, but a GTR concentration of 70% seems to be an optimum for such thermoplastic elastomers. Substitution of MAPE by HDPE gave rise to substantial decrease in blend homogeneity. MAPE/GTR compounds showed much better elastic recovery compared to samples with HDPE as the matrix (with and without coupling agent). An increase in GTR content increased the elasticity of the compounds.

SEM micrographs were used to confirm the level of compatibility between MAPE/GTR compounds, while HDPE based samples were shown to have a weak interface.

TGA results showed that the processing temperature for GTR filled compounds must be kept lower than 200°C. For compounds containing MAPE and GTR, degradation started around 200°C. Ageing tests also revealed good thermal stability of MAPE and HDPE based blends, no thermal degradation was observed after ageing at 70°C for one week. However, after one week of ageing at 90°C, significant decrease in tensile elongation at break was observed for all samples.

Rheological measurements revealed that viscosity of the blends is strongly affected by the compatibility between each phase. Thermal ageing at 90°C also led to significant increase in viscosity of the thermoplastic elastomers which can be attributed to possible cross-linking occurring with time at high temperature in the presence of oxygen.

Overall, the performances of MAPE based blends were superior to HDPE ones on all aspects evaluated in this work. This indicates that MAPE is a good candidate to produce GTR based TPE.

Acknowledgements

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Chapter 4. Degradation behavior of maleated polyethylene / ground tire rubber thermoplastic elastomers with and without stabilizers

Résumé

Dans ce travail, on étudie les effets de différents processus de dégradation (climatique, vieillissement thermique et ré-extrusion) sur le polyéthylène maléaté (MAPE), ainsi que des élastomères thermoplastiques à base de MAPE/GTR (poudrette de pneus recyclés) avec et sans stabilisants (stabilisant thermique, UVA et HALS). Les caractérisations mécaniques ont révélé que l'ajout de GTR réduit la stabilité nette du composé à 80 et 90°C. Néanmoins, l'addition de stabilisants augmente la stabilité thermique du MAPE. Toutefois, les résultats montrent que les stabilisants n'ont aucun effet sur la phase GTR. Les caractérisations mécaniques ont également montré que les conditions climatiques causent une dégradation du MAPE. Par contre, l'addition de stabilisants et de GTR augmentent de façon significative la stabilité du MAPE contre ces intempéries. La ré-extrusion a entraîné une baisse de module du MAPE (en raison d'une diminution du poids moléculaire), tandis que le module des composés avec GTR a augmenté. La ré-extrusion a également entraîné une diminution de la taille moyenne des particules de GTR, en particulier les composés avec une concentration élevée de GTR. Les analyses morphologiques ont montré que le vieillissement thermique et la ré-extrusion n'ont pas beaucoup changé la morphologie du mélange. Cependant, le changement des conditions climatiques, conduit à une dégradation remarquable des deux composés MAPE et GTR. Aussi, la compression rémanente des composés MAPE/GTR a diminué avec l'augmentation du niveau de dégradation (due à une réticulation). Enfin, la densité des échantillons a légèrement augmenté avec le niveau de dégradation (également en raison de la réticulation).

Abstract

This work investigates the effects of different degradation processes (weathering, thermal ageing and re-extrusion) on maleated polyethylene (MAPE), as well as MAPE/ground tire rubber (GTR) thermoplastic elastomers with and without stabilizers (thermal stabilizer, UVA and HALS). Mechanical characterizations revealed that GTR addition reduced neat compounds stability at both 80 and 90°C, but addition of stabilizers increased thermal stability of MAPE. However, the results suggest that the stabilizers had no effect on the GTR phase. Mechanical characterizations also showed that weathering caused degradation in MAPE, but addition of stabilizers and GTR increased significantly MAPE stability against weathering. Re-extrusion resulted in lower MAPE modulus (due to decreased molecular weight), while the modulus of GTR filled compounds increased. Re-extrusion also led to decreased GTR average particle size, especially at higher GTR contents. Morphological analyses showed that thermal ageing and re-extrusion did not change significantly blend morphology, but weathering, on the other hand, led to severe degradation of both MAPE and GTR filled compounds surface. Compression set of MAPE/GTR compounds was found to decrease with increasing degradation level (due to crosslinking). Finally, sample density slightly increased with degradation level (also due to crosslinking).

Keywords: Ground tire rubber, Thermoplastic elastomer, Thermal ageing, Weathering, Re-extrusion, Stabilizers.

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4.1 Introduction

Economical recycling of tire rubber has attracted increasing concern due to environmental issues caused by discarded tires. The matrix phase in tires is a vulcanized rubber and cannot be molten or dissolved which makes tire very challenging to reprocess. As a result, ground tire rubber is usually produced and used as filler in thermoplastics, thermosets or virgin rubbers [25,29,36,40]. Thermoplastics are the most promising matrices to produce GTR filled compounds because thermoplastic elastomers (TPE) can be produced. These materials benefit from both mechanical properties of elastomers and easy processing/reprocessing of thermoplastics [43-45]. It is believed that successful inclusion of even small amounts of waste rubber to thermoplastics can lead to a significant increase in GTR consumption due to large market share of thermoplastics [4].

Ground tire rubber, however, has only been used in less demanding applications due to low mechanical properties of GTR filled compounds. Since the rubber phase in GTR particles is highly crosslinked, rubber molecules do not have the freedom to entangle with molecules composing the thermoplastic matrix. This behavior leads to low interfacial adhesion between both phases. The most important drawback caused by this limitation is observed on tensile elongation at break of such compounds. Since elongation at break is measured at high deformations, the effect of de-bonding (disentanglement) between the matrix and GTR particles is more noticeable [4,15,47].

Numerous modification methods such as partial devulcanization (regeneration) of tire rubber, chemical surface activation of GTR particles, and inclusion of different compatibilizers have been proposed to increase the interfacial interactions between the rubber and thermoplastic phases. Unfortunately, none was proven to be effective, especially at high GTR concentrations [4]. Karger-Kocsis et al. [4] recently published a comprehensive review regarding the difficulties to produce a high quality GTR filled compounds.

In a previous investigation [19], it was shown that maleated polyethylene (MAPE) is an excellent choice for production of high quality/highly filled GTR based thermoplastic elastomers. MAPE is believed to create strong chemical bonds with vulcanized rubber through reaction of maleic anhydride groups with unsaturated C=C bonds of the rubber molecules. Production of MAPE/GTR compound is thus a more convenient approach, regarding environmental and economical aspects, compared to any other technique suggested in the literature so far. There is no need for further energy and time consuming processing (such as devulcanization and revulcanization of GTR), and the final product contains high amounts of waste rubber. For example, it was shown that compounds up to 90% by weight of GTR can be successfully produced by twin-screw extrusion using MAPE [19].

But concerns regarding environmental issues caused by discarded tires, also apply to every polymer product including MAPE/GTR thermoplastic elastomers. Such compounds must also be recycled at the end of their service life. Thermo-mechanical recycling is a common method regarding polymer recycling by using the least amount of energy [57]. In this method, polymers are first granulated and then re-processed to fabricate new products. The quality of the recycled products depends strongly on the stability of the polymers against two factors: (a) degradation during their service life, and (b) degradation during recycling (reprocessing) [57].

During its service life, environmental stresses such as heat, radiation, oxygen, humidity or combinations of these factors cause undesirable changes in the properties of polymers like loss of ductility and changes in molecular weight (M_w) [58,59]. These changes are usually consequences of detrimental chemical modifications such as [60]:

- Chain scission and cross-linking of macromolecules, which can lead to decrease or increase in molecular weight, respectively.
- Change in molecular structure of polymer macromolecules. One possibility is formation of unsaturated C=C bonds due to breakage of C-H bonds in two adjacent carbon atoms. Such double bonds are highly prone to reaction with macro-radicals (which are products of chain scission) resulting in cross-linking [58].

- Formation of small molecules such as H_2, CO, CO_2 and monomers. Once trapped in the polymer network, such molecules cause crazes and even cracks.

Reprocessing of polymers can also lead to their degradation due to thermal and mechanical stresses (during extrusion and molding processes) [49,57]. Al-Malaika and Amir [49] studied the effects of re-processing on the mechanical properties of PP/natural rubber (NR)/recycled NR compounds. They reported that mechanical properties were stable up to 4-5 regeneration cycles, after which a sharp drop in tensile strength and modulus was observed.

Introduction of fillers in thermoplastics significantly changes their properties including their resistance against degradation. The rubber phase, for instance, is usually more significantly affected by ageing due to the presence of reactive double bonds and also lower glass transition temperature (T_g) compared to polyolefins [58]. As mentioned above, the presence of such double bonds can lead to cross-linking. Increase in rubber phase cross-link density leads to embrittlement of the thermoplastic elastomer [58]. In the case of GTR filled TPE, on the other hand, the vulcanized structure of the rubber phase and also the presence of a variety of stabilizers and carbon black is expected to increase stability compared to TPE containing virgin rubber.

To date, no comprehensive work has been conducted to study the stability of GTR based thermoplastic elastomers to different degradation processes. Thus, the present paper is devoted to investigate the effects of different degradation processes (namely thermal ageing, weathering and re-extrusion) on the physical, mechanical, rheological and morphological properties of neat MAPE and MAPE/GTR thermoplastic elastomers. Different GTR concentrations (40, 60 and 80 wt.%) were used to determine the effect of GTR content on MAPE stability. The effect of three types of stabilizers (thermal stabilizer, UVA and HALS) on the degradation behavior of the compounds is also investigated.

4.2 Experimental

4.2.1 Materials and processing

Maleic anhydride grafted polyethylene, Epolene C-26, with an average molecular weight of 65000 g/mol, acid number of 8 (mg KOH g^{-1}) and melt flow index of 8 g/10 min (190°C and 2.16 kg) was supplied by Westlake Chemical Corporation. GTR was obtained from ROYAL MAT Canada and used as received. The ground tire rubber has particle sizes between 50 and 850 μm and weighted average particle size of 300 μm (weighted standard deviation of 133 μm). Acetone extract of GTR was 8%. Thermal stabilizer (IRGANOX 1010), UV absorber (TINUVIN 326) and hindered amine light stabilizer (HALS) (Chimassorb 944) were purchased from BASF Canada. IRGANOX 1010 acts as an antioxidant by chain-breaking donor and acceptor mechanisms leading to reduction in hydro-peroxides reaction rate in polymers [61]. Ultraviolet absorber (UVA) absorbs the harmful UV radiation of the light spectrum, while hindered amine light stabilizer protects the polymers against photo-oxidation by consuming damaging macro-radicals [62].

All samples were compounded using a co-rotating twin-screw extruder, Leistritz ZSE-27, with a L/D ratio of 40 and 10 heating zones. MAPE, GTR and stabilizers were fed to the first zone of the extruder (main feeder) with an overall rate of 3 kg h^{-1}. The screw speed was set at 120 rpm and the temperature profile was constant at 180°C.

Compounds with 0, 40, 60 and 80 wt% of GTR were produced. For compounds with stabilizers, thermal stabilizer, HALS and UV absorber were added with concentrations of 1, 1 and 0.5% of MAPE content, respectively. Regarding sample coding for compounds containing GTR, the concentration of waste rubber is reported in parenthesis. Samples with stabilizers are denoted by +. For instance, a sample containing 40% GTR and stabilizers is coded as GTR(40)+.

The extruded compounds were then cooled in a water bath and pelletized at the die (5.9 mm in diameter) exit. The materials were compression molded in a laboratory Carver press at 200°C to form rectangular plates. The samples were first preheated for 5 minutes and pressed for another 5 minutes in molds of 115×115×2.5 mm^3 and 115×115×6 mm^3 under a load of 1.3 MPa.

4.2.2 Degradation processes

4.2.2.1 Accelerated weathering

Effects of high energy radiation on properties of neat MAPE and MAPE/GTR (with and without stabilizers) were investigated using a xenon arc type light exposure apparatus (Atlas Weather-o-meter WT-6500). Compression molded plates (both 2.5 and 6 mm thick) were mounted on a drum rotating around the xenon arc light at a speed of 1 rpm. The temperature and relative humidity of the chamber were maintained at 50°C and 30%, respectively. Chamber temperature was chosen to be higher than ambient temperature in order to accelerate the photo-oxidation reaction [58]. It should be noted that no thermal degradation occurs to MAPE/GTR compounds under these conditions [19]. The samples were subjected to high energy radiation for a period of 400 h. The plates were then cut and characterized.

4.2.2.2 Thermal ageing

Thermal ageing of the samples was performed at two different temperatures (80 and 90°C) in an oven. Specimens for different tests were first cut from compression molded plates and then subjected to each temperature for a period of 7 days.

4.2.2.3 Re-extrusion

Each sample was re-extruded up to eight times using the same conditions as mentioned in section 4.2.1. Molding and characterization of the samples was performed after 2, 4, 6 and 8 cycles of re-extrusion.

4.2.3 Characterization

4.2.3.1 Particle size measurement

The effect of extrusion cycles on GTR particle size was investigated using an optical microscope (Stereo-Microscope, Olympus, SZ-PT). MAPE/GTR compounds were first dissolved in hot 1,2,4-trichlorobenzene (TCB). GTR particles were then separated from the solvent via filtration and dried in an oven at 70°C for 96 hours. A minimum of 200 particles were measured using the optical microscope, to obtain a weighted average particle size using the following equation:

$$\bar{L}_w = \frac{\sum_{i=1}^{n} w_i L_i}{\sum w_i} \tag{4.1}$$

where $\bar{L}_w$, L_i and w_i refer to weighted average particle size, individual particle size and individual particle weight, respectively. Assuming that the rubber particles have similar densities, equation (4.1) can be re-written as:

$$\bar{L}_w = \frac{\sum_{i=1}^{n} V_i L_i}{\sum V_i} \tag{4.2}$$

where V_i refers to individual particle volume. Particles were assumed spherical and individual volumes were calculated accordingly.

4.2.3.2 Tension test

Dog bone samples were cut according to ASTM D638 type V from the compression molded plates to perform tensile tests. The tests were done at a crosshead speed of 100 mm min^{-1} on an Instron model 5565 with a 500 N load cell at room temperature (23°C). The data reported are Young's modulus (E), yield strength (σ_Y) and tensile elongation at break (ε_b). A minimum of five samples were tested to report the average while standard deviations were less than 10%.

4.2.3.3 Rheological analysis

Rheological properties were measured on an ARES Rheometer with a parallel-plate geometry (25 mm diameter) at 170°C. A strain sweep test was initially performed to determine the linear viscoelastic range for each compound (0.5-5%). Frequency sweep tests were then performed in a range of 0.05-315 rad s^{-1}.

4.2.3.4 Compression set

Compression set of the thermoplastic elastomers was determined according to ASTM D395. Specimens, 13 mm in diameter and 6 mm in thickness, were cut from the compression molded plates. The samples were first compressed to 85% of their original thickness (specimens were placed between two metal sheets and the gap was controlled using screws) and then heated at 70°C for 24 hours in an oven. The thickness of the specimens was measured after recovering at standard conditions for 30 min. A minimum of three samples were tested to report the average while standard deviations were less than 5%.

4.2.3.5 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to study the effect of the different degradation processes on the bulk and surface properties of the compounds. In order to investigate the bulk morphology of the compounds, fractures in liquid nitrogen were performed. The surfaces were then coated with a gold/palladium alloy. Then, a JEOL model JSM-840A scanning electron microscope was used to take micrographs at a voltage of 15 kV.

4.2.3.6 Density measurements

Density data were obtained by a gas pycnometer, ULTRAPYC 1200e from Quantachrome Instruments, using nitrogen as the gas phase. The data reported are the average of five measurements while standard deviations were less than 1%.

4.3 Results and discussion

4.3.1 Particle size measurement

Effect of re-extrusion on the weighted average GTR particle size in MAPE/GTR compounds is presented in Table 4.1. It is clear that re-extrusion of MAPE/GTR compounds resulted in reduction of the average particle sizes due to particle break-up under mechanical stress. Increase in particle concentration led to more significant reductions in particle size. Average particle size of GTR(40) and GTR(80) decreased by 14 and 27% respectively, after 8 cycles of re-extrusion. This behavior can be linked to the fact that viscosity increases with increasing GTR content [19]. Thus, in compounds with higher GTR content, GTR particles are subjected to more severe stresses (i.e. more significant particle rupture). Table 4.1 also shows that reduction in particle size was more noticeable as the number of re-extrusion cycles increased. For instance, in the case of GTR(80), the average particle size decreased by 5% between the first two cycles (0 to 2), while the last two cycles (6 to 8) of re-extrusion led to a 14% decrease. This behavior can be considered as a result of GTR particles embrittlement due to their thermo-mechanical degradation. Further discussion on this topic is presented in section 4.3.2. It is also shown in Table 4.1 that the distribution of particle sizes became narrower (the values of weighted standard deviations decreased) with re-extrusion.

Table 4.1 Effect of re-extrusion on the weighted average particle size (µm) of GTR particles.

Sample	**Re-extrusion**				
	0 cycle	**2 cycles**	**4 cycles**	**6 cycles**	**8 cycles**
GTR(40)	290 (108)	280 (101)	274 (93)	267 (91)	249 (84)
GTR(60)	291 (104)	275 (98)	263 (94)	247 (88)	224 (82)
GTR(80)	279 (99)	264 (94)	256 (86)	238 (82)	205 (82)

* The values in parenthesis denote weighted standard deviations.

4.3.2 Tensile properties

Table 4.2 presents the tensile properties (E, σ_Y and ε_b) for the initial samples (no degradation), as well as samples exposed to thermal ageing (at 80 and 90°C) and accelerated weathering.

Table 4.2 Tensile properties for the initial samples, as well as samples exposed to thermal ageing (at 80 and 90°C) and accelerated weathering.

