# Study of compatibilization methods for High Density Polyethylene and Ground Tyre Rubber:

## Exploring new routes to recycle scrap tyres

Dissertation:

To obtain the doctor's degree at the Polytechnical University of Catalonia
Chemical Engineering Department

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Dr. Xavier Colom Fajula

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To those who will be happy for this new goal in my professional career and, to my parents, for their guidance and support during my studying period…

*A tots aquells que s'alegraran d'aquesta meva nova fita professional i, als meus pares, pel seu suport i consell durant tota l'etapa en la que he estat estudiant...*

“The important thing is not to stop questioning.
Curiosity has its own reason for existing”

A. Einstein

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*Primer de tot, vull agrair l'orientació rebuda pels professors F. Javier Cañavate i Xavier Colom, ambdós directors de la tesis. D'altra banda vull agrair profundament a Francesc Nogués, qui m'ha ajudat en la part experimental i ha estat disponible sempre que l'he necessitat. Als estudiants Tuomas Juhanila, Antti Palosuo, Halina Lach i Dorian Polus que d'una manera o altra han participat en la realització de la tesis. Als meus companys de l'empresa BYK-Chemie GmbH, Jaume Figueras i Joan Barceló, per les llargues i interessants converses mantingudes. Als coneixements rebuts de tot el professorat de la Universitat Politècnica de Catalunya on he cursat els estudis d'Enginyeria Tècnica en Química Industrial, un Postgrau en Materials basats en Polímers, Enginyeria en Organització Industrial i la realització de la present tesis. Finalment, vull agrair a Josep Martínez, el seu suport moral i la seva paciència al llarg de tota l'execució de la tesis.*

# Biography

Pilar Casas was born in Sabadell (Barcelona, Spain) on May the 13th, 1977. She got a Chemical Engineering degree in 2000, a Postgraduate Course in Polymer Materials in 2001, a Business Administration degree in 2004 and a Diploma in Advanced Studies in 2007, all from Polytechnical University of Catalonia. Her professional history started in 1998 when she worked for the masterbatch producer Plásticos Compuestos S.A. as lab technician; there she carried out her Chemical Engineering thesis. Just afterwards, she initiated her career as technical adviser in Comindex S.A. (Spanish agent for BYK-Chemie GmbH) and from 2003 to 2005 she worked for SUCITESA, as marketing responsible, where she carried out her Business Administration thesis. Nowadays, she is working since April 2005, for BYK-Chemie GmbH as technical adviser for coatings additives in the Spanish market.

# Biografia

*Pilar Casas i Carné va néixer el 13 de maig de 1977 a Sabadell. Va obtenir el títol d'Enginyeria Tècnica Industrial en Química Industrial i de l'especialitat de polímers i recobriments l'any 2000, el títol de Postgrau en Materials basats en Polímers l'any 2001, el títol d'Enginyeria en Organització Industrial al 2004 i al 2007 va obtenir el Diploma en Estudis Avançats en l'especialitat de Polímers, tots per la UPC. Va començar la seva experiència professional al 1998, a l'empresa fabricant de masterbatch, Plásticos Compuestos S.A., com a tècnica de laboratori fins al 2001 on va tenir l'oportunitat de realitzar el seu projecte final de carrera per l'obtenció del títol d'Enginyeria Tècnica Industrial. Es va iniciar en l'assessorament tècnic a Comindex S.A. (actual distribuïdor de BYK-Chemie GmbH), del 2003 al 2005 va treballar per SUCITESA com a responsable de màrqueting on va realitzar el projecte per l'obtenció del títol d'Enginyeria en Organització Industrial. Actualment treballa des d'abril de 2005 a BYK-Chemie GmbH com assessora tècnica d'additius per a pintures en el mercat espanyol.*

# *Abstract of the Thesis*

Cars, trucks, tractors, airplanes… all need tyres as essential component to work. Unfortunately, due to its continuous use, tyres suffer from wear and have a limited lifetime; therefore, they must be changed every certain time becoming end of life tyres (EOL tyres). Paradoxically tyres are formulated to withstand difficult conditions and among other raw materials, they contain vulcanizated rubbers, high amount of stabilizers and other additives that turn tyres into non biodegradable material. Until 2006, disposal of EOL tyres in landfills was a common practice but it was banned by the European Community (directive 1993/31/EC). This European legislation together with an increasing environmental consciousness has instigated researchers to find applications for 3.4million tonnes of used tyres generated per year in Europe. Some extended uses for EOL tyres are energy recover and civil applications but the use of tyres after separation and grinding processes (material know as Ground Tyre Rubber - GTR), has increased during the last decade. Physical and chemical properties of EOL tyres make them an interesting material for the international research community focused today on finding new ways to recycle tyres for value added applications.

A good option to recycle big volumes of discarded tyres is using GTR particles as filler in thermoplastic matrixes, although this is a difficult task due to the low compatibility between the two materials. The surface characteristics of the GTR particles are responsible of this low compatibility. Despite these facts, the particle size obtained from standard industrial grinding processes is between 400 and 600μm. These particles are too large to be entrapped easily in polymeric matrixes. These characteristics in conjunction with the fact that GTR is made of highly crosslinked rubber with difficulties to react chemically to other materials, make GTR a material very difficult to work with.

The present thesis deals with the study of different compatibilization methods for an injection moulding grade of High Density Polyethylene (HDPE) and GTR obtained from standard industrial grinding process. The HDPE resin was chosen due to its wide range of injection moulding applications. The aim is to explore different methods to mix these two materials and obtain optimum mechanical, thermal and morphological properties for injection moulding applications. The composites are optimized to obtain the highest GTR amount, adequate processability and minimum cost.

After a preliminary study of the composites based on GTR and HDPE, three different methods to improve the adhesion between these two materials are studied. The first method consists in an oxidizing treatment on GTR particles surface in order to promote mechanical anchoring. In the second method the influence of wetting additives and waxes is studied. These substances reduce interfacial tension between GTR particles and HDPE matrix. The third and last method, study the influence of Ethylene Propylene Diene Monomer (EPDM) addition with and without peroxides. In this method, GTR particles are encapsulated by EPDM and this effect can be boosted by the use of peroxides. The composites properties are quite different depending on the used method.

After a comparison of the composites obtained by the three different compatibilization methods, it is found that the one with 30% of EPDM plus two peroxides, corresponding to

30% GTR + 40% HDPE + 30% EPDM + 0.5% Trigonox 311 + 0.1% Dicumyl Peroxide

fulfil the objectives of the thesis. This composite has good adhesion between GTR and HDPE that results in high elongation, it is obtained by a cheap compatibilization process and contains a high amount of recycled tyres (30%), it is easy to process, and the most important thing, it represents a new route to recycle scrap tyres for a value added application.

# *Resum de la Tesis*

*Cotxes, camions, tractors, avions... tots necessiten els neumàtics com a component imprescindible per al seu funcionament. Malauradament, degut al desgast per ús, els neumàtics tenen una vida útil limitada que obliga a renovar-los cada cert temps passant a ser Neumàtics Fora d'Ús (NFU). Paradògicament, els neumàtics són formulats per a suportar condicions extremes d'ús i, entre d'altres matèries primeres contenen cautxú vulcanitzat, una elevada quantitat d'estabilitzants i d'altres additius que fan dels neumàtics un material no biodegradable. Fins al 2006, era possible desar els NFU en abocadors però aquesta pràctica va ser prohibida per la Comunitat Europea (directiva 1993/31/EC). Aquesta directiva conjuntament amb la creixent consciència mediambiental ha potenciat la investigació per a trobar noves aplicacions per les 3.4milions de tones de NFU que es generen a l'any a Europa. Els NFU són emprats com a font d'energia o en aplicacions civils, però cada vegada més, són emprats en autopistes o per usos decoratius després de patir un procés de separació i trituració (NFU triturat). Les propietats físico-químiques dels NFU en fan un material molt interessant per la comunitat científica internacional que es centra en buscar noves vies de reciclatge mitjançant aplicacions d'alt valor afegit.*

*Una opció per reciclar grans volums de NFU és utilitzar-los granulats com a càrrega en matrius termoplàstiques, encara que aquesta és una tasca difícil degut a la baixa compatibilitat entre aquests dos materials. Les seves característiques superficials són les responsables d'aquesta baixa compatibilitat. Cal afegir també que el tamany de les partícules de NFU obtingudes a partir de processos industrials és entre 400 and 600µm, sent aquest un tamany massa gran per poder ser fàcilment embolcallades per qualsevol matriu. D'altra banda, el cautxú dels neumàtics és troba altament vulcanitzat i, per tant, aquest reaccionarà químicament amb dificultats amb d'altres materials. Totes aquestes propietats fan dels NFU un material difícil de treballar-hi.*

*La present tesis estudia diferents mètodes de compatibilització d'un Polietilè D'alta Densitat (PEAD) de grau d'injecció i NFU triturat obtingut a partir de processos estàndards de molturació. La resina de PEAD va ser escollit com a matriu degut al seu ampli rang d'aplicacions d'injecció. L'objectiu principal és explorar diferents mètodes de compatibilització d'aquests dos materials per obtenir òptimes propietats mecàniques, tèrmiques i morfològiques en aplicacions d'injecció. Els composites són optimitzats per a* *que continguin la màxima quantitat de NFU, una adequada transformació i el mínim cost.*

*Després d'un estudi preliminar de composites basats en NFU i PEAD s'han estudiat tres mètodes diferents per millorar l'adhesió entre aquests dos materials. El primer mètode consisteix en oxidar la superfície de les partícules de NFU granulat amb tractament basats en àcids, amb l'objectiu de proporcionar rugositat per a un anclatge mecànic. En el segon mètode s'han emprat additius humectants i ceres, ja que aquestes substàncies redueixen la tensió interfacial entre les partícules de NFU i la matriu de PEAD. En l'últim mètode, es va estudiar la influència de l'Etilè Propilè Diè Monòmer (EPDM). Amb aquest mètode, les partícules de NFU són embolcallades per l'EPDM, aquest efecte pot ser millorat amb l'ús de peròxids. Les propietats dels "composites" són bastant diferents en funció del mètode emprat.*

*Després d'una comparació dels "composites" obtinguts pels tres mètodes, s'ha trobat que el que conté 30% d'EPDM i dos peròxids, corresponent a la formulació::*

30% NFU + 40% PEAD + 30% EPDM + 0.5% Trigonox 311 + 0.1% Peròxid de Dicumil

*compleix els objectius fixats en la tesis: bona adhesió entre les partícules de NFU i el PEAD on l'elevat valor d'elongació n'és una conseqüència directa, la seva obtenció mitjançant un procés de compatibilització de cost reduït, un nou material amb una elevada quantitat de NFU (30%), la seva facilitat de transformació,, i el més important, una nova via de reciclatge dels NFU per a una aplicació d'alt valor afegit.*

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# Chapter 1: General Introduction

## 1.1 The use of tyres

Nowadays recycling is becoming an increasing consciousness at all levels (domestic, industry, etc…). Generally, polymeric materials do not decompose easily and its disposal implies serious environmental problems. On the other hand, rubber is used in so many applications resulting in a growing volume of rubber waste. With the increase in demand of automobiles, the manufacturing and use of tyres has increased tremendously both in the developed and less developed countries. Since at least 65% of worldwide rubber production, and likely even higher percentage of rubber disposal consists of automobile and lorry tyres *[Ahmed 1996]*.

Tyres are essential components in cars, trucks, tractors, airplanes, etc… They are the responsible to transmit to the road the motor forces necessary for propulsion and together with the suspension dampens the unevenness of the road surface and thus ensures driving comfort. They serve as containers to keep air under pressure too. Due to their use as important component, their composition is very complex as they have to be designed according to very high standards (adhesion, flexibility, forces, pressures, etc…).

Currently, steel-belted radial passenger tyres last about 65.000Km. If these tyres are properly inflated, rotated and otherwise cared for, a lifetime of 95.000 to 128.000Km. may be achieved. A tyre loses up to 10% of its weight until it is disposed and most of the dissipated material comes from the tread, which is of rubber only. If the casing is in good state once tread is finished, tyres can generally be retreaded *[U.K. Environment Agency 1998].*

## 1.2 Tyres: production, composition and properties

The basic component used to produce tyres are synthetic and natural rubber, textile, steel and chemical additives. The proportions in which these components are used depend heavily on the specific characteristics of the tyre. This is clearly demonstrated if the ratio between natural and synthetic rubber in the different tyres is compared. Generally, truck tyres have larger natural rubber content than passenger car tyres.

Natural rubber comes from the rubber tree plantations of *Hevea brasiliensis*. Synthetic elastomers are obtained from petroleum and coal requiring several stages to be produced. The most important chemical additive is zinc oxide which is used as an activator. Carbon black is added further to improve the rubber properties, prevent oxidation and provide greater abrasion resistance. All components are finally mixed into internal mixers and vulcanised using sulphur. Vulcanisation is a thermochemical process that gives to the tyres their performance characteristics in the consumption phase of the product lifecycle, but it is also the responsible for further processing in post consumption stages as they are more difficult to process.

Approximately, 80% of the weight of car tyres and 75% of truck tyres is rubber compound. The composition of the tyres produced by different manufacturers is very similar. *Table 1.1* shows the material composition of passenger car and truck tyres.

| Material | Passenger's cars (%) | Truck/buses (%) |
|---|---|---|
| Rubber/Elastomers | 48 | 43 |
| Carbon black | 22 | 21 |
| Metal | 15 | 27 |
| Textile | 5 | - |
| Zinc oxide | 1 | 2 |
| Sulphur | 1 | 1 |
| Additives | 8 | 6 |

*Table 1.1* Tyres composition in the European Union *[SIGNUS 2007]*.

To understand the value process for tyres recycling, some of the following properties of the tyre itself (entire, grounded or in granules) have to be taken into account *[SIGNUS 2007]*:

- Vibrations absorption capacity
- Drain capacity as grounded or in granules
- Reduced weight
- High resistance to be cut as a toughening material
- High weathering resistance
- Flexibility

- High heat value

All the physical and chemical properties commented up to now make of end of life tyres an interesting material for the international research community that is focused today on finding new ways to recycle tyres in high value added applications.

### 1.3 Classification of used tyres

The following diagram summarise the various stages in the life of a tyre:

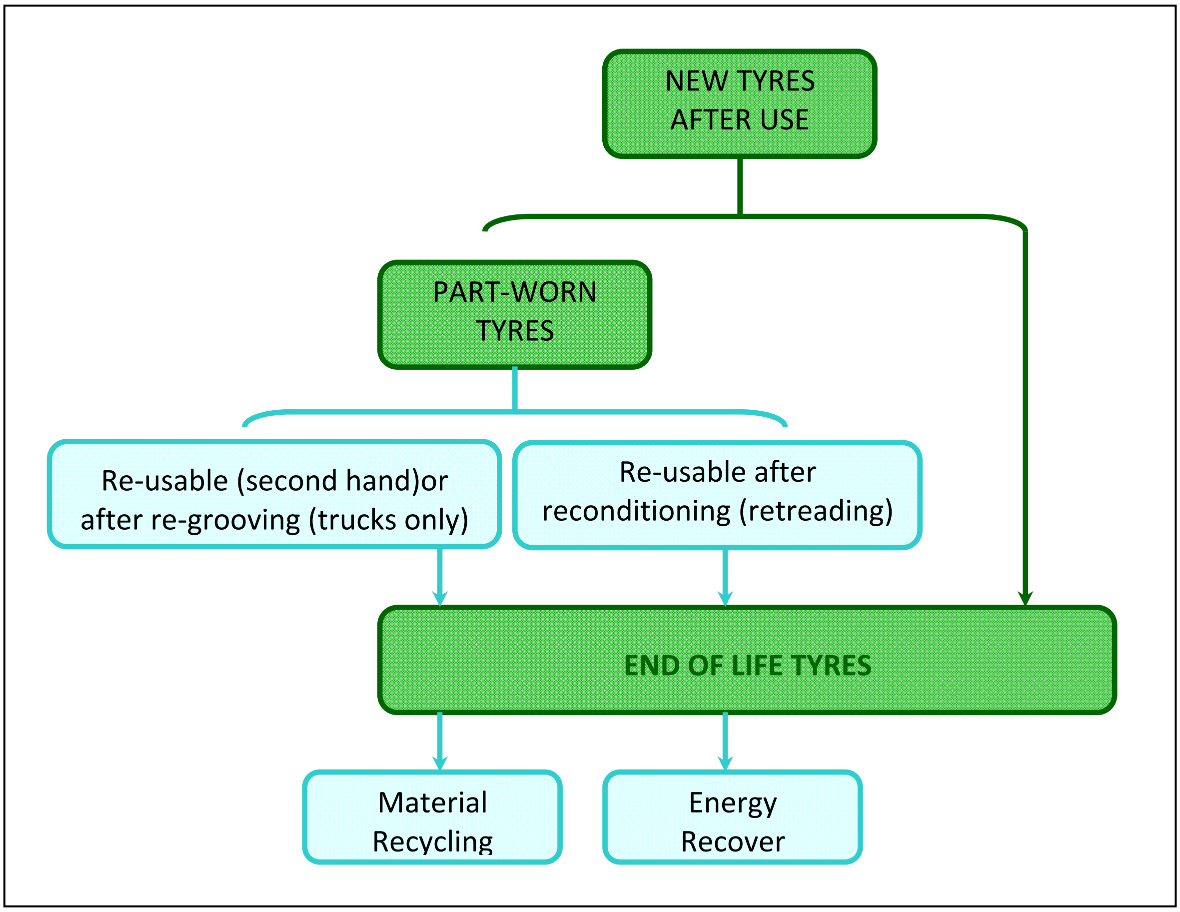


*Figure 1.2*: Identification of different categories of used tyres. *[Basel Convention 1999]*

Used tyres are transported all over the world. Many used tyres can be re-used for their originally intended purpose. Most countries accept the import of used tyres for direct re-use or for retreading. As can be seen in *Figure 1.2*, it is possible to distinguish three types of used tyres in function of their destination:

a) The used tyres that are legally re-used for their originally intended purposes are called part worn. Those tyres may have further use because a minimum tread depth remains and, subject to examining of the structural soundness, those tyres do not show wear affecting its safe and proper functioning.

b) Some used tyres cannot be re-used for its originally intended purpose but they are suitable for retreading. In this case, the used tyre may or may not have residual tread depth sufficient for further use as a part-worn tyre, but subject to an examination of the structural soundness of the casing, it can be reprocessed whereby new tread is vulcanized to the casing and the used tyre becomes a retreaded tyre. Regrooving for trucks only and retreading for all tyres are treatments considered to prolong the life of a used tyre. Regrooving is not admissible for car tyres because the tread depth in the grooves is not adequate. On the other hand, retreading maximises tyres utilization being this a preferable option because the tyre is reused in its original function. Via retreading, 80% of the original material value is available for reuse. While car tyres are retreated once, vans can be retreated twice and airplanes even up to seven times *[Schulz 1990] [Schmidt 1991]*. The process consists on adding an already vulcanized tread strip to a prepared carcass. The binding process takes place between 100-120ºC in autoclave. Selected undamaged car and truck tyre casings are sold to retreading companies. Retreaded tyre production in OECD countries, is a well developed and mature industry. In Spain, 40.000 tons of tyres were retreaded in 2007.

c) Used tyres that cannot be re-used for its originally intended purpose, and that are not suitable for retreading, are worn out. Such tyres are called end of life (EOL). This describes used tyres which fail the technical examination to determine their suitability for re-use or retreading. Such tyres may have been rejected due to age or tyre carcass damage or deterioration beyond certain limits. The recovery and eventual final disposal should take place in an appropriate collection system. According to the assessment made by each country, the lawful execution of these applications may vary. The management of end of life tyres depends very much on local economic and industrial conditions.

## 1.4 End of life tyres valorisation

The valorisation process is done by means of materials recovery or as energy source. The tyre can be used entirely, grounded or in granules. In the last two cases rubber, metal and fibber should be separated.

Some applications via components separation are as filler or base in artificial grass fields, security floors and playpens, ornamental uses or bitumen modification for motorways construction. Filler or base in artificial grass fields is one common tyre valorisation. It represents less maintenance and water consumption of the fields versus natural grass. The ground tyre can be used as a filler of the synthetic fibber or as a base of the field. An average of the used size is between 0.5 and 2.5mm, although it depends of the technical characteristics. On the other hand and due to UNE-EN1177, playpens and old people homes have to be built from high impact and weathering resistance materials. Therefore ground tyre rubber suits perfectly in this application. The ground tyre rubber size used for these applications is between 2 and 8mm. Ornamental use is another application where green areas or roundabouts can be decorated with coloured and thick ground tyre rubber (size between 12 and 25mm). Some of its advantages are easy application, security (elasticity), low maintenance and null degradability. Finally, bitumen modification for motorways construction is an application that provides noise reduction, better car adhesion to the pavement, high crack resistance, long life and low maintenance.

Tyres valorisation without components separation has been the technique for tyre recycling with a major increase in Spain. The end of life tyres to be used for civil applications must be carefully selected and must complain the ASTM 6270-98 regarding particle distribution and steel content. U.S. has been using tyres for this purpose from long time ago. Some of the applications are: drain drenches, embankment filler, drain layers for landfills, etc…

End of life tyres as energy recovery represents an alternative to fuel, with the same energy as coal but with lower percentages of sulphur. The net calorific value of a tyre is between 32 and 34MJ/kg. A ton of tyres is equivalent to a ton of good quality coal or 0.7ton of fuel oil. It is therefore, an excellent potential as a fuel, which is not surprising since tyres are mainly composed of oil products. They can be used as dedicated fuel electric in power stations or cement kilns. The combustion of a tyre, like the combustion of any hydrocarbon, produces principally carbon dioxide, water, plus inert residues. The sulphur content of tyres (approximately of 1%), is comparable to a low sulphur content or very low sulphur content fuel oil, and therefore, the level of the sulphur dioxide is as low as there other fuels. An environmentally friendly technique free of hazardous emissions was developed to generate valuable fuels or chemicals from waste tyres. The process involves breakdown of the rubber materials by selective oxidation decoupling of C-C, C-S and S-S bonds by water as a solvent or near its supercritical condition *[Lee 1996]*. During 2006, 19 tons were used in Spain as combustible in cement kilns and 2.7 tons for electric power stations.

## 1.5 Ground tyre rubber processes

The sales income of a tyre recycling plant depends on the quality of the output material and the price itself of the efficiency of the process. The modern plants have a three-stage process. Firstly, a pre-shredding process is done by a rotary shear to transform the complete car and truck tyres (up to a diameter of 1.4meters) to hand-sized pieces of tyres (shreds). Afterwards, a granulating line turns these shreds into pure granules using granulators and cutting mills. The tyre pieces are granulated in several stages to a grain size between 0 to 0.7mm, from 0.7 to 2mm and from 2 to 4mm. After every stage the steel is separated using magnets, whilst the remaining textile (fluffs) is normally extracted by suction. The last step comes the elaborate dividing and cleaning process where the highest quality standards has to be guaranteed in the end product. Granule purity levels must be around 99.99% free of steel wire and textile fluff.

The fine grinding of granules can be done in two different ways. The materials obtained from each of them have widely different properties. In the cryogenic process also called cold grinding, the rubber or granule is cooled with liquid nitrogen, making it very brittle. The rubber breaks apart like glass during the shredding process. This makes it possible to achieve very small grain sizes with low mechanical effort, meaning with little motor power. High prices for nitrogen liquid makes increasingly difficult to operate such plants economically. The other method is the rubber ground at room temperature. The process itself works like the cryogenic process with a turbo mill at the shredding stage, only without the addition of nitrogen. The granulate size is consequently larger than that achieved with cold grinding. Of course, the process is also cheaper; however, the consistency of the output material is also different. Therefore, cryogenic processing systems do offer an advantage over ambient processing systems. The cryogenically frozen rubber pulverizes much more easily than rubber at ambient temperatures, requiring less power to produce the final product of the same size. There is, however, a trade-off to the advantage of ambient systems. This is the cost of the liquid nitrogen which is obviously needed in a cryogenic system.

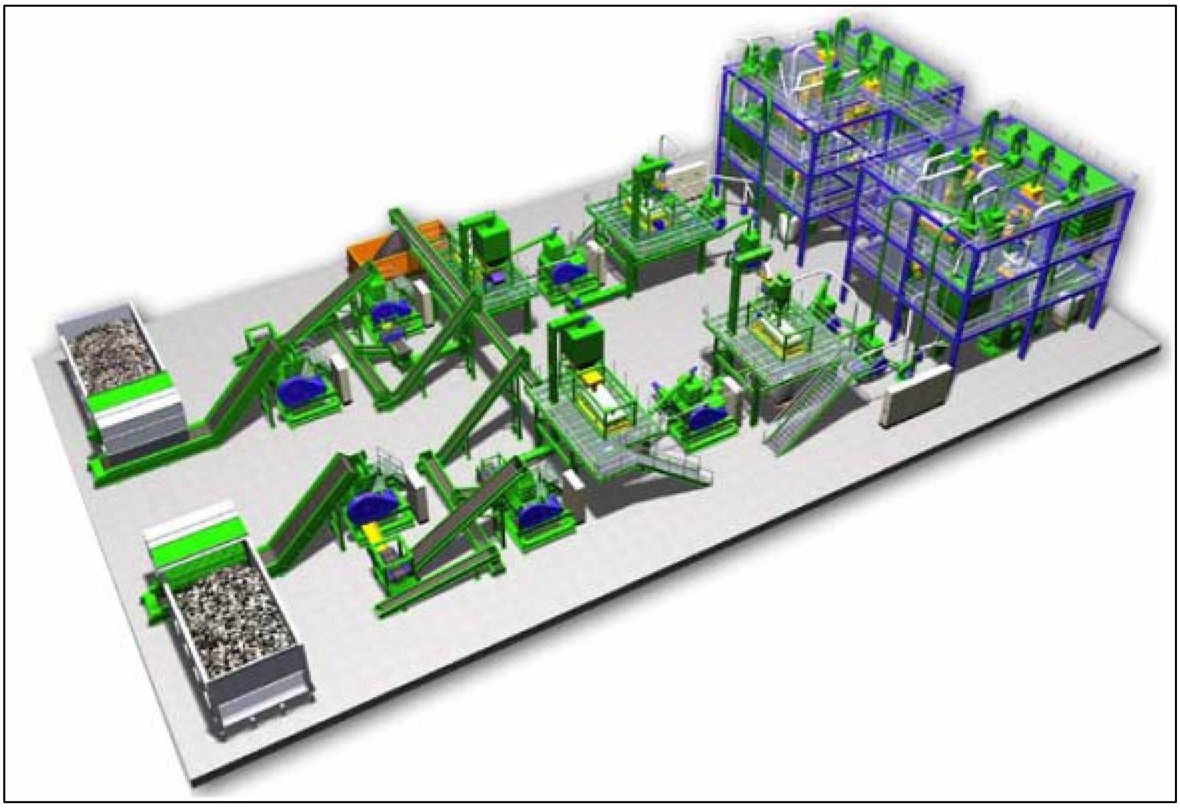


*Figure 1.3:* Granulating line *[MEWA 2007]*

### 1.6 Quality of ground tyre rubber

The granulated rubber has to comply with specific chemical and physical properties including the maximum allowed concentration of fibbers and metals. ASTM D 5603 is the standard classification for rubber compounding that characterizes the recycled vulcanizated particulate rubber. According to this standard, recycled particulate rubber are classified in bases of the feed stock and sieve analysis. The main quality properties for ground tyre rubber are the amount of steel and textile (contamination) and the particle size distribution. However, ASTM D 5603 does not inform about the physical properties and the grinding process. For this reason, surface appearance, rough or flat, is determined by microscopy most of the times. On the other hand, particle size distribution is usually determined by ASTM D 5644 in mm or mesh. Chemical composition is normally determined by ASTM D 297 (acetone extract and ash content), ASTM E 1131 (rubber content), ASTM D 1278 (heat loss), ASTM E 1131 (carbon black content) and ASTM D 3452 (natural/synthetic rubber composition).

### 1.7 Rubber reclamation of tyres

Reclaiming scrap rubber products is the conversion from a three dimensionally interlinked, insoluble and infusible strong thermoset polymer to a soft, plastic, tackier, low modulus, processable and vulcanizate essentially thermoplastic product *[Adhikari 2000]*. These reclaiming processes can be classified into physical and chemical.

In a physical reclaiming process, the rubber products are reclaimed with the help of external energy. The three dimensional network breaks down and the macromolecular rubber chain is transformed into small molecular weight fragments. The main physical reclaiming processes are: mechanical, thermo-mechanical, cryo-mechanical, microwave and ultrasonic.

The mechanical reclaiming process of crumb rubber takes place in an open two-roll mixing mill where the milling process is carried out at high temperatures. During the process, a drastic molecular weight breakdown takes place due to the mechanical shearing at high temperatures. One example is the Maxwell patent *[*Maxwell *1979]* where ground tyre is reclaimed with reclaiming agents (organic disulfides or mercaptans) by passing the rubber between a smooth stator and a cylindrical rotor arranged to provide an axial shear zone in which rubber is frictionally propelled by the rotor action.

The thermo-mechanical process consists on the degradation of the vulcanizate network by swelling the scrap rubber into a suitable solvent (aromatic and paraffinic hydrocarbon solvents) and then is transferred to a mill to form a finer powder (around 20μm) *[Harshaft 1972]*.

The cryomechanical process was developed in the middle of 1960s. This method has been widely described already in *section 1.5.* The problem is that the method only reduces the size of the ground tyre rubber particles and the reclaiming process is very weak. The process consist on placing small pieces of vulcanized rubber into liquid nitrogen which are transferred to a ball mill and ground in the presence of liquid nitrogen to form fine powder from 150 to 600μm. The main problem of this method is its elevated cost.

A controlled dose of microwave energy at specified frequency and energy level is used to cleave the C-C bonds in the microwave technique *[Makrov 1991] [Novothy 1978]*. Thus in this process elastomer waste can be reclaimed, without depolymerization, to a material capable of being recompounded and revulcanizated having physical properties essentially equivalent to the original vulcanizate. This is an economical and ecological method. Microwave energy between 915 and 2.450MHz is sufficient to break all crosslinking bonds but insufficient for polymer chain degradation. Therefore, the material is not degraded and this is an advantage versus the other processes being practised.

The last method included in the mechanical reclaiming processes is the ultrasonic method. This devulcanization process requires high energy to break the carbon-sulphur and sulphur-sulphur bonds *[Warner 1994]*. *[Yushanov 1998]* made a percolation simulation of the ground rubber tyre network degradation. They found that the experimental data and the predicted values were very close. The degree of devulcanization was characterized by the measurement of the crosslinking density and gel fraction of the devulcanized ground tyre rubber. It was reported that both crosslink density and the gel fraction decrease in the devulcanization process. For ground tyre rubber the measured gel fraction is 83% and the crosslink density of gel is 0.21kmol/m$^3$, but after ultrasound treatment at 121ºC barrel temperature it reduces to 64-65% with crosslink density of 0.02kmol/m$^3$.

On the other hand, chemical reclaiming is a growing process used for reclaim rubbers manufacturers. The reclaiming agents are generally disulfides or mercaptans exclusively selected to work at high temperature. Since 1910 so many chemical reclaiming agents have been developed for natural and synthetic rubbers, such as diphenyl disulfide, dibenzyl disulfide, diamyl disulfide *[Elgin 1949] [*Sverdrup 1949], bis(alcoxy aryl) disulfides *[Howland 1949],* butyl mercaptan and thiophenolS *[Elgin 1948]*, xylene thiols *[Gibbons 1946]* and phenols sulphides and disulphides.

The recent developments in reclaiming of rubbers have been by biotechnological processes. Biological attack of natural rubber latex is quite facile. As soon as the natural rubber polymer is converted into technical material by sulphur and numerous other ingredients, biological attack is minimized. The microbial devulcanization of particles surfaces was investigated by Loffer *et. al. [Loffler 1993],* in order to increase the possibility of producing high quality rubber products containing a larger percentage of recycled rubber. In a typical process, rubber powder (mainly SBR for old tyres) with 1.6% of sulphur content was treated with different species of Thiobacillus, T. ferrooxidans, T. thiooxidans, T. thioparus in shake flasks and in laboratory reactor. The sulphur oxidation was particle size dependant. The best results were obtained with T. thioparus with a particle size of 100-200µm. At the end, 4.7% of the total sulphur of the rubber powder was oxidised to sulphate within 40 days.

## 1.8 End of life tyres management

Nowadays, within the EU members, there are three different systems for managing end of life tyres:

- Producer responsibility
- Tax system
- Free market system

For producer’s responsibility, the law defines the legal framework and assigns to them (manufacturers and importers) the responsibility to organise the management chain of end of life tyres. This led to the setting-up of a non for profit company financed by tyre producers aiming at managing collection and recovery of end of life tyres through the most economical solutions. A reporting obligation towards the national authorities provides reliable traceability. For the end user, this system guarantees transparency of costs through a visible contribution, clearly indicated on the invoices. This system appears to be the most suitable and robust for resolving end of life tyre arising, in a sustainable manner for the long term and to achieve a 100% recovery rate in the most economical rate. On the whole, the tyre manufacturers have demonstrated a clear preference for this system and have deployed determination and commitment to take this route. Currently, the network includes 17 countries: Belgium, Czech Republic, Estonia, Finland, France, Greece, Hungary, Latvia, Lithuania, the Netherlands, Norway, Poland, Portugal, Romania, Spain, Sweden, and Turkey (Italy and other EU Members States are set to follow in the near future).

Under the tax system, each country is responsible for the recovery and recycling of the end of life tyres. It is financed by a tax levied on tyre production and subsequently passed on to the customer. This is an intermediate system whereby the producers pay a tax to the State, which is responsible overall for the organisation and remunerates the operators in the recovery chain. The countries that use this system nowadays are Denmark, Slovak Republic and Slovenia.

In the free market system, the legislation sets the objectives to be met but does not designate those responsible. In this way all the operators in the recovery chain contract under free market conditions and act in compliance with legislation. This may be backed up by voluntary cooperation between companies to promote best practices. The countries that follow this system are Austria, Bulgaria, Croatia, Germany, Ireland, Switzerland and United Kingdom.

## 1.9 End of life tyres management: situation in Spain

Signus Ecovalor is the Spanish responsible entity to promote recycled products based on reused tyres. Its activity started in October of 2006 with the aim to obey the Spanish law, RD 1619/2005, about end of life tyres management. Spain had one of the worst tyres recycling policies of the OECD. Only a very small amount of EOL tyres were corrected managed due to the lack of infrastructures. In the best case, tyres ended into landfill but the big majority, were buried or accumulated illegally *[Signus – annual report 2006].*

The EOL tyre valorisation in Spain increased to 145.536 tons in 2006. From this, 21.960 tons were used as energy source and the rest 145.536 tons, were used for different valued applications. RD 1619/2005 holds tyre's producers for the waste material after its use and establishes a waste management hierarchy which set priorities regarding what to do with the discarded tyres. In 2007, 213.542Tons of reused tyres were managed in Spain vs. 150.000Tons in 2005.

## 1.10 End of life tyres: volumes of recovery in Europe

Over 1 billion tyres are sold worldwide each year and subsequently just as many falls into the category of end of life (EOL) tyres. In 2006, about 3.23milions tonnes of used tyres were generated in Europe, of which 2.4 million tonnes were end of life tyres *[ETRMA 2006]*. Despite an increase in the service life of tyres, these volumes are constantly on the increase due to the growing number of vehicles and increasing worldwide traffic. Not surprisingly the largest volumes of arising are in the biggest countries (Germany, UK, France, Italy and Spain) where the totals vary between 300 and 600 thousand tons per annum *(see Figure 1.4).* Except Poland with 160 thousand tons, all the other countries have arising under 150 thousand tons per annum and 5 countries have 15 thousand tons or less. In 2006, 15 of EU 27 countries recovered 90% and more of their annual arising. 12 of the 15 countries recovered 100% while a further 2 attained between 80 and 90%. The remaining countries were under 77%. Countries where a producer responsibility system has been operating for over 10 years (e.g. Nordic countries) have recovery rates of 100% and stockpiles have been eliminated *[ETRMA 2007]*. Despite the heterogeneous nature of these rates, in 2006 the EU 27 had an average recovery rate of 87% while the figure for the EU 15 was 89%, which is quite favourable when compared with recovery rate of other sectors: 63.4% for papers *[CEPI 2007]*, and 47% for plastics in 2005 *[Plastics Europe Press 2007]*.

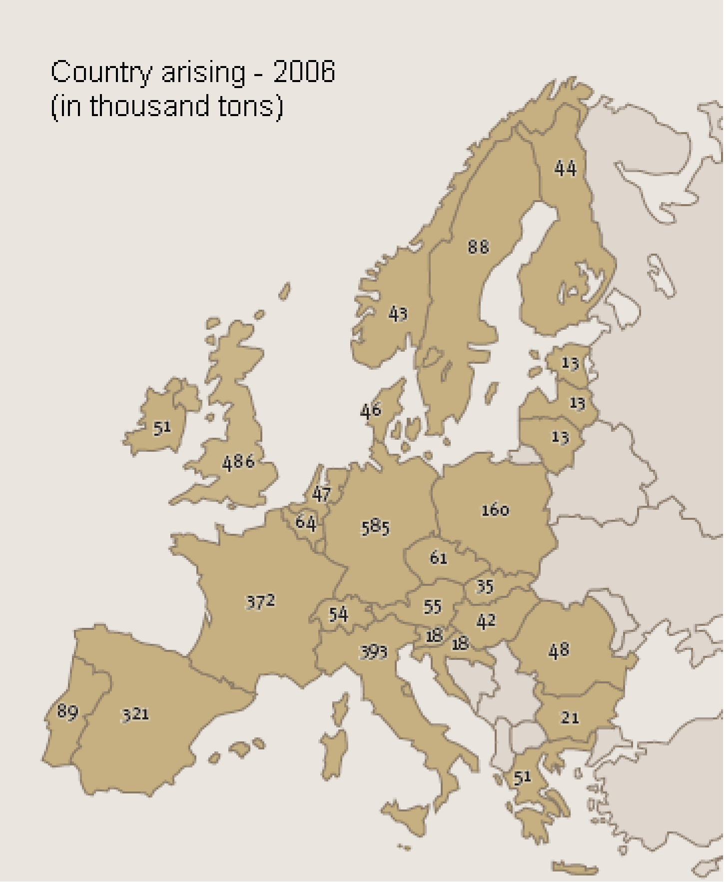


*Figure 1.4:* Volume of tyre per country in 2006 in thousand tons *[ETRMA 2007].*

### 1.11 Potential risks of end of life tyres to the environment

Despite the obvious stability of tyres, due to the fact that the different components of the rubber mixtures are trapped in the three-dimensional grid of the polymer, it is essential to ensure that tyres are not treated in a way that may cause harm to the environment.

The following leaching chemicals from tyres have to be taken into account *[MPCA 1990]*:

- Tyre samples exposed to acidic solutions leach higher concentrations of metals than those subjected to neutral or basic solutions.

- In neutral solutions (pH 7.0) tyre samples do not leach any contaminants of concern.

- Samples subjected to a pH of 3.5 produce leachate metal concentrations that exceed allowable limits for drinking water.

- Metals detected in the highest concentrations included barium, cadmium, chromium, lead, selenium and zinc.
- Soil samples taken from shredded tyre field sites displays constituent concentrations comparable to those in natural settings.

On the other hand, there are risks derived from tyres mismanagement. For example uncontrolled open air burning, which nowadays is completely banned. This technique is not environmentally acceptable. It can be released potentially hazardous levels of carbon monoxide and mono/polyaromatic hydrocarbon in the smoke plume. After open air burning, organic compounds, like pyrolytic oils, rest in the soil can cause environmental damages to the flora and fauna. Controlled stockpiling or landfilling are a risk too because under certain specifically defined climatic conditions waste tyre dumps or stockpiles can become the breeding grounds for insects, such as mosquitoes, which are capable of transmitting diseases to humans. This is of particular concern in tropical or sub-tropical regions *[Basel Convention 1999]*.

### 1.12 European legislation impact of tyre recycling

It started in 1975 with the Directive on Waste 75/442/EEC, amended by Directive 91/156/EC; End of life tyres were classified as “non hazardous waste”. In 1993, appeared the regulation on supervision and control of trans-border shipment of waste 259/93/EEC. But it is not until 1999 with the Directive on the landfill of waste 1999/31/EC, when was banned to stock used tyres (whole tyres) in landfills from July 2003 and shredded tyres from July 2006. In 2000, the European Waste List 2000/532/EC and further amendments stated that end of life were classified under code “16 01 03”. Also in year 2000, the Directive on Incineration of Waste 2000/76/EC fixed emissions standards for all cement kilns starting in 2002 and prohibited that older cement kilns burnt end of life tyres after 2008. Finally, in the year 2000 too, appeared the Directive on End of Life Vehicles (ELV) 2000/53/EC which stated that 85% of scrap cars had to be recovered starting in 2006 and tyres had to be dismantled from vehicles, increasing end of life tyres, to arise by 10%.

EU member states have to be in compliance with the EU legislation in transposing the Directives into local legislation. The members are free to set national initiatives to reach the EU targets. Regarding the development of waste management policies at national level, the landfill of waste Directives has been a major driver during the past decade. Tyre manufacturers are also facing growing environmental pressure from the general public and other stakeholders concerning illegal dumping and historic stockpiles. For all these reasons, it is in the interests of the tyre industry to continue being proactive and take responsibility collectively for end of life tyres treatment.

# Chapter 2:
# Research approach

*End of life tyres are a significant component of the overall plastics recycling challenge. Its recycling strategies are triggered by legislative actions since landfilling is not an option anymore. With the fast accumulation of scrap tyres during the last two decades, increasing awareness of their potential hazard and continuous promotion of scrap rubber recycling from government and industries have lead to new application markets and technologies development. In this chapter the reasons for the difficulties to compatibilize ground tyre rubber with other polymeric materials are explained. The research justification, the objectives to be obtained and the structure of the thesis are also explained, and finally a summary on previous studies is surveyed.*

## 2.1 Ground tyre rubber as filler in other polymer materials

The difficulty in rubber recycling lies in the fact that rubber is a thermoset material and attempts to recycle it in a manner similar to plastics often leads to non desired results. The need for fillers in polymer composites is one area that has the potential to use large volumes of discarded tyres. Ground tyre rubber in low particle size would be a good option for this application. Although, the lack of adhesion of ground tyre rubber with the rest of polymers make this practise not possible.

