POLITECNICO DI MILANO

Scuola di Ingegneria Civile, Ambientale e Territoriale
Corso di Laurea in Ingegneria per l'Ambiente ed il Territorio
Dipartimento di Chimica, Materiali ed Ingegneria Chimica "Giulio Natta"

Circular rubbers. From industrial wastes to rubber composites with low dissipation of energy

Relatore: Prof. Maurizio Stefano GALIMBERTI
Correlatore: Dr. Andrea BERNARDI

Tesi di Laurea di:
Rexhina Marku
ID number: 840605

Anno Accademico 2018 – 2019

Table of contents

INTRODUCTION AND OBJECTIVES

The present thesis is based on “circular economy”, a system which works according to the 3R approach of “Reduce, Reuse & Recycle”.

In the frame of this approach, this thesis is focussed on rubber products and, in particular, on wastes coming from industrial production. A fluorinated rubber was selected, an expensive rubber. A way to recycle and re-use a fluorinated rubber would be thus beneficial not only for the environmental impact but also from the economic point of view.

Rubber products play an important role in our lives. It is hardly possible to imagine the world without rubber products. The applications of rubber are endless. Their most important application is in tire industry. To increase the mechanical properties, tear, abrasion and aging resistance of rubbers, reinforcing fillers are used. Carbon black and silica are the most used reinforcing fillers. They can be used for many different applications of rubber composites, achieving the required properties and performances.

In the past, the disposal of end – of – life tires directly in landfills without a treatment has always been a very big problem for the environment and not only. Nowadays the disposal of tires in landfills has been banned and new methods for treating them are being studied. A steadily increasing amount of research is going on. This research has been increasingly extended to other types of end-of-life rubbers, which do not come from the tyre world. Moreover, large interest is also for wastes of the industrial process. These materials are produced during the process, remain inside a factory and are a remarkable cost, as they cannot be used for any application and, so far, have to be disposed to landfill.

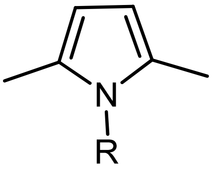
Main objective of the present thesis was to study an innovative approach for using rubber wastes coming an industrial production. Fluorinated rubbers were used: they are expensive rubbers used for very special applications. These wastes are in the form of powder and were named Rubber Powder (RP).

Main objectives of the present thesis were:

☞ to use the fluorinated rubber waste in place of either a rubber (natural rubber) or in place of silica in a rubber composites based on diene rubbers

☞ to functionalize the rubber powder, to improve its compatibility in the rubber composite, replacing either a rubber (natural rubber) or silica also with the functionalized rubber waste.

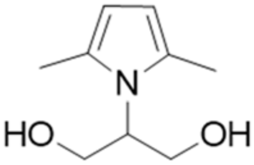
In previous studies performed by the research Group where I made my thesis, functionalization of sp^2 carbon allotropes was performed with pyrrole compound (PyC) prepared from a primary amine and 2,5-hexanedione [1, 2]. The chemical structure of the pyrrole compound is shown in the Figure below.



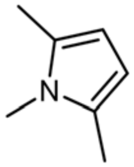
The functionalization method was found to be indeed sustainable: no solvent or catalysts were used, reagent and the carbon allotrope were simply mixed and energy (thermal or mechanical) was given. Functionalization yield was very high. Solubility parameters of the carbon allotropes were modified.

In a previous thesis [3], promising results were obtained by functionalizing the rubber powder coming from ground tyre rubber.

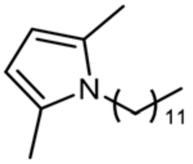
In this thesis, the first step of the activity was the preparation of pyrrole compounds. They were:



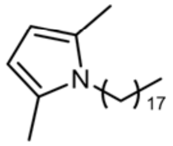
serinol pyrrole
(SP)



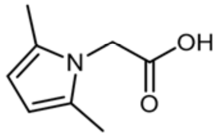
trimethyl pyrrole
(TMP)



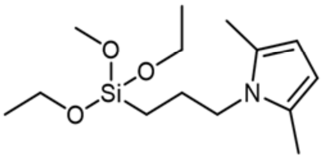
dodecyl pyrrole
(DDcP)



octadecyl pyrrole
(ODcP)



glycil pyrrole
(GlyP)



3 – (triethoxysilyl) – 1H pyrrole
(APTESP)

Then, functionalization of carbon black with these PyC was performed. The functionalization yield was determined.

Experimental activity was performed in order to estimate the solubility parameter. Dispersions of carbon black adducts with pyrrole compounds were prepared in different solvents. Calculation of Hansen solubility parameters was made by applying a method developed in the Group. Characterization of the adduct was performed.

Functionalization was then performed on Powder rubbers coming from different sources. Two of them were form commercial sources: Austin's Rubber, Lehigh's Rubber. Moreover, fluorinated rubber wastes were from a private company. Due to confidentiality reasons, we were not allowed to have information on the original commercial source of the fluorinated rubber.

Rubber composites were prepared, by replacing with the fluorinated rubber waste either a rubber (NR) or a filler (silica). The waste was either pristine or functionalized with either SP or ODcP. Objective was the investigate if the RP could be suitable to replace either a rubber or a filler and if the functionalization could promote the compatibility with the rubber matrix.

In this thesis different techniques and analysis were used, such as: ^{1}H NMR analysis, ^{1}C NMR analysis, Thermogravimetric analysis (TGA), Fourier Transformed Infrared Spectroscopy (FTIR), UV – Vis spectroscopy, Brunner – Emmett – Teller analysis (BET), Solubility tests, Contact angle, etc.