Sample	**Initial**			**Thermal (80°C)**			**Thermal (90°C)**			**Weathering**		
	E (MPa)	σ_Y (MPa)	ε_b (%)	E (MPa)	σ_Y (MPa)	ε_b (%)	E (MPa)	σ_Y (MPa)	ε_b (%)	E (MPa)	σ_Y (MPa)	ε_b (%)
MAPE	164.9	12.6	1892	164.2	13.1	1880	193.7	12.5	849	184.3	11.8	241
MAPE+	143.9	12.1	1876	143.0	12.7	1845	141.2	11.6	1586	148.6	11.7	1457
GTR(40)	56.6	9.0	519	69.7	10.4	349	97.8	10.2	128	58.9	9.6	265
GTR(40)+	52.9	9.2	567	67.9	10.6	361	79.5	9.9	185	54.3	9.5	285
GTR(60)	24.7	9.5	510	47.1	10.6	244	73.5	9.7	140	24.3	9.3	313
GTR(60)+	23.6	9.3	525	42.5	10.7	256	55.9	9.6	237	23.1	9.4	365
GTR(80)	8.5	5.5	295	14.8	8.1	207	86.3	7.2	41	9.2	6.3	234
GTR(80)+	8.1	5.4	313	14.2	8.2	188	47.9	7.6	58	8.5	6.1	250

Table 4.2 shows that inclusion of stabilizers in MAPE led to a slight decrease in its tensile modulus. Tensile modulus of MAPE+ was almost 13% lower than MAPE. This behavior is ascribed to the plasticizing effect of low molecular weight stabilizers.

Thermal ageing at 80°C did not result in neat MAPE (or MAPE with stabilizers) degradation (Table 4.2). Elastic modulus of MAPE was 164.2 MPa after ageing compared to 164.9 MPa for the initial sample. For GTR filled compounds, some degradation was observed suggesting that GTR has lower thermal stability compared to MAPE. Tensile modulus of sample GTR(60) increased by almost 90% after one week of ageing at 80°C, while its elongation at break decreased by around 50%. Chain scission followed by crosslinking in the rubber phase is believed to cause such changes (increase in modulus and decrease in GTR particles deformability). The same behavior is observed for MAPE/GTR compounds containing stabilizers. Tensile modulus of GTR(60)+ increased by 80%, while its elongation at break decreased by around 50%. This observation shows that at 80°C, thermal degradation has only occurred in the rubber phase (GTR) and not in the MAPE matrix. Since stabilizers are only present in the matrix phase, they did not improve the stability of the compounds. Thermogravimetric analysis performed in another study also showed that GTR thermal degradation starts at lower temperatures compared to MAPE indicating that GTR has lower thermal stability [19]. Tensile strength of the compounds increased slightly after ageing at 80°C. Tensile strength of GTR(60) increased from 9.5 to 10.6 MPa (12%) after 1 week of ageing at 80°C (Table 4.2).

Table 4.2 shows that thermal ageing of MAPE for one week at 90°C led to increased modulus (17%) and decreased elongation at break (55%). This is also a result of chain scission followed by cross-linking in the polymer. Inclusion of stabilizers in MAPE, on the other hand, is shown to increase its stability (at 90°C) significantly. Tensile modulus of MAPE+ did not show any noticeable change (141.6 MPa compared to 143.9 MPa for the initial sample) after one week of ageing at 90°C, while its elongation at break decreased by only 15%. MAPE/GTR compounds showed more significant degradation after ageing at 90°C compared to 80°C. Tensile modulus of GTR(60) increased by around 200% (due to crosslinking in both MAPE and GTR particles), while its elongation at break decreased by around 73%. Table 4.2 shows that addition of stabilizers led to increased stability of the compounds against thermal degradation at 90°C (unlike degradation at 80°C). Tensile modulus of GTR(60)+ increased by 137% after ageing at 90°C (compared to 200% for sample GTR(60)). This observation is ascribed to the fact that the MAPE matrix and GTR particles both undergo degradation at 90°C. Therefore, presence of stabilizers in MAPE results in higher thermal stability (at least in the matrix phase).

Table 4.2 also shows that weathering of neat MAPE led to increased tensile modulus (from 164.9 to 184.3 MPa), while its elongation at break decreased by around 87%. Reduction in elongation at break can be ascribed to its embrittlement due to crosslinking of polymer molecules. Creation of internal stresses (caused by formation and entrapment of small molecules such as CO, CO_2 and even monomers) in MAPE can also lead to premature failure of polymers [63]. Inclusion of stabilizers is shown to increase MAPE stability against weathering. Table 4.2 shows that tensile modulus of MAPE+ increased by only 3%, while its strength and elongation at break decreased by 3 and 22%, respectively.

Finally, Table 4.2 shows that increasing GTR concentration in MAPE/GTR compounds resulted in significant increase in their stability against weathering. Samples GTR(40) and GTR(80), with no stabilizer, have 49 and 21% reduction in elongation at break respectively, compared to 87% for neat MAPE. Tensile modulus data for all MAPE/GTR compounds (with and without stabilizers) do not suggest any significant degradation through weathering. Presence of carbon black in the tire rubber formulation is mostly responsible for this behavior. Increased stability of compounds containing GTR is ascribed to the fact that carbon black is an excellent absorber for visible and UV lights [64]. Small quantities of carbon black (up to 2 wt.%) are reported to give outdoor weathering stability of up to 30 years to polyethylene [64]. Introduction of stabilizers to MAPE/GTR compounds did not lead to a significant increase in their stability against weathering. Elongation at breaks of both GTR(80) and GTR(80)+ decreased by around 20% after exposure to high energy radiation for 400 hours suggesting that stability of MAPE/GTR compounds against weathering was controlled by carbon black rather than the stabilizers.

Effect of re-extrusion on tensile properties is shown in Table 4.3. Table 4.3 shows that although two cycles of re-extrusion did not cause any significant change on MAPE, further re-extrusion led to a reduction of its tensile modulus (from 164.9 to 150.2 MPa for 8 cycles of re-extrusion). Lower modulus is considered as the result of decreased molecular weight through chain scission of MAPE macromolecules. Elongation at break of MAPE increased gradually (from 1892 to 1974%) through 8 cycles of re-extrusion. Tensile strength of MAPE also decreased from 12.6 MPa to 10.8 MPa (14%) after 8 re-extrusion cycle. After re-extrusion of MAPE+, similar trends were observed for tensile properties, while changes were less dramatic (compared to neat MAPE) suggesting that improved stability against re-extrusion was obtained. Tensile modulus of MAPE+ decreased from 143.9 to 138.3 MPa (4%) after 8 re-extrusions, while its elongation at break increased from 1876 to 1914%.

Table 4.3 Tensile properties of the compounds after different re-extrusion cycles.

	2 cycles			**4 cycles**			**6 cycles**			**8 cycles**		
	E (MPa)	σ_Y (MPa)	ε_b (%)	E (MPa)	σ_Y (MPa)	ε_b (%)	E (MPa)	σ_Y (MPa)	ε_b (%)	E (MPa)	σ_Y (MPa)	ε_b (%)
MAPE	164.4	12.3	1910	160.7	12.3	1907	153.4	11.8	1943	150.2	10.8	1974
MAPE+	144.2	12.4	1884	143.6	12.0	1871	140.1	11.6	1897	138.3	11.3	1914
GTR(40)	55.2	9.9	526	56.0	9.6	512	56.7	9.5	492	55.0	9.3	487
GTR(40)+	51.7	9.3	571	51.5	8.9	552	52.1	8.9	558	52.4	8.6	533
GTR(60)	24.3	9.4	419	25.0	9.1	360	25.8	8.6	317	27.5	7.7	224
GTR(60)+	24.1	9.1	442	25.3	8.8	409	25.6	8.8	372	27.2	8.8	365
GTR(80)	9.0	4.6	202	9.4	4.5	193	9.9	4.4	168	12.2	4.3	150
GTR(80)+	7.9	4.7	225	8.8	4.7	220	10.8	4.4	183	11.5	4.5	144

Re-extrusion of MAPE/GTR compounds is shown to cause different behaviors depending on GTR content. Tensile modulus of sample GTR(40) did not show any significant change after 8 cycles of re-extrusion, while for sample GTR(80) tensile modulus increased by 43% (Table 4.3). Increase in modulus can be linked to the presence of two degradation mechanisms during reprocessing of such compounds: (i) increase in tensile modulus of thermally degraded GTR particles and (ii) reduction in GTR particle size that are stiffer (less deformable) as shown in section 4.3.1. It seems that these mechanisms were predominant in compounds with higher GTR contents. Tensile strength and elongation at break of GTR filled compounds (with and without stabilizers) generally decreased after re-extrusion. For instance, tensile strength and elongation at break of GTR(60) decreased by around 19 and 56% respectively, after 8 cycles of re-extrusion. This is also ascribed to decreased deformability of GTR particles.

4.3.3 Rheological analysis

Figure 4.1 presents the complex viscosities of MAPE and GTR(60) compounds (with and without stabilizers) before and after different degradation processes. It is obvious in Figure 4.1a that thermal ageing at 80°C did not cause significant changes in MAPE viscosity. Weathering and thermal ageing at 90°C, on the other hand, caused noticeable increase in its viscosity. These observations are in good agreement with the results obtained from tensile modulus measurements. Creation of cross-links between the broken MAPE chains decreased the motion freedom of the macromolecules leading to increased viscosity. Figure 4.1a also shows that re-extrusion of MAPE for 8 cycles resulted in viscosity reduction. Inclusion of 60 wt% of GTR is shown to increase the viscosity of MAPE significantly due to the presence of more rigid particles (Figure 4.1c). Increase in viscosity of GTR(60) after thermal ageing is ascribed to both cross-linking of MAPE matrix (at 90°C) and hardening of GTR particles (at 80 and 90°C). Re-extrusion and weathering of this compound did not alter its viscosity. For samples containing stabilizers, MAPE+ and GTR(60)+ in Figures 4.1b and 4.1d respectively, it is shown that viscosity changes were less significant compared to samples without stabilizers. Rheological analysis of samples containing 40 and 80% GTR showed similar trends as GTR(60).

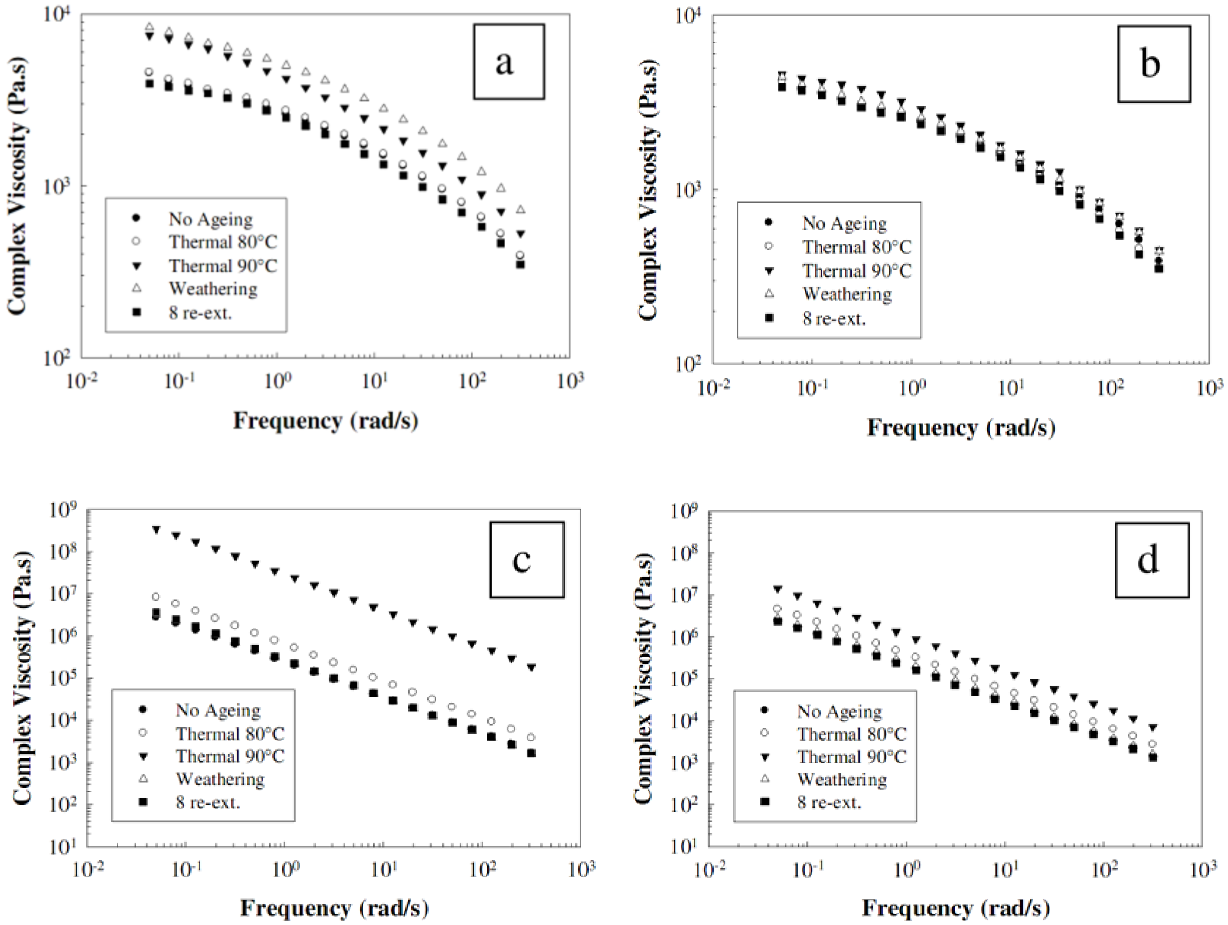

Figure 4.1 Effect of different degradation processes on the viscosity of: (a) MAPE, (b) MAPE+, (c) GTR(60) and (d) GTR(60)+.

4.3.4 Compression set

Compression set results of MAPE/GTR compounds (with and without stabilizers) are presented in Table 4.4. It is shown that adding stabilizers led to an increase in compression set (reduction in elastic recovery) of all compounds. Compression set of GTR(40) increased from 54.7 to 59.3 with stabilizers addition. Presence of small molecules (of stabilizers) in the MAPE phase increases the mobility of its macromolecules which results in increased viscous behavior. But increasing GTR concentration reduced this effect. Presence of stabilizers increased the compression set of GTR(40) and GTR(80) by 8 and 3%, respectively.

Table 4.4 Compression set (%) of the compounds before and after different degradation processes.

Sample	**Initial**	**Thermal (80°C)**	**Thermal (90°C)**	**Weathering**	**Re-extrusion**			
					2 cycles	**4 cycles**	**6 cycles**	**8 cycles**
GTR(40)	54.7	54.5	51.0	52.6	55.1	54.8	54.5	55.3
GTR(40)+	59.3	58.7	56.6	58.9	58.7	58.4	58.7	59.9
GTR(60)	48.8	47.3	44.1	48.5	48.3	49.2	49.0	49.4
GTR(60)+	51.2	50.0	48.2	51.6	50.7	51.4	51.7	51.0
GTR(80)	41.4	39.8	35.5	41.0	41.9	41.6	40.8	41.8
GTR(80)+	42.6	40.1	37.4	41.9	42.0	43.8	42.8	42.3

Thermal ageing of MAPE/GTR compounds at 80°C decreased slightly their compression set (increased elastic recovery). Cross-linking in the GTR phase is responsible for this effect. However, since no cross-linking occurred in the MAPE phase at 80°C (Table 4.2), therefore the increase in elasticity of the compounds was not significant. Cross-linking in both GTR and MAPE phases caused by thermal ageing at 90°C, on the other hand, is shown to decrease compression set more significantly. Compression set of GTR(60), for instance, decreased by 3 and 10% after one week of ageing at 80 and 90°C, respectively. Presence of stabilizers decreased this change in elastic behavior. For instance, compression set of GTR(60)+ decreased by almost 4% after ageing at 90°C. Weathering for 400 h decreased compression set of GTR(40) by 4%, while compression set of GTR(40)+ did not change noticeably. No significant changes were observed for samples with higher GTR contents due to the stabilizing effect of GTR. Re-extrusion of the compounds did not change the compression set significantly.

4.3.5 Scanning electron microscopy (SEM)

Effect of thermal ageing (one week at 90°C) and 8 cycles of re-extrusion on the surface and bulk morphology of GTR(60) is presented in Figure 4.2. It is shown in Figure 4.2 that thermal ageing and re-extrusion did not have significant effects on morphology. Although it was shown in section 4.3.1 that re-extrusion led to reduction in GTR particle size, it is difficult to see this effect using SEM micrographs since compatibility between MAPE and GTR is high; i.e. all GTR particles are well covered by the MAPE matrix.

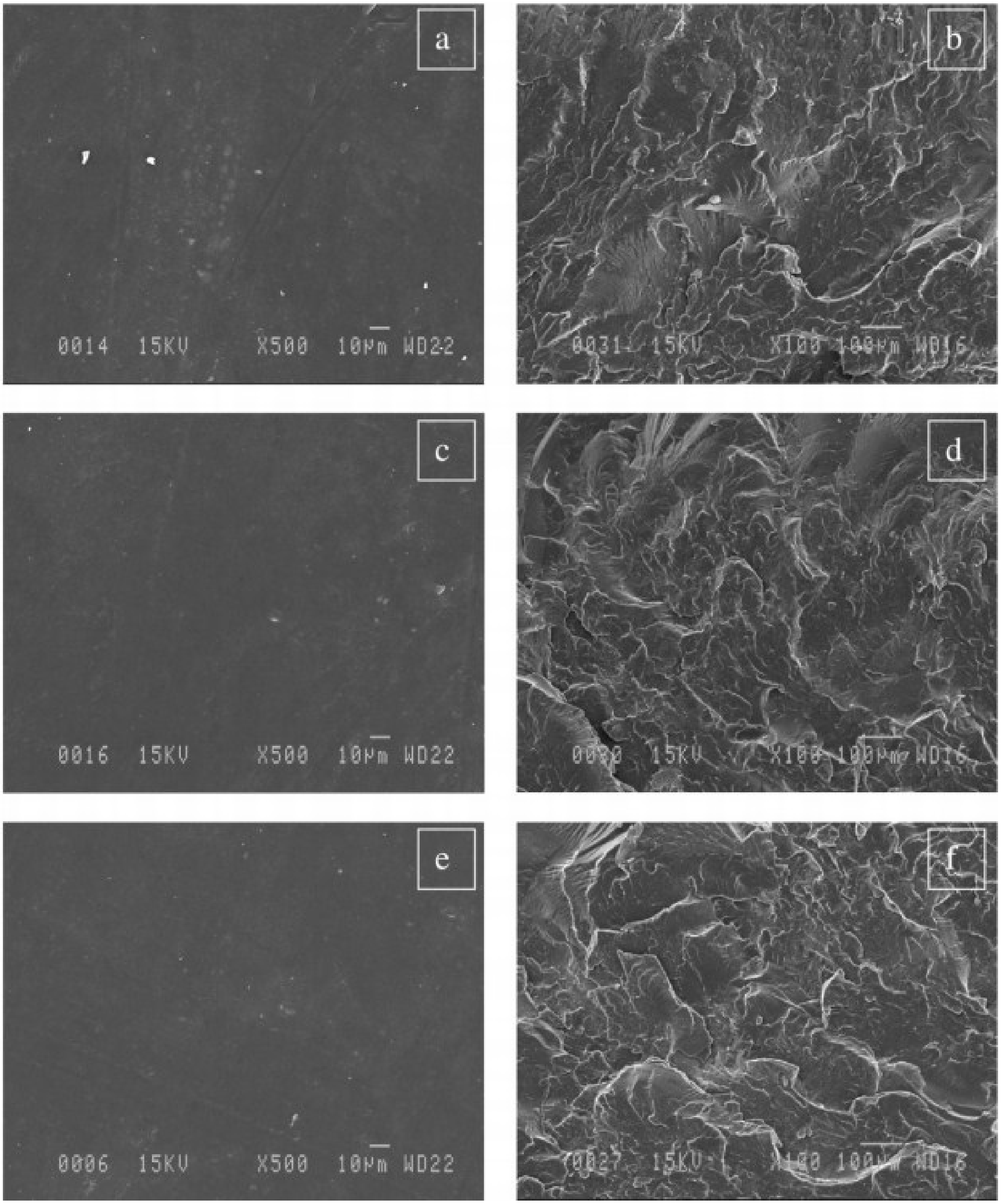

Figure 4.2 SEM micrographs of GTR(60) surface for: (a) initial sample, (c) after thermal ageing at 90°C and (e) after 8 re-extrusion cycles; as well as GTR(60) bulk for: (b) initial sample, (d) after thermal ageing at 90°C and (f) after 8 re-extrusion cycles.