From now on, the explanations will be focused on mixtures of ground tyre rubber with thermoplastic matrixes as they are larger used for industrial and household applications. Thermoplastics properties make them an ideal material for moulding applications; moreover, they are 100% recyclable products.

## 2.2 Compatibilization of ground tyre rubber with thermoplastic matrixes

The adhesion of two materials is the sum of a number of mechanical, physical and chemical forces that overlap and influence one another. As it is not possible to separate these forces from one another, it is distinguished between mechanical interlocking and electrostatic forces. Mechanical anchoring is caused by penetration in the pores and uneven parts of the surface, while electrostatic forces are caused as regard of the difference in electronegativities of adhering materials and other adhesion mechanisms dealing with intermolecular and chemical bonding forces that occur at the interfaces of heterogeneous systems.

The mechanical interlocking theory of adhesion states that good adhesion occurs only when the polymer penetrates into the pores, holes and crevices and other irregularities of the adhered surface of a substrate, and locks mechanically to the substrate. The polymer must not only wet the substrate, but also have the right rheological properties to penetrate pores and openings in a reasonable time.

Composites made out of ground tyre rubber and other polymers would have good adhesion if the ground tyre rubber would have pores, holes, crevices or other irregularities, unfortunately they do not. In *Chapter 1, section 1.5* ground tyre processes were explained. It was explained that ground rubber obtained by the cryogenic and room temperature methods are quite different. Liu *et. al. [Liu 2000]* investigated the differences in properties using ambient and cryogenically ground tyre rubber, by preparing blends with 40% wt of ground tyre rubber and 60% of Polypropylene (some of them maleated). They could see that ground method do not affect the ultimate tensile strength. However, the ultimate elongation using room temperature ground tyre showed higher elongation capability than that of the cryogenic rubber, although elongation did not exceed 20% on either of the blends.

The higher elongational capability is explained in terms of the particle shape obtained from these two processes. The cryogenically ground rubber gives a flat fracture surface, while room temperature one has a multilobed morphology. On a microscopic level the flat surface has less surface area for the same particle size than a multilobed morphology. The increase in surface area and the possible mechanical interlocking between the rubber and the polypropylene matrix provides better adhesion and therefore more favourable ultimate elongation.

*Figure 2.1* shows that the major difference between particles of rubber generated by ambient and cryogenic processing systems is their shape. Particles derived from the cryogenic process have a smooth surface, akin to shattered glass while the particles derived from the ambient process have a rough surface, giving it greater surface area relative to the cryogenically produced particle *[Adhikari 2000]*. In later sections, it will be seen how the multilobed morphology of ambient ground tyre rubber is not enough for an acceptable mechanical adhesion.

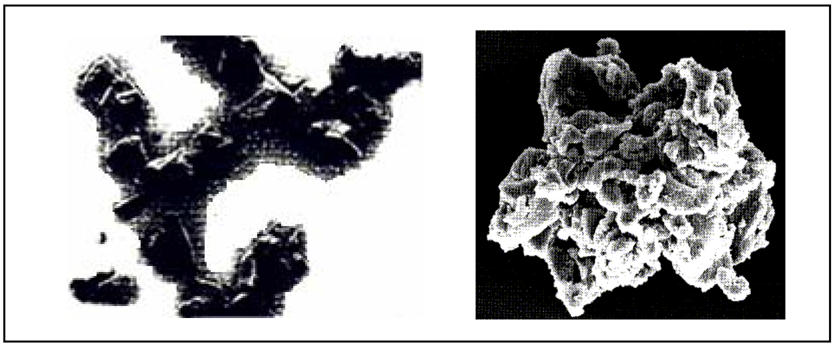


*Figure 2.1:* cryogenic ground rubber *[Burford 1982]* (x100 – left) and ambient ground rubber *[Erickson Materials]* (x325 right).

The other way to obtain good adhesion between two materials is based on the electrostatic theory of the difference in electonegativities of adhesing materials. Adhesive force is attributed to the transfer of electrons across the interface creating positive and negative charges that attract one another. As tyre formulations are complex mixtures all the different components have to be taken into account. Different rubbers and additives, such as oils, curatives, antioxidants, zinc stearate and other compounding materials can migrate onto the ground tyre rubber surface if they have a low molecular weight, and depending of their chemical nature, they can prevent adhesion or take part on the electrostatic adhesion. Interfacial strength (adhesion) is a critical parameter that not only depends of the ground tyre rubber surface chemical nature but also, the level and intensity of possible interface interactions. For this reason is necessary to have all possible tyre components into account.

The measure of surface energy is an easy method to foresee if the adhesion of two materials will be good or not. Lee *et. al. [Lee 2007]* used the measurement of contact angle as the method to evaluate the interfacial energy of GTR/PP blends with and without compatibilizers. The method consists on contact angle measurements of two or more liquids on the solid polymer surface. These liquids have known polar and dispersive components of surface tension. They used water and diiometahne for the investigation and the Owen-Wendt equation for analysis:

i) The surface tension is expressed as the sum of components due to dispersion forces ($\gamma^d$) and polar forces ($\gamma^p$)

$\gamma = \gamma^d + \gamma^p$ [1]

ii) The interfacial tension between the two phases (α) and (β) is expressed in terms of the two components of each phase:

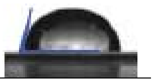
$\gamma_{\alpha\beta} = \gamma_\alpha + \gamma_\beta - 2\sqrt{\gamma_\alpha^d \gamma_\beta^d} - 2\sqrt{\gamma_\alpha^p \gamma_\beta^p}$ [2]

iii) In the case of a liquid drop forming a contact angle θ on a solid surface, the appropriate forms of *eq. [2]* can be combined with Young's equation to give:

$\gamma_L (\cos\theta + 1) = 2\sqrt{\gamma_S^d \gamma_L^d} - 2\sqrt{\gamma_S^p \gamma_L^p}$ [3]

$\gamma_L^d$ and $\gamma_L^p$ are to be found in the literature for the two chosen liquids (water and diiometahne) while $\gamma_S^d$ and $\gamma_s^p$ are the dispersion and polar components of the solid polymers.

The results were as follows:

| *Material* | *Total surface energy ($\gamma$ mJ/m$^2$)* | *Dispersive Component ($\gamma_S^d$ mJ/m$^2$)* | *Polar Component ($\gamma_S^p$ mJ/m$^2$)* | *Contact angle ($\theta$)* |
|---|---|---|---|---|
| Isotactic PP | 37.507 | 36.695 | 0.811 | 113º<br> |
| GTR/PP | 50.430 | 43.050 | 7.380 | 75º<br> |
| GTR/PP-g-MA/SEBS* | 54.040 | 43.530 | 10.510 | 63º<br> |

* SEBS: styrene-ethylene-buthylene-styrene

*Table 2.1* Contact angle measurements of Isotactic PP, neat mixture of GTR particles with PP and GTR with modified PP *[Lee 2007]*.

From the table it can be seen that the polar component of ground tyre rubber (7.380) is much higher than the one from the polypropylene (0.811). This is mainly due to the oxidation process of the ground tyre rubber (GTR) surface in contact with the oxygen from the air during the grinding and storage processes. The surface tension of polypropylene

(PP) is much lower than that of the GTR/PP blend. Therefore, the surface energy of the two materials is so different that made them totally incompatible with very poor adhesion between phases. On the other hand, the authors found that the blend containing GTR/PP-g-MA/SEBS had an increase in the polar component which means an enhancement of the specific interaction between the constituent polymers, or in other words, better adhesion.

It is important to mention too, that the highly crosslinked nature of the ground tyre rubber particles due to rubber vulcanization inhibits any molecular diffusion across the interface. Any possible interpenetration of phases is not possible, resulting in a very poor chemical interlocking.

There is one more factor responsible of the lack for adhesion which is the large ground tyre rubber particles obtained by ambient ground processes. They generate in specimen testing that the stress in the middle of it has a large degree of triaxiality (x, y and z directions of stress), meaning a stronger tendency to increase the volume absorbing little energy and leading to a crack growth *[Paul 2000]*.

Summarizing what has been explained in this section, it can be stated that ground tyre rubber is a material of difficult compatibilization with thermoplastic matrixes due to the poor mechanical and chemical interlocking.

## 2.3 HDPE: properties and characteristics

Whether used in shopping bags, packaging materials, buckets, water pipers, gas mains, oil tanks, etc… HDPE (High Density Polyethylene) is present in day to day life applications. The worldwide demand for HDPE will grow by 4.4% to 31.3Mtons in 2009. The countries and regions primarily responsible for the growth will be: China (+8.5%), other Asian countries (+5%), Latin America (+5.9%), North America (+3.1%) and Europe (+2.8%) *[Merchant Research & Consulting]*.

Hollow articles made with blow moulding processes are the most important application areas for HDPE. China, where HDPE bottles were launched in 2005, has experienced the fastest growing market for rigid HDPE packaging. India and other heavily populated markets, where infrastructures will continue to be built up, expect to have an increase of HDPE pipes and cables conductors. On the other hand, HDPE is gaining PVC (poly vinyl chloride) market share for being an environmentally friendly material. For example, today, 85% of sealing foil is manufactured from HDPE *[Ceresana Research 2008].*

Chemical composition of HDPE is poly(methylene) with a predominantly linear structure. At least, one termination group of each chain contains a methyl group, and depending of the manufacturing method, the other end group is also a methyl or vinyl. Density of commercial HDPE can vary from 0.975 until 0.935g/cm$^3$, which reflects the percentage of crystalline and amorphous phase. If lower crystallinity is required, copolimerization with alpha-olefins in small amounts (less than 5%) can be done to the linear polymer backbone. At low temperature, the only stable local chain conformation of HDPE is the flat zig-zag with a length of the C-C bond of 0.154nm and a C-C-C bond angle of 112º *[Boening 1966]*. This chain conformation also prevails in the melt and solution. Its crystallization is very rapidly and articles like films, filaments, pipes and injection-moulded articles exhibit some degree of molecular and crystal orientation, which is developed spontaneously during melt flow or introduced by stretching *[Stain 1964]*.

HDPE exhibits a high chemical resistance. Its high crystallinity and low permeability to most chemicals reduce the reactivity of the solid polymer. It is stable to alkaline and salt solutions, oxidizing agents, organic acids, HCl, HF and concentrated $HNO_3$. For MW determination, aromatic hydrocarbons and their halogen substituted derivates are used for solution-viscosity data or GPC. On the other hand, HDPE is relatively stable to heat due to its high bond energy in C-C. However, about 290-300ºC in an inert medium starts the breakage and cross-linking of chains. Oxygen is quite aggressive to the C-H bond and at melt processing temperatures, between 200-300ºC, results in a reduction of MW due to the formation of oxygen-containing groups such as hydroxyl, carbonyl, aldehydes and ketones. Moulded HDPE articles exposed to sunlight and air are attacked over time especially at wavelengths less than 400nm. Photo oxidation results in the apparition of surface cracks, brittleness, yellowing and deterioration of mechanical and dielectrical properties. Light stabilizers should be added to the matrix to avoid such undesirable phenomena.

A wide range of HDPE exists depending of the final end-use properties: stiffness, gloss or clarity, impact, tear and chemical resistance, electrical insulation properties, moulding characteristics, tensile properties to name only a few. Forced elongation of an HDPE sample into a film or rod is accompanied by structural and mechanical changes. At low deformations (e.g. 0.5% of sample length), spherulites elongate elastically. Further strain results in a partial break of bridges between crystallites in lamellae, slippage of the lamellae and other irreversible mechanical changes. At the point called “yield point”, these transformations accumulate, causing a significant change in sample appearance. The area consisting of highly oriented bundles of polymer molecules is where the “neck” develops. With further elongation, the initial morphological structures (spherulites) are disassembled and the growth of the oriented polymer area continues in the neck, causing a further strain. As a result, the sample elongates at nearly constant stress until all material in the samples becomes highly oriented. Subsequently, the oriented structure adsorbs additional small strain at increased stress and finally breaks. This ultimate stress is defined as the tensile strength. *Figure 2.2* shows an idealized strain-stress curve for HDPE *[Herman 2004]*.

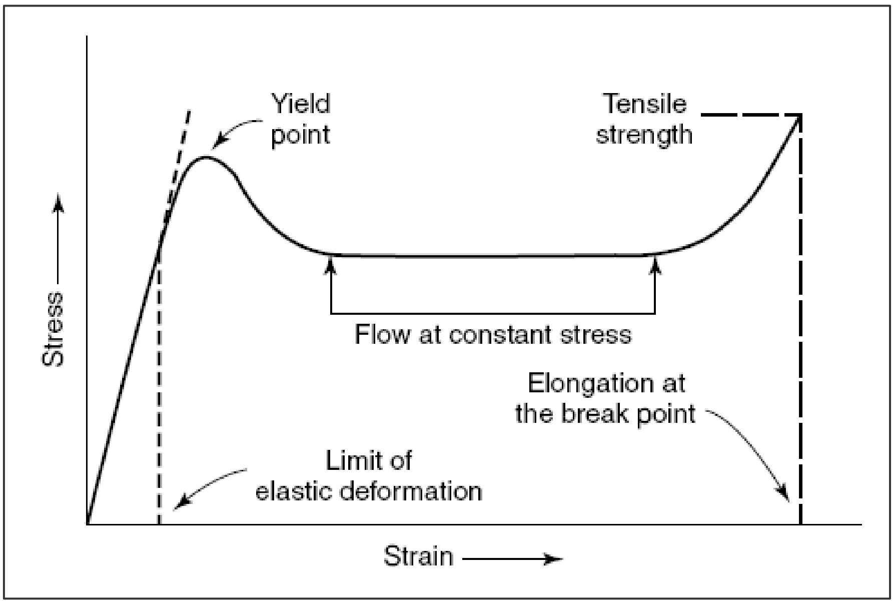


*Figure 2.2* Idealized stress-train curve for HDPE *[Herman 2004]*.

HDPE is an important injection moulding material. Uses include industrial containers, cases, pails, food tubs, containers, closures and caps, housewares, toys and a multiplicity of other applications. One large application area is that of milk bottles and other foodstuffs, household chemicals, personal toiletries and drug packaging. These take about 70% of the blow moulding market. Another substantial use area for HDPE is pipe production *[Brydson 1999].* This uses include domestic water and gas piping, agricultural piping and, on a smaller scale ink tubes for ball point pens. Its excellent electrical insulation properties have led to extensive use in cable and other wire-covering applications. One particular trend is the increasing use of crosslinked polyethylene for this usage improving heat resistance and better resistance to stress cracking.

HDPE is one of the largest used commodity thermoplastic for industrial and household applications, its mechanical properties makes of it an ideal material for moulding applications products, moreover it is a 100% recyclable material. All of these characteristics make HDPE a very interesting material and was chosen as the thermoplastic polymer to work in the present thesis. Therefore, HDPE will be used as thermoplastic matrix in all the different compatibilization studies with ground tyre rubber. A standard commercial HDPE for injection moulding will be chosen. Although, HDPE toughened with GTR is a very attractive idea for up-cycling applications, it is fraught with a number of difficulties that will have to be overcome during the development of the thesis.

## 2.4 Toughening HDPE with elastomers

For the majority of applications HDPE is a tough polymer that doesn't need further toughening. Nevertheless, there are numerous of applications under extreme conditions of strain rate and/or temperature for which its toughness needs to be substantially increased *[Bartczak 1999].* One way to increase toughness of polyethylene is by simple alterations of its chemical structure *[Wu 1999]*, or another very common method is by blending it with rubbers (mostly with EPDM as rubber component). However, by adding rubber the tensile properties such as modulus and tensile strength decrease and, as more rubber is needed for the higher crystalline HDPE's, it is a question whether in the end a better balance of properties is obtained.

To understand the fracture properties of multiphase polymers, it is often useful to first investigate the deformation mechanisms under an applied uniaxial load. Generally speaking, poor interfacial strength (adhesion) leads to poor ductibility but not vice versa. Particle debonding from the matrix prior to yielding could lead to poor tensile strength and low failure strain. Conversely, interfacial strength that exceeds the yield stress of the second phase particles can give rise to good tensile strength but not necessarily high failure strain. How global deformation occurs depends not only on particle-matrix interfacial strength but also on the local failure (stress-strain) criteria, which are intrinsic functions of particle size, elastic modulus, volume fraction, debonding mechanism and testing conditions (e.g. strain rate and temperature). Debonding of large, second phase particles create critical-size flaws, resulting in premature failure. However, flaw formation is more likely to be suppressed as the particle size decreases *[Wong 1999]*.

The brittle-ductile transition of toughened polymers can be attributed to a competition between brittle behaviour characterized by a brittle strength governed by microstructural flaws and energy absorbing plastic response (both having different temperature and strain rate dependence). While the brittle strength ($\sigma_B$) of the material can be considered to be nearly temperature independent and flaw-governed, the plastic resistance (Y), characterizing the ductile response has substantial temperature and strain rate dependence. Therefore, for a given strain rate a ductile to brittle transition can be expected to occur at a temperature where Y rises above $\sigma_B$. This transition temperature increases with increasing strain rate due to the sensitivity of Y on strain rate. Moreover, while $\sigma_B$ relates to a tensile response, the plastic behaviour responds only to a critical level of the effective stress ($\sigma_e$). In the presence of sharp notches or cracks, individual stress components can be substantially augmented by a negative pressure present in the notch field, while the effective stress producing plastic flow remains equal to Y. This together with the fact that the elevation of Y itself, due to severe strain rate concentration around notches, will lead to marked increases in the brittle-ductile transition temperature. Consequently, when structural imperfections, such as notches, crack-like flaws or poorly adhering large foreign particles, are present in the material in higher size of 10μm, they will result in a brittle response of the material. However if the structural imperfections are well controlled and foreign particles are only in the submicron range, the brittle strength of polymers can be increased somewhat to suppress the ductile to brittle transition to lower temperatures. Thus, when the yield strength falls below the brittle strength and plastic response is initiated, it often results in neutralization of the effect of some of the imperfections by molecular alignment or texture development that can significantly elevate the fracture stress across the principal direction of extension *[Muratoglu 1995].*

Bartczak *et. al.[Bartczak 1999]* in their study of toughening HDPE with either EPDM or EOR particles of less than 1μm found the following conclusion: rubber toughened HDPE undergoes a brittle to tough transition when the thickness of the matrix ligaments between adjacent rubber particles become less than a critical dimension. This critical thickness does not depend on the type of rubber or its concentration, or the size of the rubber (always < 1μm), and it is exclusively the property of the polymer matrix alone. The critical matrix ligament thickness ($\Lambda_c$) found for HDPE is approximately 0.6μm.

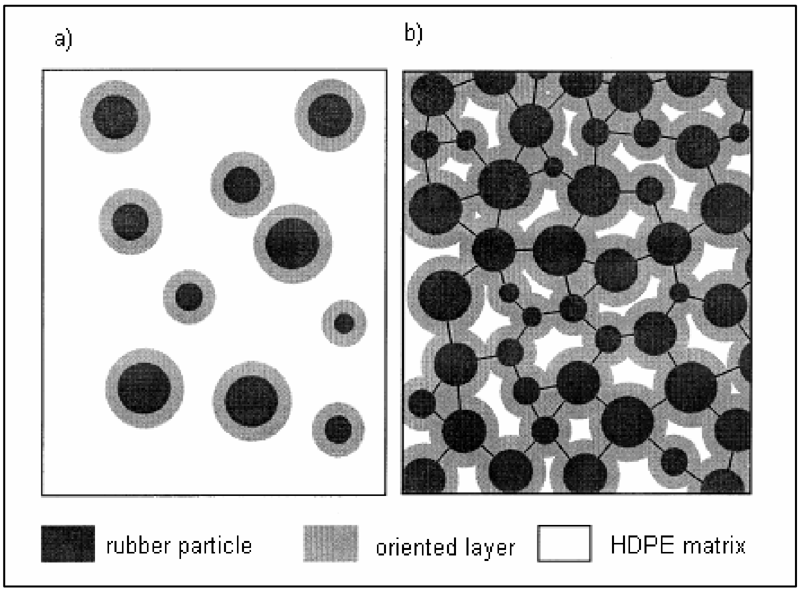


*Figure 2.3* Schematic representation of the layer of crystallites of preferred orientations: a) when ligament thickness is larger than twice the thickness of the oriented crystallization layer and material exhibits brittle behaviour; b) when ligament thickness is less than twice the thickness of the oriented crystallization layer around the particles and material with reduced plastic resistance percolates through the blend. The light grey represents the oriented layer of the matrix, while the connecting lines show the orientation of lamellae in interparticle ligament *[Ward 1983]*.

## 2.5 Research justification

Ground tyre rubber used as filler in a HDPE matrix would be an option to use large volumes of discarded tyres. On the other hand, it is foreseen that toughening HDPE with ground tyre rubber particles will not be easy. The initial constraints of the particle size that should be ideally < 1µm and actually it is 400-600µm size for standards ground tyre rubber particles and the poor interfacial strength between the two materials, clearly, are not the best conditions for this commitment.

Composites containing 5, 10, 20, 30 and 40% of ground tyre rubber particles mixed with HDPE were prepared in the laboratory. The mixtures were prepared in a two roll mill at 150-155ºC for 5min. Afterwards, the samples were pressed at 190ºC for 10min and cooled down for another 5min, refrigerated by water. The samples were properly shaped mechanically as testing specimens according to ASTM-D-412-98 specifications.

From *Figures 2.4 and 2.5*, it can be clearly seen that the more ground tyre rubber added, the more the decrease of the mechanical properties. As commented in *section 2.3* this is mainly due to the lack of adhesion with thermoplastic matrixes, the large particle size of the ground tyre rubber particles and its crosslinked nature. It is interesting to notice that elongation at break and toughness are very affected. With only 5% of GTR, elongation at break and toughness are reduced 94%. The low elongation at break is a direct consequence of the lack of adhesion between the two materials.

The results can be seen in the following two graphics:

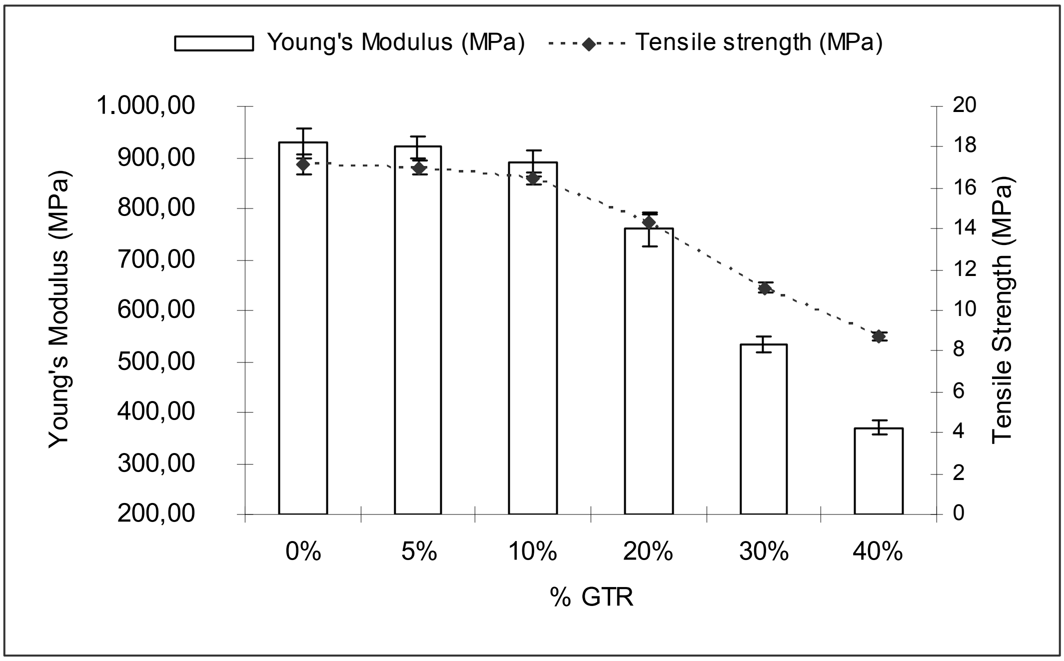


*Figure 2.4* Young’s modulus and tensile strength for HDPE/GTR composites containing 0, 5, 10, 20 and 40% of GTR.

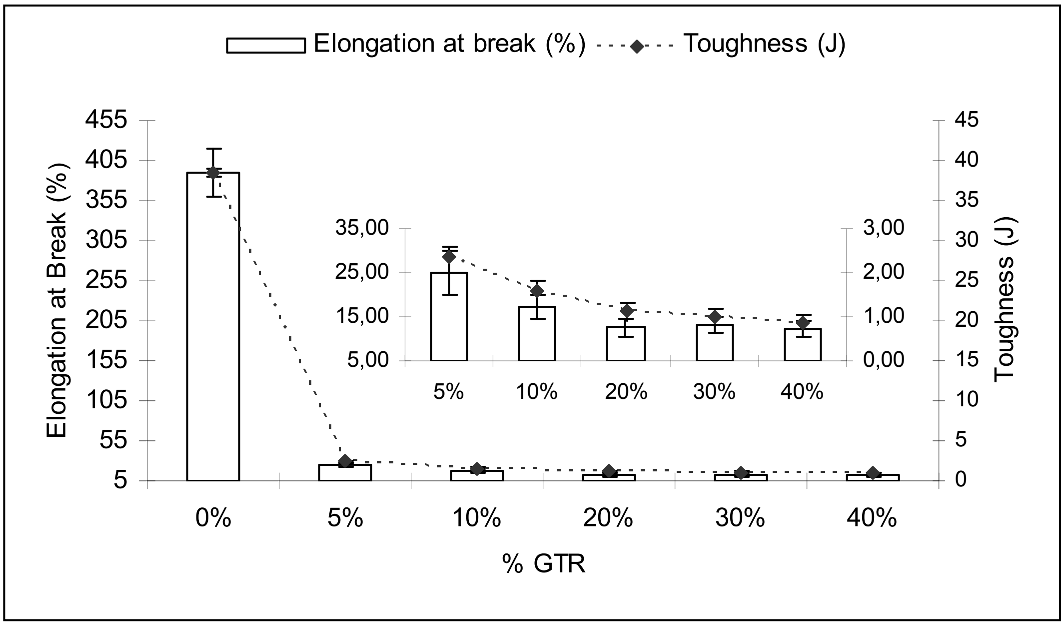


*Figure 2.5* Elongation at break and toughness for HDPE/GTR composites containing 0, 5, 10, 20 and 40% of GTR.

Therefore, the addition of ground tyre rubber into a HDPE matrix reduces its mechanical properties, and specially, elongation at break and toughness. It is also known that the lack of adhesion between the two materials is the main reason for the decrease, although, the large particle size of ground tyre rubber particles and its crosslinking nature are responsible too. The decrease of ground tyre rubber particle size is too expensive and not an option in the present thesis and de-vulcanization of ground tyre rubber (reclaimed) is an expensive technique too. However, this work is going to focus on exploring different methods to improve adhesion between the two materials.

## 2.6 Objectives of the thesis

1. Study the mechanical properties for the mixtures of HDPE and different amounts of ground tyre rubber. The results from the study show that the mechanical properties are very poor, especially elongation at break and toughness which are reduced 94% with only 5% of ground tyre rubber. These poor results are a consequence of the lack of adhesion between the two materials.

2. Study different methods to overcome the deleterious effects that the addition of ground tyre rubber particles have on HDPE.

3. Study the effect of an oxidising treatment on ground tyre rubber particles with acids. The acid treatment is expected to give roughness to the ground tyre rubber particles surface and improve mechanical interlocking adhesion. It is expected that the composites show higher stiffness than the composites without any treatment.

4. Study the effect of using waxes and wetting additives. These substances will be added into the mixture of ground tyre rubber and HDPE. Wetting additives act by means of their specific structures decreasing the interfacial tension between the two phases, on the other hand, waxes place themselves evenly between the ground tyre rubber particles and the HDPE matrix. In this method, it is expected to improve adhesion by means of adsorption (intermolecular contact) with the use of wetting additives and by means of matrix plasticization with the use of waxes.

5. Study the influence of the addition of a third component: EPDM. The addition of an elastomeric material will turn the HDPE/GTR composite into a thermoplastic elastomer (TPE) material. On the other hand, it is expected that it will provide an increase on the elongation at break and toughness due to its elastomeric nature. The addition of peroxides in order to vulcanize the EPDM and boost mechanical properties will be also studied.

6. The composites obtained by each method will be optimized regarding handling, difficulty on processing, cost and amount of GTR particles.

## 2.7 Structure of the thesis

The memory of the present thesis has been structured in six chapters.

The first chapter is focused on end of life tyres. The European directives and legislation, their management, their composition, their potential risk to the environment and nowadays ways of valorisation and rubber reclamation processes are the described points in this chapter.

Chapter 2 presents the justification for the thesis, the objectives that need to be fulfilled, the materials that will be used in each study and the characterization methods. Finally, there is a literature survey on previous studies based on ground tyre rubber with thermoplastic matrixes and the ones based on reclaimed tyre rubber (RTR).

Chapter 3 studies the effects of different particle size of ground tyre rubber pre-treated with different oxidizing acids and how this treatment influences the final HDPE/GTR properties. An understanding of the effect that acids have on the ground tyre rubber surface and how can be adhesion improved is aimed at. A detailed characterization of the composites and optimization of different particle size is also given in this chapter.

Chapter 4 includes an extensive study of the main properties bestowed by wetting additives and waxes in the composites, in order to improve adhesion. A characterization and optimization of several proposed composites are described.

The use of thermoplastics elastomers (TPE) has significantly increased since they were first produced fifty years ago. In Chapter 5 a proposal for production of thermoplastic elastomers containing ground tyre rubber is presented. The first part consists on a description of commercial TPEs and their features. A study of HDPE/GTR/EPDM composites, with TPOs characteristics is described in the second part. And as third and last part, a study of thermoplastic vulcanized (TPVs) based on HDPE, GTR, EPDM and the mixture of two peroxides is done. Mechanical, thermal and morphological characterization of the different composites is surveyed.

Finally, Chapter 6 summarizes the properties from each of the three different approaches to improve adhesion between HDPE and GTR. The properties from the composites obtained by each single method are compared. Finally, the best compatibilization method is discussed. Final conclusions of the thesis are included also in this chapter.

## 2.8 Materials

The basic materials used in the thesis are HDPE and ground tyre rubber. Those materials are described below. Other specific materials used in the different methods will be described in the corresponding chapter.

The high density polyethylene (HDPE) used as matrix was supplied by REPSOL-YPF (ALCUDIA® 4810-B), with a density of 960Kg/m$^3$. The HDPE was characterized by melt flow index ($MFI_{190/2.16}$) of 1.0g/10min, Young's modulus of 927.90MPa, tensile strength of 17.17MPa, elongation at break of 390.80% and toughness of 38.4J.

Two different suppliers provided the ground tyre rubber particles: Gestión Medioambiental de Neumáticos S.L. (GMN) in Maials (Lleida, Spain) and Alfredo Mesalles (Barcelona, Spain), both with a particle size average between 0.4 and 0.6mm.

## 2.9 General process for samples preparation

The general process for the composites preparation is as follows:

The mixing process for the HDPE with the ground tyre rubber particles was carried out in a two roll mill heated at 150-155ºC. The HDPE matrix is melted for a minute and then, the ground tyre rubber particles are added and mixed for another 5 minutes.

Composite sheets (150x150x2mm) were prepared by hot press moulding at 100kN and 170ºC for 10 minutes. After this step, the sample sheets are cooled for 5 minutes under pressure in the same press, by refrigerated water. The materials are afterwards properly shaped mechanically as test specimens according to ASTM-D-412-98 specifications.

All specific parameters applied on each compatibilization method are explained in the correspondent chapter.

## 2.10 Techniques used in the study

In this section will be described all the techniques used afterwards in all or in some of the studies. The different techniques comprises: mechanical properties, chemical characterization and thermal properties.

Mechanical properties are studied in order to determine the evolution of Young's modulus, tensile strength, elongation at break and toughness of the different composites. The tests are conducted in an Instron 3366 universal machine in accordance with ASTM D-638. The testing speed is 20mm/min, temperature of 23ºC ± 2ºC and a relative humidity of 50 ± 5%. The apparatus is fitted with an HRD automatic extensometer. The samples cross-sections are 6.1x2.0mm. Five replicate samples are analysed for each test and average and standard deviation percentages are calculated.

Shore A hardness is measured according to the ASTM D 1415 with a Teclock durometer. Three replicate samples are analysed for each test and five measurements are made of each sample. The hardness value is inversely related with the penetration of a standardized indenter in the rubber without causing its surface damage. Due to the rubber resilience the indenter penetration changes with time. Initial and after 60 seconds values are acquired.

As chemical characterization the fourier transformed infrared spectroscopy (FTIR-ATR) and the swelling degree are used.

A Nicolet 510M is used to obtain the attenuated reflectance IR spectra (FTIR-ATR). This technique allows the chemical characterization of the composites surface obtaining more information insight the chemistry and the reactivity involved.

The swelling ratio is determined using accurately weighed sample of about 0.5g of the composites. The samples are immersed in pure toluene at room temperature for 78 hours to allow the swelling to reach diffusion equilibrium. At the end of this period, the test piece is taken out and the adhered liquid is rapidly removed by blotting with filter paper. Afterwards the swollen weight is immediately measured. The swelling ratio is defined as:

$$R = (W_1-W_0)/W_0$$

Where $W_0$ is the weight of the test piece before swelling and $W_1$ is the weight of the swollen test piece after time (t) of immersion. The swelling ratio is a direct measurement of the degree of crosslinking.

In order to determine the thermal properties, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are used.

Thermal characterization is performed by means of thermogravimetric analysis (TGA) in a TGA851 Mettler Toledo unit. The samples are cut into pieces about 3 mg. The TG thermograms are obtained in the temperature range from 50 to 650ºC at a heating rate of 10 $^{\circ}$Cmin$^{-1}$. The experiments are carried out in air atmosphere.

The thermal behaviour of the composites is also analyzed using heat flow DSC. The measurements are made with a Mettler TA4000 thermoanalyser coupled with a DSC 30 apparatus. The sample mass is between 3.0 and 3.5 mg, which is low enough to avoid problems caused by heat and material transfer. Temperature and enthalpy is calibrated using In and Pb as standards. Samples are heated from 40 to 200ºC at a heating rate of 10 K/min using synthetic air as purging gas at a flow rate of 40 ml/min.

The morphological characterization is done by scanning electron microscope (SEM) technique and optical microscope.

The scanning electron microscope (SEM) is used to qualitatively study the fractured surface. The samples are examined with a JEOL JSM 6480 scanning electron microscope. Dry samples are coated with a thin layer of carbon before observation under the microscope, in order to increase the samples conductivity.

Finally, the optical microscope is the technique used to evaluate the dispersion of the ground tyre rubber particles in the HDPE matrix. A uniform dispersion of the particles would explain the enhancement of certain mechanical properties. The samples are cut into thin slices with a sharp blade and examined by a Jenaval optical microscope. Four samples of every test specimen are observed.

## 2.11 Previous studies of composites based on GTR and thermoplastic matrixes

Composites based on GTR and thermoplastics have not been deeply studied. Even so, some interesting and successful studies can be found in the literature.

Shojaei *et. al. [Shojaei 2007*] studied the behaviour of HDPE after degradation by re-extrusion. In order to improve the HDPE modulus and tensile strength, Polypropylene (PP) filled with 30 wt % of glass fibber was added. In addition, they studied the role of ground tyre rubber particles in the final product where they observed a lower stiffness due to its role (in that specific composite) as soft filler and an undesirable slightly increase in elongation. Unfortunately for them, ground tyre rubber did not produce any improvement on impact properties probably because of the low interfacial adhesion with the matrix phase. They finally concluded that the addition of ground tyre rubber particles into the final composition should be kept at low amounts (less than 10%wt).

Oliphant and Baker *[Oliphant 1993]* precoated the cryogenic ground tyre rubber (CGT) with ethylene acid acrylic copolymer and mixed it afterwards to LLDPE and HDPE matrixes. They found that the deleterious effects of the mixture could be overcome while still retaining composite processability. For example, a blend with 40 wt % with ethylene acid acrylic (EAA) coated CGT particles with LLDPE had an impact and tensile strengths of 90% compared with those of pure LLDPE. However, with HDPE they found very poor properties of the CGT/HDPE composites. This was believed to be because particles were too large to induce a brittle to ductile transition. The failure occurred largely through crack propagation, and the large CGT particles (even with moderate adhesion), acted as serious flaws, providing an easy path for the crack to follow. They concluded that the addition of CGT to a semi-brittle matrix such as HDPE, requires much higher levels of adhesion (to retard the crack growth at the particle/matrix interface), or much lower particle sizes.

Another way to modify adhesion between these two incompatible phases is via radiation. Sonnier *et. al. [Sonnier 2006]* studied the influence of $\gamma$ radiation on GTR/rHDPE (recycled) composites. Gamma irradiation allows achieving in situ compatibilisation, leading to an improvement of the mechanical properties. With irradiation doses of 25-50kGy the elongation at break and Charpy impact strength significantly increased. Only Young's modulus slightly decreased due to the fact that radiation induced also crosslinking of the rHDPE matrix.

The grafting of compatibilizers on ground tyre rubber surface is another method to improve compatibility. Fuhrmann and Karger-Kocsis *[Fuhrmann 1999] [Fuhrmann 2003]* functionalized ground tyre rubber with methacrylic acid and glycidyl methacrylate by photoiniciated polymerization. The process consists in UV radiation of ground tyre rubber in presence of air and afterwards a process of grafting compatibilization. The presence of reactive carboxy and epoxy groups was demonstrated. The idea behind these studies is the creation of polar functional groups on the ground tyre rubber surface that should result in increased reactivity and improved interfacial adhesion between the GTR and matrix polymers. Kim *et. al. [Kim 2000]* studied the mixture of HDPE filled with ground tyre rubber particles surface modified with acrylamide (AAm) using UV radiation. Ground tyre rubber particles and HDPE were extruded using a single-screw extruder and maleic anhydride-grafted polypropylene was added as a compatiblizer to improve adhesion between phases. They could see an improvement in tensile stress, strain and impact strength. Lee *et. al. [Lee 2007]* studied the effects of compatibilizers on GTR/PP composites using a co-rotating twin screw extruder. They observed that blends with small amounts of compatibilizers like SEBS-g-MA to the blends of ground tyre rubber and PP-g-MA had a considerable improve in adhesion. Coiai *et. al. [Coiai 2006]* studied the synthesis of polystyrene (PS) chains covalently bound to ground tyre rubber particles surface via free radical polymerization in situ by using azobisisobutyronitrile (AIBN) and dibenzoyl peroxide (BPO) as initiators. They state that graft polymerization provides a significant route to modify the physical and chemical properties of ground tyre rubber particles allowing the improvement of their compatibility with other polymers.

## 2.12 Previous studies of composites based on RTR and thermoplastic matrixes

Debapriya *et. al. [Debapriya 2006]* developed a new material based on virgin natural rubber (NR) and ground tyre rubber particles. They used a mechanochemical reclaiming method by tetra methyl thiuran disulphide (TMTD). The reclaimed tyre particles from this process (RTR) was blended and revulcanized with different proportion of virgin NR to produce new low-cost material product with useful properties (e.g. tyres). The process consisted in two simultaneous vulcanizations, one for the virgin NR and the other for the revulcanization of the partially devulcanized ground tyre rubber particles (even there was a co-vulcanization process for both of them). When the RTR was blended with fresh NR was found to reduce the tensile strength by about 7% with 20% of RTR and 46% with 60% of RTR. Moreover, they observed that the aging performances of the RTR containing vulcanizates are better than the control formulation, which does not contain any RTR.

Another very similar study from the one just mentioned was done by Sombatsompop and Kumnuantip *[Sombatsompop 2003]*. They made a thorough investigation about the rheology, the cure characteristics and the physical and mechanical properties of blends based on reclaimed tyre rubber (RTR) and two different grades of natural rubber (NR). The blend was vulcanized with sulphur. They found that when increasing the RTR amount the Mooney Plasticity (property taken to be proportional to the mean absolute viscosity of an elatomer *[Back 1947])* and shear viscosity increased but decreased with mastication time. They observed that the higher the molar mass of the NR, the higher the sensitivity to the change in compound viscosity due to mastication and RTR content. The hardness, heat build-up and the 100% modulus of the vulcanized rubbers were increased with the RTR content while tensile stress and elongation at break decreased. They finally suggested that the variations in the rheological and cure characteristics for the unvulcanized rubber were very much dependent on the molar mass of the NR whereas the mechanical properties for the vulcanized rubbers were influenced by the crosslink density.

An interesting work related to the aim of this thesis: mixture of ground tyre rubber particles with a thermoplastic matrix was done by Tantayanon and Juikham *[Tantayanon 2003]*, albeit they used reclaimed tyre rubber instead of ground tyre rubber. They blended RTR with polypropylene (PP). They used sulphur, maleic anhydre (MA) and dicumyl peroxide (DCP) as crosslinking agents. They made a comparison between the use of RTR and GTR and was found that RTR is much better in enhancing the impact strength. For them, the rubber chains of RTR can penetrate into the PP matrix much more easily than GTR promoting a better adhesion and higher impact strength of the blends. In addition, they found that all PP/RTR blends either crosslinked by sulphur or MA/DCP, showed higher impact strength than the ones GTR. The research also demonstrated that blends using MA/DCP exhibited even greater impact strength than that of blends that used sulphur. They concluded that RTR plays an important role in PP toughening by thorough dispersion into the PP matrix. Furthermore, during dynamic vulcanization the crosslinked rubber phase becomes finer and uniformly distributed into the PP matrix, thus attaining a stable morphology.

Recently, J. Karger-Kocsis and co-workers *[Grigoryeva 2005] [Lievana 2004]* used bitumen as the material to contribute the devulcanization of ground tyre rubber particles. Bitumen acts at the same time as a plasticizer and compatibiliser in thermoplastics blends. Bitumen may absorb and react with sulphur, during the melt processing acting as curing agent for the rubber compounds and also works as an effective compatibilizer for all the components in the blend. In their studies, they also added fresh rubber in order to encapsulate the GTR. They concluded that the reclaiming activity of bitumen on GTR depends on the temperature and storage time, as well as the compounding conditions. They results were very promising for further studies.

With all the collected information, it is obvious that adhesion of composites with thermoplastic matrixes and reclaimed tyre rubber particles (RTR) is much higher than those containing ground tyre rubber particles (GTR) and this is mainly because RTR is a partly devulcanized tyre rubber, in which the carbon-sulphur bonds that crosslink between the rubber chains have been ruptured. This fact allows the rubber chains of RTR to penetrate into the thermoplastic matrix much more easily than GTR, promoting a better adhesion and higher impact strength of the composites. However knowing in advance that this is a difficult task, the challenge of the present thesis is compatibilize GTR with the chosen thermoplastic matrix: HDPE. The main reason for that is the high cost of reclaimed tyres.