References

[1] Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152

[2] Barbera, V., Brambilla, L., Milani, A., Palazzolo, A., Castiglioni, C., Vitale, A., Bongiovanni R., Galimberti, M. (2019). Nanomaterials, 9(1), 44

[3] Ghilardi M., Thesis at Politecnico Milano, 2015/2016

SECTION I

PRIOR ART

CHAPTER 1

CIRCULAR ECONOMY

1.1 Introduction

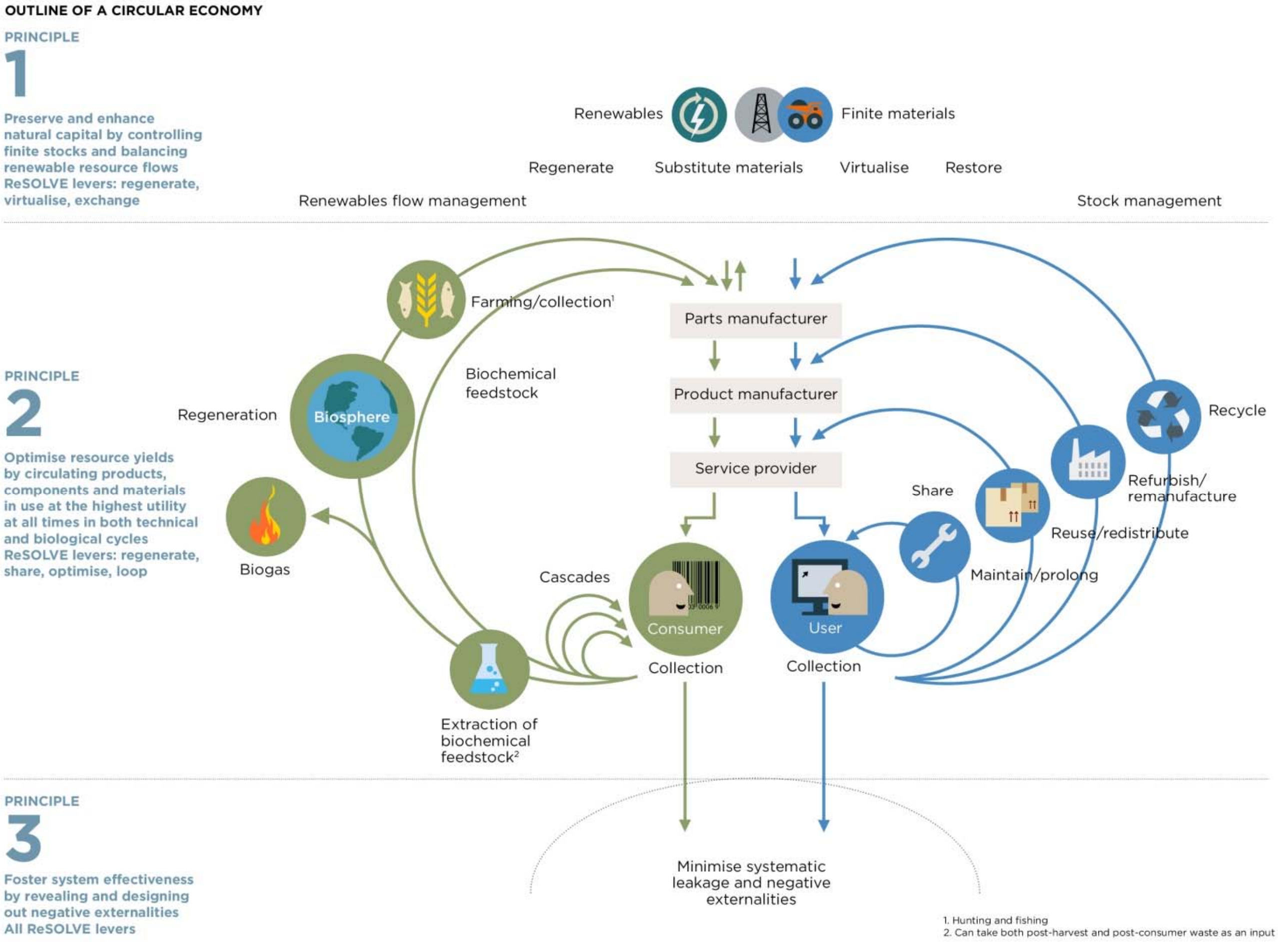
A circular economy is an economic system where products and services are traded in closed loops or ‘cycles’. A circular economy is characterized as an economy which is regenerative by design, with the aim to retain as much value as possible of products, parts and materials. This means that the aim should be to create a system that allows for the long life, optimal reuse, refurbishment, remanufacturing and recycling of products and materials.

Figure 1.1 – Conceptual diagram illustrating the Circular Economy

The circular economy brings the idea of restoration and circularity in order to replace the traditional concept of end-of-life, shifting towards the use of renewable energy, eliminating the use of toxic chemicals, and aims for the elimination of waste through the superior design of material, products, systems and business models.

It is based on three principles [1]:

- Design out waste and pollution
- Keep products and materials in use
- Regenerate natural systems



1. Hunting and fishing
2. Can take both post-harvest and post-consumer waste as an input

Source: Ellen MacArthur Foundation, SUN, and McKinsey Center for Business and Environment; Drawing from Braungart & McDonough, Cradle to Cradle (C2C).

Figure 1.2 – Circular economy system diagram

1.1.1. Closing Loops

In a circular economy material cycles are closed by following the example of natural ecosystems, therefore toxic substances are eliminated and there is no waste, because all residual streams are valuable as resource. Moreover, products are taken back after use for repair and remanufacturing in order to reuse the products a second, third or fourth time, and residual streams are separated in a biological and technical cycle [1].

1.1.2. System thinking

Circular economy asks for system thinking. All actors (businesses, people, and organisms) are part of a network in which the actions of one actor impact other actors. In a circular economy, this is taken into account in the decision making processes by including both short- and long-term consequences of a decision, considering the impact of the complete value chain, and aiming for the creation of a more resilient system which is effective at every scale [1].

1.2. Circular economy vs. linear economy

A circular economy differs from a linear economy in a fundamental way. The main differences are found in the step plan that is followed, the perspective on what sustainability is, and the quality of reuse practices.