Effect of weathering on surface morphology of MAPE, GTR(60) and GTR(60)+ is shown in Figure 4.3. It is clear in Figure 4.3a that weathering of MAPE led to severe degradation (formation of deep cracks) on its surface. It is also shown in Figure 4.3b that weathering of GTR(60) led to some degradation, while the degree of degradation was less severe compared to MAPE. Degradation of GTR(60) surface is probably related to the fact that the surface is richer in polymer matrix (MAPE). Therefore, the ability of carbon black (in GTR), regarding surface protection from high energy radiation, decreases. It is also shown in Figure 4.3c that after stabilizers addition to GTR(60), surface stability against weathering increased significantly.

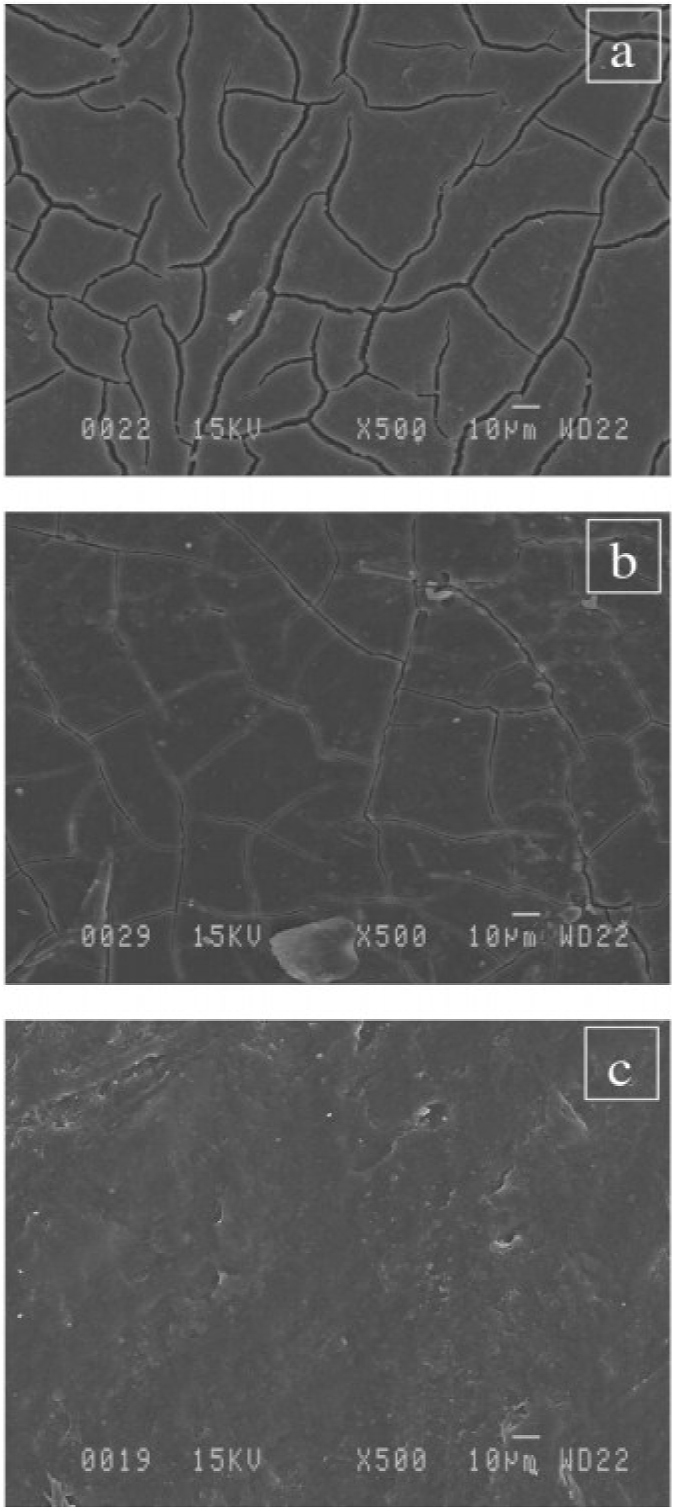

Figure 4.3 SEM micrographs of the surfaces of: (a) MAPE, (b) GTR(60) and (c) GTR(60)+ samples after 400 h exposure to weathering.

4.3.6 Density measurements

Density data of MAPE and MAPE/GTR compounds (with and without stabilizers) are presented in Table 4.5.

Table 4.5 Density (g/cm^3) of the compounds before and after different degradation processes.

Sample	Initial	Thermal (80°C)	Thermal (90°C)	Weathering	Re-extrusion			
					2 cycles	4 cycles	6 cycles	8 cycles
MAPE	0.92	0.92	0.95	0.94	0.92	0.92	0.92	0.92
MAPE+	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
GTR(40)	1.02	1.02	1.06	1.02	1.02	1.02	1.02	1.02
GTR(40)+	1.01	1.02	1.04	1.02	1.02	1.02	1.02	1.02
GTR(60)	1.07	1.07	1.11	1.07	1.07	1.07	1.07	1.07
GTR(60)+	1.07	1.07	1.11	1.07	1.07	1.07	1.07	1.07
GTR(80)	1.12	1.12	1.17	1.11	1.12	1.12	1.12	1.12
GTR(80)+	1.12	1.13	1.17	1.12	1.12	1.12	1.12	1.12

It is shown that increasing GTR concentration increased MAPE/GTR compounds density which is related to the higher density of GTR (1.2 g/cm^3) compared to MAPE (0.92 g/cm^3). Thermal ageing at 80°C did not lead to density change, while ageing at 90°C increased slightly compounds density (with and without stabilizers). For instance, densities of GTR(80) and GTR(80)+ both increased from 1.12 to 1.17 g/cm^3 after ageing at 90°C. Creation of crosslinks in MAPE and especially GTR particles during thermal ageing leads to shrinkage of the degraded material, thus increased density. Higher density is also observed for MAPE after weathering, while densities of other samples remained constant. Density of neat MAPE and GTR compounds, with and without stabilizers, remained constant throughout the 8 cycles of re-extrusion.

4.4 Conclusions

The effect of different degradation mechanisms (thermal ageing, weathering and re-extrusion) on MAPE and MAPE/GTR compounds (with and without stabilizers) was presented in this work. It was shown that thermal ageing for one week at 80°C did not change the properties of neat MAPE. But GTR addition, however, led to some degradation in MAPE/GTR compounds. Adding stabilizers did not increase the stability of such blends at this condition showing that these stabilizers have no effect on the stability of GTR particles. On the other hand, ageing at 90°C caused degradation in both MAPE and GTR phases. Incorporation of stabilizers increased the stability of the blends against thermal ageing at 90°C via stabilization of the MAPE matrix. Weathering of MAPE for 400 h led to increasing modulus and decreasing elongation at break due to cross-linking of MAPE molecules. Incorporation of both GTR and stabilizers increased significantly the stability of MAPE against weathering. For compounds with high GTR contents, addition of light stabilizers caused no significant improvement.

Re-extrusion of MAPE resulted in decreasing elastic modulus. For MAPE/GTR compounds, the results showed that GTR particle size decreased with each re-extrusion cycle and the particle size distribution was narrower. The reduction in particle size was more significant as the number of re-extrusion cycle increased and also for samples with higher GTR contents. Re-extrusion of MAPE/GTR compounds led to a slight increase in their modulus due to the thermo-mechanical degradation of GTR particles. Incorporation of stabilizers improved the stability of MAPE against re-extrusion, while the effect was not significant for GTR filled compounds. Overall, it was shown that MAPE/GTR compounds have acceptable stability against re-extrusion.

Results from rheological measurements were in good agreement with tensile characterizations. It was shown that stabilizers addition led to increasing compression set. Degradation of MAPE/GTR compounds, on the other hand, decreased their compression set. Thermal ageing and re-extrusion did not change their morphology significantly. Weathering of MAPE, however, led to severe degradation on its surface, while for MAPE/GTR compounds, the effect was less significant. SEM micrographs also revealed that addition of stabilizers increased significantly surface stability against weathering. Density of MAPE and MAPE/GTR compounds was found to increase with their degradation level due to cross-linking (sample shrinkage).

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Chapter 5. Reinforcement of maleated polyethylene /ground tire rubber thermoplastic elastomers using talc and wood flour

Résumé

Des élastomères thermoplastiques à base de caoutchouc de pneus moulus (GTR) ont été renforcés par l'incorporation de particules rigides minérales (talc) et organiques (farine de bois). Des photos prisent au microscope électronique à balayage (MEB) ont révélé que le polyéthylène maléaté (MAPE), sous forme de matrice, possède une bonne compatibilité avec la farine de bois. Par contre son adhérence aux particules de talc est plutôt faible. On a constaté que le module de traction du mélange MAPE/GTR a augmenté de façon plus significative après l'ajout de particules de talc comparé à la farine de bois. À partir d'une combinaison entre le modèle de Kerner et de Halpin-Tsai, on a pu simuler le module de traction des composites hybrides MAPE/GTR renforcés. Cette étude a permis de conclure que les modules d'élasticité dépendent fortement de deux paramètres: les relations d'aspect (géométrie) ainsi que le niveau de dispersion des particules dans la matrice. Des tests de compression ont été effectués et ont montré que la recouvrance élastique des composés diminue après l'ajout de particules solides, ce qui n'est pas le cas des échantillons ayant une meilleure compatibilité entre les particules et la matrice car ces échantillons montrent une recouvrance élastique assez élevée. Une analyse thermogravimétrique a été également effectuée et a montré que l'incorporation de particules de talc n'a pas conduit à des changements significatifs dans la stabilité thermique des composés MAPE/GTR, tandis que l'ajout de farine de bois a diminué celle-ci. Finalement, la densité et la dureté des composés MAPE/GTR ont augmenté après l'ajout des renforts particulaires.

Abstract

Ground tire rubber (GTR) filled thermoplastic elastomers were reinforced by incorporation of inorganic (talc) and organic (wood flour) rigid particles. Scanning electron microscopy (SEM) revealed that maleated polyethylene (MAPE), as a matrix, had good compatibility with wood flour, but the adhesion with talc particles was weak. Tensile modulus of MAPE/GTR increased more significantly after inclusion of talc particles compared to wood flour. Prediction of the tensile modulus of hybrid MAPE/GTR/particle composites was successfully performed using a combination of Kerner and Halpin-Tsai models. Elastic moduli were shown to depend strongly on both aspect ratio and level of particle dispersion in the matrix. Measurement of compression sets showed that elastic recovery of the compounds decreased after addition of solid particles. Samples having better particles/matrix compatibility showed higher elastic recovery. Thermogravimetric analysis showed that incorporation of talc particles did not lead to significant changes in thermal stability of MAPE/GTR compounds, while inclusion of wood flour decreased it. Density and hardness of MAPE/GTR were also shown to increase after inclusion of particulate reinforcements.

Keywords: Waste rubber, Particulate composites, Elastic modulus, Hybrid composites, Modeling.

Ramezani Kakroodi, A. and Rodrigue, D., Reinforcement of maleated polyethylene/ground tire rubber thermoplastic elastomers using talc and wood flour, J. Appl. Polym. Sci., (submitted).

5.1 Introduction

Recycling of tire rubber has attracted a great deal of attention over the past decades due to environmental concerns. The vulcanized structure of tire rubber makes it impossible to melt or dissolve, which gives rise to very challenging recycling conditions. Fabrication of GTR from tire waste is proposed as the most promising method for reprocessing such materials [25,29,36,39-42]. Sub-millimeter fractions of GTR can be introduced into different polymeric matrices such as thermoplastics, thermosets and even rubbers, to reduce their cost and modify their characteristics. Among these, thermoplastic/GTR compounds benefit from the elastic behavior of rubber combined with easy processing and re-processing conditions of thermoplastics [43-45].

Since rubber molecules in GTR are already crosslinked, they do not have the freedom to entangle with thermoplastic molecules. This behavior leads to a lack of compatibility between GTR and matrix phases [11,15,46,47] causing poor mechanical properties of GTR based thermoplastic elastomers. Several modification methods (such as surface treatment and devulcanization) have been proposed to increase the interactions at the interface of such compounds. Partial devulcanization (regeneration) of tire rubber has been performed via different techniques, while none was proven to be effective [4]. This is especially true for compounds having higher GTR concentrations. Previous investigations performed by the authors showed that MAPE, on the other hand, is an excellent choice for production of GTR filled thermoplastic elastomers [19]. MAPE is assumed to create strong chemical bonds with vulcanized rubber through reaction of maleic anhydride groups with unsaturated (C=C) bonds of rubber molecules. It was shown that compounds with GTR concentrations up to 90% by weight can be successfully produced using MAPE [19].

Inclusion of a rubber phase, both virgin and recycled, to thermoplastics is known to result in noticeable reduction in mechanical properties (especially elastic modulus). This behavior is ascribed to low mechanical properties of rubbers in comparison with thermoplastics. In our previous work [19], it was reported that adding 70 wt% of GTR to MAPE decreased its tensile modulus by 88%.

One effective method to improve the modulus of thermoplastic elastomers is addition of a reinforcing phase; i.e. particles or short/long fibers. Fiber reinforcement is known to increase the elastic modulus more significantly than particles, but processing of long fiber composites, on the other hand, is more challenging compared to particulate composites [65]. Stiff particles, both organic and inorganic, have been frequently proposed in order to balance the mechanical properties of thermoplastics [66,67]. GTR and particulate reinforcements can easily be incorporated into thermoplastics for products having a wide range of applications, while mechanical properties can be controlled by altering filler concentration.

In this paper, reinforcement of GTR filled thermoplastic elastomers is performed through inclusion of rigid (organic and inorganic) particles with different origins, namely wood flour and talc. The morphological, mechanical and physical properties of these ternary composites are then studied to evaluate the effect of each particle. Modeling of the elastic modulus of MAPE/GTR compounds and hybrid MAPE/GTR/particle composites is also performed using Kerner and Halpin-Tsai models, respectively.

5.2 Theory

For composites containing both rigid particles and soft elastomeric particles, two limiting cases with different mechanical properties have been suggested by Jancar and Dibenedetto [68]:

(i) perfect separation between the dispersed phases (rubber and rigid particles),
(ii) perfect encapsulation of rigid particles by the rubber phase.

In our case, since GTR particles are vulcanized, no encapsulation of the rigid particles by the rubber phase can be expected. Thus, our MAPE/GTR/particle composites can be considered as a clear example of case (i). According to Jancar and Dibenedetto [68], in case (i), the elastic modulus of the thermoplastic/rubber blend (E_{TPE}) can be first predicted using Kerner's model. In the case of perfect adhesion between the thermoplastic matrix and the "spherical" rubber particles, Kerner's model predicts the elastic modulus as:

$$\frac{E_{TPE}}{E_m} = \frac{(1 + AB\Phi_{GTR})}{(1 - B\Phi_{GTR})} \tag{5.1}$$

$$A = \frac{(8 - 10\upsilon_m)}{(7 - 5\upsilon_m)} \tag{5.2}$$

$$B = \frac{\left(\frac{E_{GTR}}{E_m} - 1\right)}{\left(\frac{E_{GTR}}{E_m} + A\right)} \tag{5.3}$$

where E_m and υ_m are the elastic modulus (98.5 MPa) and Poisson ratio (0.5) of the MAPE matrix, respectively. E_{GTR} and Φ_{GTR} are the average elastic modulus, taken here as 2.0 MPa [69], and volume fraction of GTR particles, respectively.

For case (i), the elastic modulus of hybrid MAPE/GTR/particle composites can then be calculated as a two phase system including MAPE/GTR blend as the effective matrix and rigid particles as reinforcement. Here, the Halpin-Tsai equation is used to predict the elastic modulus of MAPE/GTR/particle composites which is one of the most frequently used models to predict the elastic modulus of composites as [70]:

$$\frac{E_c}{E_m} = \frac{1 + \xi\eta\Phi_f}{1 - \eta\Phi_f} \tag{5.4}$$

where

$$\eta = (m - 1)/(m + \xi) \tag{5.5}$$

In equation (5.5), m is the modulus ratio (= E_p/E_m), while E_p and E_m are the elastic modulus of particles and effective matrix (= E_{TPE}), respectively. Since both particles can be considered rigid compared to the matrix, E_p is much higher than E_m, therefore η tends towards unity ($\eta = 1$). ξ is a shape factor and depends on orientation and aspect ratio of the reinforcement. It is suggested that a good prediction for longitudinal modulus of composites (with perfect orientation of reinforcements) can be obtained using the following equation for the shape factor [71]:

$$\xi = 2(l/d) \tag{5.6}$$

where l and d are length and thickness of the particles (l/d represents the aspect ratio of the particles). However, for our composites (containing randomly oriented particles), the value of ξ can be back-calculated through fitting the Halpin-Tsai equation with experimental data.