# Chapter 3:
# Oxidant treatment on GTR surface in order to improve composites compatibility

*Surface treatments are widely used to improve compatibility between two materials with low interfacial adhesion (UV or gamma irradiation, plasma or corona charge, etc…). Ground tyre rubber particles are made out of many raw materials and every tyre has been exposed to different weather conditions and handling, therefore after tyre grinding, its chemical nature can be very different. This is why the chosen surface treatment must change completely the whole surface area in one specific way. In this chapter is studied the chemical and physical modification of the reused tyre rubber particles by different chemical acids and how this modification influences adhesion between them and HDPE matrix.*

## 3.1 Previous studies of rubbers modified with acids

Rubber adhesion with the rest of polymers is a known problem. In chapter 2, *section 2.2*, was explained the reasons because ground tyre rubber particles are difficult to compatibilised with thermoplastic matrixes. It was mentioned also that electrostatic forces are caused as regard of the difference in electronegativities of adhering materials and due to other adhesion mechanisms dealing with intermolecular and chemical bonding forces that occur at the interfaces of heterogeneous systems.

It is worth to mention that intermolecular forces between two materials are matrix dependant. This means that if the matrix is a polar resin such as polyurethane or epoxy, it will be interesting to modify the ground tyre rubber surface with polar groups. On the other hand, if the matrix has an unpolar nature, such as thermoplastic matrixes, then will be interesting to not modify chemically the ground tyre rubber surface. In this later case, mechanical adhesion will be the better choice.

One clear example of rubber adhesion problem can be found in the polyurethane adhesives used to join rubber surfaces. The most frequent treatment there is the rubber surface halogenation’s which produces chemical and morphological surface modifications that enhance rubber adhesion. The better adhesion is obtained due to the surface heterogeneities creation which favours the mechanical interlocking of the adhesive on the rubber surface, the improvement of the chemical interaction via polar groups' creation and the increase of the surface energy when removing antiadherent compounds (paraffin wax and zinc stearate) from the rubber surface *[Pastor 1994]*.

*Romero et. al. [Romero 2001]* used trichloroisocyanuric acid (TCI) to chlorinate SBR. The final end-use of this study was also adhesives; therefore, some T-peel tests were performed and measured precisely to locate the joint failure. The effectiveness of the chlorination treatment is determined by factors, such as, the amount of chlorinating agent, time between the treatment and the adhesive application, formulation and components of the rubber, solvent used to apply the TCI on the rubbers, between others. In their study, they used TCI diluted in ethyl, propyl and butyl acetates. They found an influence of the solvent used to apply TCI. While propyl and butyl acetates in 0.5wt% TCI chlorinating solution makes the failure in the joint mainly cohesive, with ethyl acetate it was adhesional and cohesive.

Treatment with sulphuric acid can be used in rubbers as an alternative to halogenations with organic chlorine donors (e.g. TCI or chloramines) to improve its adhesion with other polymers. Most polymers that contain tertiary C-H bonds are suitable for sulfonation *[Erickson 1997]*. During sulfonation with sulphuric acid, the H of a C-H bond is removed and replaced by a $SO_3$ molecule, which is then halogenated to form sulfonic acid at the site of the attachment. The created sulfonic acid can be neutralized with ammonium in order to form more stable species, sometimes this is a key aspect to obtain an adequate adhesion performance. The neutralization using ammonia works extracting the H from the sulfonic acid moieties produced during the immersion of the rubber in the sulphuric acid and leaves and stabilized ion pair ($-C-SO_3^-NH_4^+$).

Returning to SBR and PU joints improvement, Cepeda *et. al. [Cepeda 2001]* studied also the influence of the styrene content of a SBR treated with sulphuric acid. It was observed that the lower the styrene content, the more significant modifications were produced on the surface, and consequently, showed the best adhesion in the T-peel test. In the ATR-IR analysis was observed severe modifications on the rubber surface. For example a strong absorption was seen in the 1200-1000cm$^{-1}$ range as an indicative of O=S=O stretching of the sulfonic acid, also the apparition of two bands at 1040 and 1167cm$^{-1}$ corresponding to the formation of sulfonic acid moieties, and finally, a new band at 1350cm$^{-1}$ due to O=S=O linkages that does not corresponds to sulfonic acid and may corresponds to a sulfonate ($-C-SO_2-OR-$). By SEM was seen how the treated sample with lower styrene showed big and deep cracks meaning a strong degradation after the treatment. Finally, it is important to mention that they observed a decrease in tensile strength and elongation at break after the treatment which corresponds to a hardening of the rubber surface.

Focusing now on surface modification of tyre wastes, some previously studies using surface treatment have been done. One example is its surface modification to be used as carbonaceous adsorbents. Having in mind that in tyre rubber, carbon black, is one of the most abundant components, the reuse of this waste can be used as a starting material for the aforesaid application. The idea behind is to treat tyre rubber surface tailoring its pore size distribution in the mesopore and macropore range trying to create them as large as possible to be used in the chemical industry, for example, in catalysis processes. These materials can accommodate a wide variety of host molecules, e.g., substances of pharmacological interest, which are much larger than those that can adsorb the traditional microporous zeolites *[Pérez 2003]*.

Therefore it is worth to mention two different studies made on this matter. In both works they use acids to create pores and roughness. One was made by Manchón *et. al. [Manchón 2004]*, where tyre rubber was first subjected to various heat (pyrolysis), chemical ($H_2SO_4$, $HNO_3$ and mixtures $H_2SO_4/HNO_3$) and combined treatments. The resultant products were characterised texturally. They found that tyre tuber is a nonporous material in all porosity ranges; this fact is one more reason of the incompatibility of tyres with the rest of polymeric materials. On the other hand, they concluded that the main porosity development occurred in the mesopore range for the heat treatment and in the macropore range for the chemical ones. The presence of $HNO_3$ in the used acid solution was determinant to create large pores in the material. On the other hand, Ariyadejwanich *et. al. [Ariyadejwanich 2003]* worked on preparing highly mesoporous activated carbons from waste tyres. They reproduced the conventional production process: carbonization followed by steam activation. However, when chars were acid treated (1M HCl) prior to steam activation, highly mesoporous activated carbons were obtained. Moreover, they found that acid treatment prior to steam activation could improve not only the mesoporosity but also the microporosity of the resulting activated carbons.

The influence of surface modified waste tyres used as cheap filler in Natural Rubber (NR) mixes was studied by Yehia *et al*. *[Yehia 2004].* The oxidant treatments were done by 30% of $H_2O_2$ and different concentrations of $HNO_3$ (10%, 20%, 30% and 60%). They observed that the tensile strength of the vulcanizates loaded with treated (20% of $HNO_3$ and 30% of $H_2O_2$) waste tyres, was improved when compared with the blend containing not treated ones. They attribute this improvement to the creation of new functional groups due to the chemical oxidation and their possible reactions. Up to 30phr of surface modified waste tyres could be safely used as filler together with HAF carbon black in NR formulations. The obtained vulcanizated had reasonable physicomechanical properties at this level of loading.

A group of investigators leaded by J. M. López Cuesta made a study using the same materials that are studied in this thesis: HDPE and GTR. In their study they tested different oxidation treatments: one wet process with potassium permanganate ($KMnO_4$) and, on the other hand, by $\gamma$-irradiation (dry process). Another special particularity of their study is that they added maleic anhydride grafted polyethylene (MAgPE) into the blend *[Sonnier 2006]*. The idea to use $KMnO_4$ comes from Liu *et. al. [Liu 2000] [Liu 2001]*. as he proposed $KMnO_4$ to break the unsaturated C=C bonds from EPDM rubber and to create hydroxyl groups. In the case of study, it was used to break the residual C=C bonds from the ground tyre rubber particles. Afterwards, the modified powder was incorporated into a polypropylene matrix containing a small amount of grafted maleic anhydride. The authors found a significant improvement on elongation at break while tensile strength remained constant. On the other hand, they performed the radiation method on ground tyre rubber particles due to its proven oxidation in other polymeric materials. Numerous studies show that the radiation energy can induce to macromolecular chain scission *[Sen 2003]* and some of the created free radicals can also recombine together to crosslink *[Banik 2000] [Lopitaux 2003]* or react with oxygen from the air to create polar groups *[Zaharescu 2001]*. Although the oxidation was proven by a specific wettability test (powder wettability meter) and FTIR spectroscopy, no significant improvement was seen for a better interfacial adhesion, in comparison with the HDPE/MAgPE/GTR blend without any previous oxidation treatment of the ground tyre rubber particles.

## 3.2 Expectations of acid treatment on ground tyre rubber particles

Sulphuric and nitric acids have been used previously to modify the rubber surface from tyre wastes resulting in a great porosity development as already commented. These results lead to consider the possibility of using the main features of the pre-treated oxidised rubber to improve the mechanical adhesion of GTR/HDPE composites. According to these previous results the chemical attack produced by the acid on surfaces creates an appropriate morphology to improve interlocking between matrix and the ground tyre rubber particles. On the other hand, it is worth to mention that acid treatments seem a financially worthwhile way to achieve a suitable material, due to the fact that their application does not require any specific equipment or complex technical processes.

In this chapter is studied the first method to improve adhesion between HDPE and ground tyre rubber. It consists on the use of various chemical acids, such as $H_2SO_4$, $HNO_3$ and a sulphuric-nitric solution (50/50% v/v), as ground tyre rubber surface modifiers. In addition, to elucidate the effect of particle size on mechanical properties of the blend, non-treated and treated ground tyre rubber particles of different sizes (<200µm, 200-400µm and 400-600µm) will be separated by sieving. The effect of the chemical and physical modifications on the ground tyre rubber particles surface and the effect of this modification on the composites performance will be monitored by determining its mechanical properties, by the use of FTIR-ATR spectroscopy, Calorimetric analysis (DSC) and SEM.

## 3.2 Experimental

The HDPE, the ground tyre rubber characteristics and the mixing process were already described in chapter 2 (*section 2.8 and 2.9 respectively*). Two different oxidant acids in aqueous solution were used: $H_2SO_4$ density, 50% v/v, $HNO_3$, 50% v/v of them. All chemicals were of analytical grade.

For each particle size category and GTR pretreatment four compositions have been studied: 5, 10, 20, and 40% weight of rubber. Above 40%, the blend was difficult to process and homogenize. A control untreated sample was also used as a reference.

The acid pre-treatments were carried out by immersion of the ground tyre rubber samples for 2 min in sulphuric acid (50% v/v), nitric acid (50% v/v), and sulphuric-nitric (50% v/v) solutions. The etching treatment was followed by reaction in air for 5 min, neutralization with 3M NaOH and rinsing the sample with distilled water at room temperature until pH 7. To ensure that no significative reduction of the particle size after the acid pre-treatment was produced, a new sieving of every size category was performed. The lost of material through the related mesh was >1% in every case.

## 3.3 Results

### 3.3.1 Mechanical properties

*Figures 3.1 to 3.4* show the results of the mechanical properties determined by tensile test. These mechanical properties were analyzed with percentage of ground tyre rubber particles content, chemical reused tyre pre-treatment and particle size category.

Tensile strength was found to decrease when increasing the tyre content. Acidic pre-treatments were found to increase the tensile strength in most of the cases when particle size is below 400μm. The effect of the acidic pre-treatment *[Cepeda 2000a] [Cepeda 2000b]* is related to the etching of the ground tyre rubber surface, the elimination of moieties and additives and the achievement of a microporous surface more suitable for mechanical adhesion. The acid pre-treated samples show similar behaviour, obtaining for the 50% sulphuric-nitric solution better results than the nitric or sulphuric acid pre-treatment, for the lowest particle size and highest ground tyre rubber content.

As expected, particle size plays an important role in tensile strength *[Cañavate 2005]*. A minor decrease of the tensile strength at high contents was obtained for small particle size category. The effect of particle size is clearly observed when comparing the three categories. Bigger particles provide a higher probability of failure cracks, whereas smaller particles may develop small microcracks with dimensions below the critical length. Quite obvious is the case of particles between 400 -600µm, showing a significant drop of the mechanical properties values for all studied cases. Also, the possibility of achieving a bigger particle size by conglomeration of particles during the process of blending should be considered. The agglomeration of particles would decrease the mechanical performance. However, the classification of particles may not be economically viable, since the increase of the blends properties is not worth the lost of tyre material that implies.

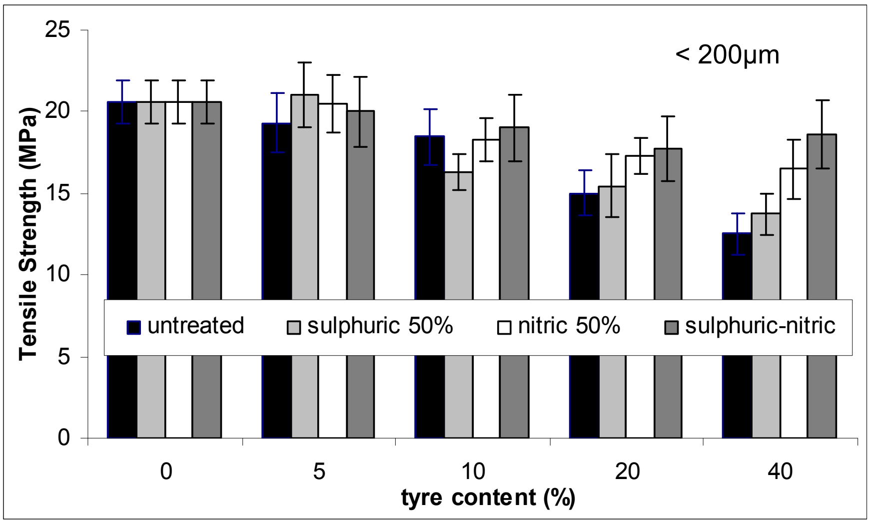


**Figure 3.1.** a) Tensile strength versus GTR content for untreated, treated with $H_2SO_4$ (50%), $HNO_3$ (50%), and $H_2SO_4$–$HNO_3$ (50%). The particle size of the GTR is below 200µm.

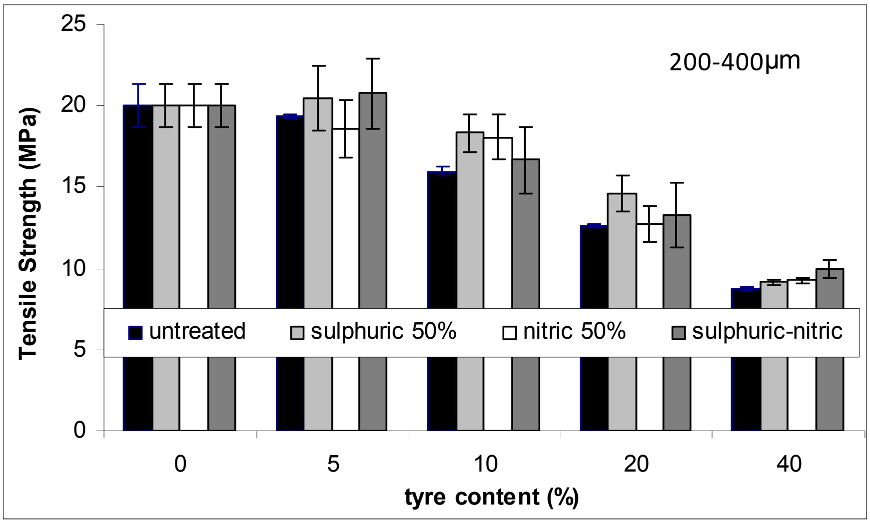


**Figure 3.1.** b) Tensile strength versus GTR content for untreated, treated with $H_2SO_4$ (50%), $HNO_3$ (50%), and $H_2SO_4$–$HNO_3$ (50%). The particle size of the GTR is between 200 and 400μm.

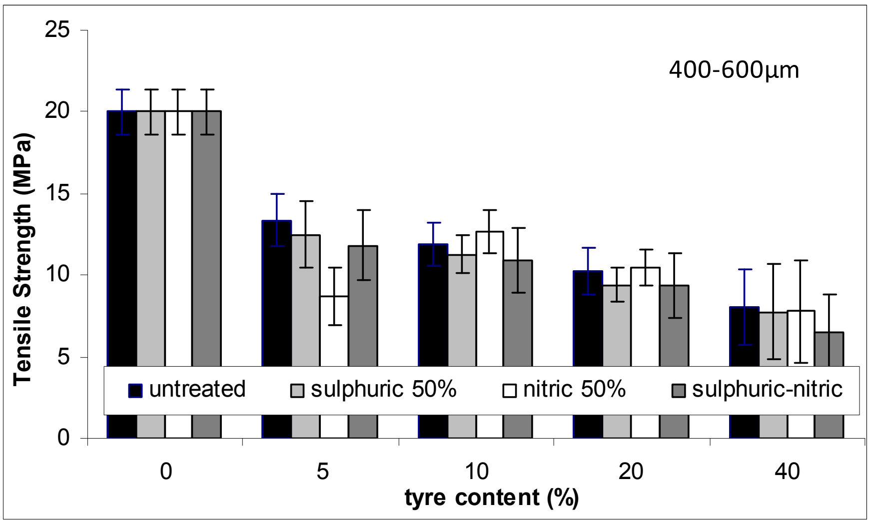


**Figure 3.1.** c) Tensile strength versus GTR content for untreated, treated with $H_2SO_4$ (50%), $HNO_3$ (50%), and $H_2SO_4$–$HNO_3$ (50%). The particle size of the GTR is between 400 and 600μm.

In addition, the effect of acids on tensile properties seems to be related to the particle size. It was observed that acid pre-treatments improve the composite tensile strength especially when the smaller particle size category was treated, whereas in particles with size between 400 and 600µm, the effect of the acid pre-treatment do not improve significantly the studied property. For example, the tensile strength was found to decrease about 25% (untreated) for compositions of 20% of ground tyre rubber when the particle size is below 200µm, meanwhile the same particle size pre-treated with sulfo-nitric blend (20% of GTR) showed only a decrease of 13%.

A significant decrease of tensile strength was observed for the composites with a ground tyre rubber amount higher than 10% w/w with particle size higher than 200µm. In case of particle size between 400 and 600µm, for a ground tyre rubber content of 5%, a 25% of decrease of tensile strength was resulted. Considering acid pre-treatments as a surface etching of the ground tyre rubber particles, the acid treatment effect is higher when increasing the surface area. In case of small particles, the increase of surface area allows a more extensive etching of the acid. At the same time, since the etching produced should be, in terms of depth, equivalent in all cases, the roughness relative to the particle size should be more important, improving the GTR/HDPE mechanical adhesion.

The composites with low ground tyre rubber content and particle size below 200µm, resulted in an increase (from 1 to 5%) of the stiffness (Young's modulus) compared with neat HDPE *(Figure 3.2.a)*. In this figure it can be seen that sulphuric-nitric treatment slightly reduces the stiffness versus neat HDPE at high ground tyre rubber amounts (20 and 40%). In contrast with other materials based on the addition of elastomers, the addition of high concentration of ground tyre rubber acts decreasing the deformation ability of the ductile and plastic HDPE matrix. Even without pre-treatment, it was observed that Young's modulus of the composites was higher than the original HDPE without ground tyre rubber, for blends with low ground tyre rubber amount (5%) and particle size comprised between 200 and 400 µm. When the content of the ground tyre rubber particles increases the poor interfacial adhesion causes a decreasing of the stiffness for similar reasons to the exposed when considering the tensile strength. Also, the decrease of the Young's modulus value is more drastic when using bigger particle size.

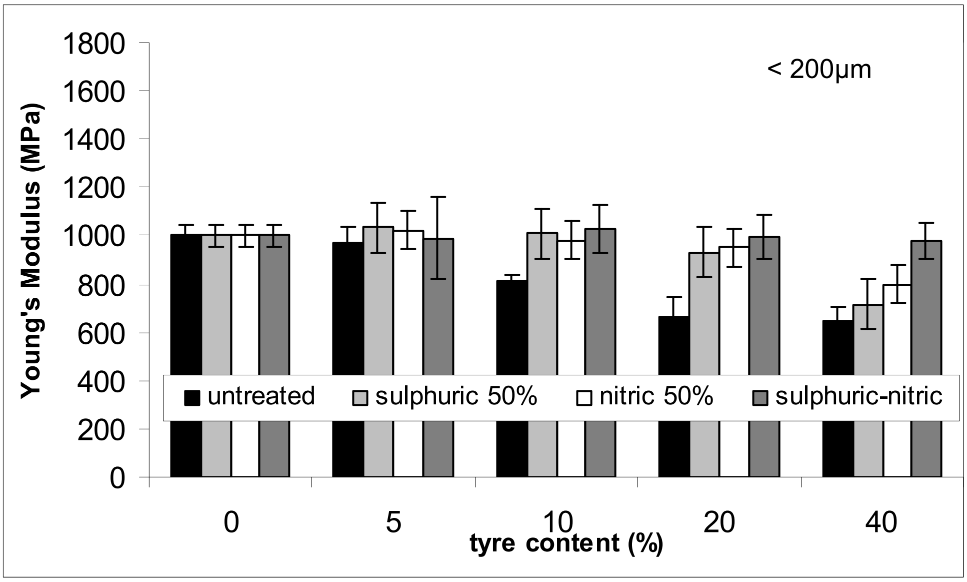


**Figure 3.2.** a) Young's modulus versus GTR content for untreated, treated with $H_2SO_4$ (50%), $HNO_3$ (50%), and $H_2SO_4$–$HNO_3$ (50%). The particle size of the GTR is below 200µm.

The effect of the acid pre-treatment on Young's modulus is clearly visible in *Figures 3.2.a, 3.2.b and 3.2.c*. The etching of the acid acts promoting mechanical adhesion, but also rigidizes the rubber by extracting the substances that may act as a plasticizer. The acid treated GTR particles have a rigid nature as it has been also observed in the studies by other authors *[Cepeda 2000a] [Cepeda 2000b]*. Then, ground tyre rubber obtained with previous acid etching are usually stiffer than not treated ones. The sulpho-nitric mixture seems to provide the best results, but in general all acids have an improving effect. As exposed previously for tensile strength blends properties, the effect of acid treatments in Young's modulus was higher when adding smaller particle size.

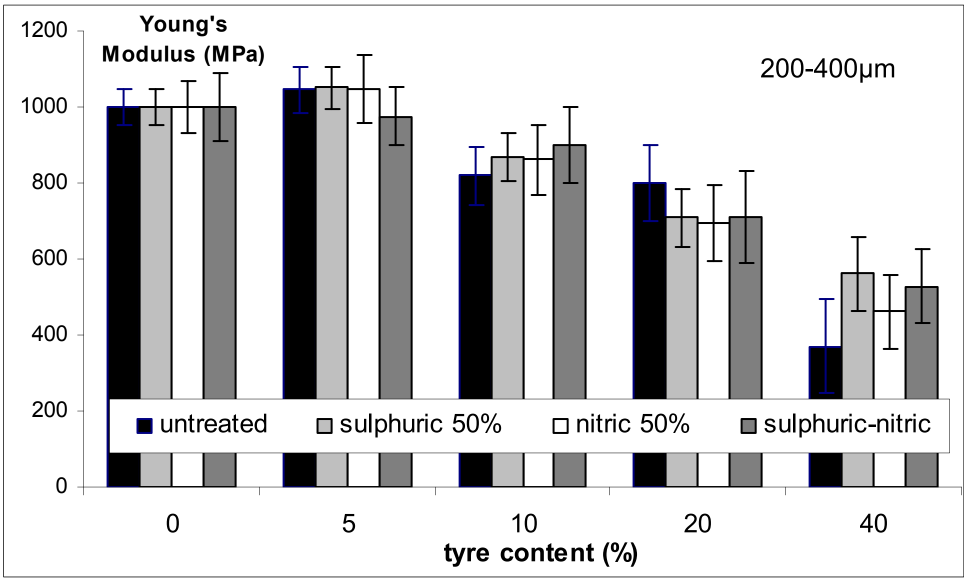


**Figure 3.2.** b) Young's modulus versus GTR content for untreated, treated with $H_2SO_4$ (50%), $HNO_3$ (50%), and $H_2SO_4$–$HNO_3$ (50%). The particle size of the GTR is below 200µm.

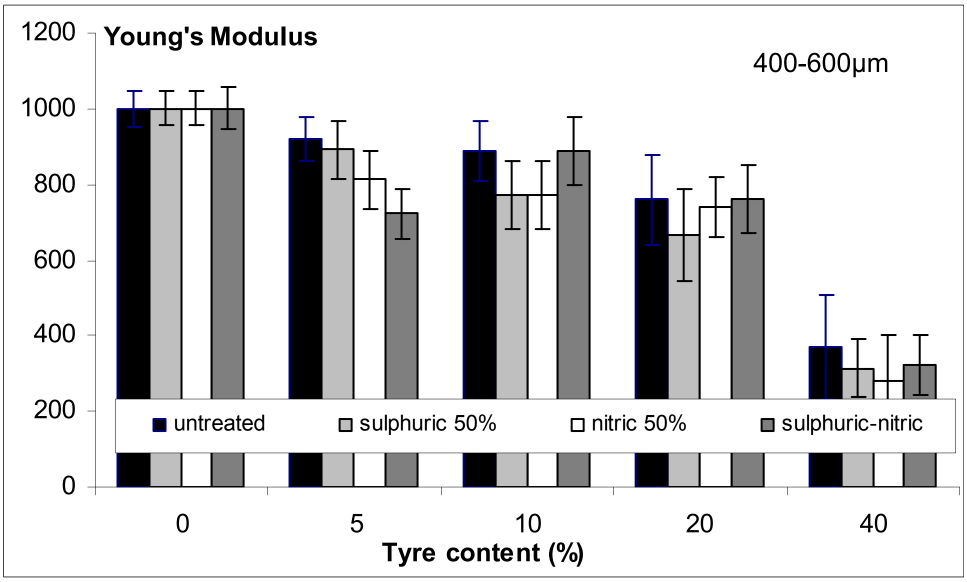


**Figure 3.2.** c) Young's modulus versus GTR content for untreated, treated with $H_2SO_4$ (50%), $HNO_3$ (50%), and $H_2SO_4$–$HNO_3$ (50%). The particle size of the GTR is between 400-600µm.

The addition of ground tyre rubber in all prepared composites produce a drastic fall of elongation at break (*Figures 3.3a, 3.3.b and 3.3.c*) and toughness (*Figures 3.4.a, 3.4.b and 3.4. c*). Toughness was calculated as the area under the load-displacement curve. Elongation at break and toughness for ground tyre rubber based composites show lower values than that of pure HDPE matrix, considerations about the particle size and type of pre-treatment are not relevant in that case. The decrease of elongation at break is related to the imperfect interfacial adhesion between components. The incidence of the poor adhesion between phases on this property is especially important. On the other hand, the compatibilizing effect achieved by the acid pre-treatments is counteracted by the increase of the stiffness of the rubber. As discussed previously, the extraction of additives, oligomers, or plasticizers of the ground tyre rubber particles by the acid produces a rigid material. The reduction of the ability of deformation of the rubber influences the decrease of elongation and subsequently the decrement of the toughness.

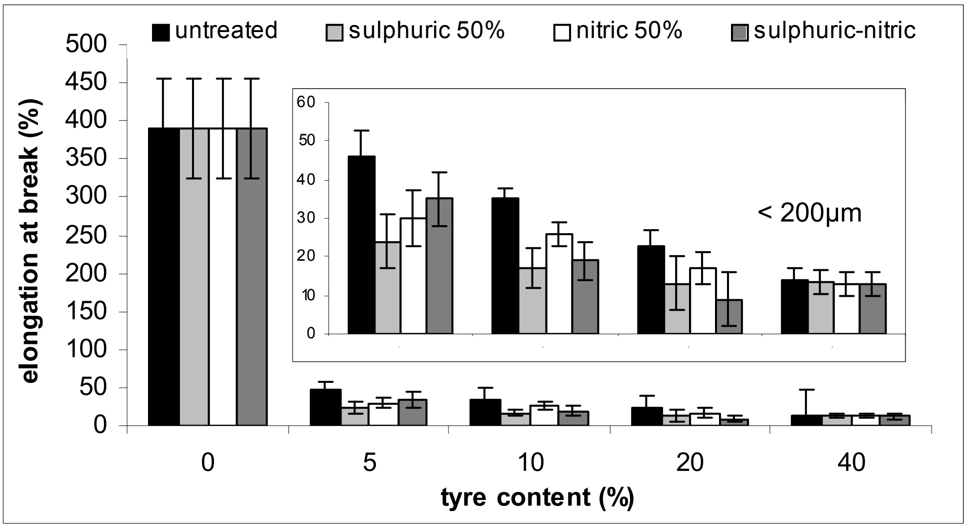


**Figure 3.3.** a) Elongation at break versus GTR content for untreated, treated with $H_2SO_4$ (50%), $HNO_3$ (50%), and $H_2SO_4$–$HNO_3$ (50%). The particle size of the GTR is below 200µm.

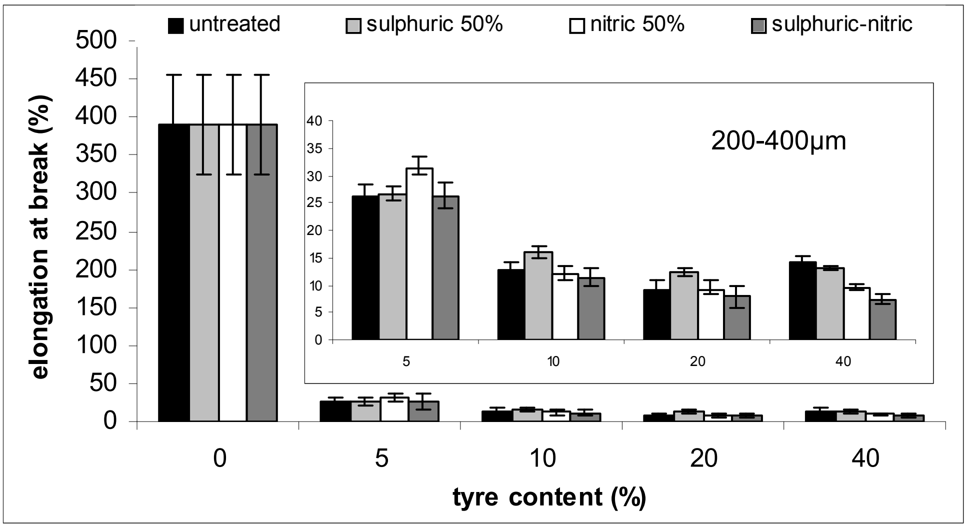


**Figure 3.3.** b) Elongation at break versus GTR content for untreated, treated with $H_2SO_4$ (50%), $HNO_3$ (50%), and $H_2SO_4$–$HNO_3$ (50%). The particle size of the GTR is between 200 and 400µm.

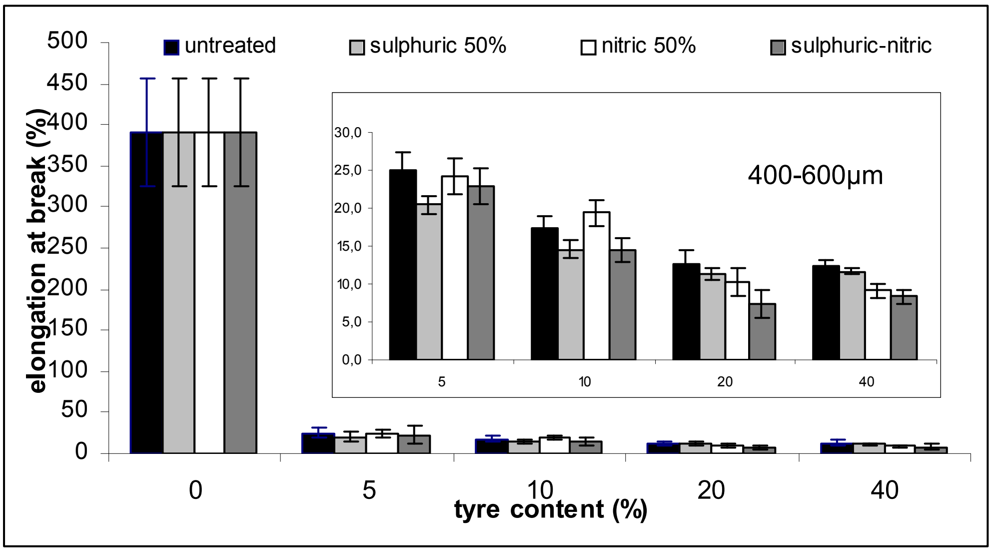


**Figure 3.3.** c) Elongation at break versus GTR content for untreated, treated with $H_2SO_4$ (50%), $HNO_3$ (50%), and $H_2SO_4$–$HNO_3$ (50%). The particle size of the GTR is between 400 and 600µm.

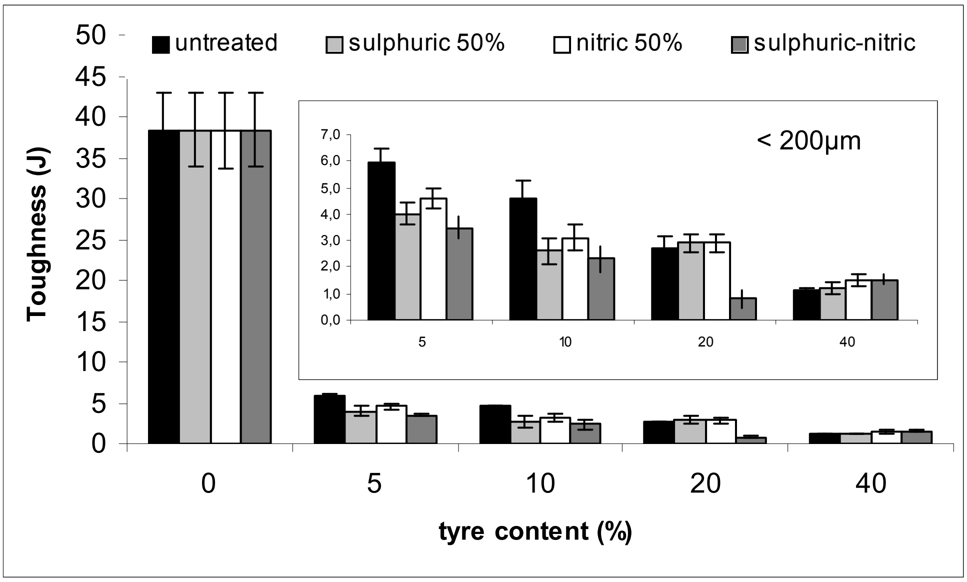


**Figure 3.4.** a) Toughness versus GTR content for untreated, treated with $H_2SO_4$ (50%), $HNO_3$ (50%), and $H_2SO_4$–$HNO_3$ (50%). The particle size of the GTR is below 200μm.

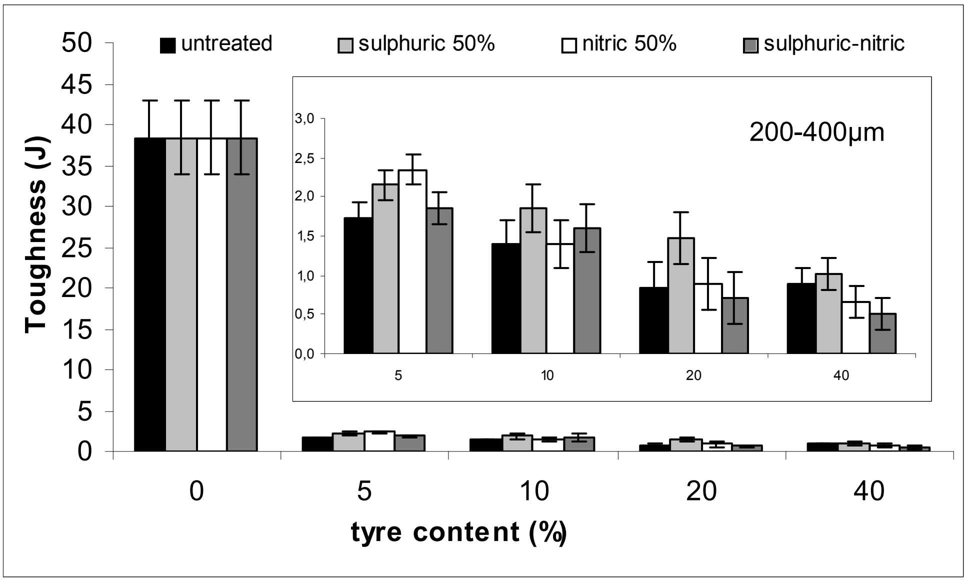


**Figure 3.4.** b) Toughness versus GTR content for untreated, treated with $H_2SO_4$ (50%), $HNO_3$ (50%), and $H_2SO_4$–$HNO_3$ (50%). The particle size of the GTR is between 200 and 400μm.

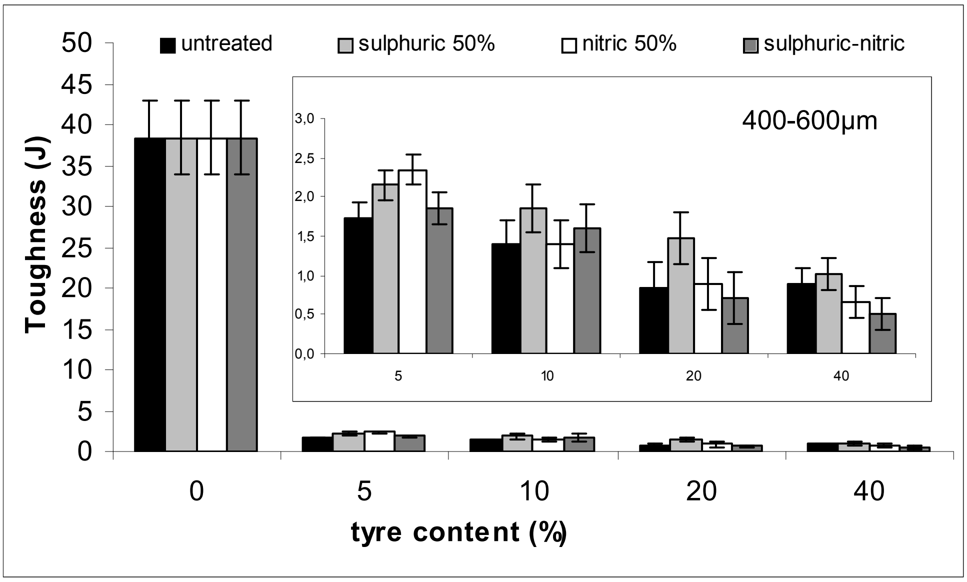


**Figure 3.4.** c) Toughness versus GTR content for untreated, treated with $H_2SO_4$ (50%), $HNO_3$ (50%), and $H_2SO_4$–$HNO_3$ (50%). The particle size of the GTR is between 400 and 600µm.

### 3.3.2 Spectroscopy study of surface treatment (FTIR-ATR)

Chemical changes produced by acid treatments on GTR particles were studied by means of FTIR-ATR spectroscopy. *Figure 3.5* shows a FTIR-ATR spectral area of 400-1800cm$^{-1}$ for the samples treated with $H_2SO_4$ and $HNO_3$ and compares these values to those for untreated ground tyre rubber particles.

To obtain this spectrum, it was chosen the band at 1026cm$^{-1}$ assigned to carbon black *[Delor 1998] [Cañavate 2000]* as a reference. The spectral analysis of untreated ground tyre rubber shows a weak band at 1739cm$^{-1}$ that is associated to the thermal oxidation that occurs as a result of the exposure of the surface to oxygen (specially during the grinding handling), and which induces the formation of an oxidation skin that includes carbonyl groups.

The strong band at 1640cm$^{-1}$ is associated to the C=C of polyisoprene, the weak band at 1540cm$^{-1}$ to zinc sterarate (an anti-adherent compound), bands at 1430cm$^{-1}$ with the scissoring vibrations of =$CH_2$ (on butadiene), the band at 875cm$^{-1}$ with the trans isopropenyl unit (-C($CH_3$)=CH-) and the band at 470cm$^{-1}$ with S-S *[ Coates 2000 ] [Smith 2004]*.

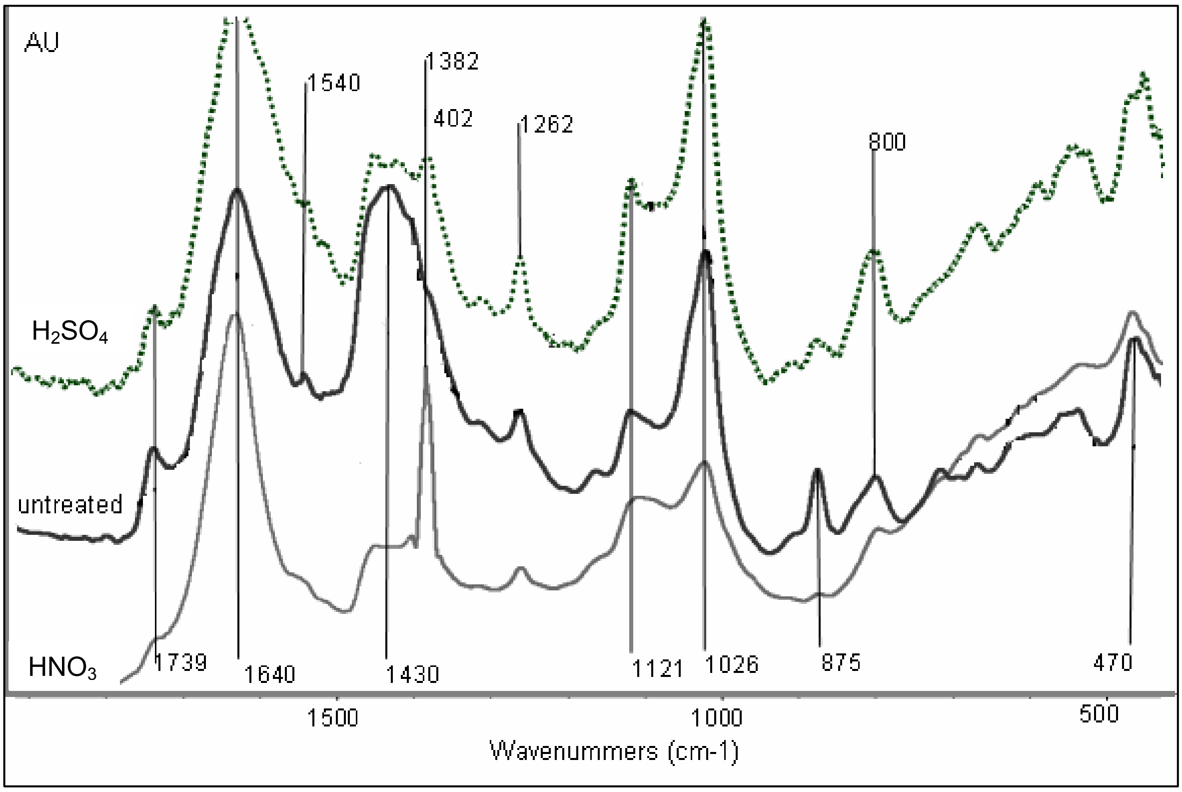


**Fig. 3.5** Spectra of GTR particles: 1) treated with $HNO_3$, 2) untreated and 3) treated with $H_2SO_4$.

The study shows that treating ground tyre rubber particles with sulphuric acid produces several chemical and degradative modifications on the tyre surface, mainly the formation of sulphonic acid, a decrease in double bonds (1640cm$^{-1}$) due to the degradation process of polybutadiene and other unsaturated components of the tyre, and a decrease in content in minor components. This phenomena may be related to the disappearance of the weak bands at 1739 and 1540cm$^{-1}$, the decreasing of bands at 1430 and 875cm$^{-1}$ and the appearance of new bands at 1402, 1121 and 618cm$^{-1}$, which is indicative of the O=S=O stretching of the absorptions of sulphonic acid. These results are in agreement with previous studies *[Cepeda 2000a] [Cepeda 2000b]*.