1.2.1. Step plan

A linear economy works according to the ‘take-make-dispose’ step plan [2]. Resources are extracted and products are produced. Products are used until their end – of – life. Value is created by maximizing the amount of products produced and sold.

A circular economy works according to the 3R approach of “Reduce, Reuse & Recycle”. Raw materials are reduced as much as possible by using less material. Products are made of reused parts and materials and after discarding a product, materials and parts are recycled. In a circular economy value is created by focusing on value retention. By keeping material streams as pure as possible during the complete value chain, the value of this material is retained. Pure materials streams can be used multiple times to provide a certain functionality or service, while only making one investment [2].

Figure 1.3 - From Linear to Circular

1.2.2. Sustainability through eco-effectiveness or eco-efficiency

In a linear economy sustainability is improved by focusing on *eco-efficiency*. This entails maximizing the economic gain which can be realized with a minimized environmental impact. This negative impact per economic profit gained is minimized in order to postpone the moment at which our system is overloaded [3].

In a circular economy sustainability is improved by enhancing the *eco-effectivity* of the system. This means that next to minimizing the negative impact of the system, the focus is put on maximizing the positive impact of the system by radical innovations and system change [3].

1.2.3. Quality of reuse practices

The main difference between eco-efficiency and eco-effectivity lies in the *quality of reuse*.

In a circular economy reuse is intended to be as high grade as possible. A residual stream should be reused for a function that is equal (functional reuse) or of a higher value (upcycling) than the initial function of the material stream. This ensures that the value of the material is retained or enhanced. For example: concrete can be grinded into grains that are used to create a similar wall as before. Or even a stronger constructive element [5].

Within a *linear economy*, reuse is mainly seen in *downcycling* practices: a (part of a) product is used for a low grade purpose which reduces the value of the material. This complicates the reuse possibilities of the material in a third life. For example: concrete is shredded and used as road filament [5].

Table 1.1 – Circular economy vs. Linear economy

	Linear	**Circular**
Step plan	Take-make-dispose	Reduce-reuse-recycle
Focus	Eco-Efficiency	Eco-Effectivity
System boundaries	Short term, from purchase to sales	Long term, multiple life cycles
Reuse	Downcycling,	Upcycling, cascading and high grade recycling.

1.3. EU action plan for the Circular Economy

On 2 December 2015, the European Commission adopted a Circular Economy package consisting of a Communication and an action plan [4] and proposals for revised legislation on waste [5]. It indicated that 'the transition to a more circular economy, where the value of products, materials and resources is maintained in the economy for as long as possible, and the generation of waste minimized, is an essential contribution to the EU's efforts to develop a sustainable, low carbon, resource efficient and competitive economy'.

The revised legislative proposals on waste set clear targets for reduction of waste and establish an ambitious and credible long-term path for waste management and recycling. Key elements of the revised waste proposal include [6]:

- A common EU target for recycling 65% of municipal waste by 2030;
- A common EU target for recycling 75% of packaging waste by 2030;
- A binding landfill target to reduce landfill to maximum of 10% of municipal waste by 2030;
- A ban on land filling of separately collected waste;
- Promotion of economic instruments to discourage land filling ;
- Simplified and improved definitions and harmonized calculation methods for recycling rates throughout the EU;
- Concrete measures to promote re-use and stimulate industrial symbiosis - turning one industry's by-product into another industry's raw material;
- Economic incentives for producers to put greener products on the market and support recovery and recycling schemes.

1.4. End – of – Life Tires

In 2015, about 3,85 million tones of used tires were managed in an environmentally sound manner. This represents a 2.3 % increase in arising compared to 2014. After sorting out the data of those tires going for reuse or retreading, an estimated 3.19 million tones of end - of- life tires (ELTs) were left to be treated [7].

This material flow went into a variety of recycling applications, public works and civil engineering or was used as a fuel substitute in cement kilns, boilers and power plants [7].

1.4.1. Tire Composition

The primary material of many tires is Natural Rubber (NR). It improves thermal stability and creates high mechanical resistance. Around 40% of the entire rubber used in tire manufacturing is natural rubber. NR is used in different parts of the tire and particularly in the tire tread. Synthetic rubber which accounts for around 60% of the rubber used in the tire structure is a petrochemical by-product which is derived from petroleum hydrocarbons. This rubber is found in the form of styrene-butadiene (SBR) and polybutadiene (PBR). The reason for using synthetic rubber - a highly complex polymeric rubber - is that it can be returned to its initial shape after the stress is relieved. SBR enables tires to resist deformation at higher temperatures, while NR deforms at comparatively lower temperatures. However, the composition of NR and synthetic rubber is not adequate for tires to tolerate forces resulting from high-speed automobiles or heavy trucks and aircrafts, so tire manufacturers apply other materials such as fillers, steel and textiles for reinforcement. The main reinforcement filler materials are silica and carbon black. By adding 30% carbon black (CB) to the tire composition, not only does the resistance increase, but CB also imparts a distinctive black color. Silica or silicon oxide (SiO2) is the main additive to rubber to increase the strength of any ruptures [8].

1.5. Scrap Tire Management

During the past few decades have been introduced many different techniques to deal with the waste tire disposal issue. Among them, land filling practice is becoming unsustainable. The approach is typically to either reuse tires in their original shape or to recycle them. Those tires that pass required tests and are identified as suitable for retreading go back into reuse. Tires that are not suitable for retreading are used in creating new products. Tires are ground using multiple techniques and used as feed for production of other polymeric materials. Combustion of waste tires to produce bio-fuel is another common way to recover the energy in the furnaces, boilers, and burners. Thermo chemical processes for liquid bio-fuels including gasification, hydrothermal liquefaction and pyrolysis are commonly used to convert scrap tires to transportation fuels. Hydrothermal liquefaction is not very applicable for scrap tires and is more suitable for woody biomass, bagasse, and algae. The most applicable method of converting tire to bio-fuel is pyrolysis [8].