5.3 Experimental

5.3.1 Materials

Maleic anhydride grafted polyethylene (Epolene C-26) with an average molecular weight of 65000 g/mol, acid number of 8 (mg KOH g^{-1}) and flow index of 8 g/10 min (190°C and 2.16 kg) was supplied by Westlake Chemical Corporation. GTR with acetone extract of 8% was obtained from Royal Mat inc. Canada. GTR particles (produced by ambient grinding method) were sieved to keep only particles between 50 and 300 μm (weighted average particle size of around 200 μm and weighted standard deviation of 46 μm). Talc powder, Stellar 410, was supplied from Luzenac America (now Imerys) and had an average particle size of 10 μm. Wood flour was a blend of sawdust from different softwood species and was kindly supplied by the Department of Wood and Forest Sciences of Université Laval, Canada. The wood flour was sieved to keep only particles smaller than 250 μm with a weighted average particle size of 170 μm (weighted standard deviation of 34 μm).

5.3.2 Compounding

All the samples were compounded using a co-rotating twin-screw extruder, Leistritz ZSE-27, with an L/D ratio of 40 and 10 heating zones. MAPE and GTR were fed to the first zone of the extruder (main feeder), while the rigid particles (talc and wood) were introduced in the fourth zone through a side-stuffer. The screw speed was set at 120 rpm to give a total flow rate of 4 kg/h for all samples. The temperature profile was constant along the screw at 180 °C to minimize material degradation (thermo-oxidation).

For MAPE/GTR/particle compounds, the ratio of MAPE/GTR was constant at 50/50 (on a volume basis), while volume fraction of rigid particles varied between 0 and 20 vol.%. For example, a composite containing 15 vol.% of talc had a formulation of MAPE/GTR/talc of 42.5/42.5/15 vol.%. The extruded composites were then cooled in a water bath and pelletized at the die (5.9 mm in diameter) exit. The compounds were then compression molded in a laboratory Carver press at 200 °C to form rectangular plates. The samples were first preheated for 5 minutes and pressed for another 5 minutes in molds of 115×115×2.5 mm^3 and 115×115×6 mm^3 under a load of 1.3 MPa.

5.3.3 Scanning electron microscopy (SEM)

Scanning electron micrographs (SEM) were used to study the morphology of the compounds and to evaluate the quality of surface adhesion between the phases. The samples were first fractured in liquid nitrogen and the surfaces were coated with a gold/palladium alloy. Then, a JEOL model JSM-840A scanning electron microscope was used to take micrographs at different magnifications at a voltage of 15 kV.

5.3.4 Tension test

Dog bone samples were cut according to ASTM D638 type V from the compression molded plates. The tests were performed at a crosshead speed of 100 mm/min on an Instron model 5565 with a 500 N load cell at room temperature (23 °C). The data reported are Young's modulus (E), tensile strength (σ_y) and tensile elongation at break (ε_b). Each composition was tested with a minimum of five specimens to get an average. Standard deviations were less than 10% in all cases.

5.3.5 Compression set

Compression sets of the thermoplastic elastomers were determined according to ASTM D395. Specimens, 13 mm in diameter and 6 mm in thickness, were cut from the compression molded plates. The samples were first compressed to 85% of their original thickness (specimens were placed between two metal plates and the gap was controlled using screws) and then heated at 70 °C for 24 hours in an oven. The thickness of the specimens was measured after recovering at room conditions for 30 min. Each composition was tested with a minimum of three specimens to get an average. Standard deviations were less than 10% in all cases.

5.3.6 Thermogravimetric analysis (TGA)

Thermal stability of the compounds was investigated with a TGA Q5000 IR (TA Instruments) at a heating rate of 10 °C/min from 50 to 700 °C. The tests were performed in both air and nitrogen atmospheres to evaluate the effects of oxidation on compounds stability.

5.3.7 Density and hardness measurements

Density was obtained by a gas pycnometer, ULTRAPYC 1200e, from Quantachrome Instruments, using nitrogen. Hardness (shore A) data was determined by a PTC Instruments Model 307L (ASTM D2240). In both tests, the data reported are the average of five measurements, while standard deviation was less than 5%.

5.4 Results and discussion

5.4.1 Morphological observations

Figure 5.1 shows SEM micrographs from cryogenically fractured surfaces of MAPE/GTR/particle compounds. Different magnifications are used for particles with different sizes.

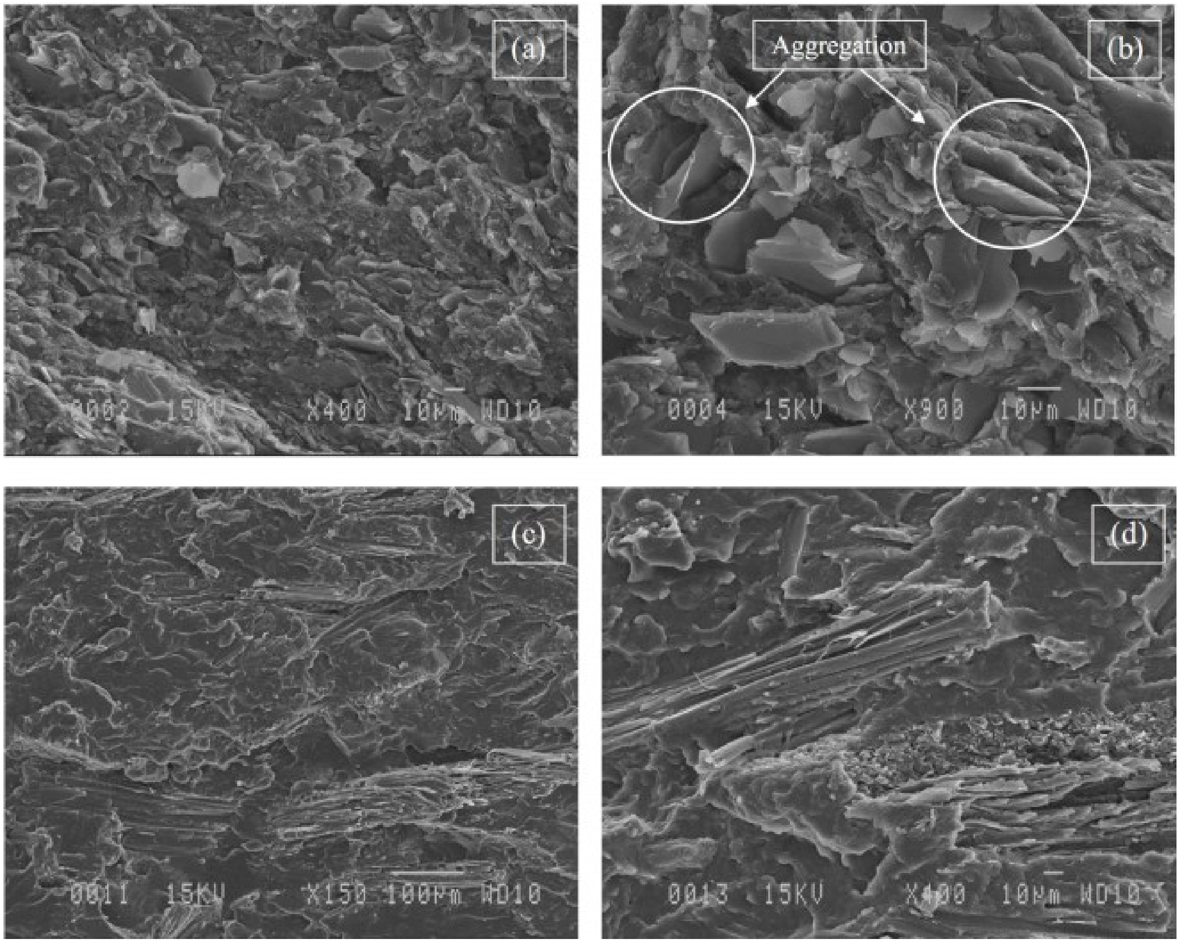

Figure 5.1 SEM micrographs of cryogenically fractured surfaces of composites based on MAPE/GTR (50/50) containing 20 vol.% of (a,b) talc and (c,d) wood flour.

The fact that no GTR particles can be detected on the surfaces of fractured samples (Figure 5.1) proves that MAPE and GTR have a high level of compatibility (also shown in [19]). Regarding particle/matrix interactions, however, different behaviors are observed. As shown in Figures 5.1a and b, the level of adhesion between the MAPE matrix and talc powder was poor. Figure 5.1 shows that surfaces of talc particles were completely clean (of matrix) and the particles can easily be spotted on the fractured surface. This observation suggests that crack propagation can occur through the weak interface. In case of compounds with good compatibility between particles and matrix, strong interface causes crack propagation to go through the matrix phase which makes particles difficult to spot. It is also shown in Figure 5.1b that the level of dispersion of talc particles in MAPE is low as signs of aggregation can be clearly seen. Wood flour, on the other hand, is remarkably well bonded to the matrix (MAPE). Figure 5.1c and d reveal that there are no gaps between wood particles and matrix. It is also seen that wood particles are broken due to the applied load. Such observations suggest that failure did not occur at the interface, indicating efficient load transfer from the matrix to the particles. High adhesion between wood flour and thermoplastic matrix is ascribed to chemical bonds between anhydride groups from MAPE and hydroxyl groups on the surface of wood particles [22].

5.4.2 Tensile properties

Figure 5.2 shows a comparison of the experimental and theoretical (calculated by Equation 5.1) values for the elastic modulus of MAPE/GTR compounds. The values of parameters A and B were calculated using equations (5.2) and (5.3) ($A = 0.67$, $B = -1.42$). It is observed in Figure 5.2 that the elastic modulus of MAPE/GTR strongly decreases with GTR concentration. For example, the elastic modulus of MAPE decreased by around 31% after adding only 16% of GTR. This reduction is ascribed to the lower modulus of rubbers in comparison with thermoplastics. Figure 5.2 also shows that the predicted values for the elastic moduli of MAPE/GTR compounds are in good agreement with the experimental results with less than 10% deviation from the experimental values.

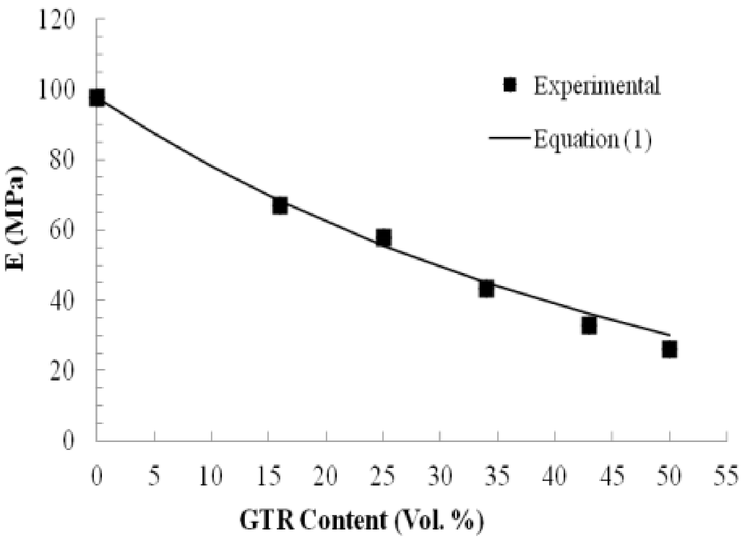

Figure 5.2 Experimental and predicted values for the elastic modulus of MAPE/GTR.

Figure 5.3 shows the experimental values of elastic modulus of MAPE/GTR compounds (E_c) reinforced with talc and wood flour. Increasing concentration of both particles increased the modulus of MAPE/GTR substantially. It is also shown in Figure 5.3 that for the range of concentration tested, elastic moduli of talc filled composites are higher compared to samples containing the same concentration of wood flour. For instance, at 20 vol.% flour, the moduli are 127 and 92% higher than the MAPE/GTR (50/50) matrix for talc and wood, respectively. Higher modulus of talc filled compounds compared to wood flour can be ascribed to higher aspect ratio of talc (average aspect ratio = 18) platelets compared to wood particles (average aspect ratio = 7) in the composites. It is also notable that average particle size of talc powder was smaller than wood flour (10 μm for talc powder compared to 170 μm for wood flour). Fu and co-workers, however, reported that for this range of sizes, elastic moduli of particulate composites are insensitive to particle size [72]. They also concluded that only when the particle size decreases to a critical value (such as 30 nm), significant changes in modulus of composites can be observed due to changes in particle size.

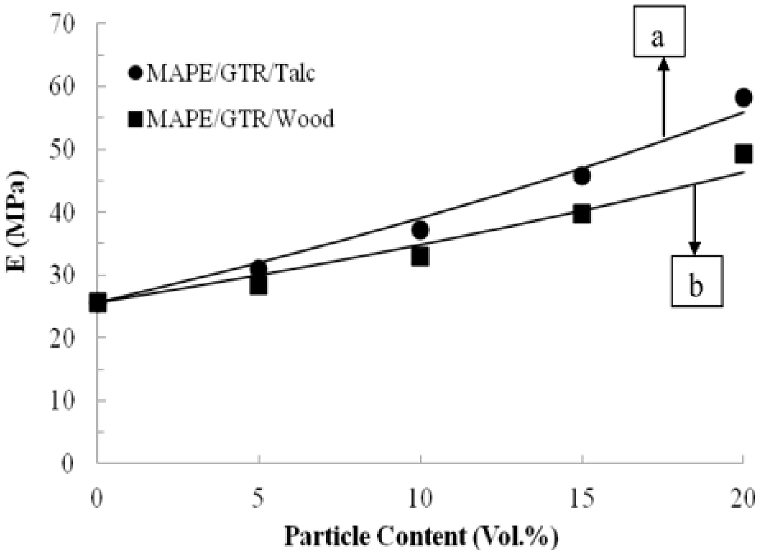

Figure 5.3 Experimental values for the elastic moduli with the predictions of the Halpin-Tsai equation for talc (line a) and wood flour (line b) composites.

Figure 5.3 also shows the fitting of experimental elastic moduli of talc and wood filled composites using the Halpin-Tsai equation. The values for effective shape factors (ξ) were calculated for MAPE/GTR/talc ($\xi = 3.7$) and MAPE/GTR/wood ($\xi = 2.2$) composites. It is shown in Figure 5.3 that, using these values for ξ, the elastic moduli can be predicted with high accuracy as deviations from experimental data are less than 5%.

Interesting conclusions can be drawn after comparing the calculated values of the effective shape factors of each particle with the values provided by equation (5.6). It is shown that the values are much lower which is mostly due to the fact that our particles are randomly oriented. Furthermore, according to equation (5.6), the shape factor for talc (ideal conditions) is 157% higher than wood (shape factors are 36 for talc compared to 14 for wood). Calculated values (by curve fitting), on the other hand, show that effective shape factor of talc is only 68% higher than that of wood. This observation is ascribed to lower compatibility between particles and matrix in talc filled composites compared to wood filled composites (as shown Figure 5.1). Presence of talc aggregates (Figure 5.1b) decreases the effective aspect ratio and the number of particles in MAPE/GTR/talc composites. In other words, the elastic modulus of our particulate composites is shown to depend strongly on both aspect ratio and level of particle dispersion in the matrix.

Figure 5.4 shows the effect of particle addition on the tensile elongation at break of the composites. It is observed that inclusion of both talc and wood particles led to significant reduction in MAPE/GTR deformability. For instance, inclusion of only 5% of each particle reduced elongation at break by almost 23%. This behavior is ascribed to: (i) low deformability of rigid particles compared to MAPE/GTR thermoplastic elastomer, (ii) stress concentration on the surface of the particles, and (iii) possible interactions between the particles at higher particle contents. It is also shown that at higher particle contents, talc filled composites have lower elongation at breaks compared to composites containing wood flour. This observation can also be linked to the low compatibility between talc and MAPE. Presence of gaps and voids at the interface increases the level of stress concentration which eventually causes the system to break more easily under tensile load [73]. Aggregation of particles is also reported to reduce the deformability of composites [74].

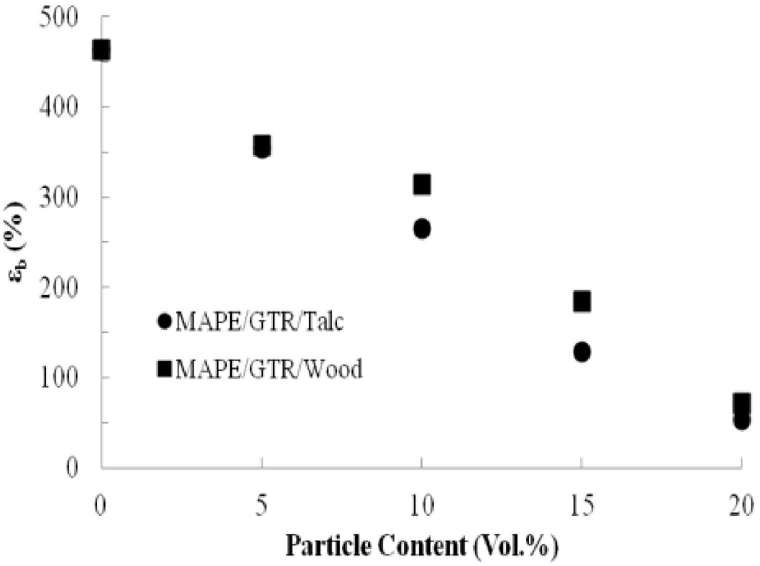

Figure 5.4 Tensile elongation at break of MAPE/GTR/particle composites.

Effect of particles on MAPE/GTR tensile strength is presented in Figure 5.5. It is shown that tensile strength also decreased after adding particles. Tensile strengths of composites containing 15% of talc and wood were 16 and 15% lower than MAPE/GTR, respectively. Reduction in tensile strength is related to premature failure caused by stress concentration on particle surfaces.