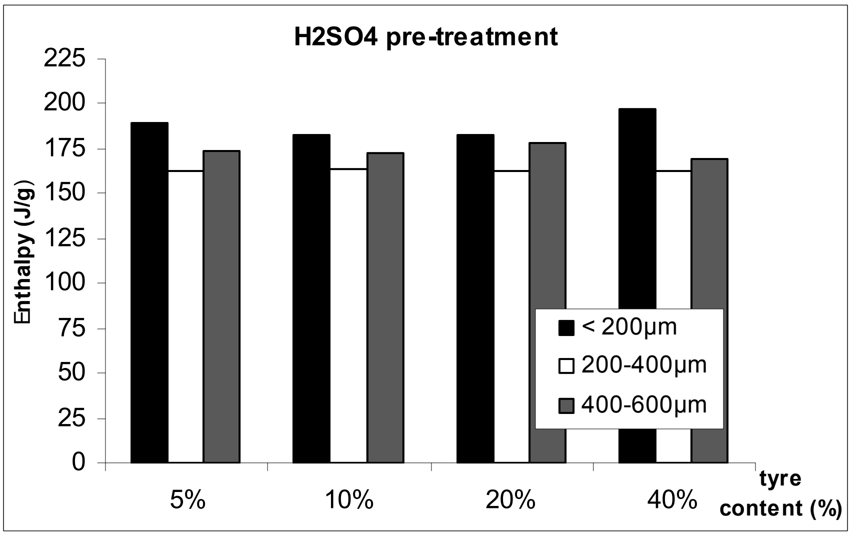
The treatment of ground tyre rubber particles with nitric acid shows similar results to the sulphuric acid treatment except for the sulphur-oxygen derivatives. As shown in *Figure 3.5*, spectra of samples exposed to nitric acid show a decrease of the same bands as those exposed to sulphuric acid (1739, 1640, 1540, 1430 and 875cm$^{-1}$), plus an increase of the band at 1382cm$^{-1}$ assigned to N-N=O *[Coates 2000]*. The bands assigned to O=S=O do not appear in this case.

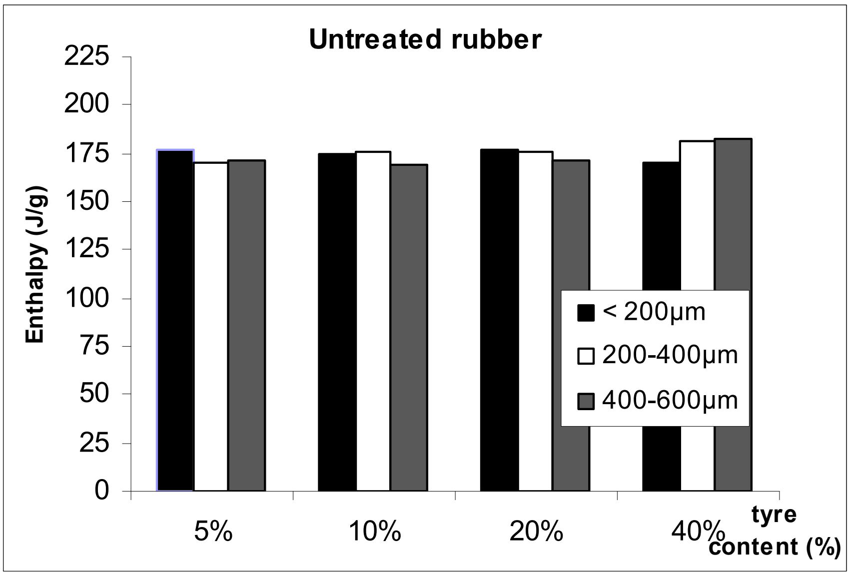
The observed chemical modifications agree with those presented in precious studies *[Figovslq 1996] [Dierkes 2003]*, sulphuric acid acts as a strong dehydrating substance that can take up hydrogen and oxygen from organic matter and cause carbonisation. $HNO_3$ is also a powerful oxidizing agent when used in concentrated solutions. They modify the surface of the material introducing sulphur and nitrogen surface groups as – $SO_3$ and – $NO_2$. There is also an increase of groups as O=S=O and C-$SO_2$-OR, a decrease of C-H and an increase of C=C.

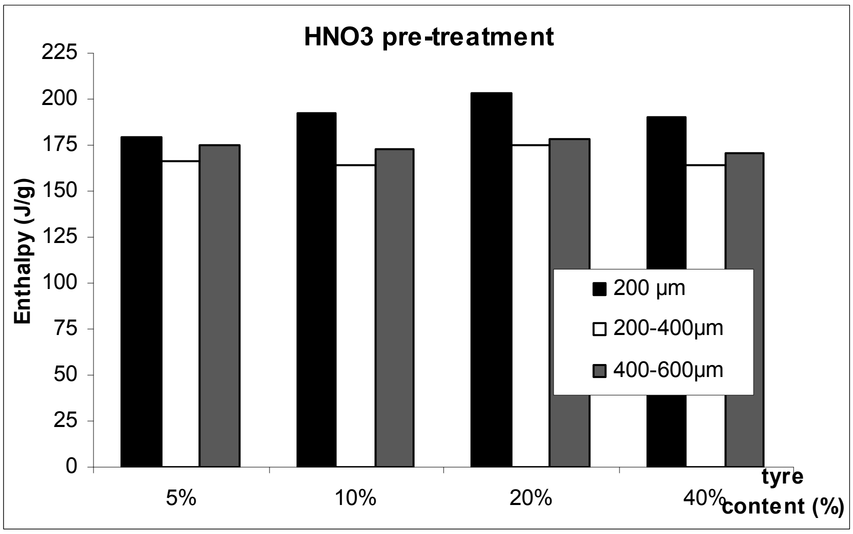
### 3.3.3 Calorimetric study of the samples

Calorimetry applied to the blends has been used as a tool to detect possible changes in crystallinity or microstructure of the matrix when adding a second component as reinforcement. By measuring the melting temperatures and the enthalpy of melting of the composites, such changes can be followed. The enthalpy and melting temperature of the samples are shown in *Figures 3.6 and 3.7*, respectively.

From the results obtained for enthalpy of the blends *Figure 3.6*, it is observed that the values remain approximately constant for all the blend compositions, regardless of the pre-treatment and particle size. That should be related to the poor interfacial adhesion between ground tyre rubber particles and HDPE matrix. Enthalpy tends to increase slightly for acid pre-treated ground tyre rubber particles for blends with the particles size below 200µm. In addition, the enthalpy of melting seems to increase when increasing the amount of the ground tyre rubber particles in the blends. This phenomenon is related to the nucleation effect of the ground tyre rubber particles in the interior of the HDPE during the preparation of the samples by melting. The small particles of ground tyre rubber act as nucleating agents increasing the compactness of the structure in their boundaries. The promotion of the crystallization results in an increase of melting enthalpy that is also related to the best performance in mechanical terms, such as tensile strength and Young's modulus.


H2SO4 pre-treatment
Enthalpy (J/g)
0
25
50
75
100
125
150
175
200
225
5%
10%
20%
40%
tyre content (%)
■ < 200μm
□ 200-400μm
▨ 400-600μm


Untreated rubber
Enthalpy (J/g)
0
25
50
75
100
125
150
175
200
225
5%
10%
20%
40%
tyre content (%)
■ < 200μm
□ 200-400μm
▨ 400-600μm


HNO3 pre-treatment
Enthalpy (J/g)
0
25
50
75
100
125
150
175
200
225
5%
10%
20%
40%
tyre content (%)
■ 200 μm
□ 200-400μm
▨ 400-600μm

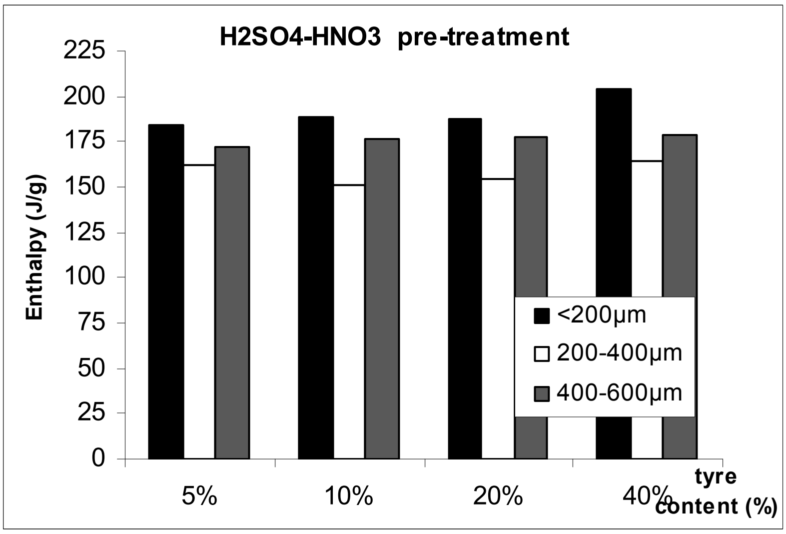
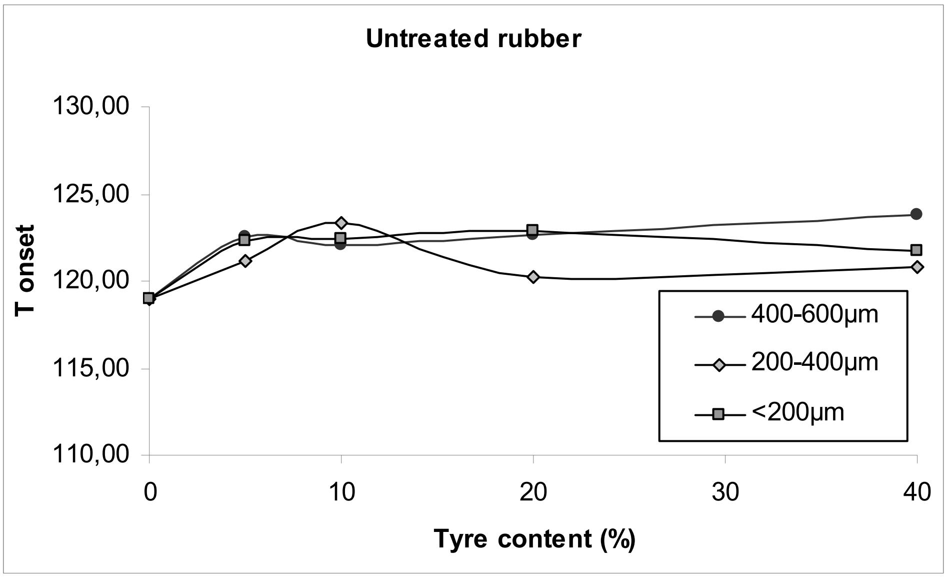


**Figure 3.6** Melting enthalpy versus content for untreated, treated with $H_2SO_4$ (50%), $HNO_3$(50%) and $H_2SO_4$-$HNO_3$ (50%). HDPE/GTR composites with several GTR particle size in microns.

Particle sizes above 200µm results always in a decrease of the enthalpy of melting. Big particles treated with acids become cracked, rough and pores where HDPE can enter in the process of melting. When the pore size is big enough, a significant amount of the HDPE in contact with the ground tyre rubber particles becomes affected this fractured surface being disturbed in the possibilities of forming a compact structure, promoting the amorphous state in this space close to the particle surface. The nucleation effect would not be present in this case because of the big size of the particles.



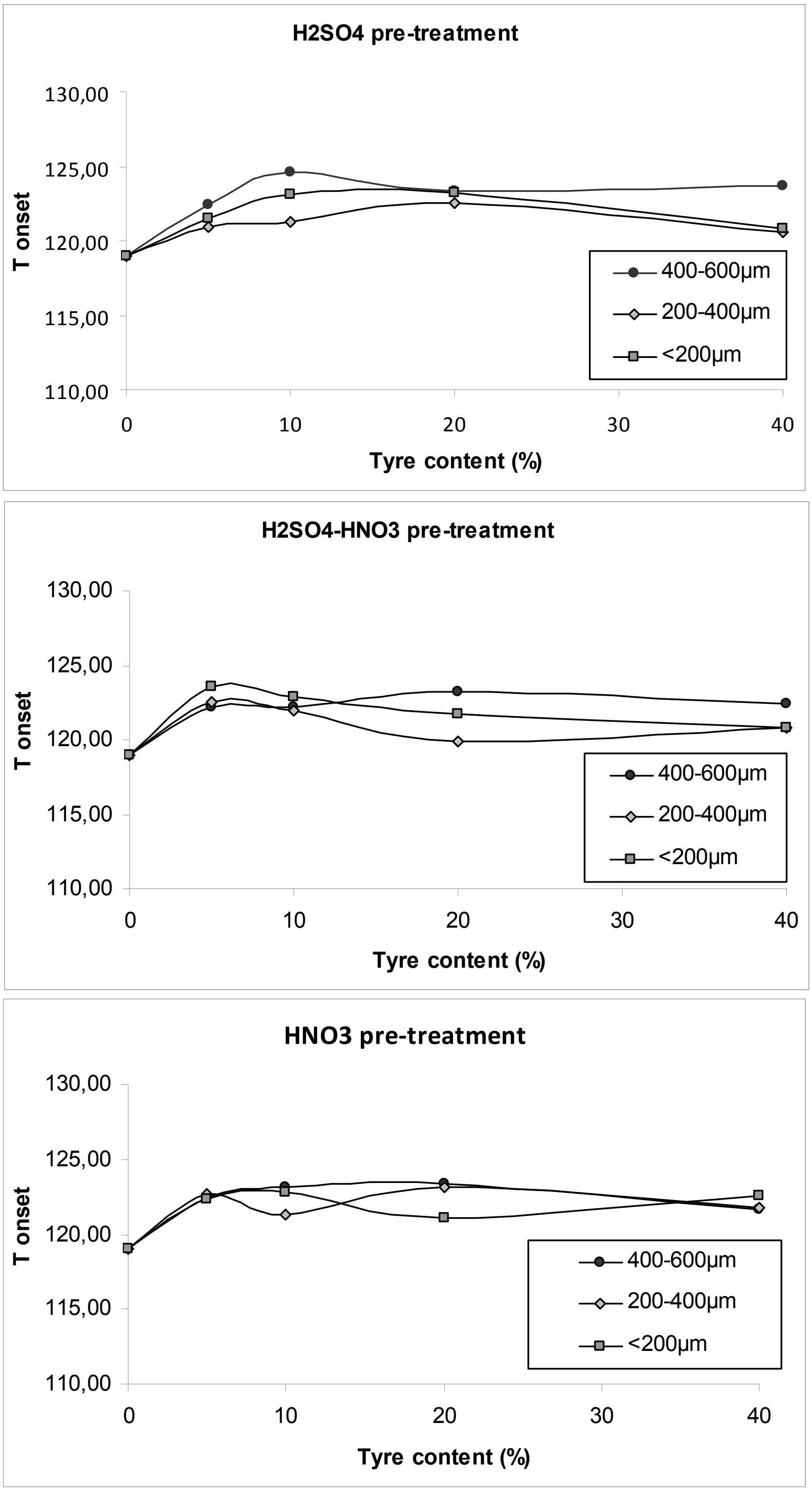


**Figure 3.7** Onset temperature versus GTR particles content, untreated, treated with $H_2SO_4$ (50%), $HNO_3$ (50%) and $H_2SO_4$-$HNO_3$ (50%). HDPE/GTR blends with several GTR particle size in microns.

The calorimetric data related to the melting temperature of the samples are shown in *Figure 3.7*. An increase in the melting temperature could be associated to a more compact crystalline structure. In this case, results show that there is a trend to higher onset in samples including GTR particles except in the case of sulpho-nitric treatment. However, the differences in temperature are not significant and it was difficult to conclude about the effect of GTR particles on HDPE microstructure. Overall, small particle sizes tend to result in higher melting temperature.

### 3.3.4 Scanning electron microscopy

Some microphotographies depicting the fracture surface of the ground tyre rubber particles composites are shown in *Figure 3.8*.

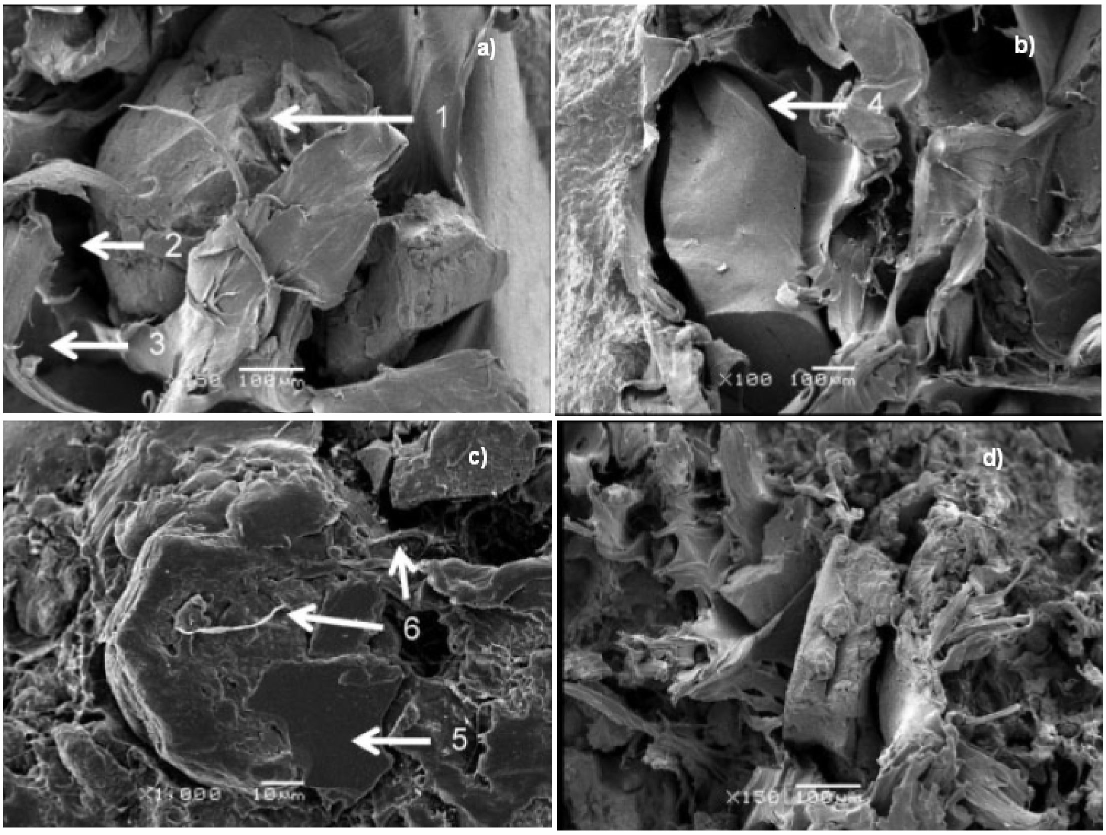


**Figure 3.8** SEM microphotographies of different fracture surfaces of GTR/HDPE. a) particle size between 400-600µm treated with $H_2SO_4$, b) particle size between 200-400µm treated with $HNO_3$, c) particle size lower than 200µm treated with $H_2SO_4$, d) particle size between 200 and 400µm treated with $H_2SO_4$-$HNO_3$ (50%).

The images show different levels of magnification, which allows the comparison of the different particle sizes. The picture “a” shows a blend sample containing sulphuric treated ground tyre rubber particles sizes between 400-600µm. In the centre appears a big particle [1], showing some cracks and pores big enough to be observed at this level of magnification. The particle is unliked to the matrix, as it can be observed by the deep voids around its contour [2]. The tyre seems to be resting on the HDPE, without being properly attached to it. On the other hand, the matrix has been strained and deformed plastically [3].

Microphotography “b” from a sample including particles with sizes between 200-400µm pre-treated with $HNO_3$ shows similar features. The interaction between both components of the blends is not good and there are many cavities [4] around the ground tyre rubber particle.

Image “c” shows a different situation, since magnification is 10 times higher, particle is much smaller. The particle seems much more integrated in the matrix, and there is an area on the right with a clean cut that indicates that the particle itself has been broken instead of detached [5], which proves the good performance of the interfacial contact, when the particles has been treated with $H_2SO_4$. The contour of the particle does not show voids around, instead some fragments of HDPE sprout from the ground tyre rubber showing points of good attachment between both components [6]. The high magnification allows the appreciation of the roughness achieved by the pre-treatment.

Picture “d” shows particles (size between 200 and 400µm) treated with $H_2SO_4$-$HNO_3$ (50%). Several medium size particles appear showing different levels of attachment.

The results of microscopy, spectrophotometry and calorimetric analysis which are summarized above suggest that the surface modification of tyres that have been subjected to different treatments influences their mechanical properties, and in some cases may also improve the interaction and compatibility between the HDPE matrix and the ground tyre rubber particles.

## 3.4 Conclusions

From the study of the mechanical properties it is concluded that: i) in most cases, acidic pre-treatments act improving the compatibility of the components resulting in better mechanical properties that untreated samples, ii) acid pre-treatments act over the ground tyre rubber particles causing etching of the surface and improving mechanical adhesion,

iii) for small particles sizes, the pre-treatment with sulpho-nitric mixture gives the best results in terms of mechanical properties, but $H_2SO_4$ has also a very positive effect, iv) smaller particle size produces blends with higher tensile strength and stiffness, v) the results of the particle sizes below 200µm, and between 200 and 400µm are both acceptable in terms of balance properties/amount of useful ground tyre rubber particles, whereas particles between 400-600µm produce a drastic reduction of mechanical properties, and vi) the effect of the acidic pre-treatment is more intense when using smaller particle sizes.

By studying the FTIR-ATR spectral bands, the main results obtained were following: i) every treatment studied produces a specific chemical modification on the ground tyre rubber particles, thus inducing the formation of specific groups; ii) several degradative effects appear in a similar way and do not depend on the acid used in the treatment (mainly the decrease in double bounds and the elimination of minor components and moieties).

Calorimetric studies show differences in melting enthalpy of the materials studied. This leads to the following conclusions: i) melting enthalpy is constant for untreated samples in every particle size, that means the matrix is not altered by the presence of the ground tyre rubber particles in terms of crystalline structure, ii) enthalpy of melting tends to be higher for the pre-treated blends with particle size below 200µm, because of the nucleation effect, may also be a cause of the better mechanical performance achieved with these samples, iii) the enthalpy of melting for the pre-treated blends with particles size below 200µm also increases with the percent of ground tyre rubber, and v) particle sizes above 200µm cause a decrease of melting enthalpy.

SEM microphotographs show differences relative to the particle size: small particles are more attached to the matrix because of the high relative roughness and relative magnitude of pores and cracks. The etched surface achieved by acids may not be enough to effectively link bigger particles to the matrix.

The results achieved for the proposed composite materials, obtained exclusively from polymeric discarded waste, allow considering them as a real alternative to value added injection moulding applications. However, further studies are still needed to improve the adhesion between the two materials and to achieve better features. Moreover, it is worth to mention that using acid pre-treatment not only is valid for low particle size ground tyre rubber but also makes the composites stiffener. This special feature must be taken into account depending on the type of the injection moulding final piece.

It is worth to set out the following question: is an acid treatment procedure environmental friendly enough? It is not an expensive procedure as no special machinery need to be used but when trying to reuse discarded tyres into a partly recycled final piece the before mentioned question must be taken into account.

# Chapter 4:

# The use of waxes and wetting additives to improve compatibility between HDPE and ground tyre rubber

*In chapter 3, acid treatment was used to modify chemically and physically the ground tyre rubber surface. In the present chapter a completely different approach is studied. The study is based on the knowledge in other fields where compatibility between resin and solid particles is also difficult (e.g. coatings, masterbatch production, etc…). The present study is focused on the influence of using substances specially designed to compatibilise resin and solid particles in GTR/HDPE composites. The aim of this work is to improve adhesion between the two phases by increasing the wetting of ground tyre rubber particles by HDPE resin. In this case, unlike acid treatment, adhesion will occur by electrostatic forces or viscosity reduction and not by mechanical interlocking. The influence of these additives in GTR/HDPE composites will be determined by mechanical properties, ATR infrared spectroscopy, DSC analysis, SEM and optical microscopy.*

## 4.1 Previous studies to compatibilize HDPE/GTR with active interface substances.

One of the most important steps in the production of pigmented coatings and plastics is the homogeneous distribution of the solid pigmented particles within the resin. If this step, which is also known as “dispersing process”, is not optimized then a wide variety of defects can occur, such as: flocculation, gloss decrease, colour shift, sedimentation and viscosity instabilities. In order to avoid those defects wetting additives and waxes are commonly used. Those areas have plenty of literature explaining how these substances help to wet pigments into the correspondent matrixes. On the other hand, it does not exist up to now, any study where these substances have been used to compatibilize ground tyre rubber into thermoplastic matrixes.

K. Oliphant and W. E. Baker *[Oliphant 1993]* studied the influence of a coating layer process upon cryogenically ground tyre rubber particles (CGT). As a coating, they used Dow Primacor 3460, an ethylene acrylic acid (EAA) copolymer. They pre-treated the cryogenically ground tyre rubber particles with the EAA copolymer. Afterwards the "coated" particles were added onto the melt LLDPE and HDPE matrixes. They observed that the deleterious effects of the cryogenically ground tyre rubber particles is more pronounced in composites with HDPE than LLDPE. For example, the impact failure for pure LLDPE was seen to be a ductile yielding process in which the dart drawn the material out as it passes through. In contrast, the failure of the pure HDPE, although it involves some plastic deformation, is observed to occur through catastrophic propagation of a crack through the impact zone. This difference in impact failure was believed to be responsible for the poorer properties of the CGT/HDPE composites. For LLDPE, where failure is ductile, large particles with moderate adhesion were easily tolerated but in CGT/HDPE composites, the failure remained semi-brittle because particles were too large to induce brittle-to-ductile transition. Failure then occurs largely through crack propagation, and the large particles, even with moderate adhesion, act as serious flaws providing an easy path for the crack to follow. They concluded that the addition of CGT to a semi-brittle matrix requires much higher level of adhesion to retard crack growth at the particle/matrix interface, or much lower particle sizes to lower the brittle-ductile transition temperature. In their study they concluded that composites of 40 to 50% of precoated CGT with LLDPE have impact properties approaching those of the pure LLDPE and retain adequate processability. This property improvement was believed to be due to an interaction between the carboxylic acid groups on the EAA copolymer with functional groups on the CGT particles surface, which result in an increase on adhesion and greater ductibility. However, poor mechanical properties were obtained with CGT/HDPE composites due to the semi-brittle nature of HDPE.

### 4.2 Mechanisms of wetting additives and waxes to increase compatibility

As mentioned already, the main reason why is not possible to have good adhesion between polyolefin's matrixes and ground tyre rubber particles is due to the different interfacial energy between the two phases. This phenomenon has been extensively studied in coatings production. Commercially available pigments for coatings production come to the market in form of agglomerates, where many pigment particles are attached to each other and form larger structures. Paint producers know that a good wetting of the pigments by the resin is very important to get optimum final properties of the coating. The very first step during the pigment grinding consists on wetting. During this phase, all the air and moisture at the pigment surface is driven off and then replaced by the resin solution. The solid/gaseous interface (pigment/air) is transformed into a solid/liquid interface (pigment/resin solution). The resin solution must penetrate the pigment agglomerate structure. It is very common the addition of wetting additives to accelerate the wetting of pigment agglomerates by the resin. The wetting and dispersing additives are used to wet and stabilize the pigment dispersion (see *Figure 4.1*).

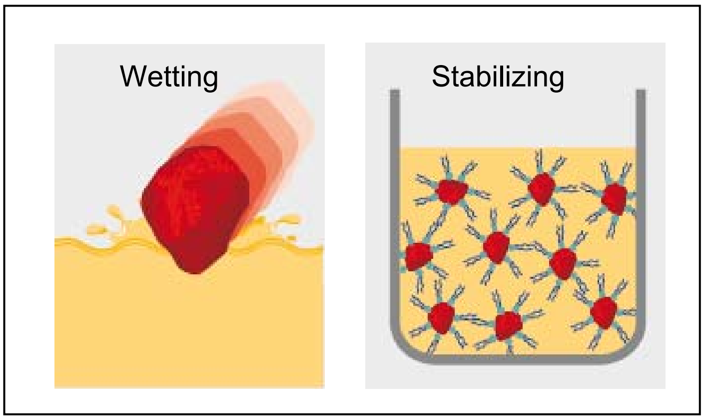


**Figure 4.1** wetting and stabilizing stages during paint production *[Scholz 2006].*

Pigment wetting by the resin solution is influenced by many factors. The penetration speed of the liquid phase into the interstices between the pigment agglomerates is expressed by the Washburn equation (under considerably simplified conditions).

$$\boxed{v = \frac{dl}{dt} = \frac{r}{2l\eta} \cdot \gamma \cos\Theta}$$

Washburn's Equation

Where:

v = penetration speed
l = penetration depth
t = time
r = capillary radius
η= viscosity of liquid
γ= surface tension of the liquid
Θ= contact angle

The capillaries between the pigment particles are assumed to be cylindrical tubes with radius r. The first factor on the right hand side of the equation shows that for fast wetting (high penetration speed) loosely packed agglomerates and low viscosity of the liquid are favourable. During paint production, the agglomerate structure can not be changed and the possibilities for viscosity reduction are fairly limited. The second factor, surface tension of the penetrating liquid and contact angle, can be easily influenced. Obviously, these two properties are not independent from each other and can be influenced by wetting additives. In practice, wetting additives are used to lower the surface tension as far as necessary to bring the contact angle close to zero.

Wetting additives can be defined as substances which are designed to reduce the contact angle between pigment and resin solution and which, as a result, speed up the penetration of the liquid into the pigment agglomerate structure. Characteristic for such substances is their surface-active structure: polar, hydrophilic structural elements along non polar, hydrophobic structural elements combined in one molecule. Because of this specific structure, such molecular combinations are interfacial active migrating, for example, to the pigment/binder solution interface.

From a chemical standpoint, wetting additives can be classified as either ionic or non-ionic according to exactly how the polar segment is incorporated into the molecule. The non polar segment is represented normally by hydrocarbon chains.

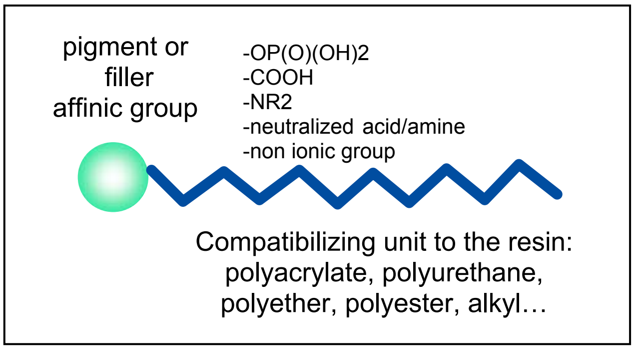


**Figure 4.2** Structure of a monofunctional wetting and dispersing additive *[Byk Chemie GmbH Literature]*.

Some of the pigment affinic groups are -$OP(O)(OH)_2$, -COOH, -$NR_2$, -neutralized amine,-non ionic groups, etc… Some classical interactions with pigment are:

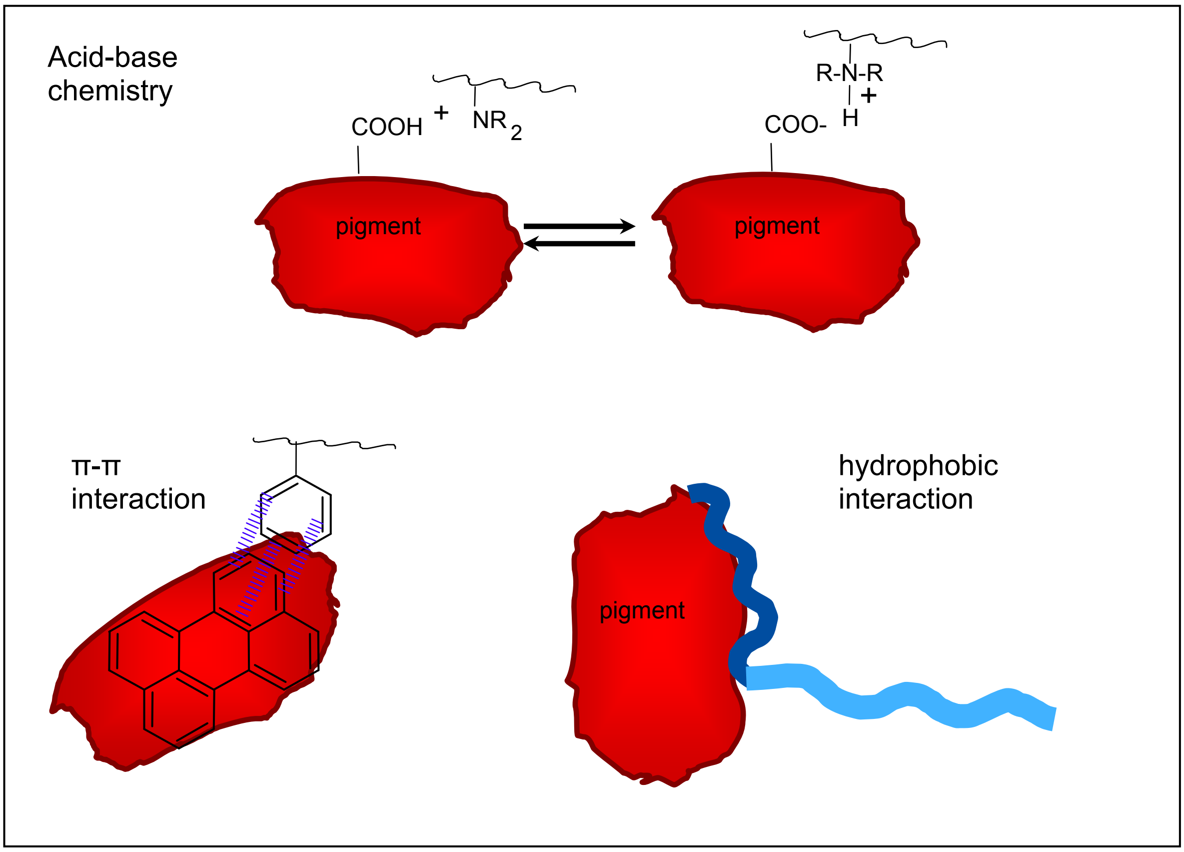
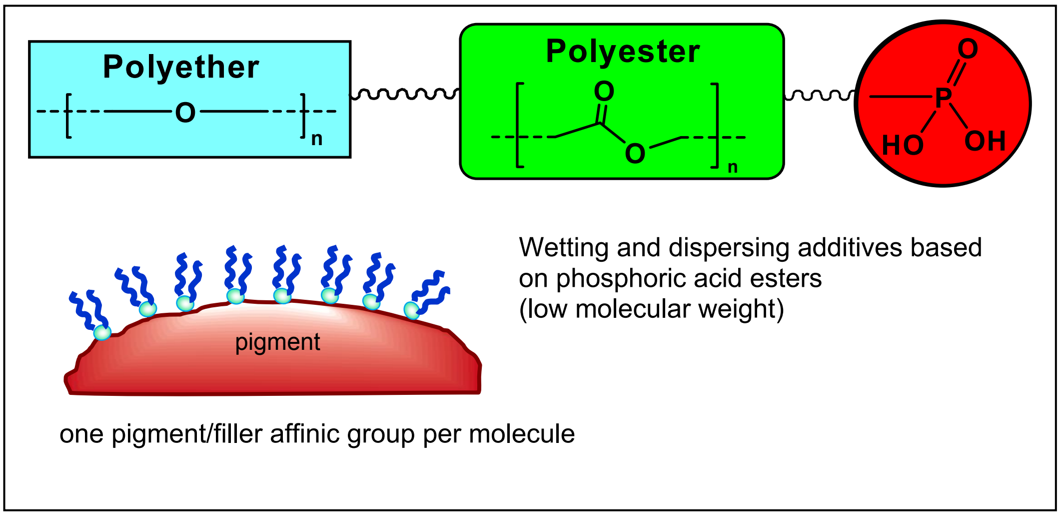


**Figure 4.3** Some examples of interactions between pigment affinic groups of wetting/ dispersing additives with pigments *[BYK-Chemie GmbH literature]*.

The resin compatible group can be very different chemically speaking. Some examples are:



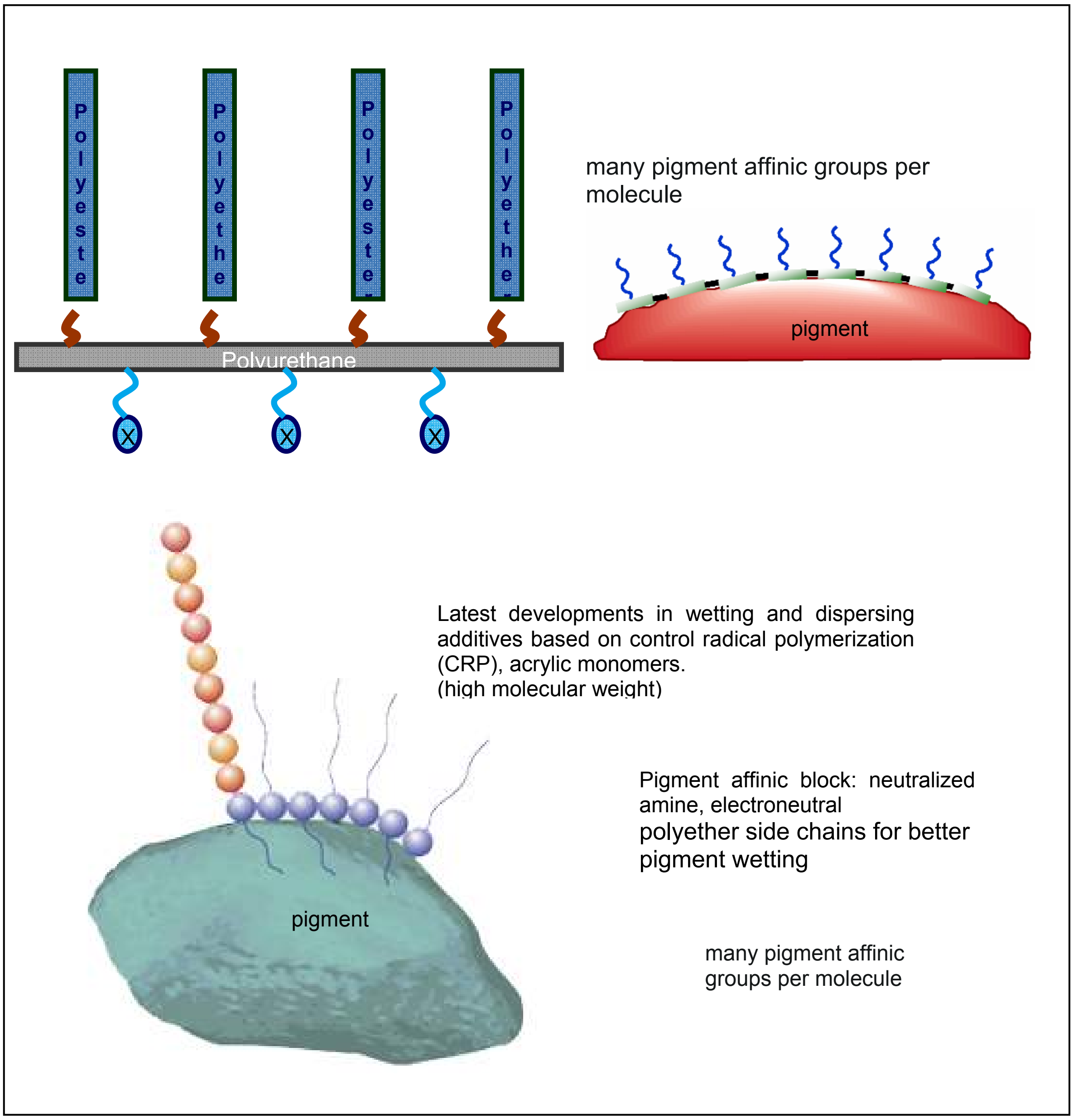


**Figure 4.4** Some examples of the most common resin compatible groups *[Byk Chemie GmbH Literature]*.

Up to now, it has been referred to the resin as a liquid (diluted in solvent) that have to wet solid pigments. Some of these wetting additives commented for coatings can be also used to wet pigment particles in thermoplastic pigment concentrates, commonly known as masterbatches. The way to give colour to plastics, such as thermoplastics, is with the use of masterbatches or pigment concentrates delivered in pellets shape. They are added to the moulding machines containing big amount of pigments, resin with lower MFI than the resin used to produce the final piece and fillers. It is very common to use waxes to wet the pigment. In *Figure 4.5* is represented how it works:

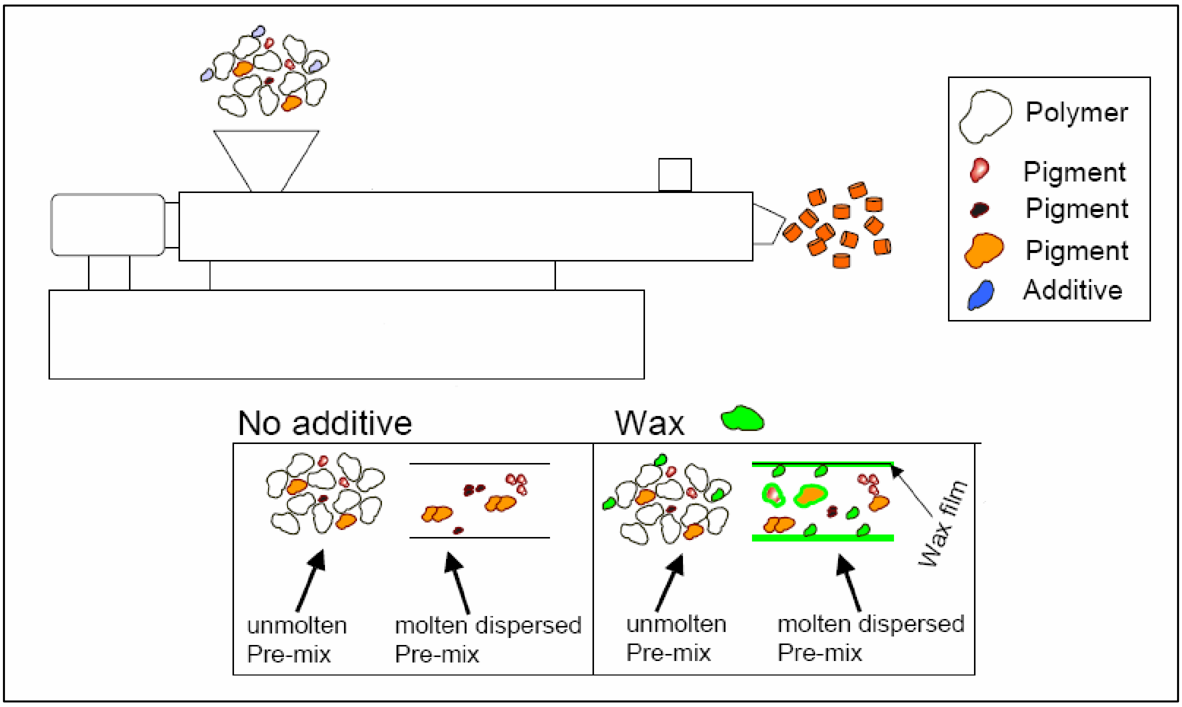


**Figure 4.5** Schematic figure of the wax influence in masterbatch production *[Byk Chemie GmbH Literature]*.

In most of the cases, masterbatch producers do not have any special machines where pigments can be dispersed effectively, but rather want to handle a good pigmentation at the processing machine (e.g. extruder). If the pigment agglomerates are very hard, then the dispersive power of the processing machine is insufficient. Masterbatches contain the optimum concentration of pigment dispersed in the carrier material. One prerequisite for coloration of plastics using such concentrates is good compatibility of the carrier material with the plastic to be coloured. The viscosity of the concentrate at processing temperature must be coordinated with the viscosity of the polymer melt. The shear effect of the polymer melt will only be sufficient to distribute the pigment concentrate homogenously if its viscosity is lower than that of the polymer.