1.5.1. Tire's environmental issues:

- Every year, more than 1.5 billion tires are removed from vehicles creating around 13.5 million tons of solid waste.
- More than half of these tires are burned or land-filled, often in parts of the world where environmental controls are poor or non-existent.
- Due to the tire's shape, land filled tires are a great breeding ground for malaria mosquitoes which reside in the still standing water remaining in the tires.

- 2.4 billion tires are manufactured each year requiring around 7.2 million tons of ‘furnace’ carbon black produced from fossil fuels.

1.5.2. The circular economy solution:

The Circular Economy for tires starts at the design stage. The raw materials are considered and how they can best be used to produce a recyclable product. Tires are designed for use, and some - the retreadable tires for aircraft, truck and Off-The-Road (OTR) markets - are designed to be reconditioned [9]. The circular economy comes into play during the use phase: to extend their life, tires need to be maintained and technology is helping by ensuring the correct pressures and loadings, reminding about wheel position rotations. Tire pressure monitoring is now mandatory on all new cars sold in Europe, the future will bring more digital input into tyre maintenance, possibly even monitoring the wear and handling performance. Commercial Vehicle and OTR tyres will be regrooved and retreaded as often as the manufacturer recommends. All this serves to extend the life of the tyre and mitigates the demand on natural resources [9].

Recycled tyres become secondary raw materials that go into new products. Cement and steel produced using tyre derived fuel (TDF) also go into new products, all of which become recyclable themselves. As a result, the tyre circular economy is open and ELTs become an enabler for several other industries (from agriculture to mining, from construction to the food industry). Achieving a “closed loop tyre-to-tyre recycling”, with materials recovered from tyres going back into tyres, is not yet within reach due to tyre high safety and environmental performance and technological constraints [9].

References:

[1] Ellen MacArthur Foundation, 2015a
[2] Bocken, Bakker & De Pauw, 2015
[3] Braungart, McDonough & Bollinger, 2007
[4] Ellen MacArthur Foundation, 2014
[5] COM (2015) 614
[6] COM (2015) 593, COM (2015) 594, COM (2015) 595 and COM (2015) 596
[7] ETRMA 2015
[8] A. Rowhani and T. J. Rainey, ‘Scrap Tyre Management Pathways and Their Use as a Fuel – A Review’, 2016
[9] ETRMA 2015 End-of-Life Tyre Report

CHAPTER 2

RUBBER

2.1 Introduction

Rubber is a material that surrounds us constantly in our everyday lives. It is found in more than 40.000 different products including tires, medical devices, gloves and many engineering and consumer products [1]. It has an important part role in many sectors such as transportation and health care. This is generally thanks to natural rubber which has unique properties such as resilience, resistance to abrasion and impact, efficient heat dispersion ect. Until now no synthetic rubber has been developed that can compete with natural rubber in these areas. Synthetic rubber is petroleum based, a non-renewable resource that is running out and growing more and more expensive [1].

Rubber compounding describes the science of elastomer chemistry and its functionalization by addition of other materials to achieve the required mechanical properties. It is therefore among the most complex disciplines in that the materials scientist requires a thorough understanding of materials physics, organic and polymer chemistry, inorganic chemistry, thermodynamics, and reaction kinetics [2].

Currently, a large number of rubber types are on the market that can be separated into more groups in according to different conditions (e.g. saturated and unsaturated, natural and synthetic, polar and non-polar, crystallizing and non-crystallizing, etc.). From view of their usage and basic properties these can be also divided onto [3]:

- rubbers for general use – they have properties complying with requirements of more products, often also with different properties, they are relatively cheap, produced and consumed in big volume
- special rubbers – except of basic elastic properties they have at least one special property, e.g. ageing resistance, resistance against chemicals, resistance against swelling in non-polar oils, resistance against high or low temperatures etc. Normally they are produced and consumed in lower volume than general rubbers and they are significantly more expensive.

2.2 Natural Rubber

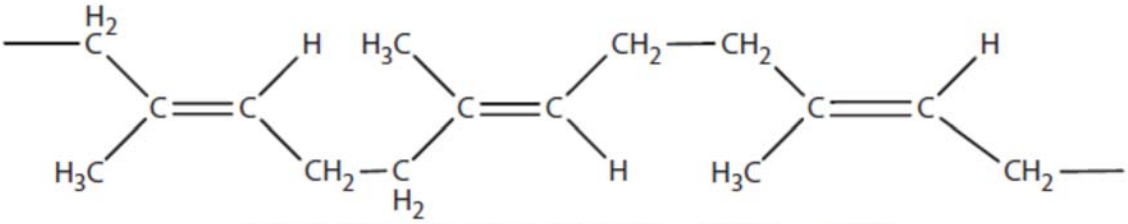
Natural Rubber (NR), which is obtained from *Hevea brasiliensis,* is a natural biosynthesis polymer possessing excellent characteristics such as high tensile strength due to its ability to crystallize upon stretching.

NR is among the most important elastomer available to technologists, since it is the building block of most rubber compounds used in products today.

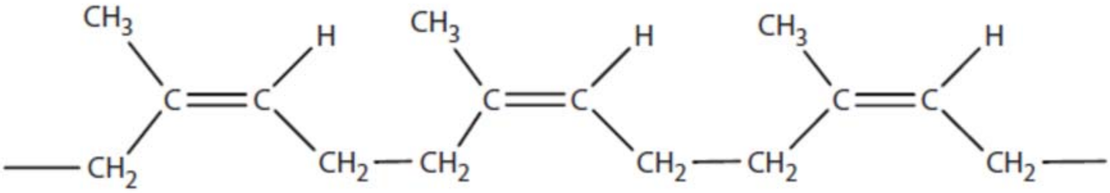
NR, which is a truly renewable resource, comes mainly from Indonesia, Malaysia, India, and the Philippines, although other extra sources of good quality rubber are becoming available. It is a material that is able of fast deformation and recovery, and it is insoluble in a range of solvents, though it will swell when immersed in organic solvents at elevated temperatures. Its properties include abrasion resistance, good hysteretic properties, high tear strength, high tensile strength, and high green strength. On the other hand, it possibly will show poor fatigue resistance. It is difficult to process in factories, and it can show poor tire performance in areas such as traction or wet skid compared to selected synthetic elastomers [2].