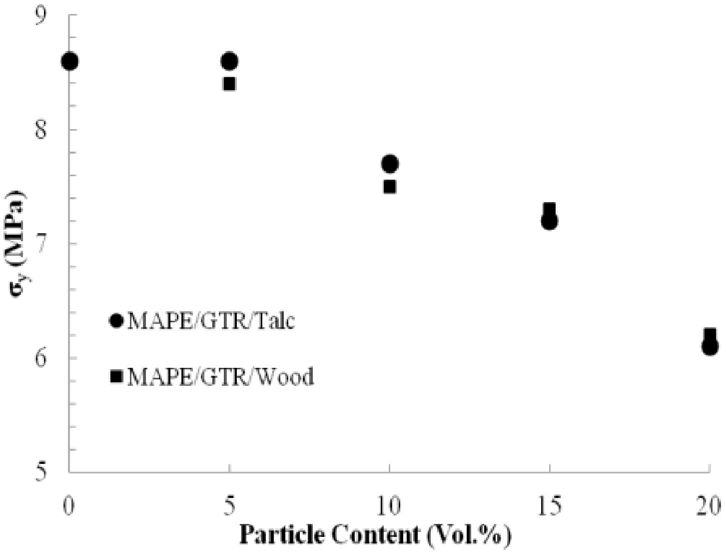

Figure 5.5 Tensile strength of MAPE/GTR/particle composites.

5.4.3 Compression set

Compression set represents the elastic recovery of elastomers or thermoplastic elastomers. It is shown in Figure 5.6 that adding particles (both talc and wood) led to higher compression set (reduction in elastic recovery) of the composites. This behavior is due to the fact that samples with higher concentrations of rigid particles have lower rubber content leading to lower elastic recovery. For instance, samples with 20% of particles contain 40% of GTR compared to MAPE/GTR blend with 50% GTR. The authors had previously shown that a decrease in overall waste rubber content in MAPE/GTR compounds increases compression set (decreases elasticity) [19]. It is also shown in Figure 5.6 that composites having better compatibility with the MAPE matrix (i.e. wood filled composites) have stronger elastic behavior. Composite with 20% talc had a compression set of 69% compared to 66% for wood filled sample of similar concentration. As the adhesion between both phases increases, the mobility of MAPE macromolecules (which are present on the interface) decreases leading to lower viscous behavior (higher elasticity) of the matrix and eventually higher elasticity of the compounds.

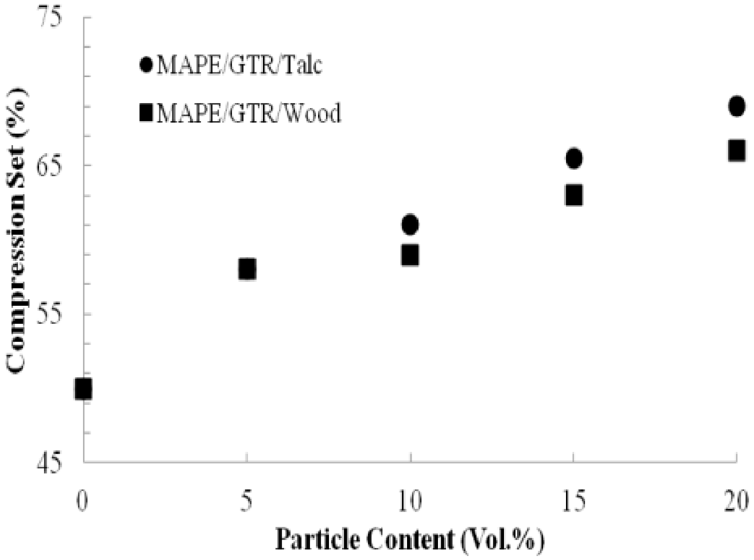

Figure 5.6 Compression set of MAPE/GTR/particle composites.

5.4.4 Thermogravimetric analysis

Results of thermogravimetric analysis, in air and nitrogen atmospheres, are presented in Table 5.1 in terms of maximum decomposition temperature ($T_{max.\ dec}$) and T_{10} (the temperature for 10% mass loss). $T_{max.\ dec}$ represents the temperature at which the rate of thermal decomposition of the sample is at its peak. It is shown in Table 5.1 that a reduction in composite stability occurred after increasing wood content. For instance, T_{10} of MAPE/GTR in nitrogen decreased from 334 °C to 293 °C after adding 20% of wood flour. Inclusion of talc particles did not produce significant changes in decomposition behavior of MAPE/GTR. It should be noted that increase in T_{10} of composites containing talc is not due to increased stability. This increase is due to the fact that degradation occurs only in

MAPE/GTR compound (not in talc), while the 10% reduction in sample weight is always measured regarding to the whole composite (including weight of talc). In other words, the increase in T_{10} is due to the presence of higher talc contents which, however, does not contribute to MAPE/GTR stability.

Table 5.1 Thermal degradation results for all samples in air and nitrogen atmospheres.

Sample	**$T_{max. dec.}$ (^oC)**		**T_{10} (^oC)**	
	in N_2	in air	in N_2	in air
MAPE	471	462	418	394
GTR	417	341	322	301
Wood flour	317	304	252	250
Talc	>600	>600	>600	>600
MAPE/GTR:50/50	463	452	338	336
MAPE/GTR/Talc(5)	459	450	356	352
MAPE/GTR/Talc(10)	463	452	363	357
MAPE/GTR/Talc(15)	460	449	371	362
MAPE/GTR/Talc(20)	458	451	379	368
MAPE/GTR/Wood(5)	465	455	328	309
MAPE/GTR/Wood(10)	462	449	307	301
MAPE/GTR/Wood(15)	460	447	305	293
MAPE/GTR/Wood(20)	457	445	293	288

As expected, presence of oxygen in air decreased the stability of all composites. Maximum decomposition rate was observed at 463 and 452 °C for MAPE/GTR compound in nitrogen and air, respectively. TGA and DTG plots of MAPE/GTR/wood composites in air are presented in Figure 5.7 and show that ultimate weight losses are less than 100%. This is due to the presence of impurities (mostly metal particles) in the GTR phase.

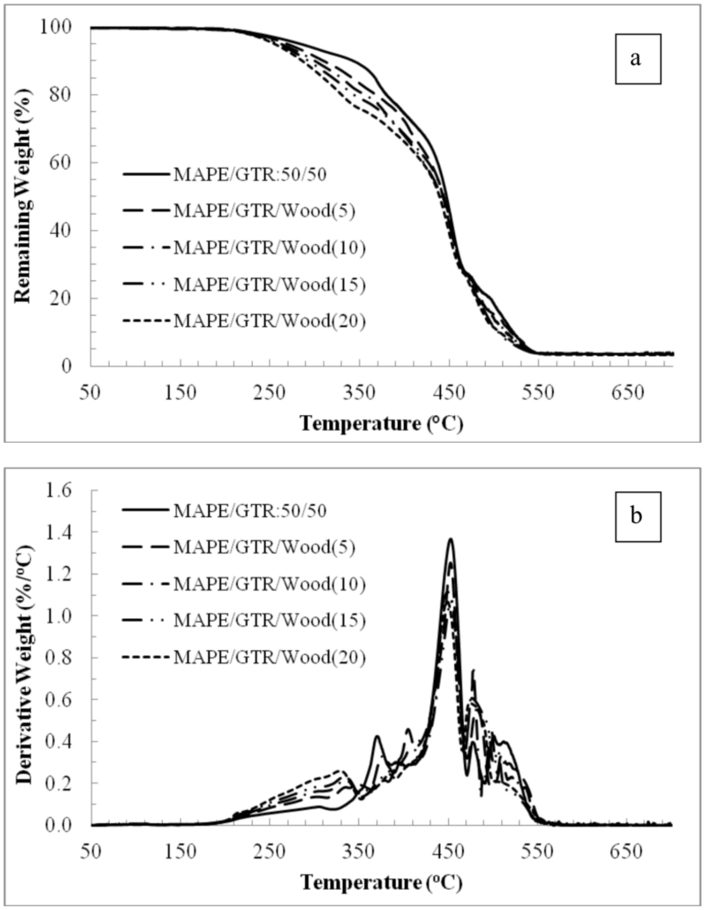

Figure 5.7 (a) TGA and (b) DTG plots for MAPE/GTR compounds with different concentrations of wood flour (in air).

5.4.5 Density and hardness measurement

Figure 5.8 shows that densities of composites filled with wood flour were considerably lower than composites with talc. For instance, densities of composites containing 20% of wood and talc were 1.13 and 1.44 g/cm^3, respectively. This behavior is due to the lower density of wood (1.4 g/cm^3) compared to talc (2.9 g/cm^3). Lower density of wood flour filled composites can result in increased specific mechanical properties (property/specific gravity). Such characteristic is of great importance for several applications such as the automotive industry.

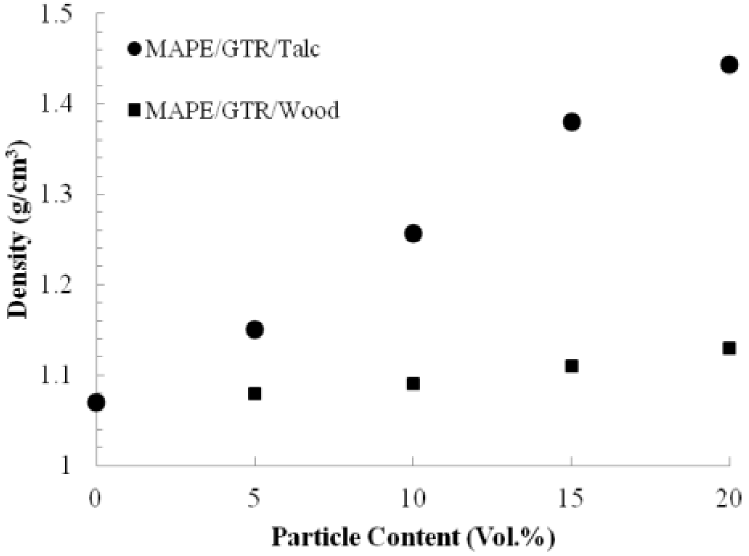

Figure 5.8 Density of the composites with different reinforcements.

Figure 5.9 shows that the addition of particles led to an increase in hardness. Hardness of composites containing talc powder was slightly higher than wood filled composites. For instance, hardness of composites containing 20% of talc and wood were 97.2 and 96.5 shore A, respectively.

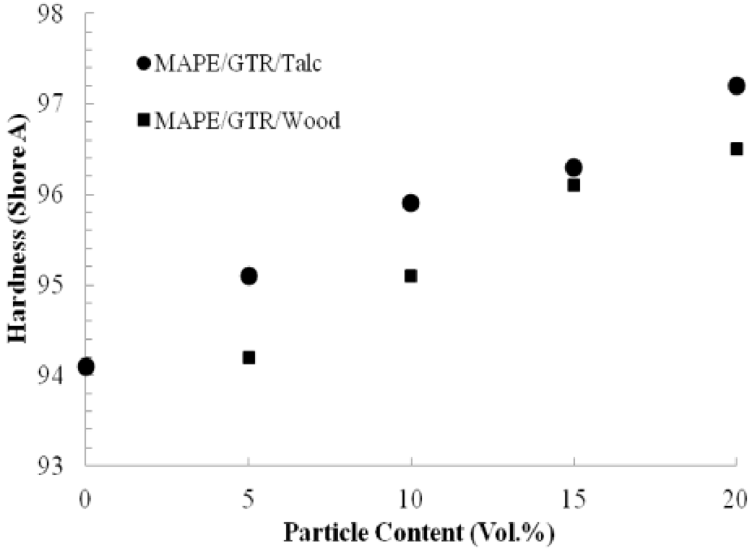

Figure 5.9 Hardness of composites with different reinforcements.

5.5 Conclusions

The effects of particulate reinforcements (talc and wood flour) on the properties of MAPE/GTR thermoplastic elastomers were investigated. SEM results revealed that MAPE had a good level of adhesion with wood flour. However, composites containing talc had low particle-matrix compatibility and signs of talc aggregation were observed. Adding both types of particles was shown to increase tensile modulus of the thermoplastic elastomers significantly. For instance, MAPE/GTR/talc and MAPE/GTR/wood composites containing 20% of reinforcement were respectively 127 and 92% stiffer than the MAPE/GTR (50/50) compound. Modeling of the elastic modulus of MAPE/GTR thermoplastic elastomers and MAPE/GTR/particle composites was successfully performed using Kerner and Halpin-Tsai equations, respectively. Fitting of the experimental data using the Halpin-Tsai equation showed that the elastic moduli depend strongly on both aspect ratio and level of dispersion of the reinforcements in the matrix. Although inclusion of both particles led to reduction in elongation at break and tensile strength of MAPE/GTR compounds, it was shown that even for composites containing up to 15% of particles, the elongation at breaks were higher than 100%.

Increasing particle concentration also resulted in lower elastic recovery of MAPE/GTR compounds. Compression set of the thermoplastic elastomers increased from 50 to 69% after adding 20% of talc powder to MAPE/GTR. Composites with higher compatibility between the particles and the MAPE matrix showed stronger elastic behavior. Thermal stability of compounds with talc powder was not affected by particle content, while inclusion of wood flour decreased thermal stability slightly. For instance, T_{10} of MAPE/GTR in nitrogen decreased from 334 °C to 293 °C after adding 20% of wood flour. The composites showed lower thermal stability in air compared to nitrogen which is linked to oxidation. Adding the particles led to increased density and hardness of MAPE/GTR, but both properties were higher for talc filled composites.

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Chapter 6. Impact modification of polypropylene based composites using surface coated waste rubber crumbs

Résumé

Des mélanges de polypropylène maléaté (MAPP) avec de la poudrette de caoutchouc recyclée (à savoir du caoutchouc de pneus moulus et les résidus de poudre d'EPDM) ont été utilisés comme modificateurs d'impact pour des composites à base de polypropylène (PP) en utilisant différents renforts tels que le chanvre, le talc et la fibre de verre. Il a été observé que ces composés (en particulier les résidus de poudre d'EPDM combinés avec le MAPP) sont très efficaces pour la modification de la résistance à l'impact des composites à base de PP. L'ajout de ces modificateurs d'impact a montré une légère diminution des modules de traction, de flexion et de torsion (jusqu'à 30%), tandis que l'augmentation de leur résistance à l'impact est considérable (plus de 80%). Par ailleurs, on a remarqué que cet effet était plus important pour les composites à base de chanvre et de verre, mais moins important pour le talc.

Abstract

Blends of maleated polypropylene (MAPP) with waste rubber powder (namely ground tire rubber and waste EPDM powder) were used as impact modifiers for polypropylene (PP) based composites with different reinforcements (hemp, talc and glass fibre). It was observed that these compounds (especially waste EPDM powder combined with MAPP) are very effective for impact modification of PP based composites. Inclusion of such impact modifiers showed slight decrease in tensile, flexural and torsion moduli (up to 30%), while increased their impact strength substantially (over 80%). The effect was more significant for hemp and glass filled composites, but less for talc.

Key words: Impact behaviour, Mechanical properties, Recycling, Polymer-matrix composites, Waste rubber crumb

Ramezani Kakroodi, A. and Rodrigue, D., Impact modification of polypropylene based composites using surface coated waste rubber crumbs, Polym. Compos., (submitted).

6.1 Introduction

Polypropylene (PP) is one of the most commonly used polymers today due to its good mechanical and processing characteristics. Nevertheless, to improve its mechanical performance, a wide range of materials have been proposed to produce PP based composites. Initially, inorganic particles like talc, glass, calcium carbonate, carbon black and mica were used [66,75-81]. Recently, organic fillers such as hemp, flax, cotton and wood flour attracted a great deal of attention. Their main advantages include low cost, environmental friendliness, low density, recyclability and relatively good specific mechanical properties [22,82-87].

Once good adhesion is obtained, incorporation of both organic and inorganic fillers leads to increased tensile and flexural properties in the composites. But their impact strength (toughness) usually decreases drastically, especially at low temperatures. Inclusion of an elastomer phase is the most common method to enhance toughness of PP based composites. In the past, several elastomers such as ethylene propylene diene monomer (EPDM), natural rubber (NR), and styrene ethylene butylene styrene tri-block copolymer (SEBS) have been proposed for this purpose [23,24,88]. But adding a virgin rubber to the composites results in lower tensile and flexural characteristics, as well as increased raw material and processing costs (such as dynamic vulcanization of elastomer phase).

Waste of vulcanized rubbers, particularly ground tire rubber and waste EPDM, on the other hand have not received much attention as impact modifiers in PP composites. Use of waste rubber in thermoplastics can be an interesting option from both economical and environmental points of view [11,14]. It is considered that successful incorporation of even a small amount of GTR (<10%) to thermoplastic resins can lead to a significant consumption of waste rubbers due to the large market share of thermoplastic materials [4,89].

The origin of low mechanical performance in compounds is usually poor compatibility between the phases; i.e. waste rubbers (vulcanized material) and PP here. The crosslinked structure of vulcanized rubber is responsible for this behaviour as rubber molecules do not have enough freedom to entangle with the matrix macromolecules and create suitable interaction [15,46,47]. Several methods have been proposed to increase compatibility between waste rubber and thermoplastic matrices. Such methods include partial devulcanization of the waste rubber, incorporation of virgin rubber to cover the surface of waste rubber (interphase) and coupling agent addition [11,15,46,47,89]. Partial devulcanization of waste rubber was investigated in a variety of forms including thermo-mechanical, chemical and even radiation methods [29].

According to previous work performed by the authors, maleated polyolefins are excellent candidates to create a strong interface with waste rubbers [19]. For example, thermoplastic elastomers (TPE) with GTR contents as high as 90% by weight were produced with tensile elongation at break superior compared to any other work reported in the literature: 431% and 219% for samples with 70% and 90% GTR, respectively.

In this work, a new approach is proposed for impact modification of PP based composites with both organic (hemp) and inorganic (talc and glass) reinforcements. The proposed protocol is to produce a masterbatch of maleated polypropylene (MAPP)-waste rubber powder (GTR and EPDM), then to add this compound to PP based composites to increase impact strength.

6.2 Experimental

6.2.1 Materials

Polypropylene, Pro-fax 6323, was purchased from Nexeo (Canada). This polymer has a melt flow index of 12.0 g/10 min (230°C/2.16 kg), a density of 0.91 g/cm^3 and a melting point of 164 °C. The maleic anhydride grafted polypropylene, Epolene G-3003, was supplied by Eastman Chemicals. This polymer has an average molecular weight (M_w) of 52 kg/mol, an acid number of 9 (mg KOH/g) and a melting point (T_m) of 158 °C. Ground tire rubber (GTR) (with acetone extract of 8%) was obtained from Royal Mat inc. Canada and used as received. Recycled EPDM (with acetone extract of 16%) was also supplied by Royal Mat inc. Both rubber powders had a particle size smaller than 850 µm and a mean particle size of around 300 µm. Hemp chips (Hempline Canada) were ground in a rotational knives grinder to reduce size. The material was sieved to keep only particles between 180 and 600 µm (average particle size of around 400 µm). Talc powder, JETFIL 350, was supplied from Luzenac America (now Imerys) and had an average particle size of 7.6 µm. Milled glass fibre, 731 ED 1/16", was purchased from Owens Corning (USA).