Dispersability can be enhanced by using micronized waxes (*Figure 4.6*), having similar particle size to modern organic pigments, allow homogenous distribution in the pre-mixture and optimally disperse and wet pigments during masterbatch manufacturing and protect against re-agglomeration.

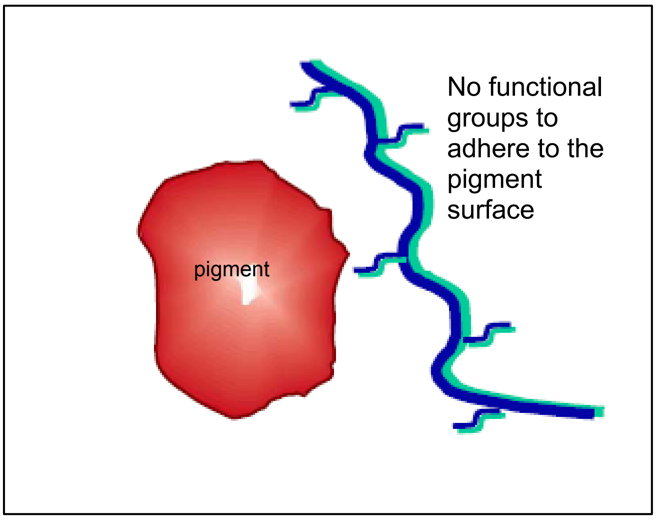


**Figure 4.6** Performance of standard PE and PP waxes during the pigment wetting process *[Byk Chemie GmbH Literature]*.

The use of waxes in masterbatch production can improve pigment wetting and distribution significantly; moreover, the melt viscosity of the pigment concentrate can be reduced considerably. Better pigment distribution results in higher tinting strength, which in turn leads to substantial saving in raw materials costs, especially when it comes to expensive organic pigments. Waxes, by lowering viscosity, ensure homogenous distribution during coloration in the processing machines, even when higher pigment concentrations are used. The ability to increase the concentration without detrimental effects can be done replacing part of the carried material with affordable fillers, e.g. calcium carbonate. The lower melting viscosity of pigment concentrates that contain waxes also permits a substantial increase in output performance *[Otto 2003]*.

It is important to notice that waxes and wetting additives behave in a different way. Waxes reduce melt viscosity of the matrix, helping to improve its wetting effect on the particle, but since waxes do not have the tensoactive structure with polar and non polar groups, do not have the interface activity of the wetting additives.

## 4.3 Discussion about the chosen additives.

If ground tyre rubber particles are considered as big pigment that must be wet by resin to obtain the optimum final properties, these additives can be used with the same purpose that are added in paint and masterbatch production. Some parameters as the chemistry of the pigment affinic group, the molecular weight or its polarity will be decisive in order to choose the ones for the study. One can foresee that the wetting additive performance can not be equal to a coating system where the resin is liquid. The average particle size of the ground tyre rubber is much bigger (between 400-600µm) than standard commercial pigments (< 1µm).

Two different kinds of additives are tested to overcome the deleterious effects of the GTR/HDPE composites. As commented before, wetting additives by means of their specific structures decrease the interfacial tension between the two phases (solid particles and resin) following Washburn's equation. Influential factors of these additives behaviour include polarities of the solid particles surface, the matrix's viscosity and geometry of the empty spaces (or pores) within the particles. Some of their groups provide adsorption onto the particle surface (ground tyre rubber particles in this case) and the non polar chains protrude into the surrounding resin. The classification of these additives is done considering its molecular weight and polarity. On the other hand, waxes place themselves evenly between the particles (ground tyre rubber particles in this case) and the polymer. Distributed among the particles, they form a fine wax film on the particles like a kind of coating after the melting process. The most important wax properties are polarity, drop point and viscosity *[Krupa 2002]*.

The additives were provided by two different companies: wetting additives by BYK-Chemie GmbH (Wesel, Germany) and waxes by Clariant Ibérica S.A. (Barcelona, Spain). In the study, four different wetting additives were chosen. Two additives were selected with basic characteristics, Disperbyk-108 of low MW and Byk-9077 with high MW. One additive with synergistic effect when combined with the two before mentioned basic additives. Finally a low MW wetting additive with acidic characteristics was chosen. The two basic additives will work if the ground tyre rubber surface has some acidic groups, and vice versa, the acidic wetting additive will work if the ground tyre rubber particles surface has some basic groups to interact. Regarding the waxes, three different chemistries were chosen, polyethylene, polypropylene and ester waxes. The commercial names and characteristics of the used additives are shown in the following table:

| **Wetting additives** | | | | | |
|---|---|---|---|---|---|
| Name | Code | Amine value (mgKOH/g) | Acid value (mgKOH/g) | MW | Description |
| Disperbyk-108 | Dis-108 | 71 | - | low | Hidroxyfuntional carboxylic acid ester with affinic groups |
| Byk-9077 | Byk-9077 | 46 | - | high | High MW copolymer with affinic groups |
| Byk-Synergist 2100 | Byk-Syn 2100 | - | - | | Insoluble pigment complex to be used together with basic wetting additives to provide better absorption |
| Byk-P 105 | Byk-P 105 | - | 365 | medium | Low MW unsaturated policarboxilic acid polymer |
| **Waxes** | | | | | |
| Name | Code | Drop point (ºC) | Acid value (mgKOH/g) | Density at 23ºC (g/cm$^3$) | Description |
| Licowax PE 520 | LPE520 | 120 | - | 0,93 | Polyethylene wax |
| Licocene PP 1502 | LCPP1502 | 86 | - | 0,87 | Polypropylene wax |
| Ceridust 5551 | Ceridust 5551 | 99 | 19 | 1,00 | Ester wax |

**Table nº 4.1** Commercial names and characteristics of the additives used.

Apart from the table summary, it is interesting to mention some more detailed information about these substances. Disperbyk-108 and Byk-9077 have both a basic character as already mentioned. Disperbyk-108 has low MW and it is based on fatty acid chemistry, while Byk-9077 has high MW and it is based on polyester-polyurethane chemistry. On the other hand, Byk-P 105 has an accentuated acid character and it is based on polycarboxilic acid chemistry. Byk-Synergist 2100 can not be included in the wetting additive definition mentioned on *section 4.2*. The additive is an insoluble blue pigment complex that must be used together with other wetting additives with basic character (Disperbyk-108 and Byk-9077 in this case). The additive provides a better adsorption of the polymeric wetting additive on non-polar surface pigments (or ground tyre rubber particles in this case). *Figure 4.7* shows a schematic drawn of how this additive works:

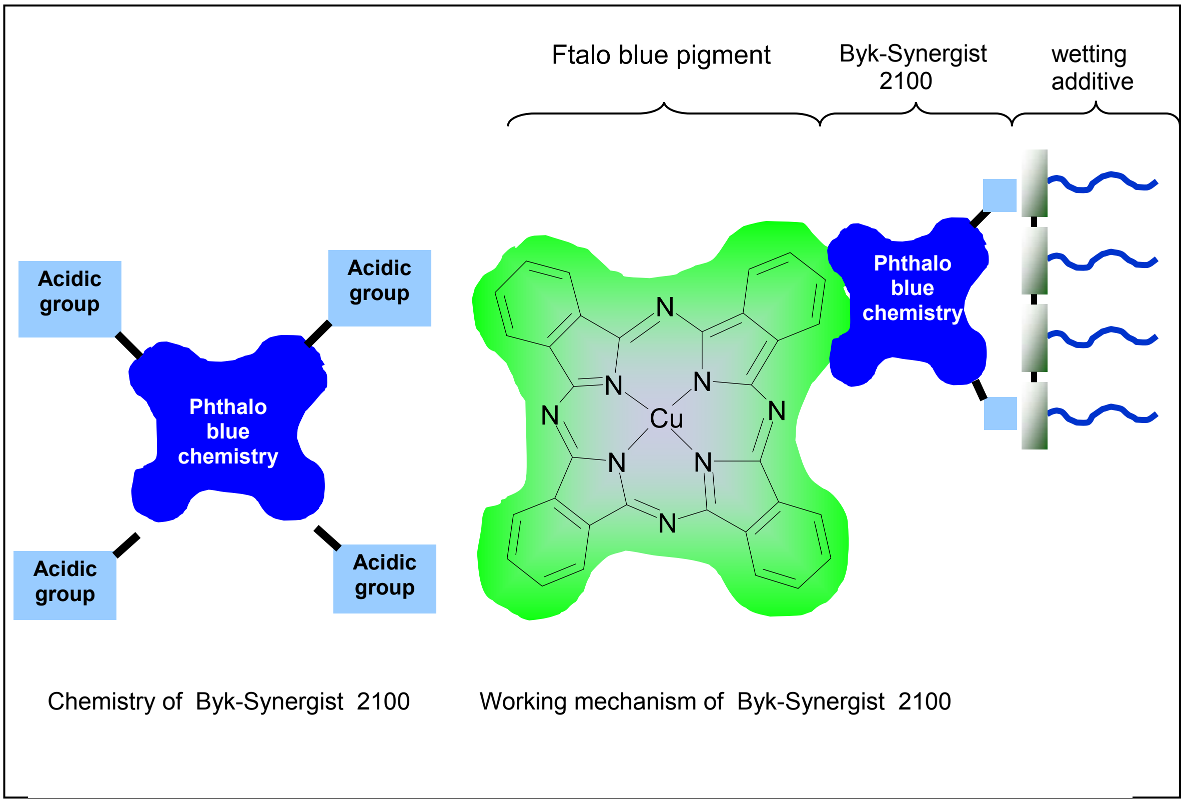


**Figure 4.7** Chemistry and working mechanism of Byk-Synergist 2100 *[Byk-Chemie Literature]*.

Waxes, on the other hand, do not work via pigment affinic groups but placing themselves evenly between the pigment and the polymer, and form a fine wax film reducing at the same time the polymer viscosity. Licowax PE waxes from Clariant are manufactured according to the Ziegler low pressure process. Licowax PE 520 is a non polar polyethylene wax, with a MW of approximately 2.000g/mol as well as relatively low density, crystallinity, hardness and melt viscosity. On the other side, Licocene PP1502 is one of the innovative Licocene® grades that are low molecular polyolefins manufactured with metallocene catalysts. This kind of waxes has been proven with good results as dispersing agents for pigments in the manufacture of masterbatches . Ceridust 5551 is a micronized ester wax that improves wetting and dispersability of organic pigments and thus boosts colour intensity. Ceridust types make pigment absorption easier when are used in polymers like polyethylene and polypropylene as binders.

## 4.4 Experimental

The HDPE, the ground tyre rubber characteristics and the general mixing process were already described in chapter 2 (*section 2.8 and 2.9 respectively*). The mixture between ground tyre rubber particles and wetting additives or waxes was previously prepared by manual stirring. If the wetting additive or wax was micronized, the blend was simply hand-stirred until a homogeneous mixture was obtained. If the wetting additive was liquid, the stirring took place until all the ground tyre rubber particles looked wet. The waxes and the wetting additives were already described in *section 4.3.*

In all cases the percent of additives refers to the amount of ground tyre rubber except in the blends HDPE/additives, where the dosage of additives was calculated considering a 80/20 composite.

## 4.5 Results

### 4.5.1 Mechanical properties

### 4.5.1.1 GTR/HDPE composites

The mechanical properties of different composites of untreated GTR/HDPE are shown in *Table 4.2*. The increase of the ground tyre rubber particles amount produces a decrease of the mechanical properties of the final composite, especially elongation at break and toughness as already was seen in chapters 2 and 3. As commented before this is due to a very weak adhesion between the two phases. The big particle size of the ground tyre rubber and its crosslinked structure, which avoid any compatibility with the thermoplastic matrix, are the main reasons of this behaviour. The brittle response of the material is related to poorly adhering large particles present in the matrix *[Bartczak 1999]*.

| %GTR | Young's modulus (MPa) | Std. Dev. | Tensile strength (MPa) | Std. Dev. | Elongation at break (%) | Std. Dev. | Toughness (J) | Std. Dev. |
|---|---|---|---|---|---|---|---|---|
| 0 | 927,90 | 27,95 | 20,67 | 2,22 | 390,08 | 22,20 | 38,4 | 3,00 |
| 10 | 889,00 | 24,94 | 16,44 | 1,53 | 17,31 | 1,31 | 1,57 | 0,23 |
| 20 | 759,65 | 33,11 | 14,34 | 2,13 | 12,55 | 1,46 | 1,13 | 0,21 |
| 40 | 370,25 | 12,84 | 8,74 | 1,72 | 12,00 | 1,73 | 0,88 | 0,15 |

**Table 4.2** Mechanical properties of untreated GTR/HDPE composites.

According to previous studies *[Colom 2006],* the composite with 20% of untreated ground tyre rubber particles is a good compromise between mechanical properties and ground tyre rubber content. Samples with higher percent of ground tyre rubber particles are more difficult to process and show an excessive decrease in Young's modulus and tensile strength. The composition with 20% of ground tyre rubber particles was used to study the effect of additives.

#### 4.5.1.2 HDPE/additives blends

These blends were prepared in order to analyze the influence of the additives in the mechanical properties of the matrix. Additive dosages are the same as those used in the mixture of HDPE with ground tyre rubber particles. *Table 4.3* shows the mechanical properties of HDPE with the different additives. In general, it is observed that additives decrease elongation at break and toughness but increase Young's modulus of HDPE. Tensile strength only increases with ester wax additive (Ceridust 5551) while it is lower with all the other additives.

Hato and Luyt *[Hato 2007]* observed similar behaviour in terms of mechanical properties when they studied a blend of paraffin wax and HDPE. They explained the results in terms of morphology, suggesting a possible cocrystallization of the mixture HDPE/wax. According to their interpretation, wax chains are short enough (9nm compared to an approximate polyethylene lamellar thickness of 10nm) to be incorporated as straight chains into the HDPE lamellae. This incorporation occurs only at low dosages of wax. The cocrystallization would be responsible for the increase in Young's Modulus and the reduction in elongation at break. Blends of polyethylene (LDPE or LLDPE) with paraffin and oxidized paraffin waxes show similar properties *[Krupa 2002]*.

| %Aditive | Young's modulus (MPa) | Std. Dev. | Tensile strength (MPa) | Std. Dev. | Elongation at break (%) | Std. Dev. | Toughness* (J) | Std. Dev. |
|---|---|---|---|---|---|---|---|---|
| 0 | 927,90 | 27,95 | 20,67 | 2,22 | 390,80 | 22,01 | 38,41 | 3,00 |
| 2.5% Dis-108 | 1.075,43 | 32,17 | 20,3 | 1,62 | 290,91 | 27,21 | 33,41 | 3,52 |
| 5% Byk-9077 | 1.087,04 | 24,13 | 19,53 | 2,61 | 317,42 | 36,01 | 32,62 | 4,44 |
| 2% Byk-Syn 2100 | 1.111,27 | 33,85 | 17,48 | 1,82 | 342,21 | 25,22 | 35,61 | 3,12 |
| 3% Byk-P 105 | 1.049,24 | 15,25 | 16,46 | 2,37 | 357,32 | 25,01 | 35,51 | 2,71 |
| 5% LPE520 | 1.088,26 | 17,48 | 16,94 | 3,14 | 337,66 | 15,90 | 34,47 | 1,61 |
| 5% LCPP1502 | 1.051,86 | 20,78 | 16,55 | 4,14 | 362,01 | 30,90 | 36,11 | 5,12 |
| 2.5%Ceridust 5551 | 1.248,99 | 36,01 | 22,19 | 2,15 | 266,21 | 16,61 | 33,00 | 3,12 |

* Toughness is calculated as the area under the load-displacement curve

**Table 4.3** Formulations showing the influence of the additives on the mechanical properties of the matrix.

#### 4.5.1.3 HDPE/20%GTR/additives composites

*Table 4.4* shows the mechanical properties of the HDPE/GTR composites with the different additives. Disperbyk-108 and Byk-9077 are both designed to interact with acid groups and, as can be seen, do not improve any of the properties of the blend. It could be assumed then that ground tyre rubber particles have a basic or rather a non polar surface. In order to improve interaction between a non polar surface and basic additives (such as Disperbyk-108 or Byk-9077) a synergic additive with acids groups can be used. As mentioned in *section 4.3* Byk-Synergist 2100 has acid groups able to interact with the basic additives and with the non polar surfaces of the ground tyre rubber particles, acting as a kind of “bridge”. It can be observed that this additive causes a significant increase in elongation at break (13.2%).

| %Additive | Young’s modulus (MPa) | Std. Dev. | Tensile strength (MPa) | Std. Dev. | Elongation at break (%) | Std. Dev. | Toughness* (J) | Std. Dev. |
|---|---|---|---|---|---|---|---|---|
| 0 | 759,65 | 33,11 | 14,34 | 2,13 | 12,55 | 1,46 | 1,13 | 0,21 |
| 2.5% Dis-108 | 760,49 | 16,44 | 13,97 | 4,38 | 12,71 | 1,27 | 1,02 | 0,13 |
| 2.5% Dis-108<br>+ 2% Byk-Syn 2100 | 737,05 | 18,69 | 13,98 | 2,88 | 14,19 | 2,33 | 1,24 | 0,11 |
| 5% Byk-9077 | 724,03 | 21,06 | 12,89 | 4,20 | 11,81 | 3,24 | 0,89 | 0,25 |
| 5% Byk-9077<br>+ 2% Byk-Syn 2100 | 712,05 | 21,02 | 13,22 | 2,52 | 14,20 | 1,96 | 1,12 | 0,29 |
| 3% Byk-P 105 | 796,47 | 26,22 | 15,08 | 3,48 | 13,19 | 2,01 | 1,25 | 0,26 |
| 5% LPE520 | 797,10 | 31,44 | 15,55 | 1,84 | 13,69 | 2,33 | 1,32 | 0,19 |
| 5% LCPP1502 | 753,07 | 29,44 | 14,59 | 4,27 | 13,51 | 1,72 | 1,24 | 0,19 |
| 2.5% Ceridust 5551 | 846,16 | 27,23 | 14,66 | 2,80 | 11,04 | 1,56 | 0,94 | 0,14 |

* Toughness is calculated as the area under the load-displacement curve

**Table 4.4 :** Influence of the additives on the mechanical properties of composites of 20% of GTR and 80% of HDPE.

Byk-P 105, designed to interact with basic groups, is the wetting additive that most improves the mechanical properties of the composite. This result is related to carbon black characteristics. Carbon black is present on tyre formulations in form of furnace black pigments in amounts between 20 to 40%. As a result of the manufacturing process, furnace black pigments always contain small amounts of basic surface oxides (pyrone-like structures) *[Buxbaum 1993]*. The presence of these basic groups on the ground tyre rubber particles surface could provide interaction with Byk-P 105. The wetting additive is anchored onto the ground tyre rubber particles surface and its non polar part is extended in the HDPE matrix. This wetting effect decreases the interfacial energy between the two phases and leads to a better adhesion. These results, obtained with an acidic wetting additive (Byk-P 105) are in concordance with the improvement in compatibility achieved by the ethylene-acrylic acid (EAA) in GTR/LLDPE composites attributed to the interaction between the acid groups on the EAA copolymer and cryogenically ground tyre rubber particles surface *[Oliphant 1993]*.

Licowax PE520 and Licocene PP1502 waxes also offer good mechanical properties, whereas the ester wax Ceridust 5551 reduces elongation at break and toughness. As discussed previously, there is an increase of Young's modulus and tensile strength when the ester wax is mixed with the matrix (*Table 4.3*). When ground tyre rubber particles are included in the composite (*Table 4*.4), the same effect can be noticed. Despite this improvement, elongation at break and toughness drastically decrease. Therefore, the effect of Ceridust 5551 seems mainly related to the matrix, being unable to create the thin coating onto the ground tyre rubber particles to improve adhesion.

The effect of Licowax PE520 and Licocene PP1502 is also related to the zinc derivatives present in tyre formulations. Pastor *et al. [Pastor 1994]*, Romero *et. al [Romero 2001].* Monteiro *et al. [Monteiro 2002]* and Colom *et al*. *[Colom 2009]* observed a diffusion and migration of different tyre additives, like zinc derivatives from the bulk of different rubbers and reused tyres to their surfaces. These additives lead to a poor adhesion between the ground tyre rubber particles and the HDPE matrix due to its low free energy (unpolar properties). As mentioned before, waxes cover the particles reducing slightly the viscosity in the layers adjacent to the matrix. During calendaring at 150-155ºC, zinc derivatives can be solubilised into the matrix due to the lower viscosity obtained by the waxes. This effect achieves a "cleaner" ground tyre rubber particles surface that is easier to wet. In order to corroborate this mechanism, a FTIR-ATR spectrum of the surface of the ground tyre rubber particles was carried out. A reference sample containing ZnO and another sample of ground tyre rubber particles submitted to the temperature effect simulating the transformation process were compared. *Figure 4.8* shows that both samples present the characteristics bands attributed to ZnO at 1.537cm$^{-1}$ and 1.398cm$^{-1}$ which proves the existence of zinc on the surface.

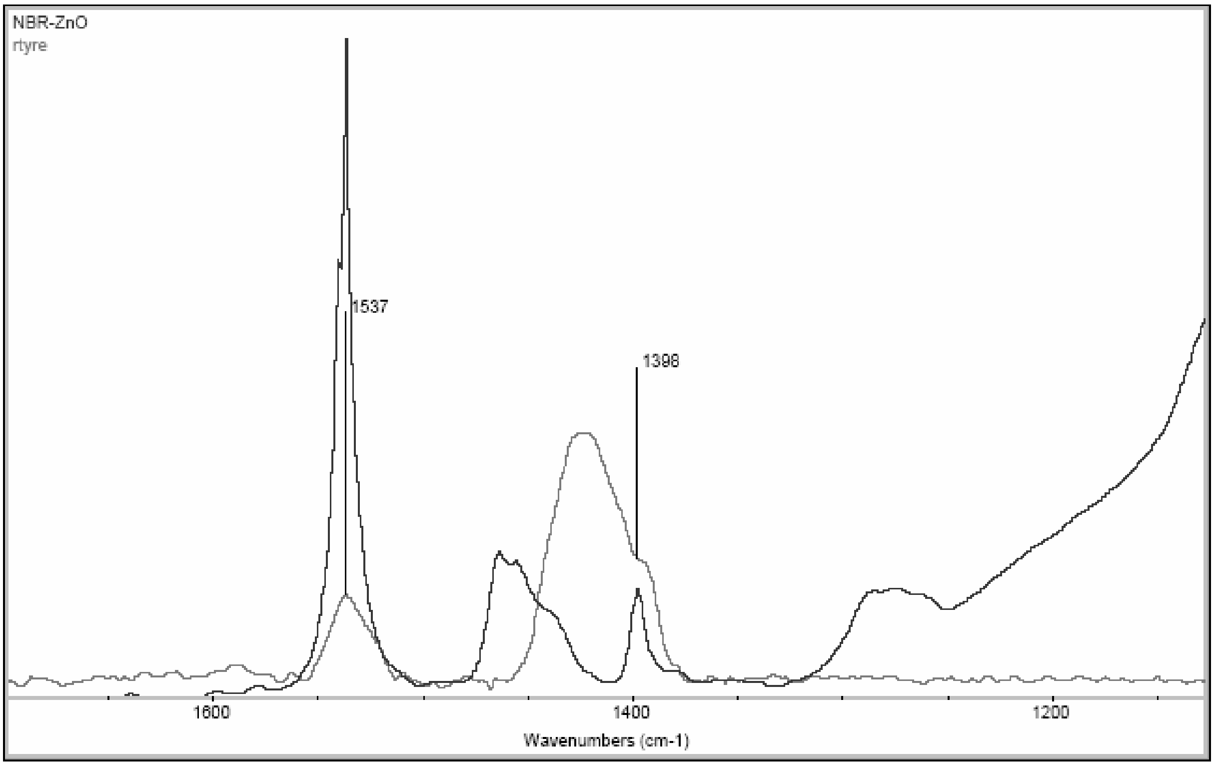


**Figure 4.8** FTIR-ATR spectrum of a sample containing ZnO and GTR submitted to the temperature effect

### 4.5.1.4. HDPE/GTR/additives composites at different percentages of GTR.

Different percentages of ground tyre rubber particles were tested with the wetting additive and waxes that gave best results (Byk-P 105, Licowax PE520 and Licocene PP1502). *Table 4.5* shows the mechanical properties of the different composites.

| % of GTR | % of additive | Young's modulus (MPa) | Std. Dev. | Tensile strength (MPa) | Std. Dev. | Elongation at break (%) | Std. Dev. | Toughness* (J) | Std. Dev. |
|---|---|---|---|---|---|---|---|---|---|
| 10% | No additive | 889,00 | 24,94 | 16,44 | 1,53 | 17,31 | 1,31 | 1,57 | 0,23 |
| 10% | 3% Byk-P 105 | 914,94 | 36,54 | 16,86 | 2,58 | 17,61 | 2,71 | 1,65 | 0,26 |
| 10% | 5% LPE520 | 933,27 | 17,48 | 16,91 | 2,80 | 14,86 | 2,59 | 1,59 | 0,16 |
| 10% | 5% LCPP1502 | 906,25 | 30,78 | 16,44 | 3,91 | 17,62 | 3,41 | 1,60 | 0,32 |
| 20% | No additive | 759,65 | 33,11 | 14,34 | 2,1 | 12,55 | 1,4 | 1,13 | 0,21 |
| 20% | 3% Byk-P 105 | 796,47 | 26,22 | 15,08 | 3,48 | 13,19 | 2,01 | 1,25 | 0,26 |
| 20% | 5% LPE520 | 797,10 | 31,44 | 15,55 | 1,84 | 13,69 | 2,33 | 1,32 | 0,19 |
| 20% | 5% LCPP1502 | 753,07 | 29,44 | 14,59 | 4,27 | 13,51 | 1,72 | 1,24 | 0,19 |
| 40% | No additive | 370,25 | 12,84 | 8,74 | 1,72 | 12,00 | 1,73 | 0,88 | 0,15 |
| 40% | 3% Byk-P 105 | 427,10 | 15,92 | 8,46 | 2,70 | 13,92 | 1,25 | 0,90 | 0,05 |
| 40% | 5% LPE520 | 421,39 | 22,41 | 9,3 | 1,82 | 14,97 | 2,04 | 0,92 | 0,14 |
| 40% | 5% LCPP1502 | 405,25 | 17,64 | 8,29 | 2,95 | 11,81 | 1,61 | 0,54 | 0,16 |

* Toughness is calculated as the area under the load-displacement curve

**Table 4.5** Influence of the dosage of GTR on the mechanical properties of the blends with HDPE and additives.

### 4.5.2 DSC analysis

In order to study the thermal effect of the additives when applied to the HDPE matrix, a DSC analysis was carried out. Obtained results are shown in *Tables 4.6 and 4.7.* From the values it may be observed that all additives, even when added in small proportion to the HDPE, produce a displacement of the $T_{onset}$ and a change in the melting enthalpy of HDPE. The DSC data shows only the HDPE melting point with no indication of any other melting point. As has been commented previously, this is due to the incorporation of the additive to the crystal lamellae of the HDPE. Composites containing Byk-P 105 and Licowax PE520 show a reduction in enthalpy of melting due to a decrease in HDPE crystallinity (Xc). This fact can be related to a better distribution of the ground tyre rubber particles (less agglomerates), which disturbs the packaging of the HDPE indicating, therefore, a better compatibility.

| % Additive | ΔH(Jg$^{-1}$) | T$_{onset}$ (ºC) | T$_{peak}$ (ºC) |
|---|---|---|---|
| Neat HDPE | 182,51 | 121,41 | 131,21 |
| 2.5% Dis-108 | 161,16 | 119,80 | 131,61 |
| 5% Byk-9077 | 175,43 | 119,58 | 130,64 |
| 2% Byk-Syn 2100 | 182,42 | 121,30 | 130,77 |
| 5% Byk-9077+ 2% Byk-Syn 2100 | 168,34 | 120,42 | 131,22 |
| 3% Byk-P 105 | 175,24 | 118,43 | 131,15 |
| 5% LPE520 | 175,08 | 119,41 | 131,09 |
| 5% LCPP1502 | 177,45 | 120,78 | 131,20 |
| 2.5% Ceridust 5551 | 177,43 | 118,81 | 132,19 |

**Table 4.6** DSC analysis of the HDPE blended with additives. The % is referred to the amount of rubber included in the 80/20 blend.

| % Additive | ΔH(Jg$^{-1}$) | T$_{onset}$ (ºC) | T$_{peak}$ (ºC) |
|---|---|---|---|
| Neat HDPE | 182,51 | 121,41 | 131,21 |
| 1% LPE520 | 175,67 | 121,65 | 131,67 |
| 3% LPE520 | 170,72 | 121,75 | 130,67 |
| 5% LPE520 | 164,85 | 119,06 | 128,67 |

**Table 4.7** DSC analysis of the HDPE/LPE520 blend.

On the other hand, results obtained for the wax Licocene PE520 at different dosages *(Table 4.7)* show that an increase in the amount of wax tends to decrease the enthalpy of the blend and coincide with the results obtained by other researchers *[Hato 2007] [Krupa 2002]*. It is known that a decrease of Tm in polymers blends is caused by the formation of less-perfect crystallites having a smaller size (interaction of both polymers). Moreover, this is always an indication of an improvement in blend compatibility.

### 4.5.3 Scanning electron microscopy

Fracture surfaces of the composites containing the additives (Byk-P 105, Licowax PE520 and Licocene PP1502) that gave better mechanical properties were examined by SEM. *Figure 4.9* contains SEM images of the composite with 20% of ground tyre rubber particles and selected additives. Figure (a) shows the composite with 20% of ground tyre rubber particles and 80% of HDPE without any additives, where ground tyre rubber particles do not display any signs of adhesion to HDPE. Figures (b), (c), and (f) corresponding to the additives combination of 2.5% Disperbyk-108 + 2% Byk-Synergist 2100, 5% Byk-9077 + 2% Byk-Synergist 2100 and 5% Licocene PP1502 respectively, show also poor interaction. Figure (d) corresponds to the composite including 3% of Byk-P 105: the particle is surrounded by the HDPE matrix but the picture does not show a perfect interaction. On the other hand, photograph (e) with 5% of Licowax PE520 shows good adhesion between the two phases. The existence of some filaments protruding from the ground tyre rubber particles indicates a strong interaction.

### 4.5.4 Optical microscope

Four samples of each specimen were examined under the microscope for dispersion quality study. The mechanical energy provided by the two roll mill during the milling stage breaks the ground tyre rubber agglomerates and creates smaller particles with larger interfaces in contact with the thermoplastic matrix. Wetting additives and waxes improve dispersion stability of single ground tyre rubber particles; consequently, better mechanical properties can be achieved.

*Figure 4.10* shows four pictures. (a) and (b) correspond to the composites without additives and with 2.5% Disperbyk-108 + 2% Byk-Synergist 2100 respectively. Both pictures show the existence of agglomerates, which can be seen as ground tyre rubber particles in contact along their edges with its interstitial spaces filled with the HDPE matrix. On the other hand, pictures (c) and (d) correspond to 3% of Byk-P 105 and 5% of Licocene PE520 respectively; both show single ground tyre rubber particles surrounded by the HDPE matrix. This lack of agglomerates means a better dispersion and stabilization of the particles, and consequently an improvement on the mechanical properties of the final blend.

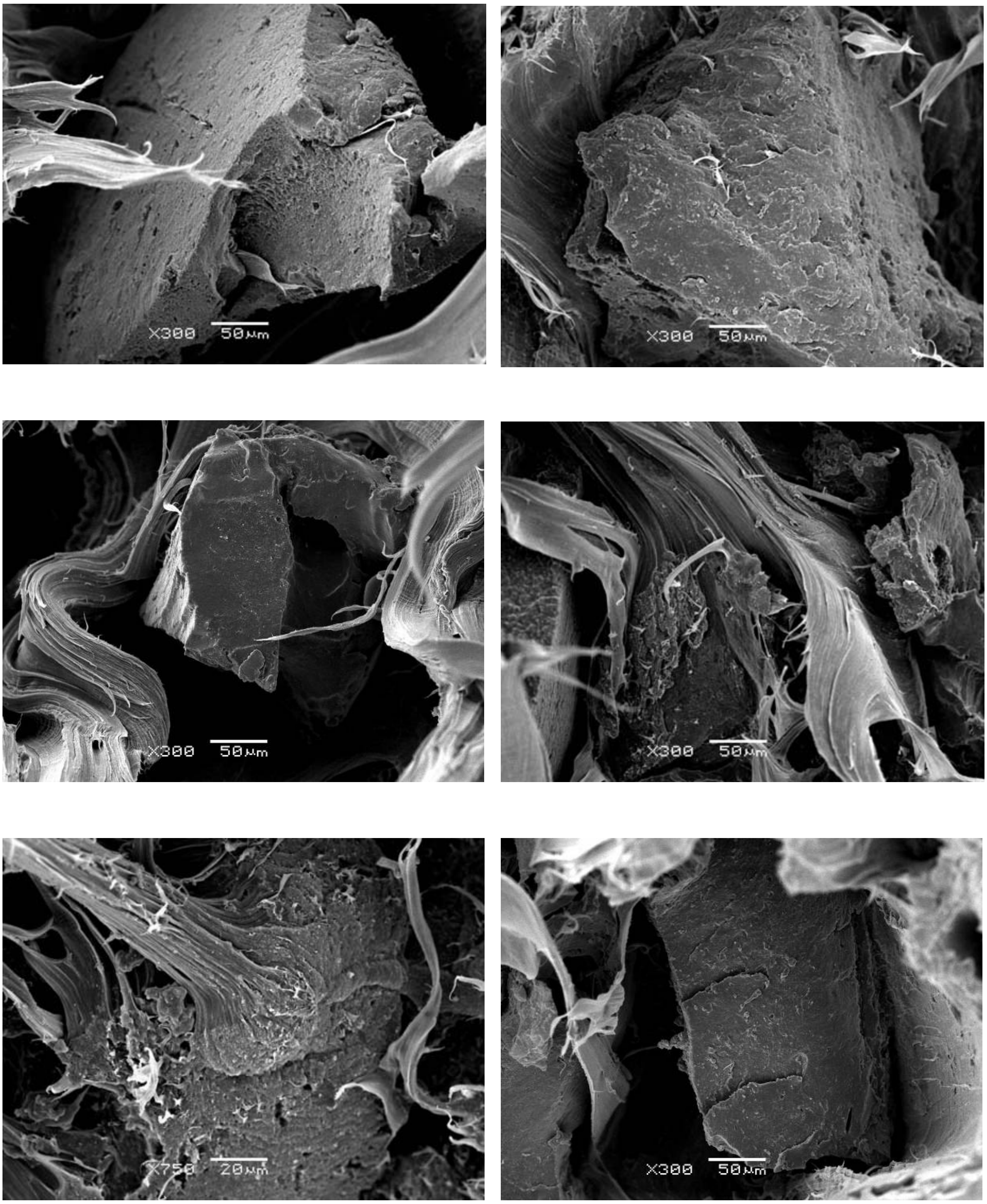


**Figure 4.9** SEM microphotographs of the composites 20% of GTR and 80% of HDPE with different additives. a) neat composite, b) 2.5% Dis-108 + 2% Byk-Syn 2100, c) 5% Byk-9077 + 2% Byk-Syn 2100, d) 3% Byk-P 105, e) 5% LPE520 and f) 5% LCPP1502.

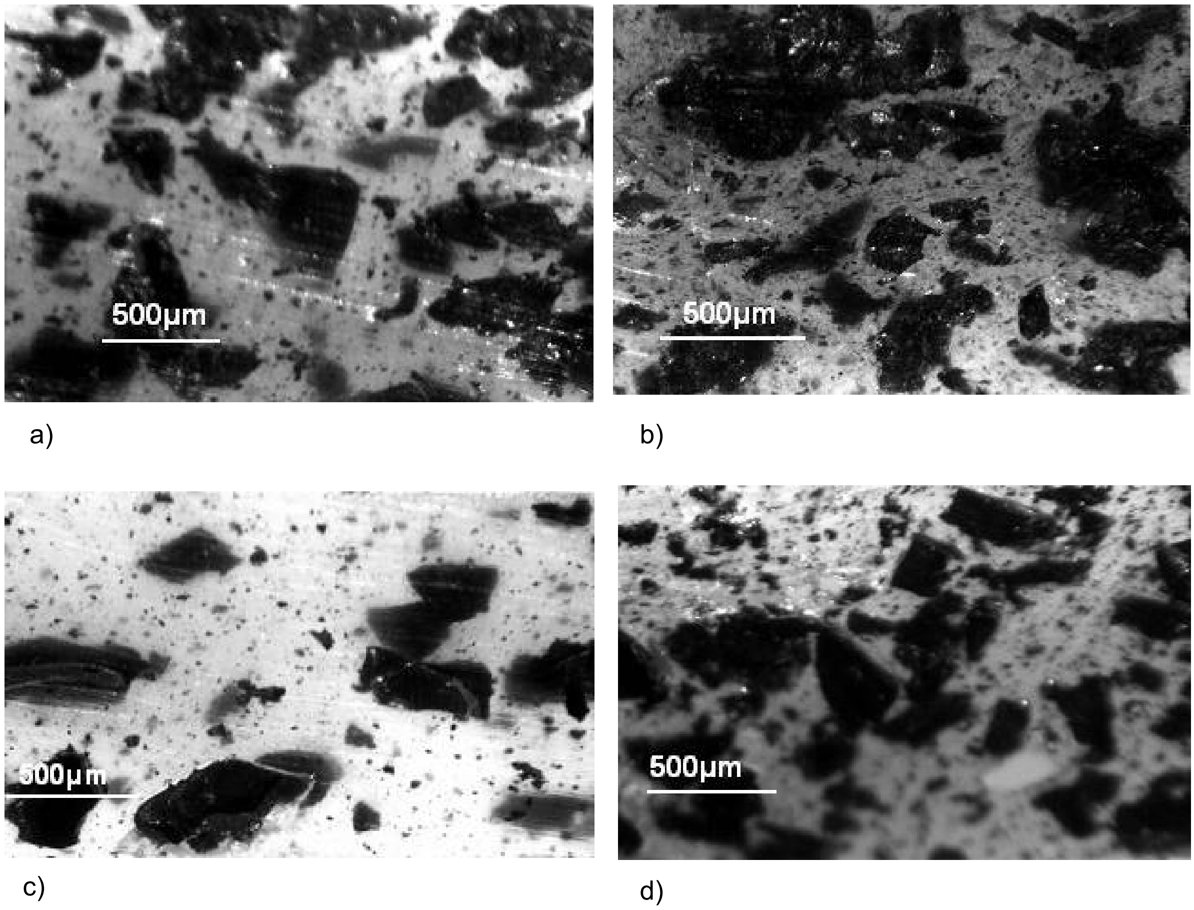


**Figure 4.10** microscope pictures of the composites with 20% of GTR and the following additives: a) neat mixture, b) 2.5% Dis-108 + 2% Byk-Syn 2100, c) 3% Byk-P 105 and d) 5% LPE520.