2.2.1 Chemistry of natural rubber

NR is a polymer of isoprene (methylbuta-1,3-diene). It is a polyterpene synthesized in vivo through the enzymatic polymerization of isopentenyl pyrophosphate. Isopentenyl pyrophosphate undergoes constant condensation to yield *cis*-polyisoprene through the enzyme rubber transferase. This enzyme can be also found in the latex serum as it is bound to the rubber particle. Structurally, *cis*-polyisoprene is a highly stereo regular polymer with an –OH group at the alpha terminal and three to four *trans* units at the omega end of the molecule (Figure 2.1). The molecular-weight distribution of natural rubber shows considerable variation from clone to clone, ranging from 100,000 to over 1,000,000. NR has a wide bimodal molecular-weight distribution. The lower – molecular – weight fraction will facilitate the ease of processing in end product manufacturing, while the higher-molecular-weight fraction contributes to high tensile strength, tear strength, and abrasion resistance [2].



trans-Polyisoprene (repeat units, $n = 100$; $M_w = 7000$)



cis-Polyisoprene (repeat units, $n = 1{,}500–15{,}000$; $M_w = 100{,}000–1{,}000{,}000$)

Figure 2.1 – *cis*- and *trans*- Isomers of natural rubber

As mentioned above NR is obtained by "tapping" the tree *H. brasiliensis*. Tapping starts when the tree is about 5 to7 years old and continues until it goes around 20 to 25 years of age. A knife is used to make a downward cut from left to right and at about a 20°–30° angle to the horizontal plane, to a depth approximately 1.0 mm from the cambium [2]. Latex then exudes from the cut and can flow from the incision into a collecting cup. Rubber occurs in the trees in the form of particles suspended in a protein-containing serum, the whole constituting latex, which in turn is contained in specific latex vessels in the tree or other plants. Latex constitutes the protoplasm of the latex vessel. Tapping or cutting of the latex vessel creates a hydrostatic pressure gradient along the vessel, with consequent flow of latex through the cut. In this way, a part of the inside of the interconnected latex vessel system can be drained from the tree. In the end when the flow stops, turgor is reestablished in the vessel, and the rubber content of the latex is restored to its initial level in about 48 h.

The tapped latex is made of 30% to 35% rubber, 60% aqueous serum, and 5% to 10% other constituents, for example: fatty acids, amino acids and proteins, starches, sterols, esters, and salts. Some of the non-rubber substances such as lipids, carotenoid pigments, sterols, triglycerides, glycolipids, and phospholipids can influence the final properties of rubber such as its compounded vulcanization characteristics and classical mechanical properties [2].

2.2.2 *Properties of natural rubber*

One of the fundamentally important properties of natural rubber is elasticity. Rubber is unique in the extent to which it can be distorted, and the rapidity and degree to which it recovers to its original shape and dimensions. It is, however, not perfectly elastic. The rapid recovery is incomplete. One part of the distortion is recovered more slowly and the other part is maintained. The extent of this permanent distortion, called permanent set, depends upon the rate and duration of the applied force. The slower the force and the longer it is restored, the greater is the permanent set. Because of rubber's elasticity, however, the permanent set may not be complete even after long periods of applied force. This quality is of obvious value in gaskets and seals.

The rubber's polymer network allows elasticity and flexibility to be combined with crystallization-induced strength and toughness when stretched. The elastic nature of this network also accounts for the exceptional resilience of cured rubber products. Because of this resilience, less kinetic energy is lost as heat during repeated stress deformation. Products that are made from natural rubber, compared to other elastomers, are less likely to fail from excessive heat buildup or fatigue when exposed to extreme dynamic conditions. This makes the natural rubber the most preferred sidewall elastomer in radial tires.

Another important and almost unique quality of uncured natural rubber compounds is building tack. When two fresh surfaces of milled rubber are pressed together they bond into a single piece. This facilitates the building of composite articles from separate components. In tire manufacture, for example, the separate pieces of uncured tire are held together solely by building tack. During cure they fuse into a single unit.

2.2.3 Production of natural rubber

Total global rubber consumption in 2014 was approximately 27.3 million metric tons of which 11.8 millions tons (43%) was NR and the remaining was synthetic rubber [4]. The world production of natural rubber was up by nearly 14% was NR from the same period in 2010 as economies improve their performance from low points in 2008 and 2009. The major regional consumers of NR have undergone a major shift from the period 2000 to 2004 with China being the largest followed by the European Union, North America, India and Japan. It is also anticipated that western European and Japanese consumption will increase due to economic growth in both areas, with sustained economic expansion in the United States; the net impact will be further growth in consumption toward 14.0 million tons/year. Further, NR consumption will then increase slowly, this being dependent on global economic conditions (Figure 2.2). Globally, NR consumption is split – tires consuming around 75%, automotive mechanical goods at 5%, nonautomotive mechanical goods at 5% - 10%, and miscellaneous applications such as medical and health – related products consuming the remaining 5% - 10% [5].