6.2.2 Compounding

A co-rotating twin-screw extruder, Leistritz ZSE-27, with a L/D ratio of 40 and 10 heating zones was used to compound the materials at a constant temperature of 180 °C and a screw speed of 120 rpm for all compounds (overall flow rate of 4 kg/h). The materials were cooled in a water bath at the die (5.9 mm in diameter) exit and then pelletized.

6.2.2.1 Composites without rubber crumb

Composites with different reinforcements (hemp, glass or talc) were produced at a concentration of 30 wt% of filler. Coupling agent (MAPP) was added with a concentration of 3 wt%. PP and MAPP were introduced in the main feed (zone 1), while all the fillers were introduced via a side-stuffer located at the fourth zone of the extruder to limit thermal degradation and to produce similar thermo-mechanical processes.

6.2.2.2 Composites with rubber crumb

First, MAPP/rubber powder masterbatches were produced by compounding MAPP with recycled rubber (GTR or EPDM) at a level of 70 wt% of waste rubber and pelletized. Then, the pellets produced in the first step (MAPP/rubber powder masterbatch) were introduced in the main feeder along with PP and MAPP at two concentrations (15 and 25 wt%) in a second extrusion process, while the fillers were again introduced via a side-stuffer located at zone four (30 wt.%). The compounds were then pelletized to be used later. All the formulations with coding are presented in Table 6.1.

Table 6.1 Formulation and coding of the samples produced.

Sample	PP	Filler*	MAPP	MAPP/EPDM	MAPP/GTR
PP	100	0	0	0	0
Un-modified	70	30	0	0	0
Compatibilized	67	30	3	0	0
GTR(15)	52	30	3	0	15
EPDM(15)	52	30	3	15	0
GTR(25)	42	30	3	0	25
EPDM(25)	42	30	3	25	0

* Hemp, talc or glass fibre.

The compounds were then compression moulded in a laboratory Carver press at 200 °C to form rectangular plates. The compounds were first preheated for 5 minutes and pressed for another 5 minutes in moulds of 115×115×2.5 mm^3 under compressive stress of 1.3 MPa.

6.2.3 Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

Scanning electron micrographs were used to study the morphology of the compounds and to observe the quality of surface adhesion between the different phases. The samples were first fractured in liquid nitrogen and the surfaces were coated with a gold/palladium alloy.

Then, a JEOL model JSM-840A scanning electron microscope was used to take micrographs at different magnifications at a voltage of 15 kV. GTR was also investigated by Energy Dispersive Spectroscopy using the same microscope to identify impurities (contamination).

6.2.4 Mechanical testing

Dog bone samples were cut according to ASTM D638 type IV from the compression moulded plates. The tests were performed at a crosshead speed of 5 mm/min on an Instron model 5565 with a 500 N load cell at room temperature (23 °C). The data reported are Young's modulus (E), tensile strength (σ_y) and tensile elongation at break (ε_b). Each composition was tested with a minimum of five specimens to get an average. Standard deviations were less than 10% in all cases.

Samples with dimensions of 75×12×2.5 mm^3 were also cut in the compression moulded plates according to ASTM D790. Flexural tests (60 mm span) were conducted using a crosshead speed of 5 mm/min on an Instron model 5565 with a load cell of 500 N at room temperature (23 °C). Each composition was tested with a minimum of five specimens to get an average for flexural modulus (F_m). Standard deviations were less than 10% in all cases.

Torsion modulus (T_m) was measured using an ARES Rheometer. A strain sweep test was performed first on each composite to determine their linear viscoelastic range. Then dynamic frequency sweeps were performed at a strain rate of 0.03%. Moduli of the composites are reported at a frequency of 1.25 rad/s for comparison. Each composition was tested with a minimum of three specimens to get an average for torsion modulus. Standard deviations were less than 10% in all cases.

For notched Charpy impact test, rectangular specimens (110×12×2.5 mm^3) were cut from the moulded plates according to ASTM D6110. The samples were then notched with an automatic notcher Dynisco model ASN 120m. For each composition, ten samples were tested on a Tinius Olsen model Impact 104 to extract an average for impact strength (I_s). Standard deviations were less than 10% in all cases.

6.2.5 Thermogravimetric analysis

Thermal stability of the compounds was investigated with a TGA Q5000 IR (TA Instruments) at a heating rate of 10 °C/min from 30 to 600 °C. The tests were performed in nitrogen and air atmospheres to evaluate both thermal and oxidative resistance of the composites.

6.2.6 Density and hardness measurements

Density was obtained by a gas pycnometer, ULTRAPYC 1200e from Quantachrome Instruments, using nitrogen as the gas phase. The data reported are the average of five measurements. Hardness (shore D) data were also determined by a PTC Instruments Model 307L (ASTM D2240).

6.3 Results and discussion

6.3.1 SEM and EDS results

Figure 6.1 presents the effect of adding a compatibilizer (MAPP) on surface interactions between the matrix and different fillers. Due to significant difference in sizes between the fillers, the micrographs are presented at different magnifications to focus on the interface.

It can be seen in Figure 6.1 that the interface quality, in case of hemp and glass filled compounds, is improved noticeably after adding MAPP. For samples without coupling agent, presence of gaps and voids between the phases is clearly observed. Surface of the exposed fillers is also very clean, indicating poor adhesion. These observations prove that the interface between the fillers and PP, is poor leading to substantial decreases in mechanical properties of the compounds (pull-out is occurring). Surface interaction between talc and PP, on the other hand, looks stronger even without a compatibilizer (Figure 6.1c).

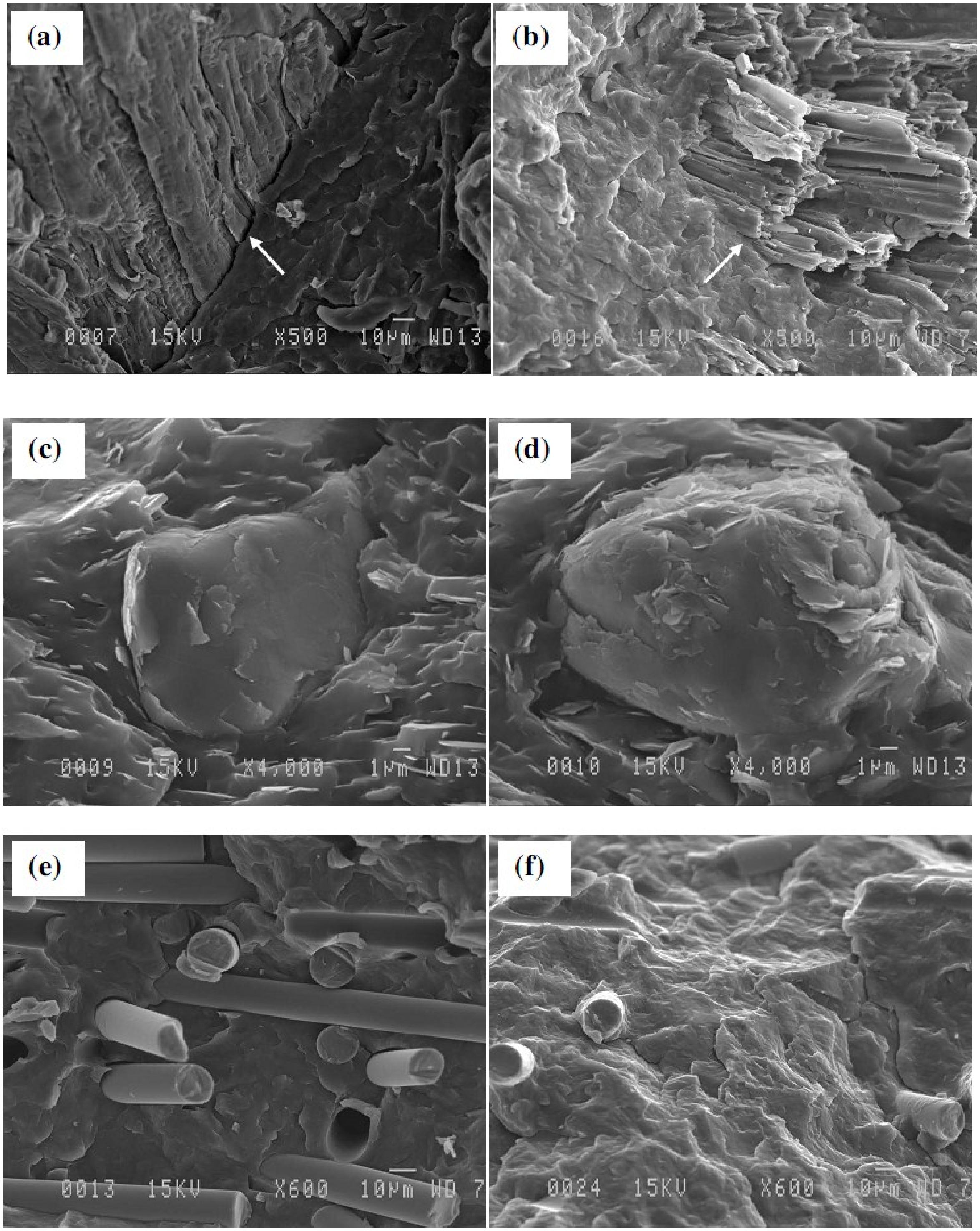

Figure 6.1 SEM micrographs of PP composites with (a,b) hemp, (c,d) talc and (e,f) glass reinforcements (a,c,e) without and (b,d,f) with compatibilizer (MAPP).

SEM micrographs of compatibilized samples, on the other hand, demonstrate a different behaviour. The gaps and voids at the filler/matrix interfaces disappeared and the surface of the particles are not as clean. Also, it can be seen that the hemp and glass fibres are broken at the level of the fractured surfaces and no pull-out is detected. All these observations suggest that the fillers are well embedded in the matrix which is a result of a strong interface (better adhesion). High filler/matrix interaction is expected to increase the composite strength through effective load transfer.

Figure 6.2 shows SEM micrographs of impact modified glass filled samples. It is clearly seen that almost no GTR (or EPDM) particles can be seen on the fractured surfaces. This observation proves that surface coating of waste rubber crumb using MAPP is an effective method for creation of a thick interface and to compatibilize waste rubber powder with polyolefins. Similar observations were obtained for maleated polyethylene (MAPE)/high density polyethylene (HDPE) compounds from previous work [19].

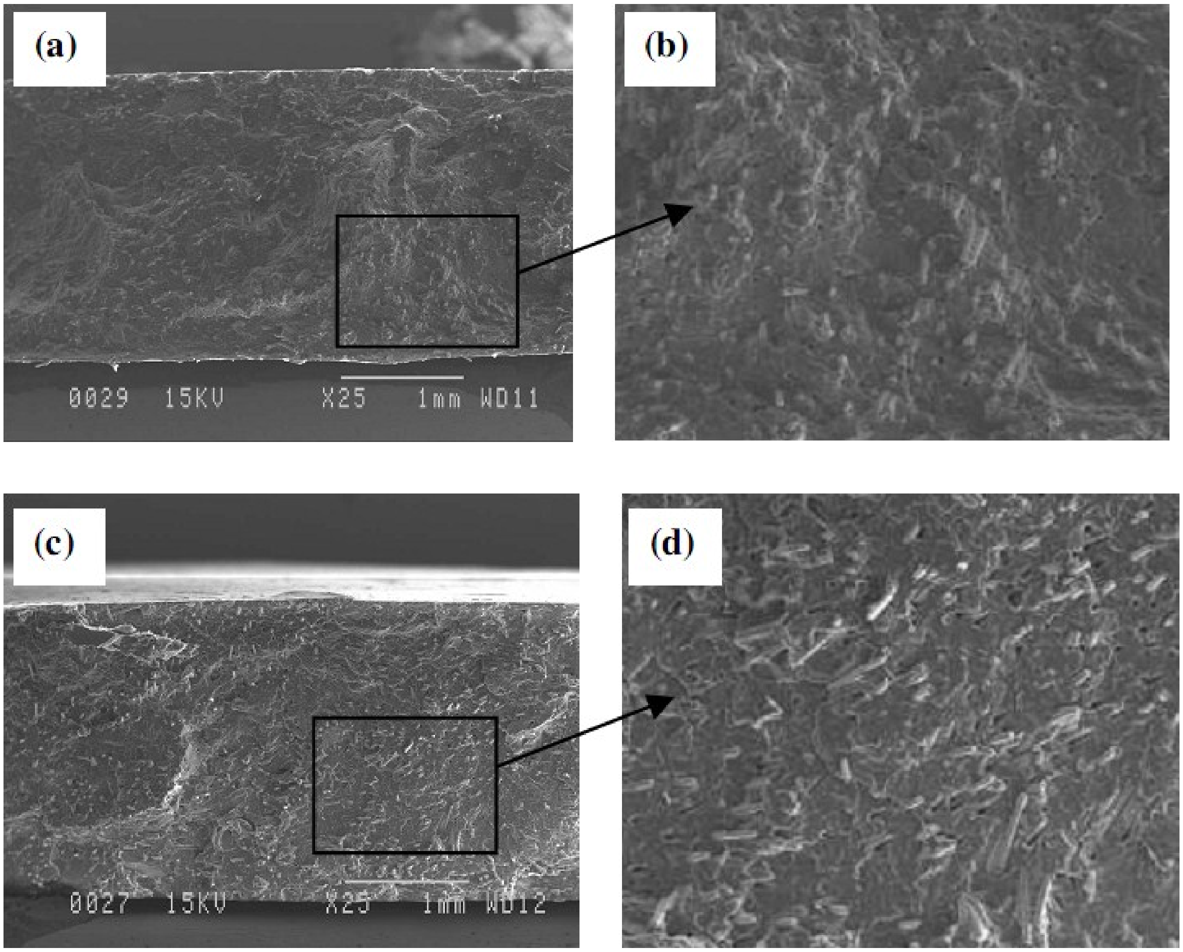

Figure 6.2 SEM micrographs of glass fibre filled PP with (a,b) EPDM and (c,d) GTR as impact modifiers.

Figure 6.3 illustrates the conventional compatibilization method compared to surface coating of waste rubber phase, proposed in this research. Adding MAPP as a compatibilizer to a PP-GTR compound (Figure 6.3a) leads to a slight increase in their compatibility. The effect is not significant because only a part of MAPP is actually located at the interface. On the other hand, adding a mixture of MAPP/GTR (with high GTR content) to neat PP through an extrusion process (Figure 6.3b) benefits from remarkably enhanced compatibility between the rubber and thermoplastic phases. High compatibility between MAPP and waste rubber is believed to be related to chemical bonds created between the maleic anhydride group of MAPP and unsaturated C=C bonds on the rubber surface. Needless to say that effectiveness of this approach combined with its simplicity provides good economical and environmental opportunity in recycling different types of waste rubbers as fillers, or even modifiers, in thermoplastics.

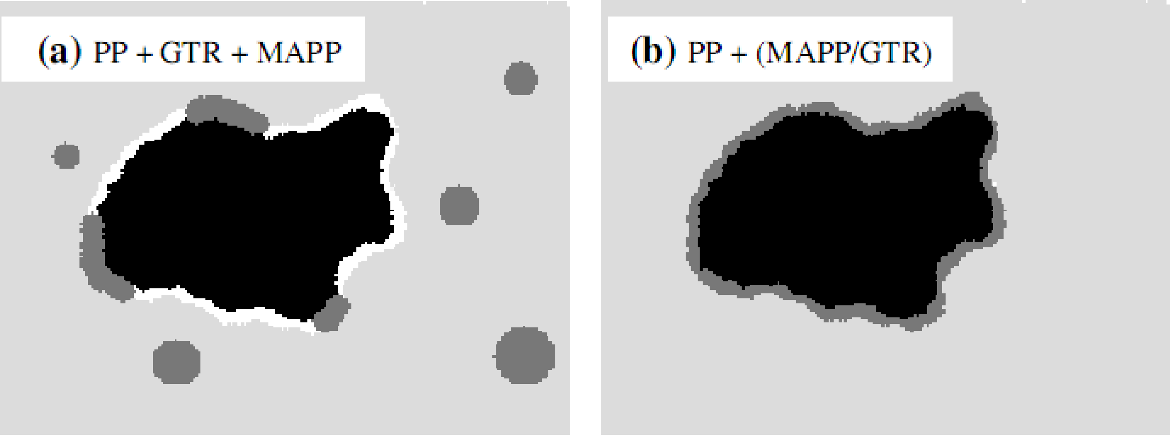

Figure 6.3 Schematic representation of impact modification of polypropylene (PP) using ground tire rubber (GTR) and maleated polypropylene (MAPP). (3a) GTR (black) in PP (light gray) matrix with MAPP (dark gray) as compatibilizer and (3b) surface coating method used in this work.

Presence of a wide variety of materials in tires usually results in some impurity in GTR. Figures 6.4 and 6.5 show examples of such impurities using SEM and energy dispersive spectroscopy (EDS), respectively. The results (Figure 5) revealed that these impurities were mostly metal alloys from Fe, Cu and Zn (Figure 6.4a) or other polymeric materials (Figure 6.4b), such as polyester fabrics [90], which are used for reinforcement of parts of tires.