## 4.6 Conclusions

From the study of the mechanical properties, the following conclusions can be drawn: i) the increase of the ground tyre rubber particles amount in neat composites produces a decrease of the mechanical properties in the final composite, especially in elongation at break and toughness as already seen in chapters 2 and 3. The mixture with 20% of ground tyre rubber particles gives a balanced compromise between the amount of ground tyre rubber particles and good mechanical properties; ii) the wetting additive Byk-P 105 and the wax Licowax PE520 give the best performance in the blends with 10, 20 and 40% of ground tyre rubber particles; iii) all additives produce an increase in the Young's modulus and tensile strength of the HDPE matrix. This increase is attributed to cocrystalization of the waxes with HDPE.

DSC data support the existence of cocrystalization of the additives with HDPE, since only one melting temperature related to HDPE appears and there is a variation of the enthalpy and melting temperature of HDPE/additives blends. In the case of Licowax PE520, the variation is greater, due to the higher content in wax.

SEM microphotographs show that Licowax PE520 acts adequately promoting adhesion. Fracture surface reveals fragments of HDPE attached to the particles. On the other hand the Byk-P 105 image shows particles better wrapped in thermoplastic than with any other wetting additive.

Optical microscope's photographs show that samples including Byk-P 105 and Licowax PE520 contain fewer agglomerates. The homogeneous dispersion of the ground tyre rubbber particles in the matrix produces better mechanical properties.

This study explores for the first time the advantages of improving HDPE and ground tyre rubber particles composites by incorporating wetting additives or waxes to the blend. It opens a wide field to the use of other additives. The method does not require special equipment to transform the materials and constitutes an environmentally friendly and economically competitive technique. Moreover, the process carried out on a two roll mill in this study, can be easily reproduced on an extruder or a brabender plasticorder.

# *Chapter 5:*
# *Formulations for thermoplastics elastomers based on HDPE and GTR*

*Thermoplastic Elastomers (TPE) are environmental friendly and value-added materials. The combination of rubbery elasticity, easy thermoplastic transformation and design flexibility makes them to get importance in replacing rubber and plastics in final end uses like weather strips, seals, airbags covers, grips, etc… Rubber articles, like tyres, are not recyclable or re-processible due to its vulcanized structure. On the other hand, the price increase of some elastomers, such as EPDM, during the last decade has lead to look for substitutes. Therefore, the attempt to replace as much elastomer as possible by ground tyre rubber particles in TPEs formulations seems to be a good option for cost reduction of the final formula plus an up-cycling application for GTR. In this chapter two attempts of GTR containing TPEs are studied in Thermoplastics Olefins (TEO) and Thermoplastics Vulcanizates (TPV) formulations.*

## 5.1 Thermoplastic elastomers: characteristics and properties

A thermoplastic elastomer (TPE) is a rubbery material with properties and functional performance similar to those of a conventional vulcanizated rubber at room temperature, although, it can be processed in the molten state as a thermoplastic *[Walker 1988]* *[Bhowmick 1988]*. Most of the TPEs meet the standard ASTM D 1566 *[ASTM D 1566*] definition of a rubber since:

a) they recover quickly and forcibly from large deformations
b) they can be elongated by more than 100%
c) their tension set is less than 50%
d) they are insoluble in boiling organic solvents

The birth of TPEs occurred in 1950 when in the laboratories of BF Goodrich, Schollenberger and co-workers *[Kolycheck 1993]* resulted with the invention, development and commercialization of thermoplastic polyurethane elastomers (TPU), the first member of this unique polymer class. Nowadays, the global demand for TPEs is of 3.1 million metric tons *(see Figure 5.1)* and the sells will remain concentrated in the developed markets of the US, Western Europe and Japan with the notable exception of China. The replacements for natural and synthetic rubber, as well as for rigid thermoplastics and metals will be where these materials will find the majority of their usage, particularly, for higher performance materials such as copolyester elastomers (COPEs) and thermoplastic vulcanizates (TPVs) *[Fredonia 2005]*.

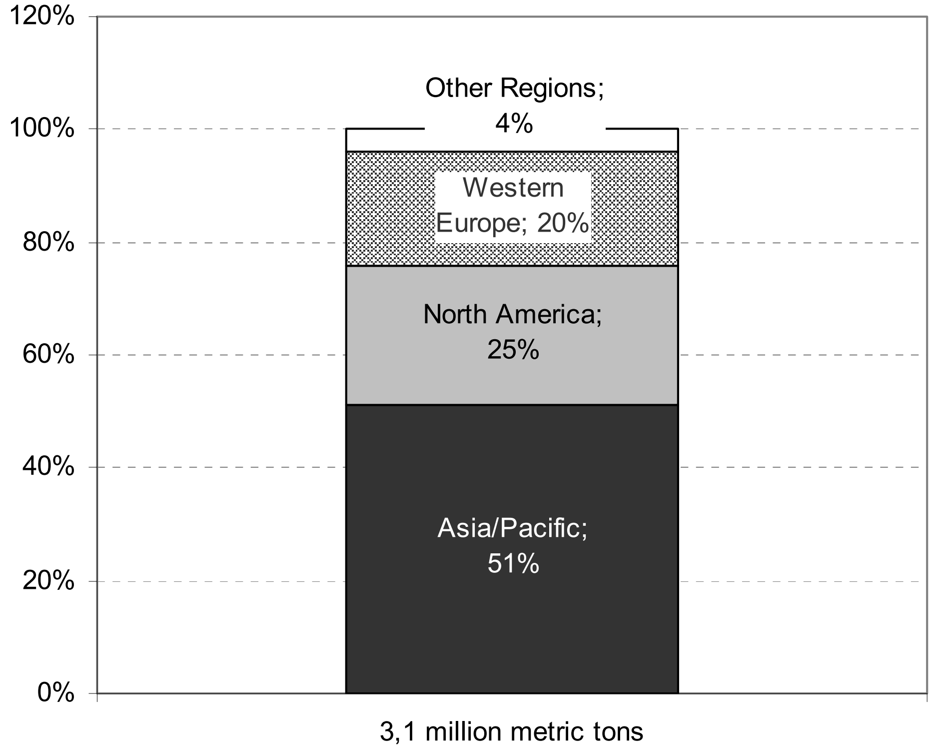
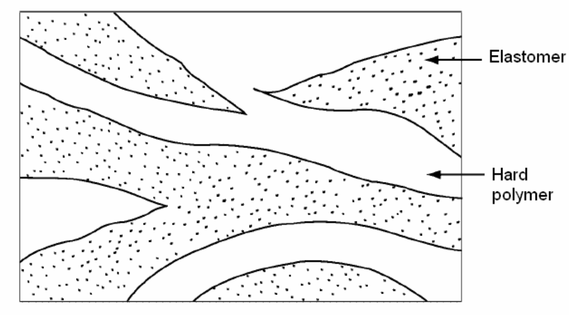


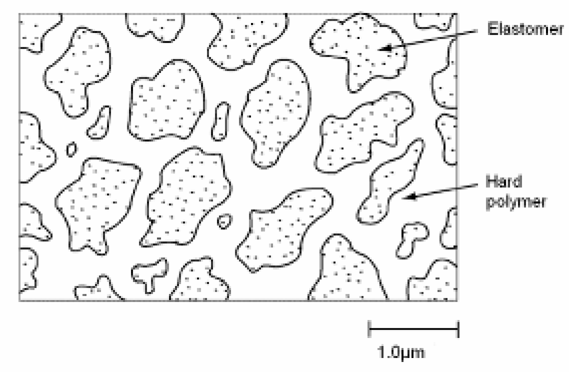
**Figure 5.1** World TPEs demand by region in 2009.

### 5.1.1 Chemistry, morphology and properties of TPEs

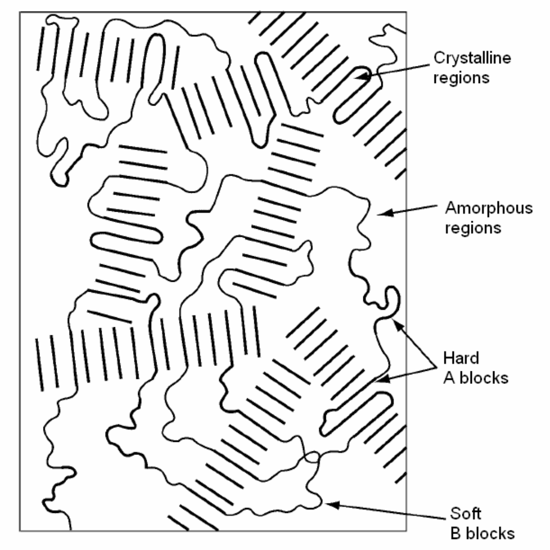
All TPEs are composed of at least two polymeric phases: a hard thermoplastic phase and a soft elastomeric phase. The two phases may result from the simply mixing of two different polymers, as in a blend of a hard thermoplastic such as polypropylene (PP) with a soft elastomer such as ethylene-propylene dyene rubber (EPDM rubber), to give a thermoplastic elastomeric olefin (TEO). Dynamic vulcanization, under conditions of high shear and temperature of the elastomer phase result into a thermoplastic vulcanizated (TPV), with properties much closer to those of vulcanizated rubbers. The two phases may also be present as alternating hard and soft segments in block copolymers, the basis for many commercially important TPEs (*see Figure 5.2*)



a) Phase arrangement of TEOs



b) Phase arrangement of TPVs



c) Phase arrangement in crystalline block copolymers

**Figure 5.2** Schematic phase arrangements of a) TEOs b) TPVs and c) block copolymers *[Herman 1986]*.

Thermoplastic vulcanizates (TPV) are prepared by a process of dynamic vulcanization, defined as the process of intimate melt mixing of a rubbery polymer and a thermoplastic to vulcanize (or crosslink) the rubbery polymer and thus generate a thermoplastic elastomer (TPE) with properties closer to those of a thermoset rubber than those of a comparable unvulcanized composition. Upon melt mixing of the thermoplastic and rubbery polymers under high shear, the less viscous thermoplastic will tend to become the continuous phase with the more viscous rubber dispersed in it. The dispersed rubber particles will then vulcanize, forming a three-dimensional polymer network within each particle and become trapped since they can not recombine into larger aggregates.

Since most of the TPEs are phase-separated systems, they show many of the characteristics of the individual polymers that constitute the phases. The characteristics contribution of every phase into the final TPEs properties can be summarized in the following table *[Rabe 2009]*:

| **Hard Phase – the thermoplastic** | **Soft phase – the elastomeric** |
|---|---|
| Processing temperatures | Lower service temperature limits |
| Continuous use temperature | Hardness |
| Tensile strength | Flexibility |
| Tear strength | Compression set and tensile set |
| Chemical and fluid resistance | |
| Adhesion to inks, adhesives and over-molding substrates | |

**Table 5.1** Characteristics contribution of every phase into the final TPE.

Each phase has its own Tg or Tm (if it is crystalline). These determine the temperatures at which a particular TPE goes through transitions in its physical properties. Thus, when the modulus of a TPE is measured over a range of temperatures, there are three distinct regions: at very low temperatures, both phases are hard and so the material is stiff and brittle. At higher temperature the elastomer phase becomes soft and the TPE now resembles a conventional vulcanizated elastomer. As the temperature further increase, the modulus stays relatively constant (region often called “rubbery plateau”) until finally the hard phase softens. At this point, the TPE becomes fluid. Therefore, TPEs have two service temperatures. The lower one that depends on the Tg of the elastomer phase, while the upper one depends on the Tg or Tm of the hard phase.

The morphology of a thermoplastic vulcanizate (TPV) is best understood as a dispersion of very small, highly crosslinked elastomer particles in a continous phase of hard thermoplastic. The size of the elastomer phase particles is one key to the performance of the TPV. As the size of these particles decreases, the ultimate tensile properties of the TPV increase.

The second key to thermoplastic vulcanizates (TPV) performance is the degree of crosslinking of the soft elastomeric phase. It has been demonstrated that highly crosslinking the elastomeric phase gives properties that are quite good and allows TPV to capture many of the thermoset rubber applications.

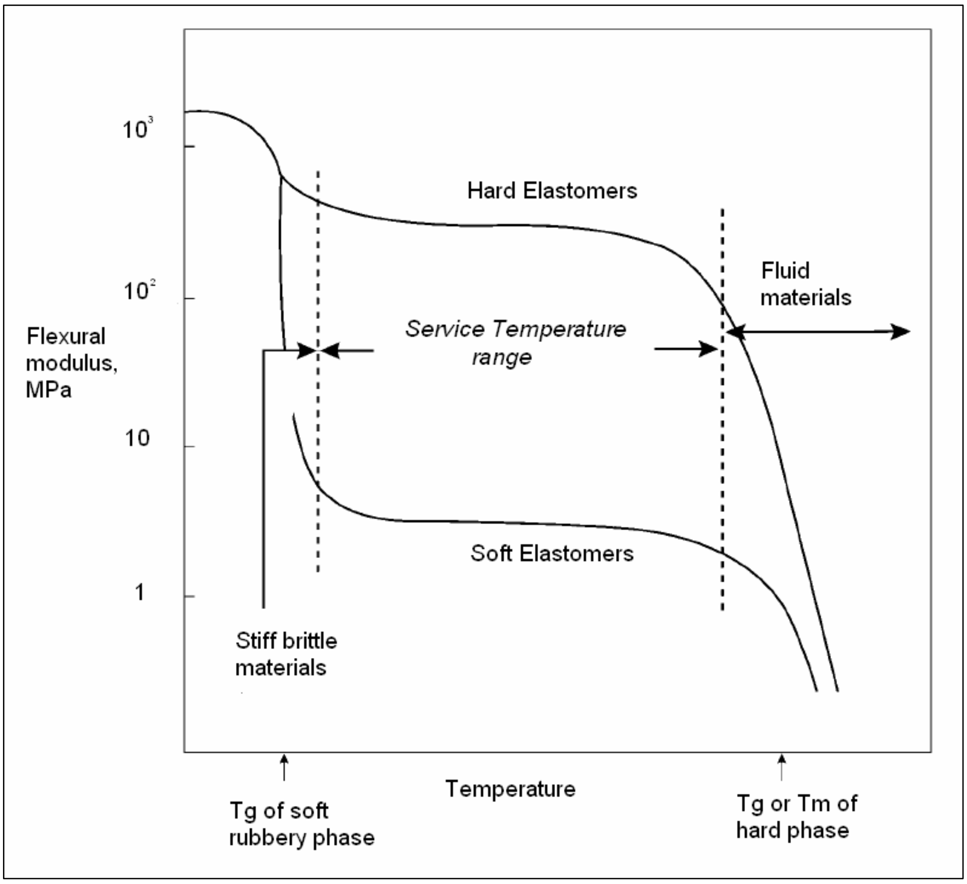


**Figure 5.3** Modulus of a TPE measured over a range of temperatures *[Herman 1986]*.

### 5.1.2 Applications

The applications of TPE are mainly the substitution of conventional vulcanized rubbers *[Kresge 1997]*. PP and EPDM blends were the first hard polymer/elastomer combinations to be developed by conventional mixing. Ethylene-propylene copolymer (EPR) has largely replaced EPDM in this application due to its lower cost. These simple blends had no tensile strength or oil resistance because of the unvulcanized EPDM or EPR and only the hard products (those containing small amounts of elastomer) showed satisfactory properties. Later on, products based on dynamic vulcanization were produced. The improved properties of the elastomer phase allowed value added applications, giving quite soft products (even 35 on the Shore A scale). Compared to EPDM or EPR mixtures with PP, the corresponding dynamic vulcanizates have lower compression set and better oil resistance.

Natural (NR) and butyl rubbers (BR) have been used to replace EPDM in similar dynamically vulcanized products *[Tinker 1988] [Abdou-Sabet 1989].* The NR ones are lower in cost and have properties between the EPDM based dynamic vulcanizates and the simple EPDM based mixtures. On the other hand, those based on butyl rubber have lower gas permeability and high damping, thus can be used as vibrator isolators or vapour barriers. However, butyl rubber have an advantage when polar engineering thermoplastics, such as poly(butylene terephthalate) (PBT) and polyamides (PA) are inserted-molded against butyl rubber, showing an excellent adhesion *[Sherman 2008]*. Molding and extrusion of these combinations of PP with EPDM, EPR, butyl and natural rubbers are similar to those for PP, and the scrap is reusable. Important applications are wire insulation, appliance parts and automobile exterior and interior parts (painted and unpainted).

### 5.1.3 New uses for TEOs and TPVs

The presence of TEOs and TPVs in automotive interiors and exteriors represent half of its use. They are replacing costlier and heavier TPUs, other TPEs and PVC materials. New metallic pigmented TEOs are used in order to replace paint and they are starting to appear on smaller exterior parts. All efforts are nowadays on placing TEOs in large exterior vertical panels, where “molded-in color” (MIC) is the preferred route (*see Figure 5.4 b*).

Auto interiors have increasingly adopted unpainted TEO for soft-touch, low gloss overmolding of consoles, pillars, door trim, shifter knobs and brake handles (*see Figure 5.4 a*). TEOs are being developed with excellent low-temperature impact for airbag covers and new TPVs are starting to encroach on sealing systems long dominated by thermoset EPDM.

But TEOs and TPVs are also growing in non-automotive markets such as medical parts, appliances, packaging seals, wires, cables and hand tools (*see Figure 5.4 c)*. Better over mould bonding (injection moulded over or around a compatible substrate resulting in hard-soft structures) to rigid plastics is a key trend, as is the development of softer and more chemical and heat resistant grades. These new application trends have produced changes in basic composition of olefinic TPEs. One example is the large-scale replacement of EPDM rubber in TEOs by metallocene-based ethylene-octene and ethylene-butene specialty elastomers. In industrial and consumer applications, novel olefinic elastomers hold equal promise, a challenge to traditional TPVs and TEOs. The initial market penetration for these new materials has been in overmolded grips for tools and personal care products, as well as seals, tubing wire and cable.

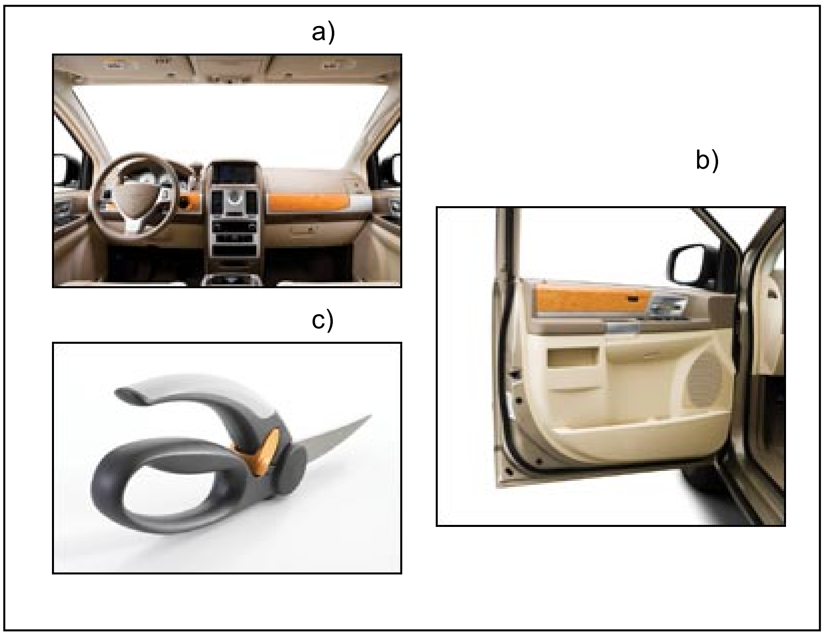


**Figure 5.4** Examples of valued added applications with TEOs and TPVs: a) in auto interiors replacing TPUs, styrenic TPEs, thermoset PUR and vinyl plastics b) two-shot molding TPV used in Chrysler door panels and c) TPV in overmold bondability for grips to get the desired soft-touch effect *[Sherman 2008]*.

In production of soft TEOs, other new tools are emerging. These include alloys and grafted TPE “hybrids” of olefinic and styrenic or other TPEs. These hybrid combinations are a trend to replace existing rubber systems TEOs. Also new TEOs are expanding opportunities for thermoformable sheet in truck rockers, cab interiors parts, as well as, marine and other applications *[Sherman 2008]*.

### 5.1.4 Reprocessing

Easy reprocessing is one of the great advantages that TPEs have over conventional vulcanized rubbers. The scrap can be reground and is usually blended with virgin material before being reworked. TPEs can be also used together with other regrinds, that is, they can be blended with reground scrap from conventional TPE to restore impact strength and reduce brittleness. Many applications, e.g. coextrusion, generate scrap which often has very poor properties. TPE can convert this into useful materials *[Lutz 1989] [Sarkar 1998]*.

## 5.2 Aim of this work

Based on this information, this work is aimed to develop and characterize thermoplastic elastomeric olefins (TEOs) and thermoplastic vulcanizates (TPVs). The following points will be studied:

- Production of thermoplastic elastomer olefins (TEO) containing ground tyre rubber. In order to obtain such material two different waxes, ethylene vinyl acetate (EVA) and ethylene propylene diene monomer (EPDM) will be added into the composite.
- Production of thermoplastic vulcanizates (TPV) containing ground tyre rubber, HDPE, ethylene propylene diene monomer (EPDM) and peroxide as crosslinker.
- A detailed study regarding the influence of each component in the final mechanical properties will be performed.
- Morphological, chemical and thermal characterization of the final material will be done too.

## 5.3 Previous studies based on thermoplastic elastomeric olefins or thermoplastic vulcanizates.

Thermoplastic elastomeric olefins and thermoplastic vulcanizates contain both elastomeric and thermoplastic phases. In the case of thermoplastic elastomeric olefins there is no crosslink. Sarkar *et. al. [Sarkar 1998]* and Bartczak *et. al. [Bartczak 1999]* both researchers studied the properties and characteristics of thermoplastic elastomer olefins. Sarkar *et al*. studied rheology, structural and mechanical properties of hydrogenated styrene-butadiene rubber (HSBR) with LDPE and HDPE. Those properties were compared to those of SBR/LDPE blends. It resulted that HSBR/LDPE blend had highest tensile strength, modulus and work-to-break with the lowest elongation at break. The improvement in the mechanical properties and the uniform morphology were correlated with the interfacial adhesion and compatibilisation of the HSBR/LDPE blend through ethylene segments. On the other hand, Z. Bartczak *et al.* worked with the mechanical response of rubber-modified HDPE. The rubbers were EPDM or ethylene-octene copolymers (EOR) blended into HDPE at volume fractions of up to 0.22. It was found that the single parameter that controls the notch toughness of the blends is the matrix ligament thickness between rubber inclusions. The critical thickness for HDPE-rubber systems was found around 0.6μm, independent of the type of rubber used. Above this critical value, the blend toughness remains as low as that of the unmodified HDPE.

Some works made on thermoplastic vulcanizates based on HDPE are those of J. George *et al. [George 2000]* and K. Yamauchi *et. al. [Yamauchi 2005].* J. George and co-workers studied the mixtures of Acrylonitrile Butadiene Rubber (NBR) and HDPE even though, as was already seen in chapter 2, these two materials have a large difference in surface energy. In their study the rubber/plastic ratio was maintained constant meanwhile the dicumyl peroxide concentration was varied. Blends properties such as mechanical, dynamic mechanical, flow and morphology were studied. They concluded that dynamic vulcanization can be employed as means of technological compatibilisation of HDPE/NBR blends. On the other hand, K. Yamauchi *et al.* studied the structures of thermoplastic vulcanizates based on NR/HDPE. In their study they used transmission electron microscopy (TEM), small-angle-X-ray scattering (SAXS) and small angle neutron scattering (SANS). From TEM observations, it was revealed that NR and HDPE were phase-separated but the structure became smaller by dynamic vulcanization during mixing. They wanted to observe which performance of the carbon black pigment was. It was found that carbon black was dominantly incorporated in the natural rubber domains. The extremely low contrast for SANS between crystalline and amorphous HDPE enable them to measure the interface thickness between NR and HDPE (5-6nm) and between NR and carbon black (2.4nm).

It is of interest which properties have the commercial thermoplastic elastomers that are sold nowadays. M. Montoya *et al. [Montoya 2004]* did a systematic study of physical characterization on a series of commercial thermoplastic elastomers based on PP and EPDM. They examined formulations from different manufacturers, having a wide range of Shore hardness values (from A45 to D51). It was found that EPDM used for the different formulators is very similar in ethylene content and thermal properties. Therefore, the TPE hardness is mainly controlled by the PP content and only nice elastomeric behaviour was observed in grades with dominant proportion on EPDM. Grades with higher hardness values and dominant proportion of PP showed a mechanical response corresponding to a toughened thermoplastic. A. Nicolini *et al. [Nicolini 2008]* compare the behaviour of two different curing agents: one conventional dicumyl peroxide (DCP) and a mixture of DCP/bismaleimide (BMI), in thermoplastic vulcanizates based on PP/EPDM 35/65 w/w. The thermoplastic vulcanizates obtained by using DCP presented lower tensile strength, lower swelling degree and remarkable lower deformations than those obtained with BMI/DCP system. The hardness properties were not significantly affected by the content of the curing agent, showing only a slight decrease when DCP content was increased. The study of the morphology evolution showed the rubber phase undergoes crosslinking after adding the curing agent.

Focusing on researches made out of composites containing ground tyre rubber particles, it can be found several studies. They can be differentiating in the two types of Tthermoplastic elastomers already commented. The thermoplastic elastomeric olefins (TEO) without any curing reactions, this is only the blend of the rubber and plastic phase, and those based on dynamic vulcanization. There are not too many studies of thermoplastic elastomers olefins based on ground tyre rubber when they are compared to thermoplastic vulzanizates.

Two significant studies can be found on thermoplastic elastomeric olefins based on ground tyre rubber. The first one was already commented in *chapter 4*, it was done by K. Oliphant *et al. [Oliphant 1993]* They pre-coated cryogenically ground tyre rubber particles with ethylene-acrylic acid copolymer (EAA) and mixed with Linear Low Density Polyethylene (LLDPE) and HDPE, afterwards they studied some of the mechanical properties. They found that the blends of 40% of pre-coated cryogenically ground tyre rubber particles with LLDPE have impact and tensile strengths that are 90% of those for the pure LLDPE, representing increases of 60 and 20% respectively, over the blends with uncoated particles. It was believed that specific interactions between the Ethylen Acid Acrylic (EAA) copolymer and ground tyre rubber particles do in fact occur. For HDPE, however, was shown that the obtained moderate adhesion is not sufficient to produce useful composites. A more recent work has been reported by L. Mészáros *et. al. [Mészáros 2008]* .They prepared thermoplastic elastomeric olefins based on LDPE, ground tyre rubber particles and ethylene vinyl acetate copolymer (EVA) as compatibilizer to improve the adhesion and achieve better rubber-like properties. Based on the results, it was found that the application of EVA is essential to ensure rubber-like properties but as the content is increased, only less additional improvement can be detected.

Much more studies on dynamical vulcanization based on ground tyre rubber particles have been reported. The different works can be put together depending on the thermoplastic matrix, if they include or not a grafted component and if some devulcanizating agent for ground tyre rubber is included into the final blend.

S. Tantanyanon *et.al*. *[Tantanyanon 2003]* worked with a thermoplastic vulcanized based on PP and reclaimed tyre rubber (RTR) particles, dynamically vulcanized with sulphur, maleic anhydride (MA), DCP or the combination of MA and DCP. They concluded that the major increase in interfacial adhesion resulted when MA/DCP was used which caused the crosslinking in the rubber and plastic chains. However, the amount of reclaimed tyre rubber particles in the blend is limited by the amount of carbon black. The same study but with HDPE instead of PP was also done by the same group of researchers managed by P. Punnarak *et. al. [Punnarak 2006]*. However, in this case the results showed that sulphur vulcanization produced the blend with the highest impact and tensile strength, while the peroxide curing method was the poorest.

K. Naskar *et.al*. *[Naskar 2002]* studied a thermoplastic vulcanizate formulation containing Ethylene-co-acrylic acid (A-HDPE) and ground tyre rubber maleated with maleic anhydride (MA) and dicumyl peroxide (DCP). They observed that the MA moiety in the grafted ground tyre rubber particles exist mainly in the ionic form due to the interaction between the unreacted ZnO remaining in the ground tyre rubber and the acid anhydride of the modified ground tyre rubber particles. This fact enhances the ground tyre rubber hydrophility and, therefore, increases its surface energy resulting in greater physical properties of the blend. The same group of researchers, K. Naskar *et.al*. *[Naskar 2001]*, studied thermoplastic vulcanizates consisting on A-HDPE, cryogenically ground tyre rubber particles and EPDM dynamically vulcanized with dicumyl peroxide (DCP). From their detailed study on mechanical properties and process conditions, they saw that blends with higher rubber content showed poor processability and physical properties, while the compositions with higher plastic content behave like toughened plastics. However the 60:40 rubber/plastic blend was found to behave as a commercial thermoplastic elastomer and it was observed that 50% of EPDM could be replaced by cryogenically ground tyre rubber particles without deterioration in properties.

Similar to the work of K. Naskar and co-workers, Y. Li *et.al*. *[Li 2003]* studied the effect of DCP on blends of HDPE and ground tyre rubber particles with the addition of the following fresh rubber: ethylene-octylene copolymer (POE), ethylene-propylene copolymer (EPR) or EPDM. They observed that after dynamic vulcanization the tensile strength and elongation at break of the blend containing POE was higher than those with EPR and EPDM. A good bonding between the ground tyre rubber particles and the matrix is observed in all dynamically vulcanizated systems.

As already commented in *chapter 2*, functionalization of the thermoplastic phases as well as ground tyre rubber particles is a way to increase adhesion between the two phases. A. Tolsov *et al. [Tolsov 2007]* studied the performance of recycled polyethylene (LDPE and HDPE) and ground tyre rubber functionalized. The functionalization was performed by free radical grafting of reactive monomers, maleic anhydre (MA) and acrylamide (AAm), using addition of dicumyl peroxide (DCP) or $\gamma$-irradiation technique. Interactions between the anhydride and amide functional groups of reactive polymers or between anhydride functionalized thermoplastics and coupling agents with amine/amide groups led to compatibility enhancement between the thermoplastic matrix and the dispersed ground tyre rubber particles. As a result, the tensile properties of the thermoplastic elastomer containing ground tyre rubber particles funtionalized were improved.

An attempt to make the mixing and reaction in a reactive injection moulding (RIM) was studied by R. J. Sanderson and A. Crosky*. [Sanderson 2005].* Their blends were also HDPE and ground tyre rubber but these materials were compatibilizated by a brominated dimethylol-phenolic resin and DCP. They concluded that the highest properties regarding tensile and impact strength were achieved between 25 and 35% by weight of ground tyre rubber.

And last but not least, C. R. Kumar *et al. [Kumar 2002]* produced thermoplastic vulcanizates out of ground tyre rubber particles thermomechanically decomposed in presence and absence of processing oil and LDPE. The fresh gums were SBR, NR and EPDM. The composition was constant at 50:25:25 wt%, this is, LDPE:fresh gum :GTR and dynamic vulcanization occurred either by sulphur or by peroxides curatives. Based on the thermomechanical and mechanical properties of the resulting thermoplastic elastomers , the best performance was achieved by recipes containing GTR in absence of processing oil and EPDM after vulcanization with sulphur. E. Lievana and J. Karger-Kocsis *[Lievana 2004]* worked on blends consisting on ground tyre rubber previously mixed with bitumen, LDPE and EPDM. The study is based on the fact that bitumen contributes to the devulcanization of ground tyre rubber and act at the same time as plasticizer and compatibiliser in the blends. From the study, they got thermoplastic elastomers with outstanding mechanical properties fulfilling commercial thermoplastic elastomer requirements.

From all these previous works can be concluded that addition of fresh rubber with good matrix compatibility (similar surface energies) helps to encapsulate the ground tyre rubber particles creating a co-continuos phase and improving the adhesion between the thermoplastic and rubber phase. Several factors that affect morphology have to be taken into account like plastic/rubber composition, mixture conditions and the type of curing agent used to crosslink the elastomeric phase.

## 5.4 Study of thermoplastic elastomeric olefins based on ground tyre rubber.

This first part of the study consisted on producing thermoplastic elastomeric olefins (TEO) based on ground tyre rubber, HDPE and four different compatibilizing agents: two waxes, EVA as a polymer that approaches elastomeric materials in softness and flexibility and EPDM as fresh rubber. As the work will be based in TEOs no reaction (crosslinking/vulcanization) will take place and the final material will consist on a simple blend of the two phases: rubber and thermoplastic. The objective consists on getting a final formulation with the maximum content of ground tyre rubber particles with the less deleterious effects on the final blend properties.

### 5.4.1 Experimental

The HDPE, the ground tyre rubber characteristics and the mixing process were already described in chapter 2 (*section 2.8 and 2.9 respectively*).

The Ethylene Acid Acrylic (EAA) and the Fischer-Tropsch waxes were supplied BYK-Cera. Their commercial names are CERAFAK 103 and CERAFLOUR 940 respectively. CERAFAK 103 will be named from now on as CFK. It contains 6% of active substance in xylene/butyl acetate/n-butanol. On the other hand, CERAFLOUR 940 is a micronized Fischer-Trosph with a melting point of 115ºC. From now on, it will be named CFL. The fischer-tropsch wax is a paraffin made out of CO and $H_2$.

EVA was supplied by REPSOL-YPF too. Its commercial name is ALCUDIA® PA-539, with a density of 937Kg/$m^3$ and a vinyl acetate content of 18%. It was characterized by melt flow index ($MFI_{190/2.16}$) of 2.0g/10min, with a tensile strength of 22MPa (ISO 527, -1, -3) and a tensile strength at break of 640% (ISO 527, -1,-3).

The EPDM rubber (Buna® EP G 6470) was supplied by Lanxess Chemicals, S.L., with a Mooney viscosity of 59 [$ML_{(1+4)}$ at 125ºC], 4.7wt% of ethylidene norbornene (ENB) and 70wt% of ethylene content. An ethylene rich version of EPDM was chosen in order to be fairly compatible with HDPE.

### 5.4.2 Results and discussion

#### 5.4.2.1 Mechanical properties

The type of compatibilizing agent used is the most important factor that will affect the final thermoplastic elastomeric olefin properties but also the plastic/rubber composition will be determinant. For this reason, two different steps have been done to study the mechanical properties. First of all, the impact of the different compatibilizing agents has been tested in formulas containing 30% of ground tyre rubber particles and varying the compatibilizer dosage between 5 to 20%. The second part consists on the study of different plastic/rubber composites where the compatibilizing agent was kept constant at 30%.

*Figure 5.5.a-d* shows the influence of the compatibilizer dosage on the mechanical properties of blends with constant GTR amount of 30%. Some conclusions can be drawn from the study of the graphic.

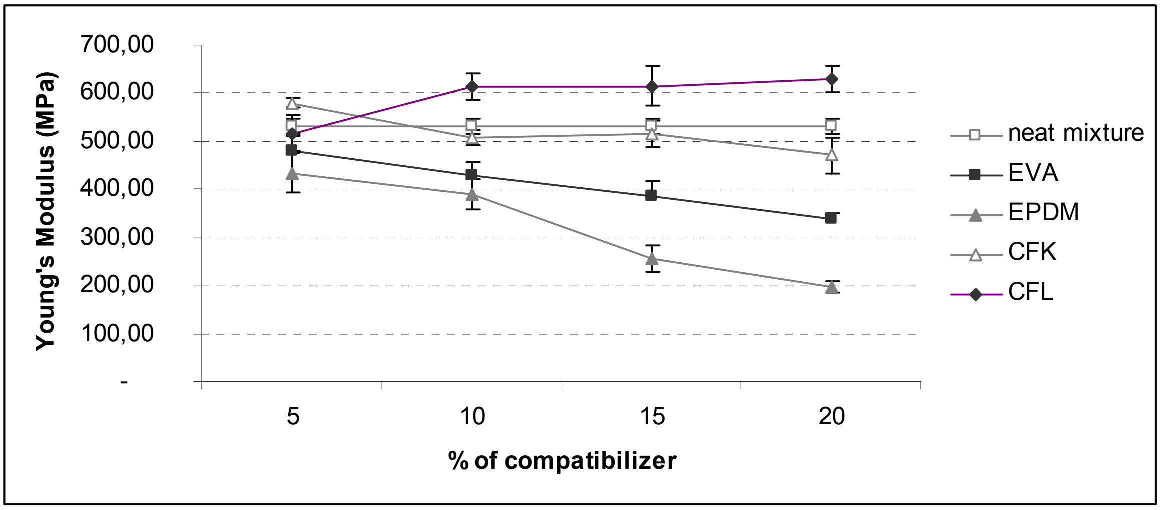


**Figure 5.5.a** Young’s modulus vs. different amounts of compatibilization agents at a constant amount of GTR of 30%.

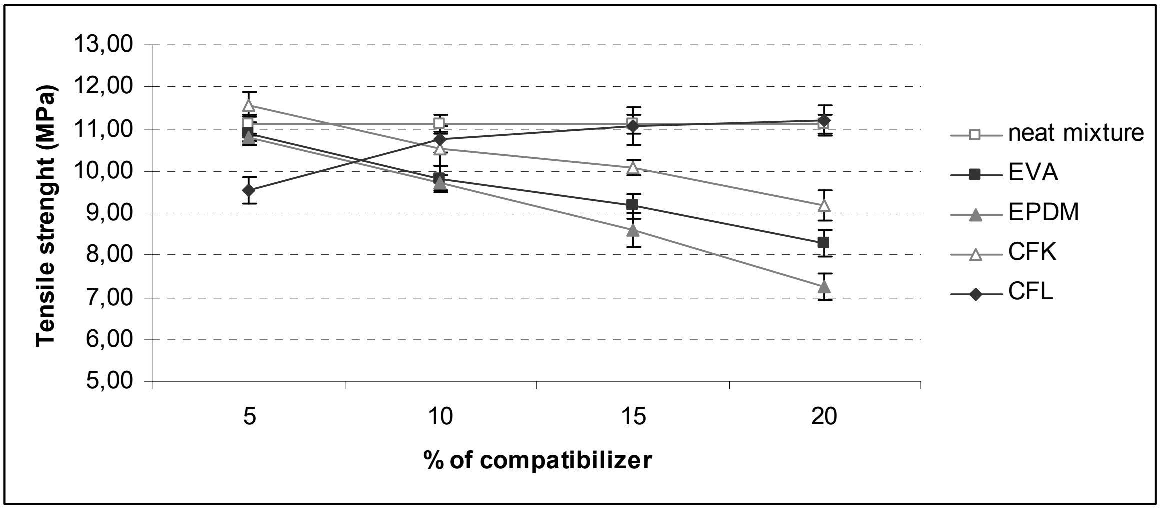


**Figure 5.5.b** Tensile strength vs. different amounts of compatibilization agents at a constant amount of GTR of 30%.

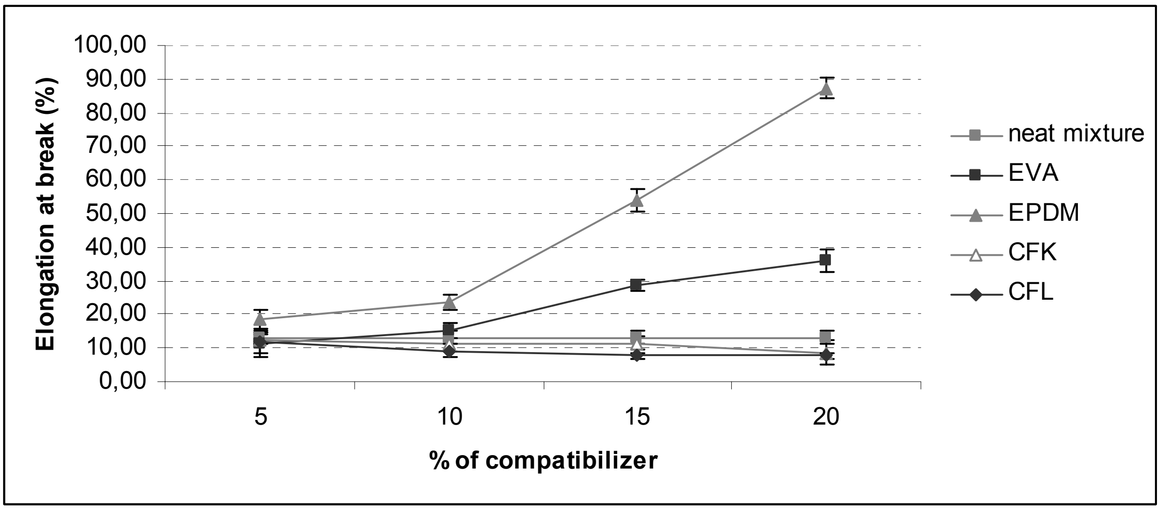


**Figure 5.5.c** Elongation at break vs. different amounts of compatibilization agents at a constant amount of GTR of 30%.

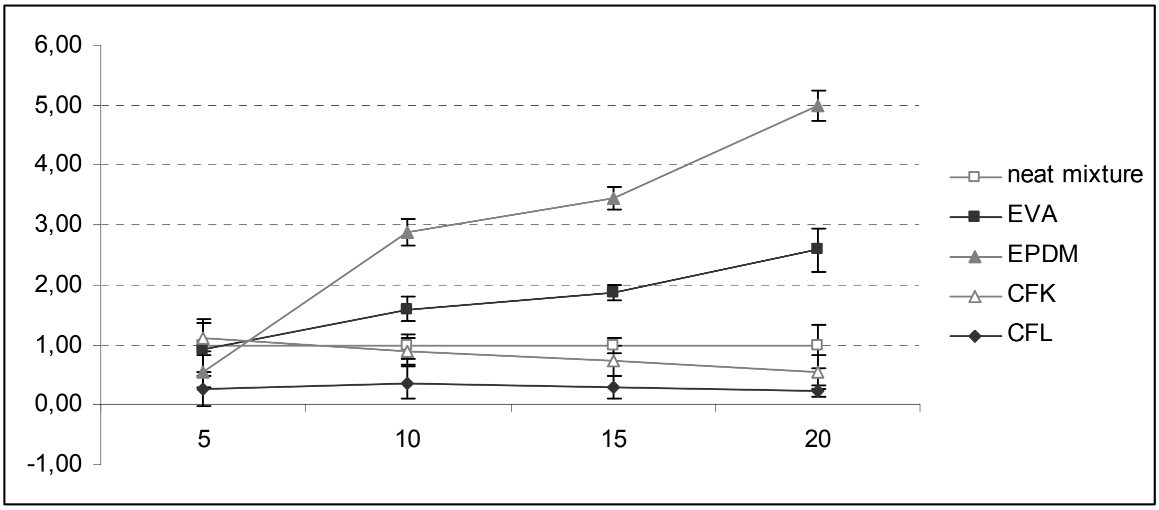


**Figure 5.5.d** Toughness vs. different amounts of compatibilization agents at a constant amount of GTR of 30%.

The increases of the two waxes content do not improve elongation at break nor toughness. However, Ceraflour 940 seems to slightly increase the Young’s modulus and the tensile strength. This was the opposite effect expected in this study were Young’s modulus and tensile strength should be reduced due to the final rubber-like behaviour. This could be related, as already studied in *chapter 4* of the present thesis (*see section 4.5.1.2*), due to a possible co-crystallization of the mixture HDPE/wax. As wax chains are short enough, they can be incorporated as straight chains into the HDPE lamellae. Cerafak 103, however, do not have any significant benefit in any property. It could be that the low active substance of the wax (only 6%) is not enough to obtain appreciable results.