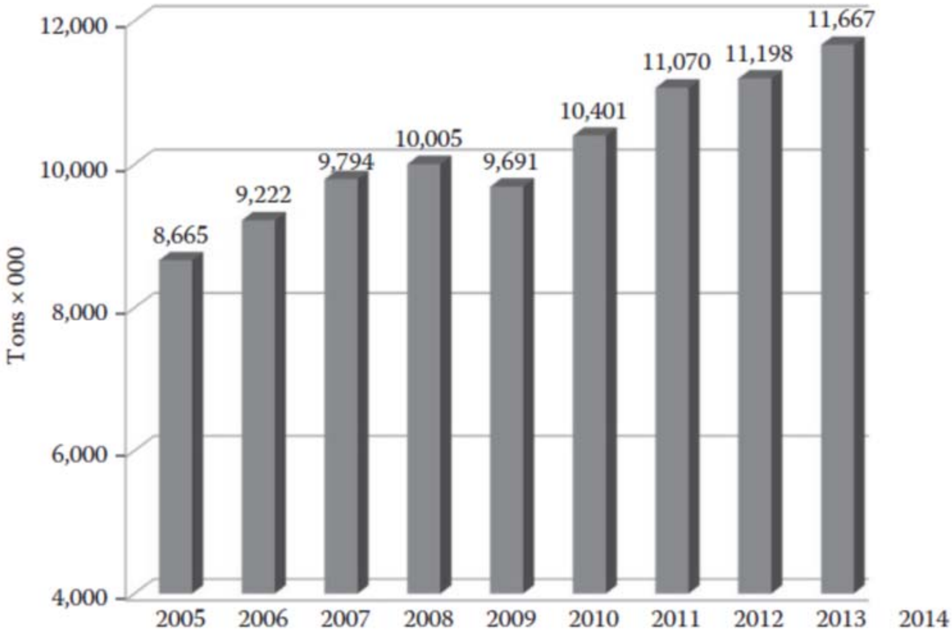


Figure 2.2 – Global natural rubber productions (millions of tons)

2.3 Synthetic Rubber

There are several synthetic rubbers in production. The polymerisation is the chemical process by which the synthetic rubbers are produced. Synthetic rubbers have mostly been developed with unique properties for specialist applications. Styrene-butadiene rubber and butadiene rubber are synthetic rubbers mostly used for tire manufacture. Butyl rubber, being gas impermeable, is generally used for inner tubes.

2.3. 1 Styrene-Butadiene Rubber (SBR):

SBR is the most widely produced elastomer. It has a vast range of applications and is relatively inexpensive compared to other elastomers [6].

SBR was synthetized for the first time in Germany in 1929 by German chemist, IG Farbenindustrie and in 1933 it was improved and patented by Eduard Tschunkur and Walter Bock with the name of Buna-S. It has become more and more important during WWII cause of the difficult reperibility of Natural Rubber (i.e. Roosevelt financed a series of studies for the so called GR – S, government rubber styrene).

Nowadays SBR represents the most abundant synthetic rubber produced worldwide and it covers about 36-37 % of the market. The overall production in 2014 was of 7 250 000 t / y. [7, 8]. Its single largest application is in passenger car tires, particularly in tread compounds for superior traction and treadwear. Other applications are: in footwear, foamed products, wire and cable jacketing, belting, hoses, and mechanical goods.

Summary of pros and cons:

Advantages of SBR rubbers: good abrasion and aging resistance; good elasticity; low price. Disadvantages of SBR rubbers: inferior mechanical properties (require reinforcements); adhesion properties; poor oil resistance; poor ozone resistance; do not resist aromatic, aliphatic or halogenated solvents; low elongation at break [7, 9].

Comparison with NR:

The processing of SBR compounds in general is similar to that of natural rubber in the procedures and additives used. Compared to natural rubber, SBR is typically compounded with better abrasion, crack initiation, and heat resistance. SBR extrusions are smoother and keep their shape better than those of natural rubber.

SBR needs more reinforcing filler than natural rubber to achieve good durability, tear and tensile strength. NR also has higher resilience than SBR [7].

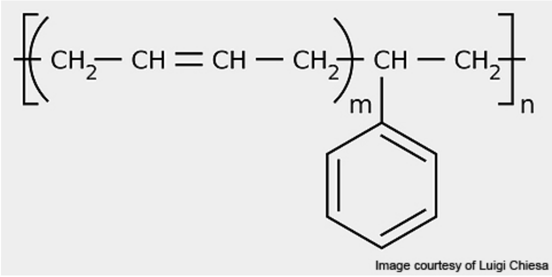


Image courtesy of Luigi Chiesa

Figure 2.3 – Styrene Butadiene Rubber (SBR)

2.3. 2 Butadiene Rubber (BR):

1,3-Butadiene, (chemical formula C_4H_6; chemical structure $CH_2=CH-CH=CH_2$) is a reactive colorless gas produced as by-product of the synthesis of ethanol or from the dehydrogenation of butane, butane or by the cracking of petroleum distillates. It is then dissolved in hydrocarbon solvents and polymerized to polybutadiene by the action of anionic or Ziegler-Natta catalysts.

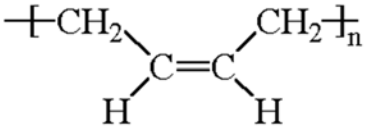


Figure 2.4 – Butadiene Rubber (BR)

BR are mostly used in passenger car tires, primarily in blends with SBR or NR to improve hysteresis (resistance to heat buildup), abrasion resistance, and cut growth resistance of tire treads. The type of BR used depends on which properties are most important to the particular compound. BR is also used for improved durability and abrasion and crack resistance in tire sidewalls and carcasses, as well as in elastomer blends for belting. High BRs are also used in the manufacture of high impact polystyrene.

2.3. 3 Butyl Rubber (IIR):

Butyl rubber is the common name for the copolymer of isobutylene.

The unique properties of butyl rubber are used to advantage in tire inner tubes and air cushions (air impermeability), sheet roofing and cable insulation (ozone and weather resistance), tire-curing bladders, hoses for high temperature service, and conveyor belts for hot materials (thermal stability with resin cure).

2.3. 4 Polyisoprene (IR):

Polyisoprene is made by solution polymerization of isoprene (2 methyl-1,3- butadiene). The isoprene monomer, the structural unit of the natural rubber polymer, can polymerize in four isomeric forms: trans 1,4 addition, cis 1,4 addition, 1,2 addition, leaving a pendant vinyl group, and 3,4 addition. The production of a synthetic analogue to natural rubber was stymied for over 100 years because polymerization of isoprene resulted in mixtures of isomeric forms. In the 1950s, rubber-like elastomers with >90% cis 1,4 isoprene configuration were finally produced using stereospecific catalyts.