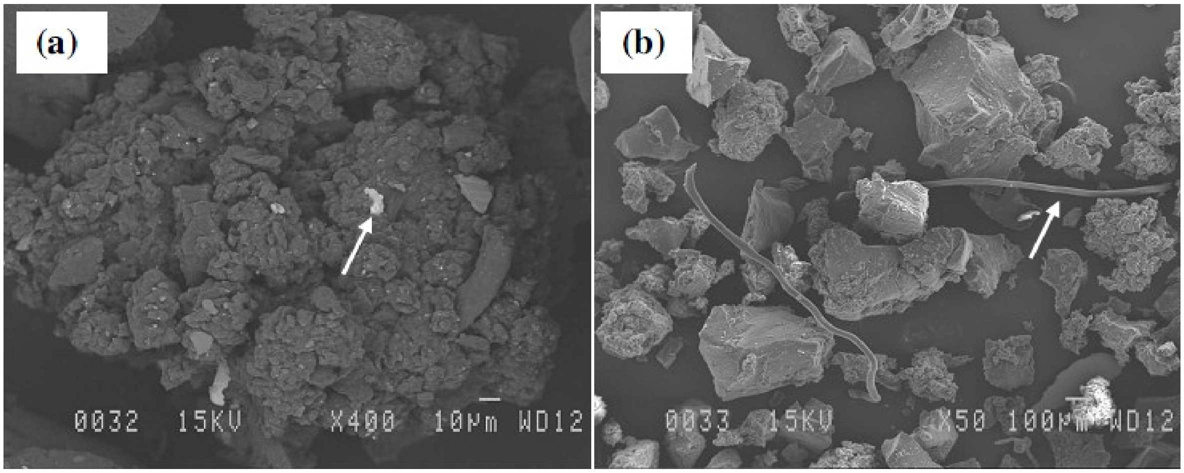

Figure 6.4 Typical examples of impurities in waste rubber powder.

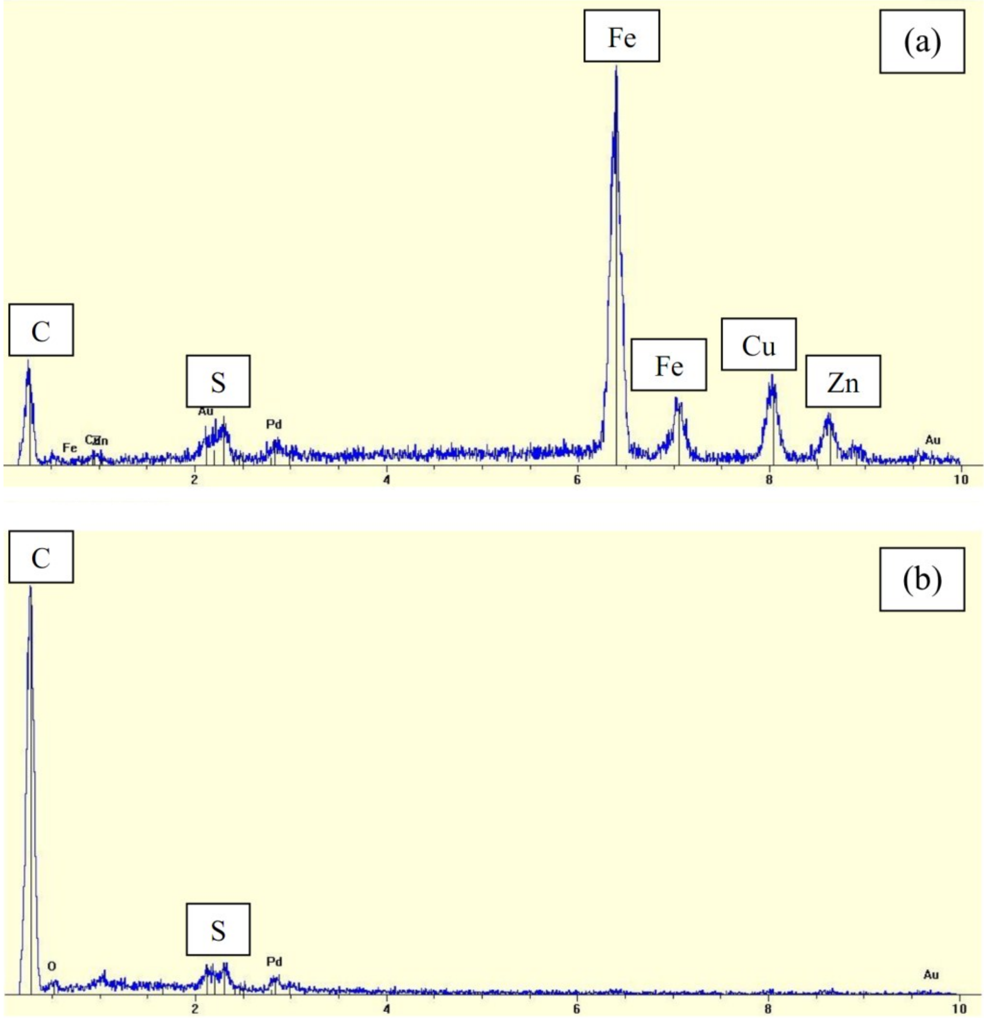

Figure 6.5 EDS plots for impurities seen in (a) Figure 6.4a and (b) Figure 6.4b.

6.3.2 Mechanical properties

Figures 6.6-6.11 present the mechanical properties of the PP based composites before and after incorporation of the additives. As presented in Figure 6.6, tensile strength of all composites, without coupling agent, were lower compared to neat PP (30.7 MPa). This behaviour is ascribed to poor interaction between fillers and matrix. After coupling agent addition, tensile strength increased for all composites with a greater effect for hemp (50%

improvement) and glass fibre (45% improvement). Although compatibilization of PP-talc composite also improved tensile strength, the effect was not as strong as the others (21% improvement). It is also interesting to mention that hemp fibre showed comparable (and in some cases even better) reinforcing effect compared to other fillers (especially talc).

It is well established in the literature that adding a rubber phase leads to a decrease in tensile properties of thermoplastics [23,24,91]. This observation is conceivable due to the fact that a part of the thermoplastic matrix (with high tensile properties) is substituted with a soft rubber phase. For example, Ruksakulpiwat et al. [92] added virgin EPDM and natural rubber as an impact modifier to PP-vetiver grass composite. No impact modification effect was reported for samples with rubber contents lower than 20%. For samples with 20% rubber, however, tensile strength and modulus of the composite decreased by 43% and 23%, respectively.

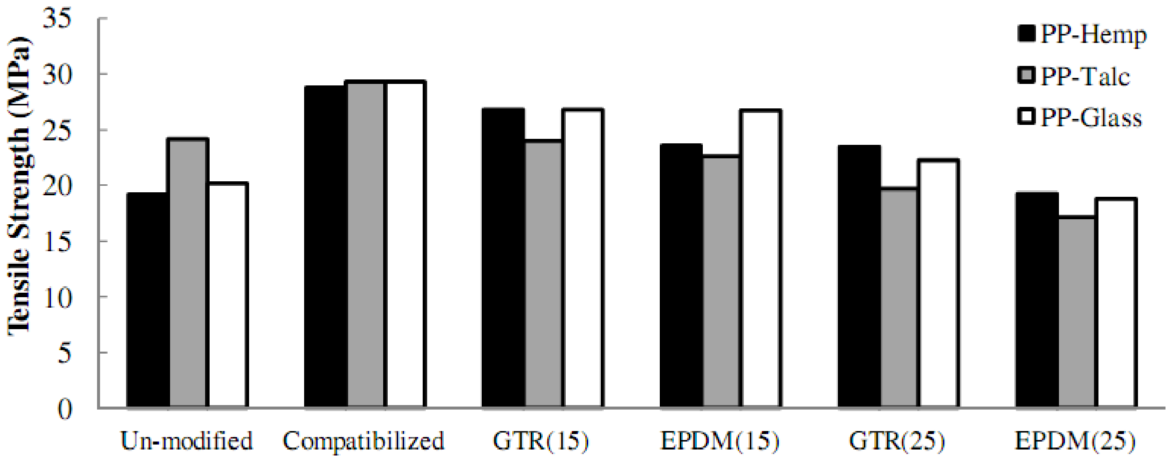

Figure 6.6 Effect of different modifications on tensile strength.

In our previous work [93], regenerated GTR was also introduced as an impact modifier for HDPE-flax composites. The results showed that although regenerated GTR increased impact strength of the composites, the reduction in mechanical properties was noticeable: adding only 15% of regenerated GTR increased the impact strength of composites (with

15% flax) around 38%, while tensile strength dropped from 17.5 to 11.6 MPa (34% decrease).

As shown in Figure 6.6, inclusion of surface coated waste rubber, on the other hand, led to a gradual decrease in tensile strength of the PP based composites. This effect was more noticeable for EPDM modified samples. Tensile strength of PP-glass composite decreased by only 9%, while PP-talc and PP-hemp composites showed 22 and 18% reduction, respectively. Increasing EPDM concentration led to lower tensile strength in all composites. Adding 15% of GTR led to 9% reduction in tensile strength of PP-glass composite, while the strength of PP-talc and PP-hemp also decreased by only 18 and 7%, respectively.

Figure 6.7 shows the effect of different modifications on tensile modulus. It is observed that inclusion of reinforcements led to a noticeable increase in modulus of PP (0.63 GPa). This behaviour is due to incorporation of rigid fillers with significantly higher stiffness compared to PP. Adding a coupling agent also increased tensile modulus of all composites. Tensile modulus of PP-glass composite increased by almost 21%, while the increase for talc and hemp filled samples were 12 and 17%, respectively. Adding waste rubber led to a slight decrease in modulus. Figure 6.7 also reveals that GTR led to a less significant reduction of tensile modulus compared to EPDM. Adding 15% GTR decreased the modulus of hemp filled composites by 4%, while the same amount of EPDM decreased it by 12%. Incorporation of a higher content of both rubbers led to more reduction in tensile modulus. It is also noteworthy to mention that even samples with 25% rubber have higher tensile modulus than neat PP. It should be considered that such samples contain around 50% of virgin material, while the rest is from cheap and environmentally friendly sources. It should also be noted that the PP matrix can also be of recycled origin.

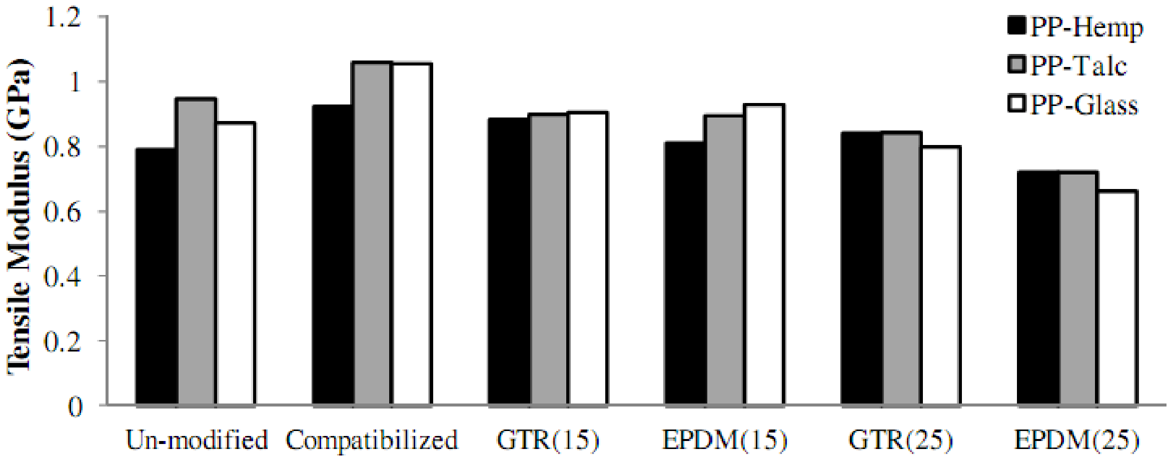

Figure 6.7 Effect of different modifications on tensile modulus.

As presented in Figure 6.8, tensile elongation at break of the composites was lower compared to neat PP (23%). It is also expected that adding coupling agents should decrease the elongation at break in composites even more significantly. Improved interaction between the dispersed phase and matrix combined with low elongation at break of fibres are responsible for this effect. This behaviour is obviously observed for PP-glass composites (Figure 6.8). Adding waste rubber to the composites did not increase their elongation at break. This observation is probably a result of large rubber phase particle size and their crosslinked structure which leads to lower elongation at break. The most noticeable increase is observed for PP-glass composite with 25% of waste EPDM with an increase from 5.3% to 8.5%.

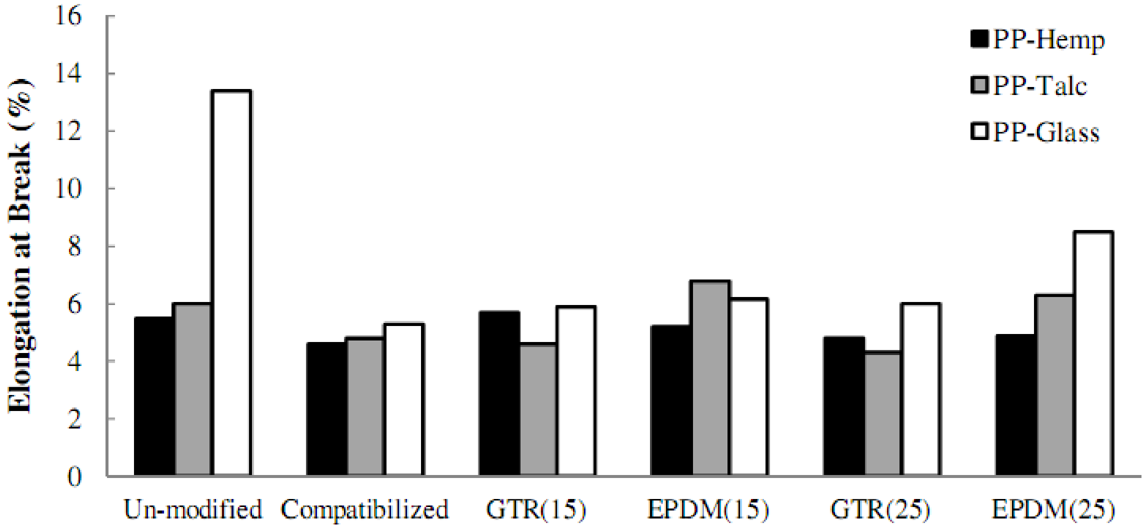

Figure 6.8 Effect of different modifications on tensile elongation at break.

Flexural modulus of different composites is presented in Figure 6.9. It is shown that PP-talc composites had the highest flexural modulus (2.99 GPa) compared to neat PP (1.43 GPa). Adding a coupling agent did not significantly modify the flexural modulus of the composites. Adding rubber phases, on the other hand, decreased the flexural modulus of all compounds; the reduction being more significant for PP-talc composites. Flexural modulus of talc filled composite decreased by almost 30% with 25% of GTR.

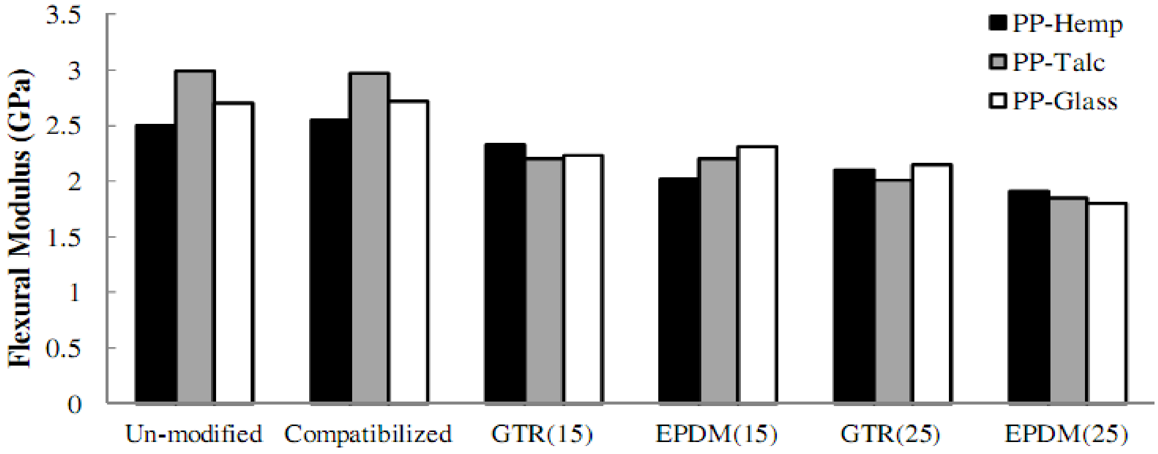

Figure 6.9 Effect of different modifications on flexural modulus of the composites.

Figure 6.10 shows the torsion modulus of PP based composites with and without coupling agent and impact modifier addition. Torsion modulus and tensile modulus show a similar trend. Adding reinforcements increased the modulus of PP from 0.65 GPa to over 1.00 GPa. Inclusion of a coupling agent increased torsion modulus, while waste rubber decreased it. For instance, adding 15% GTR decreased torsion modulus of PP-hemp by about 11%, from 1.10 GPa to 0.98 GPa.

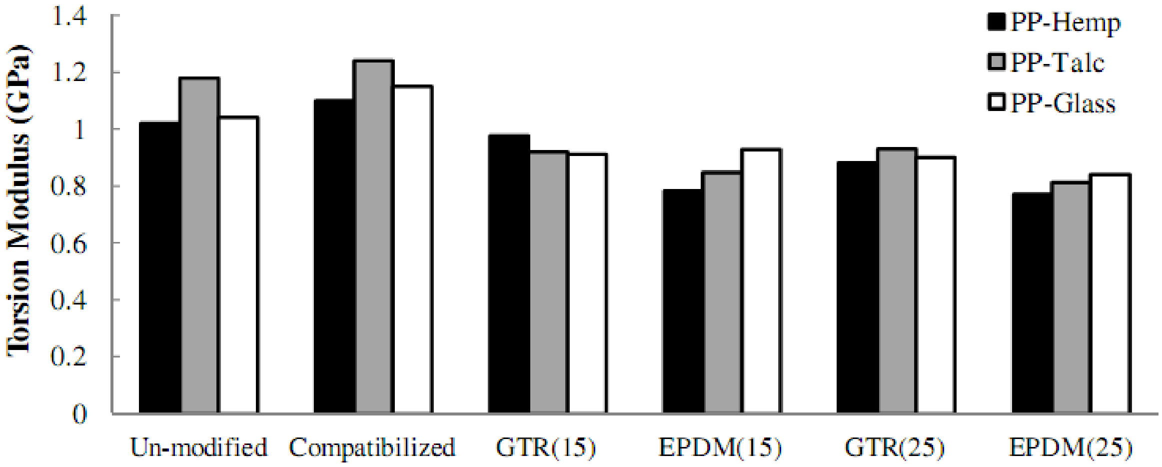

Figure 6.10 Effect of different modifications on torsion modulus.