On the other hand, if fresh EPDM or EVA are incorporated into the blend, elongation at break and toughness increase immediately, but Young’s modulus and tensile strength provided by the thermoplastic matrix abruptly decrease due to the incorporation of a rubber-like phase. For example, if the samples with 20% of EPDM or EVA are compared to the sample containing the neat mixture (30%GTR and 70%HDPE), it can be seen how the elongation at break is increased 628% in case of the EPDM and 250% in the case of EVA. Toughness is increased 509% and 263% for EPDM and EVA respectively.

The plastic/rubber composition has an important influence in the final material properties. *Figures 5.6.a-d* shows different compositions of plastic/rubber phases with a fixed compatibilizing agent content of 30%. It can be observed that when ground tyre rubber particles content is increased all the blends containing compatibilizers agents decreases all the mechanical properties with the exception of the Young’s modulus of Ceraflour 940 due to a possible cocrystalization with the matrix.

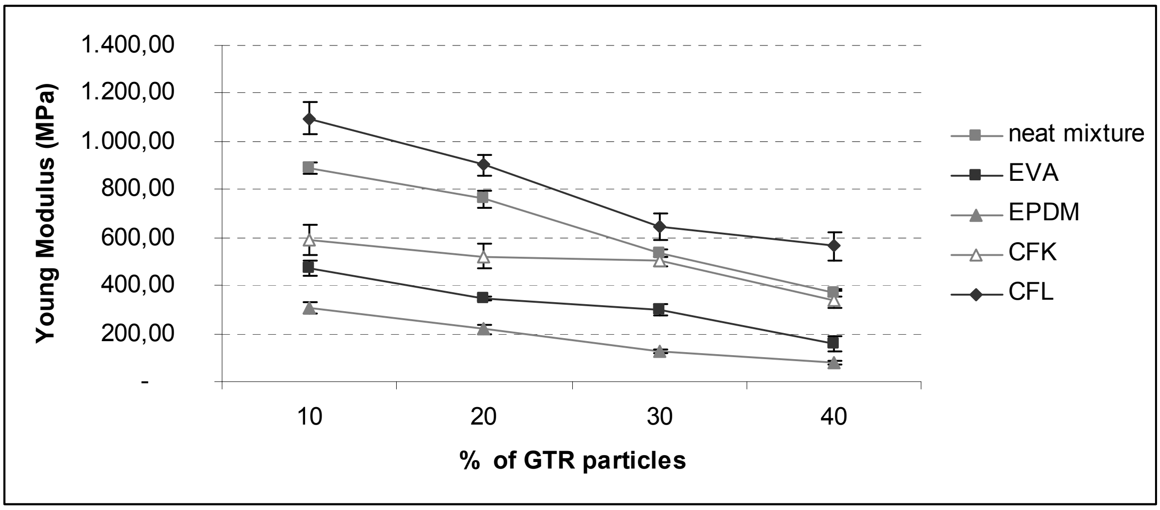


**Figure 5.6.a** Young's modulus vs. different amounts of GTR particles at a constant amount of compatibilizing agent at 30%.

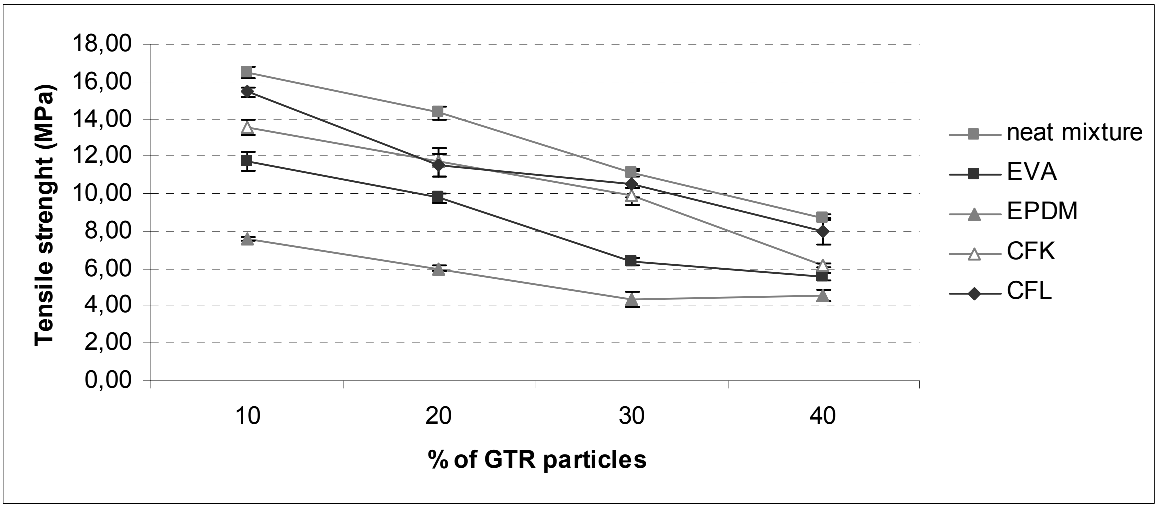


**Figure 5.6.b** Tensile strength vs. different amounts of GTR particles at a constant amount of compatibilizing agent at 30%.

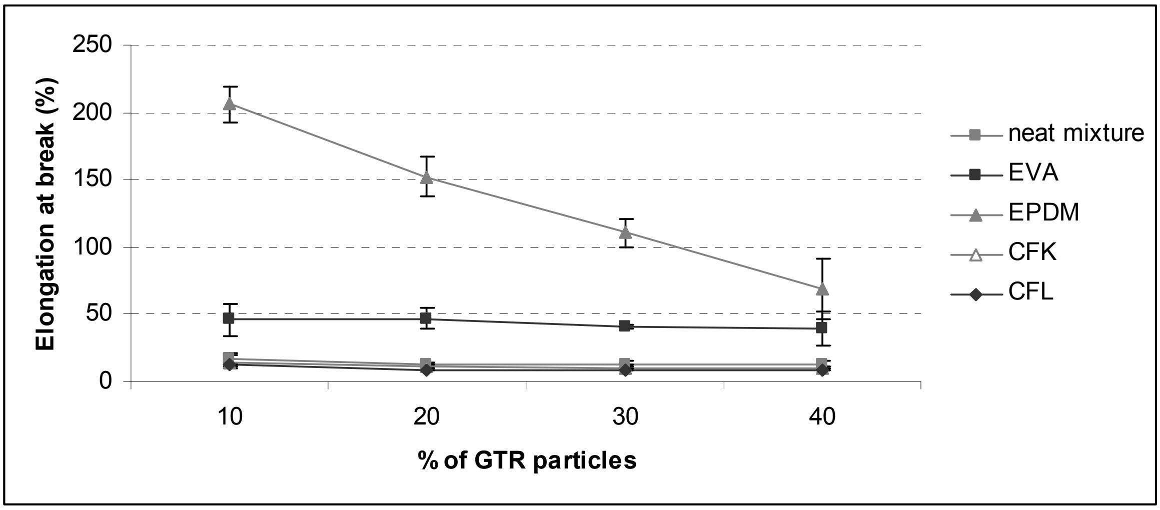


**Figure 5.6.c** Elongation at break vs. different amounts of GTR particles at a constant amount of compatibilizing agent at 30%.

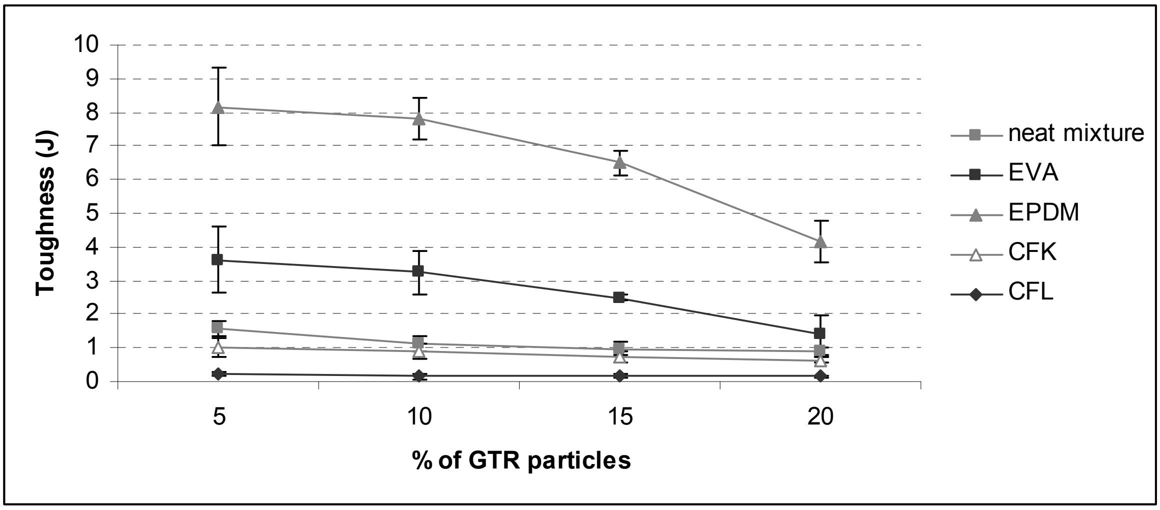


**Figure 5.6.d** Toughness vs. different amounts of GTR particles at a constant amount of compatibilizing agent at 30%.

For Young's modulus property, the tendency in all blends decrease when the amount of ground tyre rubber is increased. Besides the blend with Ceraflour 940, all the blends have lower values than the neat mixture without any compatibilizing agent. The exception of the blend containing Ceraflour 940 is again due to a possible co-crystallization of the mixture HDPE/wax. The more affected blends are those containing EPDM and EVA due to the rubber-like effect.

For tensile strength all values for all blends at different ground tyre rubber particles amounts are below the values of the neat mixture. Once again, the samples containing EPDM and EVA are the ones with lower values due to the rubber-like effect.

On the other hand, the values of elongation at break and toughness are reduced when ground tyre rubber particles amount is increased with all compatibilizing agents. In spite of that, EPDM and EVA are the compatibilizers that give higher values (especially EPDM which values are the highest by far).

The fact that these two properties do not increase when the amount of ground tyre rubber particles is getting higher in the composites means that these two fresh polymers do not act as expected: they do not perform the encapsulating effect for the ground tyre rubber particles as was though in the beginning of the study. Therefore, the adhesion between the two materials is not good and they do not perform thermoplastic elastomeric properties materials characteristics. Moreover only the values obtained by the blend containing EPDM are acceptable.

### 5.4.3 Conclusions

From the results obtained in the study of mechanical properties from the mixtures of ground tyre rubber particles with HDPE and compatiblizing agent in order to produce thermoplastic elastomeric olefins, the following conclusions can be drawn:

- The mechanical properties of the thermoplastic elastomeric olefins produced by calendaring with HDPE/GTR and the following compatibilizing agents: Ethylene Acid Acrylic wax, Fischer-Tropsch wax, EVA and EPDM, do not fulfil the mechanical properties of the commercial thermoplastic elastomers.

- The waxes are clearly not good compatibilazing agents to obtain TPEs properties. Even with the Fischer-Tropsch wax, the blend behaves more brittle and less rubber-like due to a possible co-cristallization with the matrix. The wax based on EAA do not improve any of the studied properties, this fact could be related to the low active substance of the wax.

- Although some authors got satisfactory results using EVA, the results obtained with our processing conditions were not enough to improve the mechanical properties of the TPEs produced. This fact can be clearly seen in elongation at break and tensile strength, where EVA is not able to encapsulate the GTR particles.

- Finally, we got promising results with EPDM. At a constant amount of ground tyre rubber particles at 30%, the values for elongation at break and toughness showed the rubber-like characteristics but also due to a good compatibility between phases, being the blends containing this compatibilizing agent the ones that showed the maximum elastomeric thermoplastic properties. Besides these goods results, the tendency change when higher amount of GTR are included. The higher the amount of the ground tyre rubber particles the lower the values for the elongation at break and toughness. This fact means that this mixture should be improved in order to obtain TPE's characteristics.

- As results from the conclusions of this first study, EPDM was chosen as a compatibilizing agent in the next work for thermoplastic vulcanizates where is believed that properties will improve and will better fulfil with those of TPEs due to the partial crosslinking of the fresh rubber with peroxides that will encapsulate much better the ground tyre rubber particles creating a three-dimensional network.

## 5.5 Formulations for thermoplastics vulcanizates based on HDPE, EPDM and GTR.

Thermoplastic Vulcanizates (TPV) are a specific group of the so called Thermoplastic Elastomers (TPE). The main characteristic is the existence of a crosslinked rubber phase obtained by dynamic vulcanization in the presence of the thermoplastic matrix. In this second part, TPV’s based on ground tyre rubber, HDPE and Ethylene Propylene Diene Monomer rubber (EPDM) including other additives and the crosslink by a new peroxide developed to resist high temperatures are studied. The aim of this study is optimize the formulation in order to include ground tyre rubber particles maintaining a good balance of properties in the final TPV material. The use of ground tyre rubber particles would improve the possibilities of recovering tyre waste. A detailed study regarding the influence of each component in the final mechanical properties will be performed. The swelling properties, ATR infrared spectroscopy, TGA and DSC analysis will be used in order to study the final TPV material. The morphology of the composites will be studied by scanning electron microscopy (SEM).

### 5.5.1 TPVs production

Thermoplastic vulcanizates have special production conditions parameters and machines. In general co-rotating twin screw extruders with high L/D ratio are suitable for TPVs preparation in continuous process. Internal mixers are generally used for batch processes. TPVs with high rubber phase are not easy to produce. The higher the rubber content the more difficult to produce, and therefore, less output is obtained. S. Abdou-Sabet and K. Shen *[Abdou-Sabet 1982]* found that the proper conditions to produce PP/EPDM TPVs with high content of elastomer was in a co-rotating twin screw extruder, a mixing shear ratio of 2000s$^{-1}$ and melting temperature for the PP between 170 and 230ºC. With those conditions they got higher tensile strength, elongation at break and better processability. In that concrete case the vulcanization was done within 20 to 60 sec.

In the present work factors, such as plastic/rubber composition, crosslinking density and process and cure conditions will be detailed studied due to the importance in the final TPV production.

### 5.5.2 Peroxides

The mechanism of crosslinking polymers by peroxides can be divided in three steps (*see Figure 5.6*). The first step, which determines the rate of the overall reaction, is the homolytic decomposition of the peroxide and the generation of the free radicals. The second step consists of the hydrogen abstraction by the alkoxy radical derived from the peroxide. This results in stable polymer radicals and peroxide decomposition products. The third and last step is the combination of two polymers to form the C-C crosslinks. However, additional reactions may be important to have into account: for example, Yamazaki and Seguchi *[Yamazaki 2000]* have reported studies on the chemical crosslinking mechanism of PE using peroxides at elevated temperatures and have identified alkyl radicals and allyl radicals, the latter apparently, formed via disproportionation of two polymer radicals and further reaction (*see Figure 5.7*). Sometimes, the utilization of peroxides can present as disadvantage, the degradation of the thermoplastic, because peroxides are not selective for unsaturated elastomers. Therefore, undesired side reactions such as disproportionation or β-chain scission can also take place during the crosslinking process (*see Figure 5.8*).

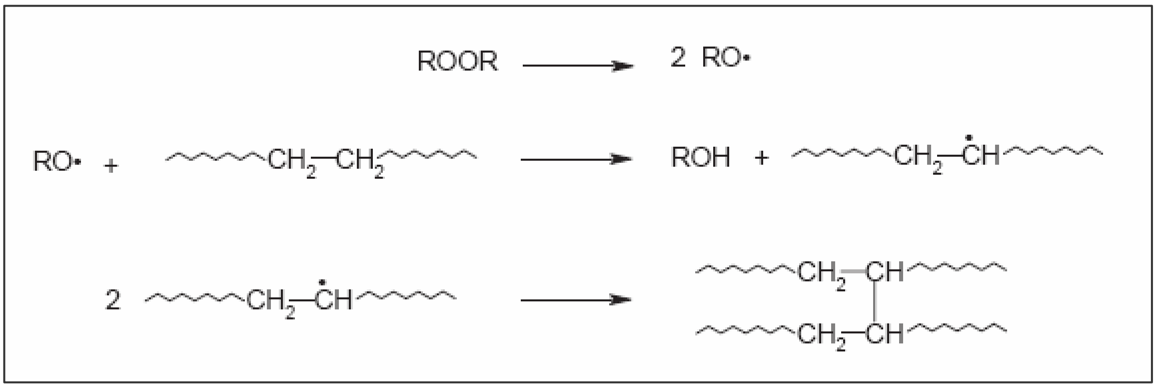


**Figure 5.6** Crosslinking reaction scheme for PE in the presence of peroxide *[Camara 2006].*

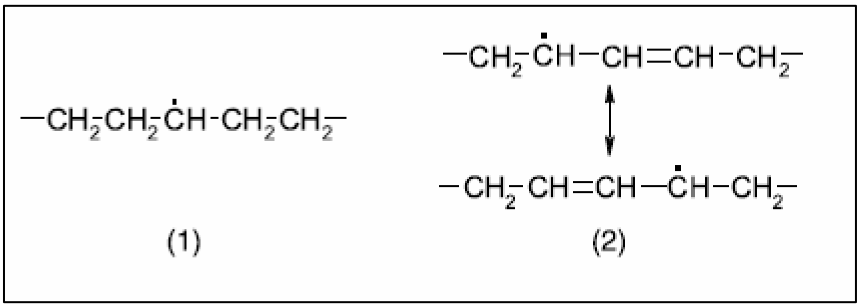


**Figure 5.7** 1) alkyl radicals and 2) allyl radicals formed from the crosslinking mechanism of PE using peroxides at high temperature *[Camara 2006]*.

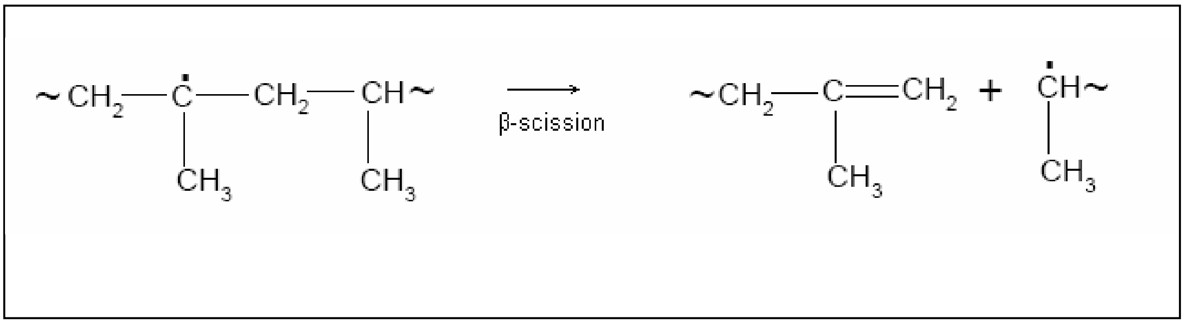
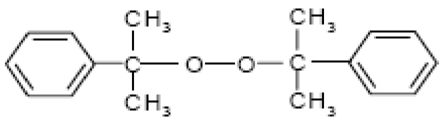


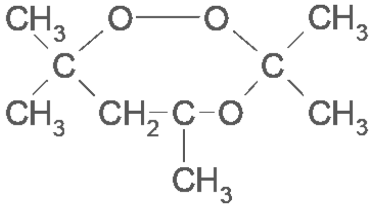
**Figure 5.8** Undesired side reaction: β-chain scission *[Camara 2006]*.

The chemical structures and commercial names of the peroxides used in present study are:

Dicumyl Peroxide (DCP)
98% of purity from Sigma-Aldrich



Trigonox® 311
3,3,5,7,7-pentamethyl-1,2,4-trioxepane
95% pure
active oxygen content of 9,18%
from Akzo Nobel Polymer Chemicals



The dialkyl peroxides, like DCP, are the most widely used, as they are cost-efficient for most crosslinking applications. Until recently, crosslinking of polyethylene always took place using conventional crosslinking peroxides like this one. To prevent premature decomposition of these peroxides in the extruder, processing temperatures were limited to 160-170°C.

Trigonox 311 has a decomposition temperature significantly higher compared to any other commercially available crosslinking peroxide, resulting in a safe processing temperature of 20-30°C above those of conventional organic peroxides. The use of this peroxide at higher temperatures, results in a less viscous, more homogeneous melt which not only improves extruder output but also has a positive effect on final properties of the cured article *[Nijhof 2008]*.

Peroxide crosslinking efficiency is defined as the number of moles of chemical crosslinks formed per mole of reacted peroxide. It depends on the peroxide type and polymer radicals formed during the process. The most used peroxide types for rubber based compounds crosslinking are: dialkyl (belongs to the thermally most stable ones), alkyl-aralkyl, diaralkyl, peroxy-ketales and peroxy esters *[Cheremisinoff 1993].*

The decomposition rate of peroxides depends on the bond strength of the weakest bond; this is the O-O bond. The chemical nature of the hydrocarbon group attached and the polarity of the substrate in which the peroxide is dispersed, will affect the O-O bond strength. The chemical nature of the hydrocarbon group will influence on structure effects like steric, inductive and the resonance stabilization of the free radicals generated on the peroxide decomposition.

The chemical nature of the peroxides resulting free radicals are very important on determining the final product properties. The most useful peroxides are those which primary free radicals are sufficiently reactive to abstract hydrogen atoms from the polymer chain to form the corresponding macro-radicals. The relative reactivity or stability of the free radicals generated is again related to the hydrogen bond dissociation energy of the parent compound.

From the values of bond dissociation energy, it can be deduced that radicals like phenyl, methyl, tert-butoxy and alkoxy are highly reactive and are good hydrogen abstractors but radicals such as ethyl, isopropyl and tert-butyl are lower in energy and are poor hydrogen abstractors *[Vroomen 1991].*

Decomposition products of DCP, primarily generates cumyloxy radicals, which further undergo β-cleavage to form acetophenone and methyl radicals. Both the cumyloxy and methyl radicals have enough energy to abstract hydrogen atoms from most sites available in a polymer. Moreover, the methyl radical is not as sterically hindered as the initial cumyloxy radical and may more efficiently involve in reactions where steric hindrance is a limitation *[Dluzneski 2001]*. DCP is known as very efficient peroxide due to the reactivity and amount of generated radicals. The decomposition products of DCP are methane, acetophenone, 2-phenylpropanol-2, α-methylstyrene and water.

The major decomposition products for Trigonox 311 are methane, acetone, isopropyl acetate, 3-hydroxy-1,3-dimethylbuthyl acetate and 3-oxy-1-methylbuthyl acetate. The decomposition reaction can be seen in *Figure 5.9.*

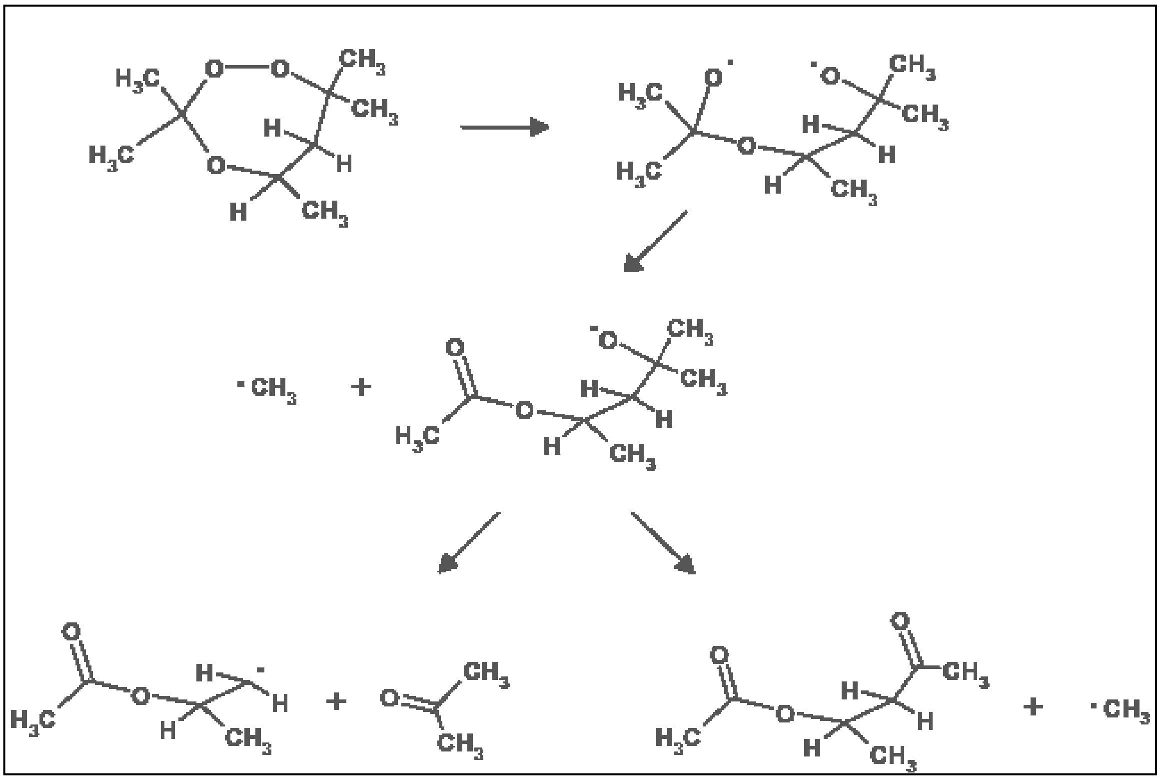


**Figure 5.9** Major decomposition products of Trigonox 311: methane, acetone, isopropyl acetate, 3-hydroxy-1,3-dimethylbuthyl acetate and 3-oxy-1-methylbuthyl acetate *[Nijhof 2008]*.

### 5.5.3 EPDM: characteristics and properties.

From previous works in literature, as well as, the study on thermoplastics elastomeric olefins in the first part of this chapter, it is clear that the election of EPDM as fresh rubber in the composite is the best option. The chosen EPDM for the present study has been Buna® EP G 6470 with a high ethylene content of 70% in order to make it as compatible as possible with the thermoplastic matrix of HDPE.

The main factors that will influence the peroxide crosslinking efficiency of EPDM are:

- the type and amount of termonomer
- ethylene/propylene ratio
- randomness of monomer distribution
- polymer molecular weight
- molecular weight distribution

Some EPDM characteristics to take into account are *[Buna 2007]*:

- Molecular weight and Mooney viscosity:
  Mooney viscosity of EPDM gives an indication of the polymer molecular weight and can be varied within a relatively wide range during its polymerization. In general, higher molecular weight provides the following properties:

  - Higher capacity for filler or oil loading
  - Lower compression set
  - Better tear resistance

  Polymer molecular weight has a substantial influence on the collapse resistance of extrudates at elevated temperatures, and this, is of special importance for the continuous production of extruded products.

- Influence of the diene:
  Copolymers can only be crosslinked with peroxides or radiation while terpolymers can be crosslinked both with peroxides and with sulphur. The cure rate and the crosslink density increase with increasing diene content. Terpolymers with high levels of Ethylidene Norbornene (ENB) are particularly suitable for the production of profiles by continuous vulcanization or for co-vulvanizations with diene rubbers.

- Influence of the ethylene/propylene ratio

  If ethylene and propylene contents are approximately equal, both monomers within the polymer molecule are evenly distributed, meaning the rubber is amorphous.

  If the ethylene content is over roughly 65% weight, ethylene sequences form in increasing number and length. These sequences are able to form crystallites.
  In the vulcanizate, the crystallinity of the polymer results in improve tensile strength and increased hardness, but also with higher compression set at low temperatures.

  Other effects of increasing ethylene content include:

  - Good extrudability
  - High filler and plasticizer loading capacity

### 5.5.5 Results and discussion

#### 5.5.5.1 Mechanical properties

The most important factors that affect thermoplastic vulcanizates morphology and mechanical properties are: a) type of curing agents used to crosslink the elastomeric phase, b) plastic/rubber composition (including EPDM/GTR proportion on the rubber) and c) degree of crosslinking. Four different experimental sets were designed in order to perform an accurate study of the thermoplastic vulcanizates mechanical properties. The first set was carried out on composites 40/30/30 (HDPE/EPDM/GTR) with peroxide contents from 0.1 to 3% using Trigonox 311 (*Table 5.1*). The influence of the Trigonox 311 content on thermoplastic vulcanizates mechanical properties was studied. In order to assess the previous results, a second set of samples containing only DCP was tested. Different temperatures of curing, related to peroxides activity, were examined too (*Table 5.2*). Moreover, the influence of the plastic/rubber composition of the composites was tested at constant EPDM/GTR ratio and peroxide content (*Table 5.3*). Finally, ground tyre rubber was substituted at different concentrations by EPDM in a fixed plastic/rubber and peroxide content composition (*Table 5.4*). These last sets of samples were tested in order to determine the amount of EPDM that can be replaced by ground tyre rubber particles maintaining a good balance of mechanical properties of the thermoplastic vulcanizates.

| Composite | % of HDPE | % of EPDM | % of GTR | % of Trigonox 311 | Young's Modulus (MPa) | Std. dev % | Tensile Strenght (MPa) | Std. dev % | Elongation* at break (%) | Std. dev % | Toughness* (J) | Std. dev % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 40 | 0 | 60 | 0 | 440.45 | 14.80 | 9.56 | 0.23 | 12.88 | 1.92 | 1.03 | 0.12 |
| 2 | 40 | 30 | 30 | 0 | 98.99 | 6.00 | 5.12 | 0.25 | 153.03 | 21.63 | 8.93 | 2.13 |
| 3 | 40 | 30 | 30 | 0.1 | 116.91 | 10.80 | 5.1 | 0.23 | 145.98 | 34.81 | 8.69 | 2.84 |
| 4 | 40 | 30 | 30 | 0.2 | 126.71 | 9.70 | 5.32 | 0.42 | 170.14 | 40.03 | 8.90 | 2.01 |
| 5 | 40 | 30 | 30 | 0.5 | 120.99 | 4.60 | 5.6 | 0.22 | 190.19 | 32.72 | 9.35 | 2.32 |
| 6 | 40 | 30 | 30 | 1 | 126.71 | 4.45 | 5.85 | 0.12 | 268.36 | 29.15 | 11.34 | 1.31 |
| 7 | 40 | 30 | 30 | 2 | 128.26 | 7.61 | 6.22 | 0.15 | 260.93 | 29.21 | 11.08 | 1.33 |
| 8 | 40 | 30 | 30 | 3 | 130.83 | 6.43 | 6.55 | 0.95 | 228.53 | 48.43 | 10.73 | 5.32 |

* Toughness is calculated as the area under the load-displacement curve

***Table 5.1*** Mechanical properties of the composites containing HDPE/EPDM/GTR ratio of 40/30/30 and different contents of Trigonox 311. The table includes the composite of 40% HDPE with 60% GTR.

| Composite | % of HDPE | % of EPDM | % of GTR | % of Trigonox 311 | % of DCP | Temperature (ºC) | Young's Modulus (MPa) | Std. dev % | Tensile Strenght (MPa) | Std. dev % | Elongation at break (%) | Std. dev % | Toughness* (J) | Std. dev % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 9 | 40 | 30 | 30 | 0 | 0.1 | 170 | 116.26 | 6.12 | 6.98 | 0.23 | 221.94 | 21.52 | 13.91 | 1.22 |
| 10 | 40 | 30 | 30 | 0.5 | 0.1 | 210 | 94.98 | 10.01 | 4.99 | 0.81 | 156.24 | 24.74 | 7.03 | 3.93 |
| 11 | 40 | 30 | 30 | 0.5 | 0.1 | 190 | 97.51 | 5.32 | 7.06 | 0.67 | 297.33 | 30.62 | 17.17 | 3.52 |
| 12 | 40 | 30 | 30 | 0.5 | 0.1 | 180 | 90.34 | 8.49 | 6.74 | 0.42 | 281.41 | 28.91 | 15.86 | 4.01 |

* Toughness is calculated as the area under the load-displacement curve

***Table 5.2*** Mechanical properties of the composites containing HDPE/EPDM/GTR ratio of 40/30/30 with 0.1% of DCP and mixtures of 0.1% DCP + 0.5% Trigonox 311, at different temperatures.

| Composite | % of HDPE | % of EPDM | % of GTR | % of Trigonox 311 | % of DCP | Young's Modulus (MPa) | Std. dev % | Tensile Strenght (MPa) | Std. dev % | Elongation at break (%) | Std. dev % | Toughness* (J) | Std. dev % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 13 | 10 | 45 | 45 | 0.75 | 0.15 | 9.78 | 0.21 | 2.45 | 0.21 | 360.00 | 35.02 | 8.33 | 1.9 |
| 14 | 20 | 40 | 40 | 0.67 | 0.13 | 23.75 | 1.43 | 4.00 | 0.42 | 337.00 | 44.81 | 12.72 | 2.1 |
| 15 | 30 | 35 | 35 | 0.58 | 0.11 | 55.49 | 4.52 | 6.04 | 0.51 | 293.42 | 48.23 | 15.31 | 2.3 |
| 16 | 40 | 30 | 30 | 0.5 | 0.1 | 97.51 | 5.32 | 7.06 | 0.67 | 297.33 | 30.62 | 17.17 | 2.5 |
| 17 | 50 | 25 | 25 | 0.42 | 0.08 | 209.00 | 12.23 | 7.10 | 0.31 | 135.00 | 12.31 | 9.04 | 0.7 |
| 18 | 60 | 20 | 20 | 0.33 | 0.07 | 263.15 | 18.81 | 8.25 | 0.22 | 107.70 | 24.21 | 7.91 | 4.9 |
| 19 | 70 | 15 | 15 | 0.25 | 0.05 | 385.52 | 16.62 | 10.44 | 0.41 | 154.63 | 45.01 | 5.68 | 4.9 |
| 20 | 80 | 10 | 10 | 0.17 | 0.03 | 637.47 | 14.61 | 14.59 | 0.51 | 42.26 | 10.83 | 3.51 | 1.3 |
| 21 | 90 | 5 | 5 | 0.08 | 0.01 | 783.07 | 60.61 | 16.70 | 0.44 | 30.80 | 7.82 | 2.70 | 1.4 |
| 22 | 100 | 0 | 0 | 0 | 0 | 927.90 | 27.91 | 17.17 | 0.52 | 390.80 | 22,01 | 38,41 | 3.0 |

* Toughness is calculated as the area under the load-displacement curve

***Table 5.3*** Mechanical properties of formulations showing variation of the rubber/plastic composites at fixed peroxide dose and constant EPDM/GTR ratio of 1:1.

| Composite | % of HDPE | % of EPDM | % of GTR | % of Trigonox 311 | % of DCP | Young's Modulus (MPa) | Std. dev % | Tensile Strenght (MPa) | Std. dev % | Elongation at break (%) | Std. dev % | Toughness* (J) | Std. dev % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 23 | 40 | 60 | 0 | 0.5 | 0.1 | 41 | 2.32 | 14.22 | 0.53 | 751.21 | 18.84 | 54.61 | 3.46 |
| 24 | 40 | 50 | 10 | 0.5 | 0.1 | 65.59 | 6.95 | 10.92 | 0.53 | 592.65 | 19.14 | 39.42 | 2.36 |
| 25 | 40 | 40 | 20 | 0.5 | 0.1 | 89.19 | 11.84 | 7.26 | 1.14 | 417.68 | 32.68 | 22.89 | 3.98 |
| 26 | 40 | 30 | 30 | 0.5 | 0.1 | 97.51 | 5.32 | 7.06 | 0.67 | 297.33 | 30.62 | 17.17 | 2.52 |
| 27 | 40 | 20 | 40 | 0.5 | 0.1 | 132.93 | 10.19 | 6.14 | 0.16 | 121.38 | 22.27 | 6.3 | 1.61 |
| 28 | 40 | 10 | 50 | 0.5 | 0.1 | 161.37 | 14.36 | 6.23 | 0.42 | 33.54 | 11.75 | 1.72 | 0.72 |
| 29 | 40 | 0 | 60 | 0.5 | 0.1 | 172.42 | 10.32 | 6.33 | 0.45 | 25.78 | 4.46 | 1.24 | 0.32 |

* Toughness is calculated as the area under the load-displacement curve

***Table 5.4*** Mechanical properties of the 40:60 plastic:rubber composites at different rubber (EPDM:GTR) ratios.

*Table 5.1* shows the influence of the peroxide content on the mechanical properties of composites where the plastic/rubber and EPDM/GTR ratios were kept constant at 40/60 and 50/50 respectively. A reference sample without EPDM and without peroxide (only HDPE/GTR) is also included showing a brittle performance (*composite nº1*). When EPDM is incorporated to the composite, elongation at break and toughness increase immediately, however, Young's modulus and tensile strength decrease due to the incorporation of a rubber-like phase. As peroxide content increases, all properties show higher values due to crosslinking, but at higher contents of Trigonox 311 (2 and 3%) elongation at break start decreasing. This could be related to the reaction of the peroxides with the thermoplastic matrix, because they are not selective for unsaturated elastomers *[Loan 1963] [Camara 2006]*. Similar results were reported in previous studies *[Kumar 2002] [Naskar 2001].* In polymer composites, an increase in elongation at break is directly related to a better compatibility between phases. Therefore it can be concluded that composite 6, containing 1% of Trigonox, shows maximum elastomeric thermoplastic properties. In other words, from this experiment, 1% of Trigonox produces the best results to crosslink EPDM and seems to be effective creating a network to encapsulate ground tyre rubber particles.

Processing conditions are important issues regarding final properties of the cured composite. DCP, as standard peroxide for TPV's studies, was also tested in combination with Trigonox, in order to study synergetic effects and compare processing and physical properties of the composites. Although 1% of Trigonox showed maximum performance in the first study, the content was reduced to 0.5% when adding DCP as additional peroxide, in order to avoid excess of peroxide. That would be also beneficial for cost savings. *Table 5.2* shows the mechanical properties of the DCP alone and in combination with Trigonox 311, at different processing temperatures. Composite 9, with 0.1% of DCP, was consolidated at 170ºC and did not show difficulties in handling. However, its properties were not as good as those of composite 6. Composites with higher DCP contents lead to premature crosslink in the two roll mixer (working temperature 150-155ºC) and those pressed at higher temperatures became very sticky and difficult to remove from the press being impossible to measure. The synergy effect of both peroxides at 210, 190 and 180ºC was studied in composites 10, 11 and 12. Consolidation temperature seems to have an important role in the final properties. Different conditions for composites containing 0.5% of Trigonox and 0.1% of DCP were tested. Composite 10 was difficult to take off the press too but composites 11 and 12 showed no handling problems. Composite 11 shows better elongation at break and toughness than 6. Therefore a combination based on 0.5% of Trigonox and 0.1% of DCP respectively seems to give the maximum elastomeric thermoplastic properties. Nicolini *et al.* [*Nicolini 2006*] also found that the mixture of two curing agents, DCP/bismaleimide, in TPVs based on PP/EPDM 35/65 w/w gave the best mechanical properties and much better ones than DCP alone.

The plastic/rubber composition has also an important influence in the final material properties. *Table 5.3* shows the mechanical properties of composites where EPDM/GTR ratio was kept constant at 1:1, and peroxide combination of 0.5% Trigonox 311 and 0.1%DCP. As HDPE content increases from 10 to 40%, Young's modulus, tensile strength and toughness gradually increase too. Elongation at break decreases due to the incorporation of a plastic phase. With even higher contents of HDPE (more than 50%), Young's modulus and tensile strength increase while elongation at break and toughness decrease. The higher the HDPE content the less toughening effect of the elastomeric phase. Therefore the mixture with 40% of HDPE and 60% of rubber phase shows the highest desired properties. Similar results were found by A. K. Naskar *et al.* *[Naskar 2001].*

The last set of samples study mechanical properties when fresh rubber is replaced by ground tyre rubber particles. Up to this point, the best properties have been obtained with the 40/60 composition of plastic/rubber phase. Therefore, the HDPE phase and peroxide content are maintained while EPDM content is varied from 60% to 0%. *Table 5.4* shows the results. When ground tyre rubber particles content increased the loss in mechanical properties due to the incompatibility between ground tyre rubber particles and HDPE is clear. From 60% to 30% of EPDM, the composite becomes gradually less toughened but when 40% of ground tyre rubber particles is included, EPDM seems to loose its encapsulating and compatible effect leading to an important decrease of elongation at break and toughness. It's interesting to notice that the composite with 60% of ground tyre rubber particles is even more brittle than the one containing 10% of EPDM. It seems that peroxides only vulcanizes EPDM and do not react with the possible existing active sites of ground tyre rubber.

After this study an overall vision of composites behaviour is acquired. In order to assess the substitution of EPDM for ground tyre rubber, two composites are selected for comparison. Composite 23 does not contain GTR (40%HDPE + 60%EPDM + 0.5%Trig + 0.1%DCP) and composite 26 has 30% of EPDM substituted by GTR (40%HDPE + 30%EPDM + 30%GTR + 0.5%Trig + 0.1%DCP). Results show (*Table 5.4*) that even with the considerable amount of 30% in ground tyre rubber particles, the 297% value in elongation at break fulfils the major criteria for a thermoplastic elastomer: which this value must be higher than 100% [*Lievana 2004*]. However, if the ground tyre rubber particles amount is increased to 40% the elongation at break drastically drops down to 121% which is almost in the limit. Therefore, 30% of ground tyre rubber in the composite is the optimum amount for the desired balance: maximum ground tyre rubber particles quantity with acceptable mechanical properties.

#### 5.5.5.2 Hardness measurements

*Figure 5.10* shows an increasing hardness tendency when peroxide dosage (Trigonox) is increased in the blends where the plastic/rubber and EPDM/GTR ratios were kept constant at 40/60 and 50/50 respectively. Figure 5.11 shows the effect on hardness, when EPDM is substituted by GTR (*Table 5.4*). At high GTR dosages, from 40 to 60%, the hardness value is maintained constant at values of 89-90, in those cases, EPDM (less than 20%) is not able to form the co-continuous phase to encapsulate the dispersed GTR particles and give the rubber-like property on the final blend. This is in concordance with the results obtained in the mechanical properties, where composites with less than 30% of EPDM suffer an important decrease in elongation at break and toughness.