Polyisoprene compounds, like those of natural rubber, show good building tack, high tensile strength, good hysteresis, and good hot tensile and hot tear strength. The characteristics which differentiate polyisoprene from natural rubber arise from the former’s closely controlled synthesis. Polyisoprene is chemically purer − it does not contain the proteins and fatty acids of its natural counterpart. Molecular weight is lower than natural rubber's. Polyisoprene is therefore easier to process, gives a less variable (although generally slower) cure, is more compatible in blends with EPDM and solution SBR, and supplies less green strength (pre-cure) than NR. Polyisoprene is added to SBR compounds to improve tear strength, tensile strength, and resilience while decreasing heat buildup. Blends of polyisoprene and fast curing EPDM combine high ozone resistance with the good tack and cured adhesion uncharacteristic of EPDM alone.

Polyisoprene is generally used in favor of natural rubber in applications requiring consistent cure rates, tight process control, or improved extrusion, molding, and calendering. The synthetic elastomer can be produced with the very low level of branching, high molecular weight, and relatively narrower molecular weight distribution that contributes to lower heat buildup compared to natural rubber. Therefore, certain grades of polyisoprene are used as an option to natural rubber in the tread of high service tires (truck, aircraft, off – road) without losing abrasion resistance, groove cracking, rib tearing, cold flex properties, or weathering resistance. Other applications are footwear and mechanical goods. Polyisoprene rubber is widely used in medical goods and food- contact items (baby bottle nipples, milk tubing, and hospital sheeting) because of polyisoprene's high purity and the high tensile strength of its compounds.

2.4 Vulcanization

Vulcanization is the conversion of rubber molecules into a network by the formation of cross links. Vulcanizing agents are needed for this cross linking. The rubber compound changes from the thermoplastic to the elastic state during the irreversible process of vulcanization. Two types of vulcanization methods exist [10]:

- Pressure vulcanisation: a batch (non-continuous) method in which the product is moulded under simultaneous pressing and heating. The heat is transferred through the metal of the mould. This is the most frequently used non-continuous (batch) method.
- Free vulcanization: this continuous method is usually used for large and/or endless products shaped by the extrusion process (for example, conveyor belts and water hoses), when `pressure vulcanisation' is not possible. Hot air, steam, `salt baths' or occasionally microwave systems are used for this method [10].

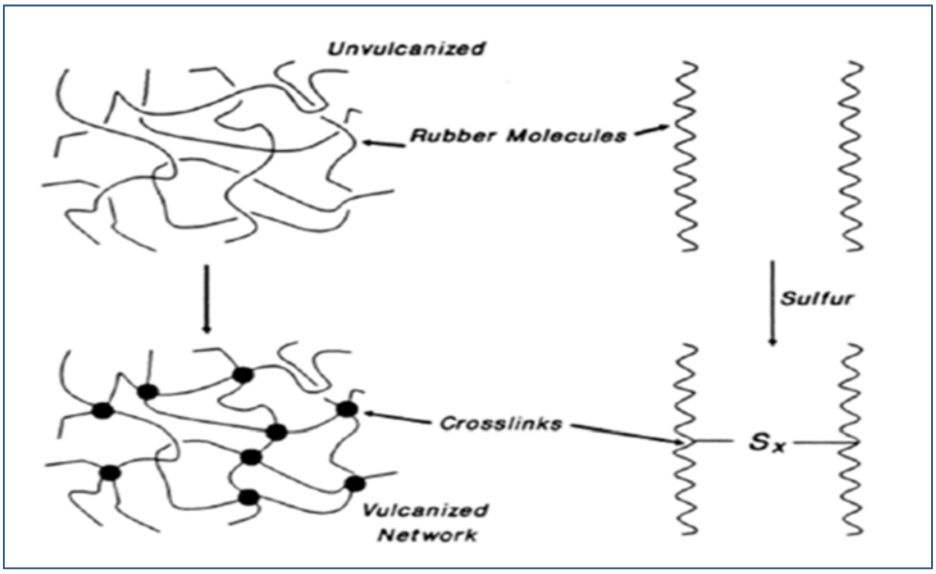


Figure 2.5 - Crosslinked and uncrosslinked rubber

Vulcanization technique comprises the following principal stages [11]:

- **Mixing** of crude rubber with about 5-30% of sulphur (cross-linking agent) and other additives such as:
    - activator (commonly zinc oxide or stearic acid),

- accelerator (guanidines, thiazoles, dithiocarbamates, xanthates, thiurams) ,
- coagulants (acetic acid, calcium chloride),
- anti-oxidants (amines, phenolics, phosphites),
- colour pigments,
- surfactants,
- softeners (oils),
- ant-foaming agents,
- anti-tack agents (Rosin derivates, coumarone-indene resins, aliphatic petroleum resins, alkyl-modified phenol-formaldehyde resins).

Slow cross-linking starts at this stage. It is required to avoid active vulcanization during mixing, which may cause cracks formation at the molding stage.

- **Molding (shaping)** the rubber mixture. The rubber must be shaped before heating stage becausecross-linking makes shaping impossible.
- **Heating** the mixture to 120-200ºC. Increased temperature speeds up the vulcanization process resulting in fast and complete cross-linking. C-S bonds replace C-H bonds linking chain polyisoprene molecules. Each link is formed by one to seven sulphur atoms.

Density of cross-links must be controlled in order to prevent formation of brittle rubber.

Properties of rubber improved by vulcanization:
- tensile strength;
- elasticity;
- hardness;
- tear strength;
- abrasion resistance;
- resistance to Solvents.