The main idea behind the addition of virgin rubbers to composites is to increase ductility. Successful use of waste rubber, instead of virgin rubber, benefits from lower cost, environmental friendliness and simpler processing conditions (since there is no need to vulcanize waste rubber). Figure 6.11 shows the results of different modifications on impact strength of the composites. Adding all reinforcements led to a significant decrease in notched impact strength of PP. Impact strength of PP-hemp composite is less than 21 J/m compared to 37.4 J/m for neat PP. Dispersed particles are known to act as stress-concentrators in the structure of composites, this decreases strength especially at high deformation rates (such as impact tests). Samples with talc and glass as dispersed phase, without modification, showed slightly higher impact strengths compared to hemp filled ones. This is believed to be due to smaller particle size of glass and talc and also lower loading, on a volume basis, of these fillers (glass and talc have a density of 2.6 and 2.9 g/cm^3, respectively, while the density of hemp is around 1.4 g/cm^3). It is shown that adding coupling agent had a slight effect on increasing the impact strength of hemp and glass fibre filled composites, while almost no effect is observed for PP-talc composites.

Substantial enhancement in impact strength for all composites is obtained after adding both types of rubber wastes. This effect was more significant for compounds containing MAPP/EPDM as impact modifier. This behavior can be ascribed to chemical similarity of EPDM with PP (due to presence of propylene blocks) and/or possibility of presence of higher content of C=C bonds in EPDM which provides stronger interactions with MAPP. Adding 15% of the MAPP/EPDM blend increased impact strength of PP-glass composites from 23.1 to 41.9 J/m (over 81% increase). Increase in impact strength of both PP-talc (34%) and PP-hemp (49%) composites are also observed. Adding higher concentration (25%) of MAPP/EPDM did not change its effectiveness on impact modification of PP-talc and PP-glass composites significantly. Impact strength of PP-hemp composite with 25% MAPP/EPDM showed a 16% improvement over the compound with 15% of this modifier.

MAPP/GTR blend did not increase significantly the impact strength of composites at concentration of 15%, while noticeable increase is observed for samples with 25% MAPP/GTR. Impact strength increased by 78% for PP-glass composites, while the value increased by almost 60% and 40% for PP-hemp and PP-talc composites, respectively.

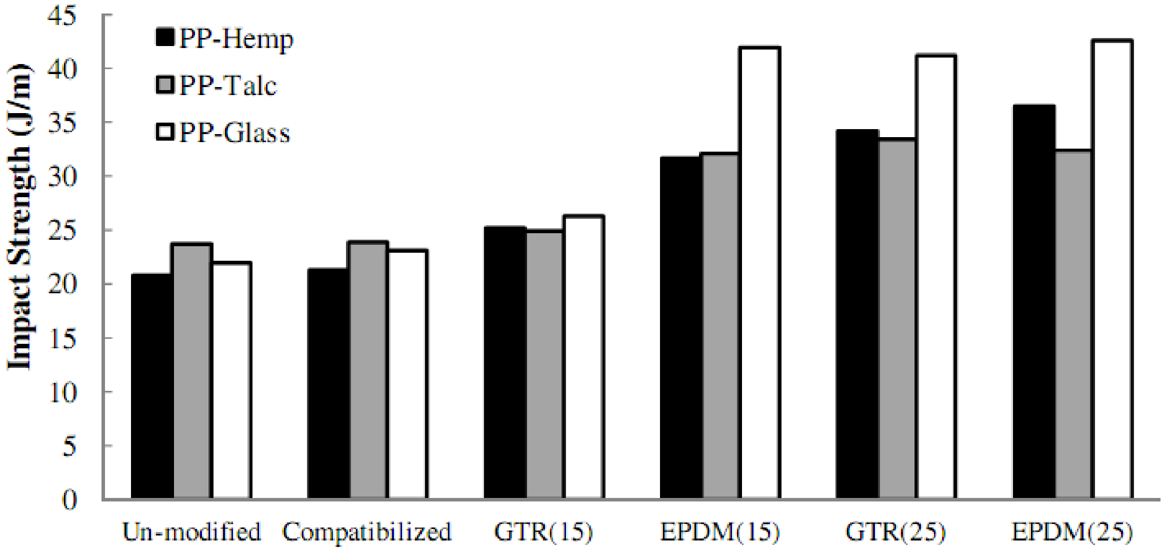

Figure 6.11 Effect of different modifications on notched impact strength.

Considering the effect of adding waste rubbers on other mechanical properties (tensile, flexural, torsion) of the composites, it is possible to conclude that incorporation of 15% of MAPP/EPDM or 25% of MAPP/GTR is probably the most interesting approach to impact modification of the composites produced.

6.3.3 TGA results

Thermogravimetric analysis was performed on the samples to compare their thermal and oxidative stabilities. The results presented in Table 6.2 are reported in terms of maximum decomposition temperature ($T_{max.\ dec}$) which represents the temperature at which the rate of thermal decomposition of the sample is at its peak, as well as T_{10} and T_{50} which are the temperatures for 10 and 50% mass loss, respectively. In almost all cases, degradation temperatures were much higher in nitrogen atmosphere compared to air. For PP-hemp composite with MAPP as coupling agent, compatibilized (hemp), T_{10} was 267°C in air, while it increased to 304°C in nitrogen. This shows that oxidation plays an important role during thermal degradation of these composites.

Table 6.2 Thermal degradation data for all samples in air and nitrogen.

Sample	**$T_{max. dec.}$ (^oC)**		**T_{10} (^oC)**		**T_{50} (^oC)**	
	Air	N_2	Air	N_2	Air	N_2
PP	360	424	289	334	342	420
Hemp	317	341	251	239	316	335
Talc &Glass	-	-	> 600	> 600	> 600	> 600
EPDM	325	390	272	300	437	505
GTR	341	417	301	322	471	438
Unmodified (hemp)	345	405	266	306	323	394
Unmodified (talc)	398	402	325	372	394	411
Unmodified (glass)	372	402	297	359	367	410
Compatibilized (hemp)	349	407	267	304	325	398
Compatibilized (talc)	406	412	331	375	400	415
Compatibilized (glass)	380	404	298	352	370	403
GTR15 (hemp)	371	419	273	298	355	409
GTR15 (talc)	392	422	305	341	376	389
GTR15 (glass)	397	431	323	382	397	434
EPDM15 (hemp)	406	435	284	343	389	424
EPDM15 (talc)	411	451	332	358	406	431
EPDM15 (glass)	405	442	327	378	403	440
GTR25 (hemp)	393	440	282	304	371	421
GTR25 (talc)	398	417	311	365	419	440
GTR25 (glass)	420	444	334	380	410	442
EPDM25 (hemp)	412	432	290	354	396	438
EPDM25 (talc)	420	448	333	373	417	445
EPDM25 (glass)	415	450	326	381	411	448

Composites with talc and glass showed higher thermal stability compared to hemp filled ones, which is ascribed to the higher stability of these fillers. In air, $T_{max.dec}$ of compatibilized PP-hemp composites was 349°C compared to 406 and 380°C for PP-talc and PP-glass, respectively.

6.3.4 Density and hardness measurements

Figure 6.12 shows the density for the different materials. As mentioned before, talc (2.9 g/cm^3) and glass (2.6 g/cm^3) have higher density compared to hemp (1.4 g/cm^3), leading to increasing density with content. Inclusion of MAPP did not change density of the composites. Adding both rubber phases, on the other hand, increased slightly density since the density of EPDM (1.3 g/cm^3) and GTR (1.2 g/cm^3) are higher than neat PP (0.91 g/cm^3).

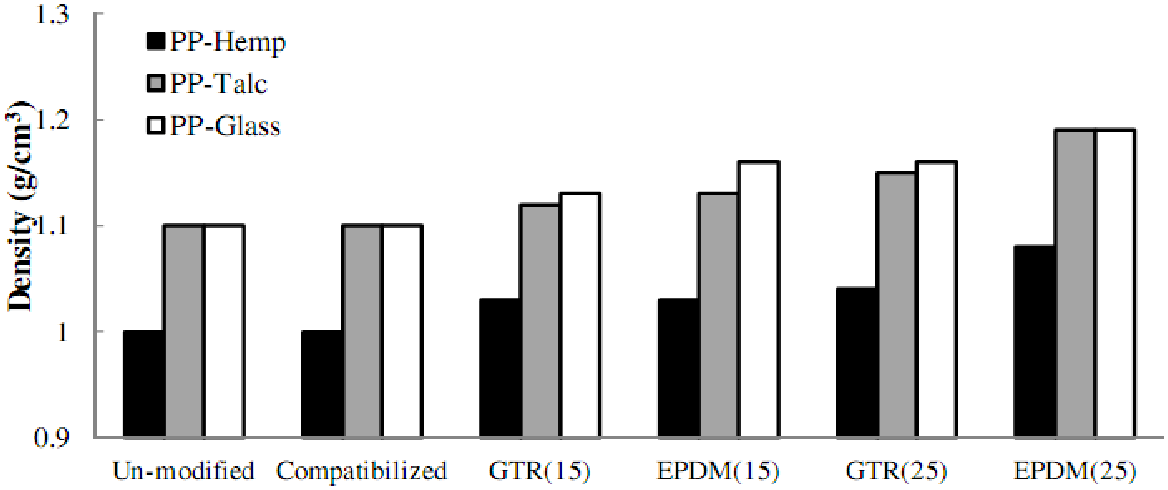

Figure 6.12 Density of the different composites, before and after modifications.

Hardness (shore D) data are presented in Figure 6.13. It is observed that hardness of the composites is higher than neat PP (70), while adding waste rubber decreases slightly the values.

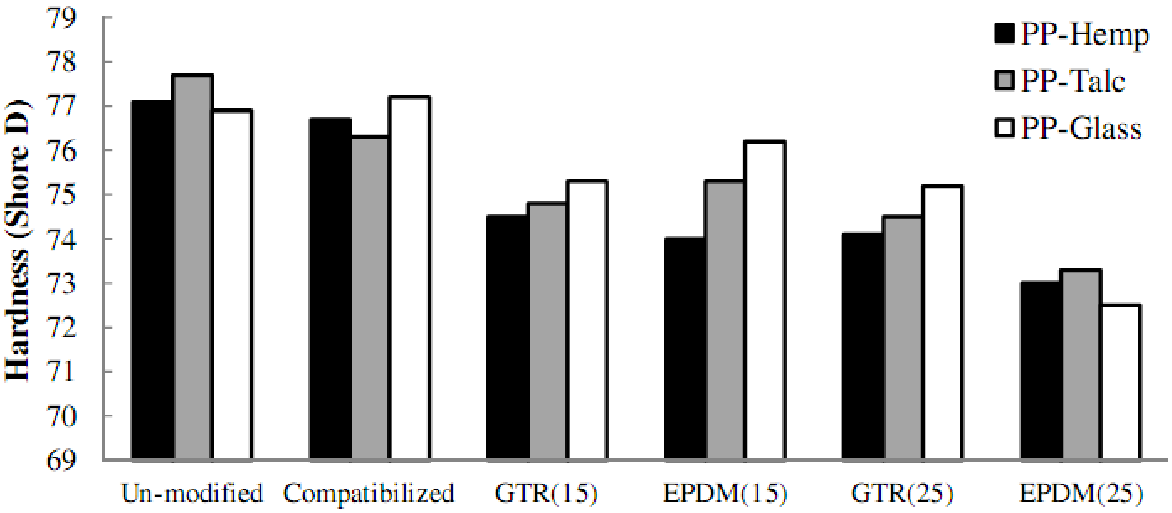

Figure 6.13 Hardness of different composites, before and after modifications.

6.4 Conclusions

Surface coating of waste rubber powder with maleated polypropylene (MAPP) was investigated for impact modification of polypropylene (PP) based composites. Polypropylene composites based on organic (hemp) and inorganic (talc and glass fibre) reinforcements were produced with and without MAPP as a coupling agent. Adding reinforcements led to an increase in moduli (tensile, flexural and torsion) of PP, while tensile strength decreased (around 20-40%). Coupling agent addition, on the other hand, led to an increase in both tensile strength (up to 50%) and moduli (up to 21%) of all the composites produced. Hemp fibre showed comparable (and in some cases higher) mechanical properties compared to inorganic reinforcements. For instance, tensile strength of all composites with compatibilizer was around 29 MPa. SEM micrographs revealed that surface covering of waste rubber particles with MAPP led to very good surface interaction with the PP matrix. The results were also confirmed with mechanical characterisations. Adding waste rubber powder decreased tensile, flexural and torsion moduli of the composites. On the other hand, impact strength of such composites showed a noticeable increase over the original compounds. Significant improvement (up to 81%) in impact strength was achieved after adding only 15% of MAPP/EPDM blend. Suitable impact modification (up to 78%) was also observed after adding 25% of MAPP-GTR compound. Thermal degradation of hemp filled composites was proven to occur at lower temperatures than inorganic fillers. In air atmosphere, T_{10} of PP-hemp composite was 266 °C compared to 325 and 297 °C for PP-talc and PP-glass, respectively. Densities of PP-talc and PP-glass composites (both 1.1 g/cm^3) were observed to be higher compared to PP-hemp composite (1.0 g/cm^3). Finally, hardness increased with reinforcement addition, while the presence of a rubber phase decreased it.

Acknowledgements

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Chapter 7. Conclusions and recommendations

7.1 General conclusions

This research work was devoted to contribute in the field of waste rubber recycling (especially tire rubber) via the production of high quality compounds based on a thermoplastic matrix and waste rubber powder. The key conclusions are presented as follows:

In the first step, maleated polyethylene studied and shown to be an excellent matrix in order to create strong interfacial adhesion with rubber particles. Compounds with intermediate to high concentrations of ground tire rubber GTR (between 50 and 90% by weight) were produced. The compounds showed very good properties as thermoplastic elastomers (high elongation at break and low compression set). Substitution of MAPE by HDPE (as matrix), however, gave rise to substantial decrease in blend homogeneity. SEM micrographs were used to confirm the level of compatibility between MAPE/GTR compounds, while HDPE based samples were shown to have weak interfacial adhesion. Rheological measurements were performed on both MAPE and HDPE based compounds. The results revealed that viscosities of the blends were strongly affected by the compatibility between the phases.

One of the most important benefits of using thermoplastics as matrix for waste rubber powder is the potential for further reprocessing and recycling of the compounds. Thus, the ability for the compounds to withstand different degradations (during service life and reprocessing) is of interest. The effects of different degradation mechanisms (thermal ageing, weathering and re-extrusion) on MAPE and MAPE/GTR compounds (with and without stabilizers) were presented in the second phase of the work. It was shown that GTR addition led to lower stability against thermal degradation in MAPE/GTR compounds. Incorporation of stabilizers increased the stability of the blends against thermal ageing only via stabilization of the MAPE matrix (no effect was observed on GTR). Weathering of MAPE for 400 h led to increased modulus and reduced elongation at break due to crosslinking of MAPE molecules. Incorporation of both GTR and stabilizers increased significantly the stability of MAPE against weathering. For compounds with higher GTR contents, addition of light stabilizers caused no significant improvement.

Re-extrusion of MAPE resulted in decreased elastic modulus. For MAPE/GTR compounds, the results showed that GTR particle size decreased with each re-extrusion cycle and the particle size distribution was narrower. The reduction in particle size was more significant as the number of re-extrusion cycles increased and also for samples with higher GTR contents. Incorporation of stabilizers improved the stability of MAPE against re-extrusion, while the effect was not significant for GTR filled compounds. Overall, it was shown that MAPE/GTR compounds have acceptable stability against re-extrusion.

In the third phase, the effects of particulate reinforcements (talc and wood flour) on the properties of MAPE/GTR thermoplastic elastomers were investigated. SEM results revealed that MAPE had a good level of adhesion with wood flour. However, composites containing talc had low particle-matrix compatibility and signs of talc aggregation were observed. Adding both types of particles was shown to increase tensile modulus of the thermoplastic elastomers significantly. Modeling of the elastic modulus of MAPE/GTR thermoplastic elastomers and MAPE/GTR/particle ternary composites was successfully performed using Kerner and Halpin-Tsai models, respectively. Fitting of the experimental data using the Halpin-Tsai equation showed that the elastic modulus depended strongly on both aspect ratio and level of dispersion of the reinforcements in the matrix. Increasing particle concentration resulted in lower elastic recovery of MAPE/GTR compounds. Composites with higher compatibility between the particles and the MAPE matrix showed stronger elastic behavior.

As the last step of the work, surface coating of waste rubber powder with MAPP was performed to study the ability of low GTR concentrations and waste EPDM powder to serve as impact modifiers for PP based composites. Polypropylene composites based on organic (hemp) and inorganic (talc and glass fiber) reinforcements were produced with and without MAPP as coupling agent. SEM micrographs revealed that surface covering of waste rubber particles with MAPP led to very good surface interaction with the PP matrix. The results were also confirmed with mechanical characterizations. Adding waste rubber powder decreased tensile, flexural and torsion moduli of the composites. On the other hand, impact strength of such composites showed a noticeable increase (over 80%) compared to the original compounds.

7.2 Recommendations for future works

The following directions are suggested in order to extend the applications of GTR filled thermoplastics:

1) Maleated polyethylene was shown to be an excellent matrix to produce GTR filled thermoplastic elastomers. The author believes that this idea has strong potential to be used at an industrial scale. Feasibility study for industrial implementation of this idea is of high interest, including more advanced economics/life cycle/mechanical analyses.
2) Different grades of maleated polyethylene or polypropylene can be used to optimize the mechanical properties of thermoplastic elastomers. For instance, acid number and molecular weight of the maleic anhydride grafted thermoplastics both play important roles in the level of compatibility and characteristics of the resulting compounds.
3) In this thesis, only maleated polyethylene and polypropylene were used to produce waste rubber filled thermoplastic elastomers. In the future, maleated forms of different types of thermoplastics and even bio-based thermoplastics (such as maleated thermoplastic starch) can also be used for this purpose in order to get products with more diverse characteristics and applications.
4) In order to decrease the cost of final products and reduce the environmental concerns caused by the process, maleation of recycled thermoplastics can also be considered to produce new matrices for fabrication of all recycled GTR filled thermoplastic elastomers.

5) It was shown that maleated polyethylene has lower mechanical properties compared to high density polyethylene. In order to increase the mechanical properties of thermoplastic/waste rubber compounds, pre-impregnation of GTR particles in a solution of maleated polyethylene (in a suitable solvent) can be considered. After drying, pre-impregnated particles can be combined with high density polyethylene.
6) In this thesis, thermoplastic elastomers were reinforced using particulate reinforcements. In order to increase the mechanical properties of the compounds, inclusion of short and continuous fibers can also be investigated.

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