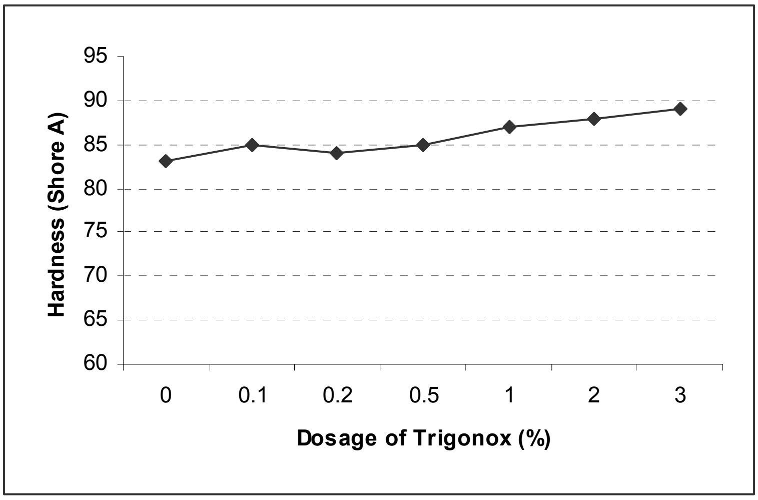


**Figure 5.10** Hardness as function of Trigonox dosage.

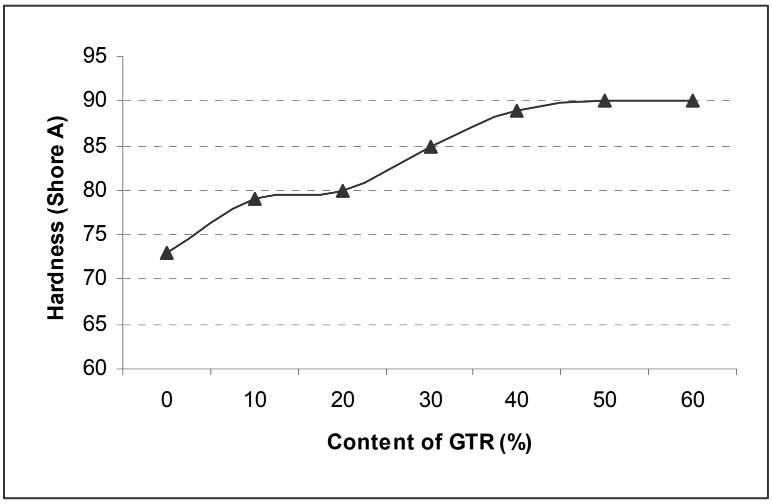


**Figure 5.11** Hardness as function of GTR dosage.

### 5.5.5.3 Swealling measurements

*Figure 5.12* shows the swelling measurement of the composites where the plastic/rubber and EPDM/GTR ratios were kept constant at 40/60 and 50/50 respectively. The influence of the peroxide content was studied. As expected, when peroxide amount increase, the swelling decreases. High concentrations of peroxide (more than 1%) lead to crosslinked structures related to the observed decrease of elongation and toughness.

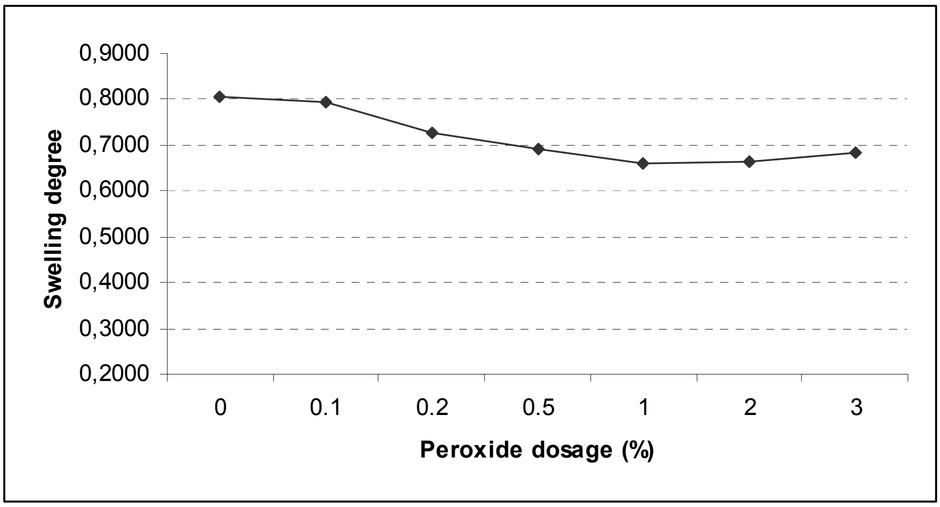


**Figure 5.12** Influence of peroxide dosage on the swelling degree on blends where the plastic/rubber and EPDM/GTR ratios were kept constant at 40/60 and 50/50 respectively.

#### 5.5.5.4 Attenuated total reflectance FTIR spectroscopy

ATR-FTIR spectroscopy was used to study the chemical changes involved after dynamic vulcanization. The main peroxides reaction consists on the hydrogen atoms abstraction from the polymer chain and formation of the corresponding macroradicals [18]. The reactivity of the generated free radicals depends on the hydrogen bond dissociation energy [*Naskar 2004*]. Trigonox 311 major decomposition products are methane, acetone, isopropyl acetate, 3-hydroxy-1,3-dimethylbuthyl acetate and 3-oxy-1-methylbuthyl acetate, while, major DCP decomposition products are methane, acetophenone, 2-phenylpropanol-2, α-methylstyrene and water.

Peroxide cross-linking of unsaturated rubbers and polymers is achieved via free-radical mechanism that involves three steps: the first is the generation of radicals by thermal decomposition of the peroxide, on second place the radical attack on the polymer chain via hydrogen abstraction to generate polymer radicals, and third and last, the combination of two polymer radicals to form carbon-carbon crosslinks [*Yamazaki 2000*].

In order to investigate the chemical changes on composites with Trigonox 311, the sample's spectra with constant 40/30/30 ratio of HDPE/EPDM/GTR and an increasing peroxide dose from 0 to 3% were examined. The studied bands have been referenced by Choudhury et al. [*Choudhury 2007*] analyzing similar composites based on milk pouches (LDPE-LLDPE), EPDM and DCP. The spectra are shown in *Figures* 5.13.a, 5.13.b and 5.13.c.

In *Figure 5.13.a*. can be seen, the presence of different C=O stretching bands (1744, 1592, 1586 cm$^{-1}$) associated to carbonylated products such as ketones, aldehydes or other products that can be generated by the Trigonox decomposition. The C=O peak intensity is observed to be higher for the composites cured with higher peroxide amount, indicating an oxidative degradation of the matrix polymer due to the higher peroxide concentration.

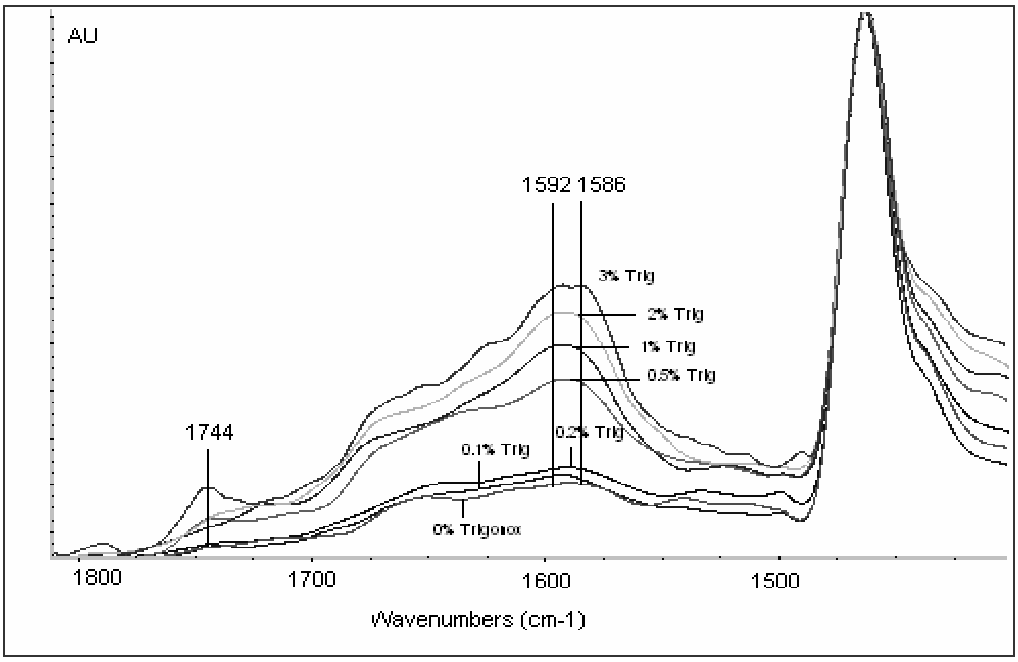


**Figure 5.13.a** ATR-FTIR spectres of samples with HDPE/EPDM/GTR ratio of 40/30/30 and an increasing peroxide dose (from 0 to 3%) for the area between 1800 and 1400 $cm^{-1}$.

*Figure 5.13.b* shows the spectra between 1400 and 1000$cm^{-1}$. Bands at 1374, 1258, 1090 and 1025$cm^{-1}$ are assigned to the asymmetric stretching vibrations of C-O-C bonds of esters and ethers linkages during the curing reaction between peroxide free radicals and the polymeric macroradicals. The C-O-C band absorbance increases up to 1% of Trigonox but it decreases at higher peroxide dose (2 and 3%) due to the preferred oxidative degradation reaction of the peroxide with the matrix. The results are in concordance with the mechanical properties, where the composite with 1% of Trigonox showed the more interesting mechanical behaviour.

Finally, the spectral region between 850 and 700 is shown in *Figure 5.13.c*. The band at 804$cm^{-1}$ corresponds to the double bond –C=C- of the ENB unit of EPDM. Its significant intensity decrease is associated to the disappearance of the double bonds as a consequence of the crosslinking.

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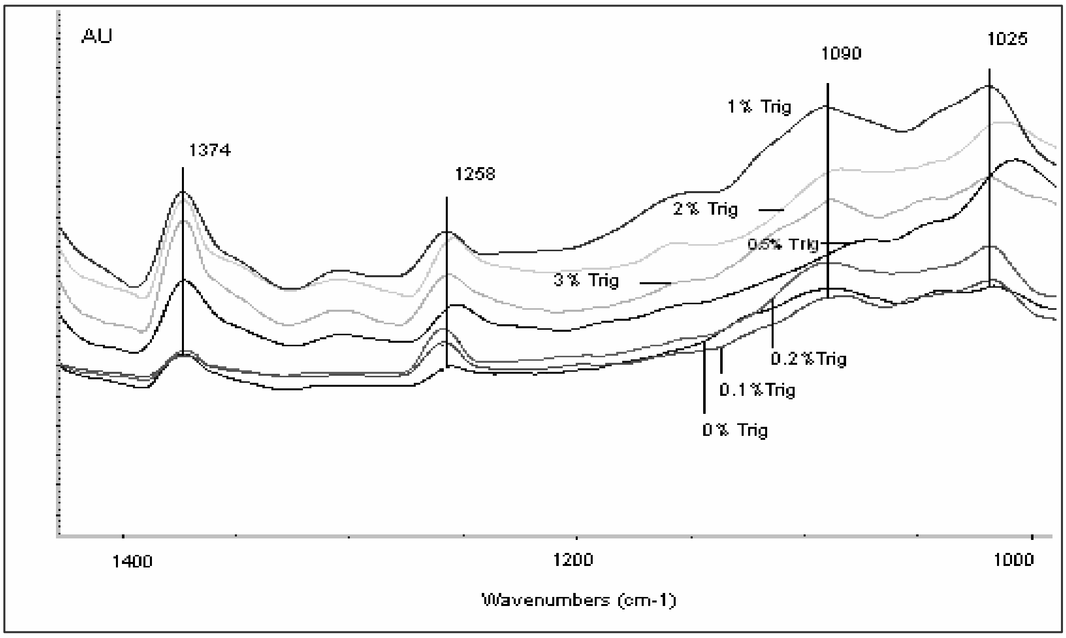

**Figure 5.13.b** ATR-FTIR spectres of samples with HDPE/EPDM/GTR ratio of 40/30/30 and an increasing peroxide dose (from 0 to 3%) for the area between 1400 and 1000 cm$^{-1}$.

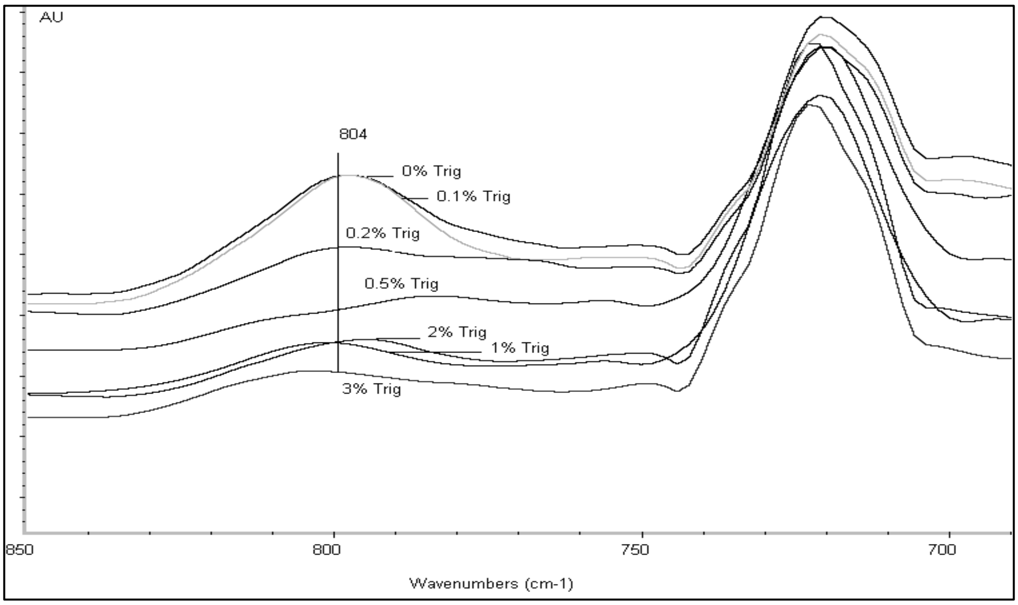

**Figure 5.13.c** ATR-FTIR spectres of samples with HDPE/EPDM/GTR ratio of 40/30/30 and an increasing peroxide dose (from 0 to 3%) for the area between 850 and 700cm$^{-1}$.

### 5.5.5.5 Thermogravimetric analysis (TGA)

*Figure 5.14* shows the DTG curves of ground tyre rubber particles, the composite 11 (40%HDPE 60%EPDM 0.5%Trigonox 0.1%DCP) and a new composite composed of 40%HDPE 30%EPDM 30%GTR 3%Trigonox and 0.6%DCP. For the ground tyre rubber particles thermal decomposition, two peaks can be observed at 350 and 402ºC which corresponds to 48.5% of elastomeric components (e.g. SBR, NR and BR) [25]. The first stage, between 200 and 350 is related to the decomposition of the extender oil decomposition and other organic non-polymeric additives present in the rubber compound [*Punnarak 2006*]. The high char residue of 51.5% includes carbon black and other fillers such as calcium carbonate or zinc oxide.

The two composites containing 40%HDPE 30%EPDM 30% GTR and peroxides show two thermal decompositions processes between 230 and 500 ºC. The first decomposition at 382ºC corresponds to the elastomeric components. The second process appears at 473ºC for the composite with lower peroxide amount and 467ºC for the one with higher peroxide amount. It corresponds to the HDPE and EPDM decomposition [*Montoya 2004*]. The slight displacement to lower temperatures, for the peak corresponding to HDPE and EPDM, can be related to the high peroxide dose and the increase in carbonyl groups observed by FTIR-ATR analysis.

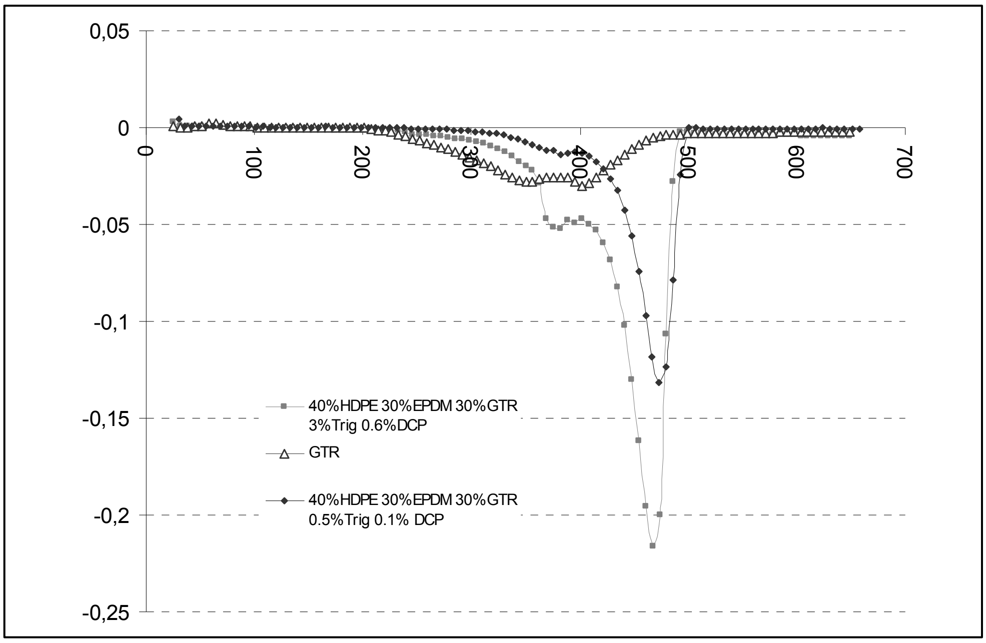

**Figure 5.14** DTG curves corresponding to GTR itself, an standard blend with 40%HDPE 60%EPDM 0.5% Trigonox 0.1% DCP and a blend with 40%HDPE 30%EPDM 30%GTR 3%Trigonox 0.6%DCP.

### 5.5.5.6 DSC analysis

*Table 5.5* shows the DSC characteristics for the individual components and the composites. Both components (EPDM and HDPE) show a reduction in enthalpy of melting, related to the decrease in crystallinity when mixed with ground tyre rubber particles [*Aggarwal 1975*]. This decrease is related to the interaction of both polymers which disturbs the packaging and is an indicative of compatibility.

A decrease of the melting temperature ($Tm_{peak}$) is also found for the HDPE components of the different composites. It is known that a decrease of Tm in polymers of composites is caused by the interaction of both polymers [*Mark 1996*] and is always an indication of an improvement in composite compatibility. A displacement of $Tm_{peak}$ is also found for the ethylene component in EPDM phase.

Crosslinked composites have lower crystallinity than composite 2 (40%HDPE 30%EPDM and 30%GTR) which is not crosslinked. When peroxide content increases, the higher crosslinking degree produces a decrease of enthalpy of melting in both components (EPDM and HDPE).

| **Mixture** | **$Tm_{peak}$ (ºC)** | | **$Tm_{onset}/Tm_{end}$ (ºC)** | | **ΔHm (J/g)** | |
|---|---|---|---|---|---|---|
| | EPDM | HDPE | EPDM | HDPE | EPDM | HDPE |
| HDPE | - | 132.83 | - | 132.83/137.07 | - | 250.56 |
| EPDM | 46.17 | - | 38.39/53.14 | - | 9.07 | - |
| 1 | - | 127.83 | - | 119.05/131.84 | - | 243.37 |
| 2 | 47.17 | 128.00 | 41.78/51.49 | 118.11/132.02 | 2.60 | 227.22 |
| 3 | 47.17 | 126.50 | 41.98/51.45 | 117.87/132.26 | 2.26 | 224.40 |
| 5 | 46.67 | 127.67 | 41.13/52.59 | 118.12/132.36 | 1.80 | 215.12 |
| 8 | 46.83 | 127.33 | 41.21/52.73 | 117.62/132.42 | 1.46 | 210.08 |
| 11 | 48.50 | 126.67 | 43.71/54.15 | 116.32/132.35 | 0.76 | 195.35 |

**Table 5.5** DSC characteristics for the individual components (HDPE, EPDM) and the produced blends.

#### 5.5.5.7 Scanning electron microscopy (SEM) analysis

Figure 5.15 shows the SEM micrograph of the following composites: a) 40%HDPE 60%GTR, b) 40%HDPE 30%EPDM 30%GTR, c) 40%HDPE 30%EPDM 30%GTR 3%Trigonox and d) 40%HDPE 30%EPDM 30%GTR 0.5%Trig 0.1%DCP.

Figure 5.15.a shows the composite without EPDM and peroxides, only HDPE and GTR. These two materials are incompatible due to their different chemical composition as can be seen in picture 5.15.a where ground tyre rubber particles appear almost isolated without being wet by the HDPE matrix. Without any kind of compatibility between the two materials, very little adhesion is possible, leading to very poor mechanical properties as already described.

The influence of EPDM addition into the HDPE-GTR composite is shown in Figure 5.15.b. The addition of an elastomeric component which, at the same time contains high amount of polyethylene should help to improve compatibility between HDPE and ground tyre rubber particles. Particles are not as isolated as in the composite without EPDM. However, can be observed as some ground tyre rubber particles parts are still not surrounded neither by HDPE nor EPDM. In other words, EPDM still is not able to encapsulate all ground tyre rubber particles.

As expected, the encapsulation effect is seen in Figures 5.15.c and 5.15.d with peroxides addition. In both pictures can be observed how ground tyre rubber particles are encapsulated by EPDM. In the case of Figure 5.15.d corresponding to the composite with 0.5%Trigonox + 0.1%DCP, the encapsulating effect is much more visible. The fact that ground tyre rubber particles are completely encapsulated means that EPDM has formed a three-dimensional network within them, and at the same time, EPDM creates a co-continuous phase with HDPE. This effect leads to a much better adhesion and better mechanical properties as already observed.

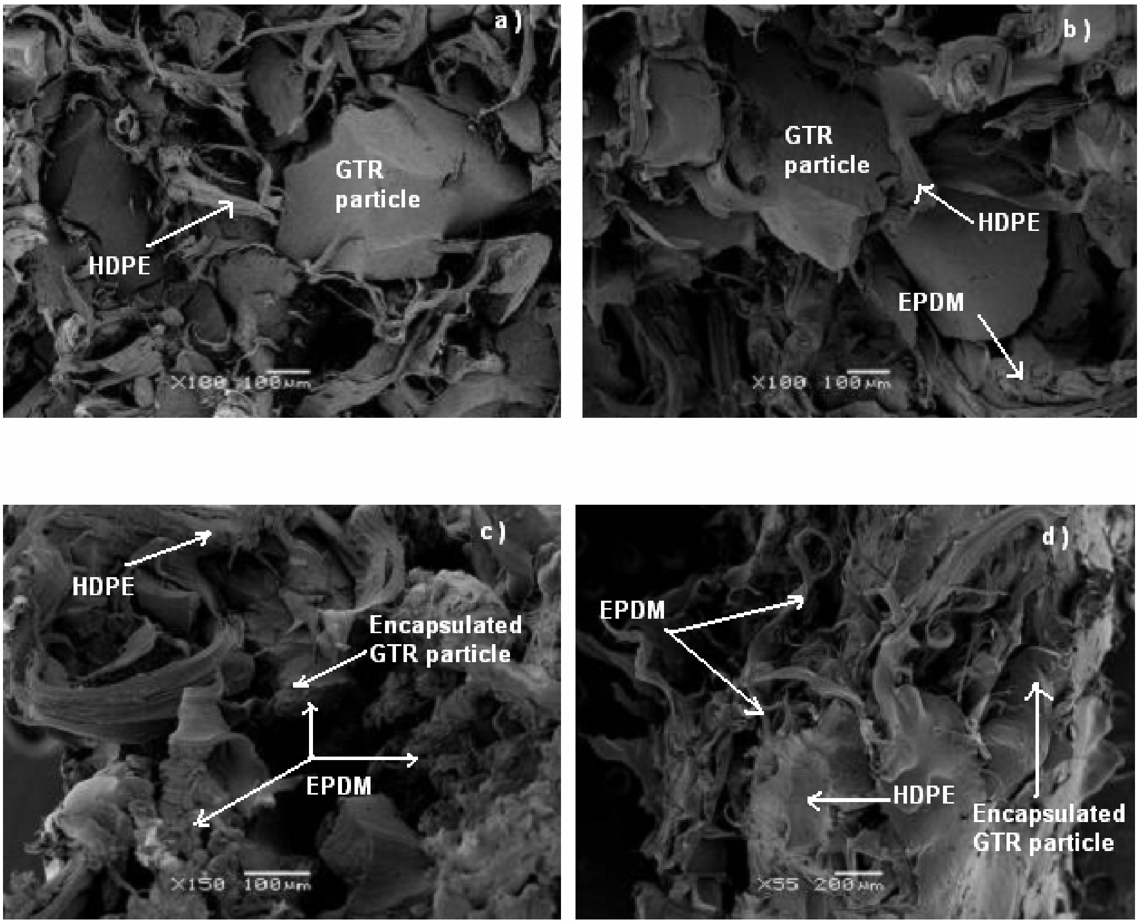

***Figure 5.15.a-d*** shows the SEM micrograph of the following composites: (a) 40%HDPE 60%GTR, (b) 40%HDPE 30%EPDM 30%GTR, (c) 40%HDPE 30%EPDM 30%GTR 3%Trigonox and (d) 40%HDPE 30%EPDM 30%GTR 0.5%Trig 0.1%DCP.

### 5.5.6 Conclusions

The following conclusions can be drawn from the present study:

- The composition consisting on 40% HDPE 30% EPDM 30% GTR 0.5% Trigonox 311 and 0.1% DCP gives the best balance regarding GTR amount (30%) and mechanical properties. It is proved that process conditions, such as press temperature, have an important role in the final mechanical properties. The mixture of two different peroxides types give the best synergist effect. High peroxide amount has a negative impact on crosslinking due to a possible thermooxidative degradation of the thermoplastic matrix as observed by FTIR-ATR and TGA analysis.

- The encapsulation phenomena of EPDM over GTR particles can be observed in SEM pictures. An optimization of composite components for maximum adhesion between GTR particles and HDPE matrix is studied during the mechanical properties test. Good adhesion is only possible if GTR particles are encapsulated by fresh rubber: EPDM. Good adhesion between phases is directly translated as good mechanical properties in the final composite.

- GTR can be up-cycled if is used as a rubber component in TPV production. In the present study, 30% of fresh rubber can be substituted by this recycled material, still fulfilling the major criteria for this kind of materials.

# *Chapter 6:*
# *Conclusions and future outlook*

## 6.1 Comparison of composites obtained by each compatibilization study

This work was devoted to study different compatibilization methods for HDPE and ground tyre rubber particles obtained from standard industrial grinding process. In this way, new routes to recycle scrap tyres are explored.

Based in the knowledge from the literature and the preliminary screening works three different methods to compatibilize HDPE and ground tyre rubber were tested:

1. acid pre-treatment on the ground tyre rubber particles in order to cause mechanical interlocking to improve mechanical adhesion.
2. the addition of wetting additives and waxes in order to modify the interfaces between the two materials improving adhesion by chemical interactions.
3. with the incorporation of fresh rubber and peroxides in order to encapsulate the ground tyre rubber particles and create a thermoplastics vulcanizates or a thermoplastic elastomer olefins materials depending if the blend contains or not peroxide respectively.

The final mixture should have the following premises:

1. good adhesion between ground tyre rubber and HDPE
2. considerable amount of ground tyre rubber particles without deleterious effects on the mechanical properties in the final blend
3. cheap compatibilization process
4. easy handling of the compatiblization process

The compatibilization study for the different methods has consisted in mechanical, thermal if necessary and morphological characterization. Besides these three characterizations, the mechanical properties give a directly information of the compatibilization characteristics for the two materials.

The three compatibilization methods have been studied in chapters 3, 4 and 5. Each of them concluded with one amount of the studied compatibilizer that gives the highest mechanical properties. In order to have an overview on the mechanical properties the *Table 6.1* compares the mechanical properties of different blends obtained via different compatibilization methods. All of them contain 20% of ground tyre rubber particles as basic parameter to be compared between them.

| Compatibilization | Young modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) | Toughness (J) |
|---|---|---|---|---|
| neat mixture[a] | 759.65 | 14.34 | 12.55 | 1.13 |
| Sulpho-nitric treatment[b] | 762.25 | 9.34 | 7.3 | 0.48 |
| with 3%Byk-P 105[c] | 796.47 | 15.08 | 13.19 | 1.25 |
| with 5%Licowax PE 520[d] | 797.10 | 15.55 | 13.69 | 1.32 |
| with 30%EPDM (TPO)[e] | 219,35 | 5,99 | 152,19 | 14,32 |
| with 40%EPDM + peroxides (TPV)[f] | 89.19 | 7.26 | 417.68 | 22.89 |

[a] 20%GTR + 80%HDPE

[b] 20% of pre-treated GTR with the sulpho-nitric mixture of acids + 80%HDPE

[c] 20%GTR + 80%HDPE + 0.6%Byk-P 105

[d] 20%GTR + 80%HDPE + 1%Licowax PE 520

[e] 20%GTR + 50%HDPE + 30% EPDM

[f] 20%GTR + 40%HDPE + 40% EPDM + 0.5%Trigonox 311 + 0.1%DCP

**Table 6.1** Mechanical properties of the blends obtained by different compatibilization methods containing 20% of GTR.

From *table 6.1* the following conclusions can be taken:

i) The mechanical properties directly depend from the compatibilization method used.

ii) The acid treatment do not improve any of the properties from the neat mixture and as explained in chapter 3 this is due to the big particle size of the used ground tyre rubber particles. If lower particle size is used, for example lower than 200μm, then the values are much higher regarding Young's modulus and tensile strength (994MPa and17.7MPa respectively). These values show that the final composite shows a brittle performance compared to the neat mixture (20% of GTR and 80% of HDPE).

iii) The values obtained with the waxes and wetting additives are slightly better than the neat mixture for all the studied mechanical properties characteristics.

iv) The blend containing 30% of EPDM shows the rubber-like characteristics of thermoplastic elastomeric olefins. While Young's modulus and tensile strength suffer and important decrease, elongation at break and toughness increases do to the incorporation of the fresh rubber.

v) If 20% of EPDM instead of 30% is used with the addition of peroxides as a crosslinking agent, the rubber-like characteristics commented before are much better increased. This fact means a better encapsulation of the ground tyre rubber particles by EPDM fresh rubber and can be directly translated for a better compatibility between phases.

A second important point to choose the best compatibilization method is the amount of ground tyre rubber particles incorporated in the mixture without deleterious defects in the mechanical properties. One of the aims of the thesis was to incorporate as much GTR as possible into the blend in order to help the reduction of EOL tyres. *Table 6.2* shows the mechanical properties from the same mixtures from *table 6.1* but at 40% of GTR in the blend.

| **Compatibilization** | **Young modulus (MPa)** | **Tensile strength (MPa)** | **Elongation at break (%)** | **Toughness (J)** |
|---|---|---|---|---|
| neat mixture[a] | 370,25 | 8,74 | 12.31 | 0.15 |
| Sulpho-nitric treatment[b] | 323.04 | 6.45 | 7.8 | 0.42 |
| with 3%Byk-P 105[c] | 427.10 | 8.46 | 13.92 | 0.90 |
| with 5%Licowax PE 520[d] | 421.39 | 9.30 | 14.97 | 0.92 |
| with 30%EPDM (TPO)[e] | 79.09 | 4.54 | 68.97 | 4.17 |
| with 40%EPDM + peroxides (TPV)[f] | 132.93 | 6.14 | 121.38 | 6.3 |

[a] 40%GTR + 60%HDPE

[b] 40% of pre-treated GTR with the sulpho-nitric mixture of acids + 60%HDPE

[c] 40%GTR + 60%HDPE + 1.2%Byk-P 105

[d] 40%GTR + 60%HDPE + 2%Licowax PE 520

[e] 40%GTR + 30%HDPE + 30% EPDM

[f] 40%GTR + 40%HDPE + 20% EPDM + 0.5%Trigonox 311 + 0.1%DCP

**Table 6.2** Mechanical properties of the blends obtained by different compatibilization methods containing 40% of GTR.

From *table 6.2* similar conclusions than in *table 6.1* can be taken:

i) The acid treatment does not improve any of the studied properties except for toughness at that particle size.

ii) The use of wetting additives and waxes improve slightly all the properties.

iii) The compound with fresh rubber improves the rubber-like properties (elongation at break and toughness) although these values are much lower than with 20% of ground tyre rubber particles. This is related to an insufficient encapsulation of the GTR rubber. On the other hand, the blend with EPDM and peroxides improves the rubber-like properties by far. The addition of peroxides into the blend helps to a better encapsulation of the ground tyre rubber particles and therefore to a better compatibilization of the two phases.

A third point to have in consideration in order to establish the best compatibilization method is the cost of the final formula. A quotation of the different formulas containing 20% of GTR is done in *table 6.3*:

| **Component** | **Price (€/Kg)** | **Acid Pre-treatment** | **Wetting additives** | **waxes** | **With EPDM** | **With EPDM and peroxides** |
|---|---|---|---|---|---|---|
| HDPE | 0.8 | 80%→ 0.64€/Kg | 80%→ 0.64€/Kg | 80%→ 0.64€/Kg | 50% → 0.4€/Kg | 40% → 0.32€/Kg |
| GTR | 0.2 | 20%→0.04€/Kg | 20% →0.04€/Kg | 20% →0.04€/Kg | 20% → 0.04€/Kg | 20% →0.04€/Kg |
| EPDM | 2.5 | | | | 30% → 0.75€/Kg | 40% → 1€/Kg |
| Sulpho-nitric[a] | 0.41 | 0.083 €/Kg | | | | |
| Byk-P 105 | 17 | | 3%→ 0.51€/Kg | | | |
| Licowax PE 520 | 1.90 | | | 5% → 0.095 | | |
| DCP | 7 | | | | | 0.1% → 0.007€/Kg |
| Trigonox 311 | 35 | | | | | 0.5% → 0.175€/Kg |
| **Total** | | **0.07€/Kg** | **1.19€/Kg** | **0.77€/Kg** | **1.19€/Kg** | **1.54€/Kg** |

[a] 50% v/v solutions

**Table 6.3** Estimation costs in €/Kg. of the formulas obtained from different compatibilization methods, all of them with 20% of GTR.

From the estimation cost calculation it can be concluded that the formula of thermoplastic vulcanizates is the highest in cost. If the formula is compared to the thermoplastic elastomeric olefins, there is a difference of 0.35€/Kg that comes from the peroxides use. The cheapest formula is the one with acid compatibilization methods. From this study, it can be seen that the use of waxes is cheaper than the use of a wetting additive. As the result with these two compatibilizers is quite similar, the fist option between them both is the use of a polyethylene wax additive.

And last but not least, the handling of the compatibilization process is another important parameter to take into account. The easiest of the process will also lead to a low cost production. As commented already in chapter 3 the use of acid treatment leads to the question if this procedure is enough environmental friendly. Of course, it is not an expensive procedure as no special machinery is needed but when trying to reuse discarded tyres into a partly recycled final piece the before mentioned question must be taken into account. The handling of the process using wetting agents and waxes, as well, as the ones using EPDM with or without peroxides do not need any special requirement for manufacturing the compounds and there is no negative impact on the environment.

Finally it can be stated that the blend:

30% GTR + 30% EPDM + 40% HDPE + 0.5% Trigonox 311 + 0.1% Dicumyl Peroxide

fulfil the fixed aims of the thesis: good adhesion between GTR and HDPE, its mechanical properties can be classified as Thermoplastic Elastomer (TPE) (e.g. elongation at break > 100%) cheap compatibilization process, new material containing recycled material with TPE characteristics, easily processed (injection moulding), and the most important thing, a new route to recycle scrap tyres with a high value final application.

## 6.2 Final conclusions

After the complete study of the three compatibilization methods and the comparison of the mechanical properties, estimation costs, maximum amount of ground tyre rubber particles and easiness of production of the final compound, the following final conclusions can be taken:

- A detailed study of the composites obtained by each compatibilization method was done. In the three methods there has been a mechanical properties study, a thermal, chemical and morphological study.

- The effectiveness of the compatibilization method can be check with mechanical properties of the blends. Mechanical properties are method dependant.
    - Acid treatment does not improve any of the properties with the chosen particle size. The acid causes etching on the surface of ground tyre rubber particles improving, in this way, mechanical adhesion. A brittle performance of the compound can be observed at lower particle size (< 200µm).
    - Addition of waxes and wetting additives has a slightly improvement of all mechanical properties. The best results were obtained with the wetting additive Byk-P 105 and the wax Licowax PE 520. Byk-P 105 interacts with the basic groups present in the ground tyre rubber particles surface. Licowax PE 520 acts covering the ground tyre rubber particles and reducing slightly the viscosity in the layers adjacent to the matrix.
    - Thermoplastic elastomeric olefins characteristics were only obtained with EPDM. Although the rubber-like properties where obtained at low ground tyre rubber particles amounts it was not sufficient at higher ground tyre rubber particles dosages. To improve these properties peroxides were added. Peroxides are use for dynamic vulcanization and the blend is transformed into a thermoplastic vulcanizate. A mixture of peroxides is used. Trigonox 311 which is designed to work at high temperatures and DCP, as standard peroxide for TPV's studies, to study synergetic effects and compare processing and physical properties of the composites. The composition consisting on 40% HDPE 30% EPDM 30% GTR 0.5% Trigonox 311 and 0.1% DCP gives the best TPV mechanical properties.

- The mechanical properties results described are accorded in all cases to thermal and morphological characterization.

- The maximum amount of ground tyre rubber particles in the final blend was desired in order to help the global reduction of EOL tyres. The blend consisting on 40% HDPE 30% EPDM 30% GTR 0.5% Trigonox 311 and 0.1% DCP gives the best balance regarding ground tyre rubber amount (30%) and mechanical properties without deleterious defects.

- If an estimation of the cost of the composites is done the thermoplastic vulcanizate is the one with the high cost and the one with acid treatment the one with the lowest. Between the two additives which gave similar mechanical properties results, the cost to use a wax in the formula is lower than the use of the selected wetting additive. Therefore, in this case, the use of the wax would be the first choice.

- Due to cost savings, it was a premise to have a compatibilization method that does not need many complications to be applied (e.g. especial machines, etc…). Besides the acid treatment, which need an step more in order to apply the pre-treatment onto the ground tyre rubber particles, the rest of the methods do not need any special handling or special equipment as the raw materials used can be add directly to the mixture.

## 6.3 Future outlook

In order to check the possible applications of the newly developed thermoplastic vulcanizates and its commercialization, further investigation are necessary. This includes standardizes and non-standardized techniques.

Based on the results obtained in this thesis, HDPE could be replaced by recycled HDPE. Therefore more recycled material would be included into the mixture.

Mechanical and visual properties of the composites make them interesting for their use as insulators. It could be very interesting to check the acoustic and dielectric performance of the produced thermoplastic vulcanizate as elastomers, in general, improve acoustic characteristics in some frequencies.

## Abbreviations

| | |
|---|---|
| AIBN: | Azobisisobutyronitrile |
| ATR-FTIR: | Attenuated total reflectance FTIR spectroscopy |
| BMI: | Bismaleimide |
| BPO: | Dibenzoyl peroxide |
| BR: | Butadiene Rubber |
| BR: | Butyl Rubber |
| CGT: | Cryogenic Ground Tyre |
| COPE: | Copolyester Elastomer |
| DCP: | Dicmuyl Peroxide |
| DSC: | Differential Scanning Calorimetry |
| EAA: | Ethylene Acid Acrylic |
| $E_b$: | Elongation at Break |
| EOL | End Of Life |
| EOR: | Ethylene-octene copolymers |
| EPDM: | Ethylene Propylene Diene Rubber |
| EPR: | Ethylene-propylene copolymer |
| EPR: | Ethylene-propylene copolymer |
| EVA: | Ethylene vinyl acetate copolymer |
| GPC: | Gel Permeation Chromatography |
| GTR: | Ground Tyre Rubber |
| HAF | High Abrasion Furnace |
| HDPE: | High Density Poly(ethylene) |
| HDPE: | High Density Polyethylene |
| HSBR: | Hydrogenated Styrene-Butadiene Rubber |
| IR: | Isoprene Rubber |
| LDPE: | Low Density Polyethylene |
| LLDPE: | Linear Low Density Polyethylene |
| MA: | Maleic anhydride |
| MIC: | Molded-in color |
| MW: | Molecular Weight |
| NBR: | Acrylonitrile Butadiene Rubber |
| NR: | Natural Rubber |
| NR: | Natural Rubber |
| PA: | Polyamide |
| PBT: | Poly(butylene terephthalate) |
| PBT: | Poly(butylene terephthalate) |
| POE: | Ethylene-octylene copolymer |
| PP: | Polypropylene |
| PS: | Polystyrene |
| PVC: | Poly (vinyl chloride) |

| | |
|---|---|
| PVC: | Poly(vinyl chloride) |
| rHDPE | recycled High Density Polyethylene |
| RIM: | Reactive Injection Moulding |
| RTR: | Reclaimed Tyre Rubber |
| SANS: | Small Angle Neutron Scattering |
| SAXS: | Small Angle X Ray Scattering |
| SBR: | Styrene Butadiene Rubber |
| SBR: | Styrene-Butadiene Rubber |
| SEBS: | Styrene Ethylene Buthylene Styrene |
| SEM: | Scanning Electron Microscopy |
| TCI: | Trichloroisocyanuric acid |
| TEM: | Transmission Electron Microscopy |
| TEO: | Thermoplastic Elastomeric Olefin |
| Tg: | Glass-transition temperature |
| TGA: | Thermogravimetric Analysis |
| Tm: | Melting point |
| TMTD | tetra methyl thiuran disulfide |
| TPE: | Thermoplastic Elastomer |
| TPU: | Thermoplastic Polyurethane Elastomer |
| TPV: | Thermoplastic vulcanizated |
| Xc: | Cristallinity |

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