2.4.1 Sulphur vulcanization

Sulphur is the oldest vulcanization agent for unsaturated rubbers used in rubber practice. It is effective and fast link in form of cross-links to rubber macromolecules takes place only in the presence of activators and accelerators. If these are missing the reaction of sulphur with rubbers will be very slowly and it bonds to rubbers in a form of side - cyclic structures not in a form of sulphur cross-links. These ingredients affect the kinetic parameters of vulcanization (temperature and time) and melting time of vulcanized compounds and sulphur content necessary for creation of optimal network of vulcanizates. Type and the content of present accelerators and also the accelerator: sulphur ratio in rubber compounds affect final properties of vulcanizates mainly their thermo-oxidative stability and some of their tensile and dynamic properties.

Sulphur vulcanization of unsaturated rubbers is preceded in three stages:

- In the first stage, by element interaction of vulcanization system, the transitional complex is created. This complex together with rubber creates active curing agent.
- In the second stage is created the primary network of vulcanizate with mainly polysulfide cross-links.
- In the third stage the primary network of vulcanizate is restructured by modification of cross-links (sulfidity decrease) and rubber macromolecules (isomerization, dehydrogenation, and cyclization) and in the end the final network of vulcanizate is created.

From the chemistry point, the first stage adopts the concept about ion character of reactions leading to the creation of reactive curing agent. During the next curing stages the reaction with radical character are allowed. These reactions lead to the formation of reactive cross-linking fragments and also to the single creation of cross-links between macromolecules of present rubber, finally to their changes in the last stage of vulcanization.

Sulphur vulcanization is a complicated system. Its basis is network created by rubber macromolecules which are connected with chemical cross-links: sulphur-sulphur or carbon-carbon character. There are different types of physical bonds. These are not only bonds created between individual macromolecules or segments of sulphur macromolecules following their chemical structure (e.g. hydrogen bridges; polar forces) but also their intermolecular and inter-molecular snarls. The three dimensional network of sulphur vulcanization is not ideal because of the complicated curing course, the possibilities of cross-links re-structuralization in the third vulcanization stage, formation of cross and others bonds by reactions of rubber macromolecules with other elements of rubber compound mainly with accelerators and fillers, the possibility of incomplete mixing of homogenous ingredients to the whole volume of rubber matrix. In the network there are also present the others ingredients attending in vulcanized rubber compounds in chemical transformed as well as in original form [3].

2.5 Reinforcing Fillers

Fillers commonly have a significant effect on compound and vulcanization properties of rubbers. Fillers that are used to modify the properties of rubbers, typically obtain an important functionality which is able to bond to the rubber matrix, therefore improve the processability and final product performance. These active fillers are classified as reinforcing fillers. Farther, the fillers which show intermediate or a low ability of property improvement are identified as semi- and non-reinforcing types, respectively. The basic characteristics which determine these categories of fillers are particle surface activity, particle size, particle surface area and particle structure.

2.5.1 Factors influencing filler reinforcement

- *Particle surface activity* – Functional or active fillers can give a strong interaction between filler and rubber matrix when compared to inactive fillers, which relates to the affinity for and ability to react with rubber [12]. Chemical interaction between filler and rubber depends on the type or form of the functionality on the filler surface. Some filler need to be modified in order to match the surface chemistry to a specific rubber.
- *Particle size* – Particle size of filler is one of the basic parameters which strongly affect rubber properties. Silica and carbon black have very small primary particle sizes in the range of 10 – 100 nm and are classified as reinforcing fillers which can significantly improve rubber performance. Fillers with particle size in the range of 100 – 1000 nm and 1000 – 10000 nm are classified as semi- and non – reinforcing fillers, respectively. When the particle size is greater than 10000 nm which greatly exceeds the polymer interchain distance already, the filler causes an area of localized stress, leading to elastomer chain rupture on flexing or stretching, and hence deterioration in rubber properties.
- *Particle surface area* – In the case of reinforcing fillers, they have a high surface area which provides more active contact sites, which provide a higher potential to contribute to strong filler – rubber interactions in rubber compounds.
- *Particle structure* – The primary particles of reinforcing fillers; carbon black and silica are generally spherical. However, these particles are not stable during their production, but form aggregates/agglomerates or bundles because of self – association of the active functionalities on their surface [13]. The higher the structure, the better the reinforcement efficiency.

2.5.2 Carbon Black

Carbon black is most commonly used as reinforcing filler in the rubber industry because of its high capability for reinforcement. The surface chemistry of carbon black is primary composed of carbon with presence of a low percentage of other hydrocarbon or oxygen – containing groups on its surface, e.g. phenol, carboxyl, ketone, quinine, lactone and pyrole [14].

The relatively non – polar surface is compatible with hydrocarbon rubbers that are widely used in rubber compounding. The black has a limited number of chemically active sites which arise from broken carbon – carbon bonds because of the methods used to manufacture the black. However, the presence of oxygen complexes is not essential for reinforcement in most general purpose rubbers. The reinforcing activity is mainly attributed to mechanical interlocking of the rubber onto the carbon black surface, the chemisorptions of the rubber onto the filler surface due to free radical interactions between carbon atoms in the filler and in the rubber, and the Van der Waal forces between carbon black and rubber [14].

2.5.3 Silica

As carbon black can only be used in black rubber articles, a need for alternative active fillers which permit the production of highly durable colored products led to the development of non – black fillers. Early, the use of silica as non – black reinforcing filler instead of carbon black caused different problems such as higher compound viscosity and more difficult processing. This is because of a significant difference in polarity between the silica surface and rubber hydrocarbons. The surface of silica aggregates or particles is virtually covered by silanol groups (-Si-OH) that are very polar and considerably chemically active [15]. This feature leads to low compatibility with general purpose rubbers, thus weak filler – rubber interaction.

However, with the aid of coupling agents, properties of silica – filled rubber such as physical/mechanical properties or elasticity can be successfully improved [16]. Therefore, silica is now used next to carbon black as a main filler to increase the usefulness of rubbers in different applications. Carbon black and silica, as fillers, are able to increase the strength of vulcanized amorphous rubbers more than tenfold. Therefore, relatively few applications of elastomers are used in the unfilled or gum state. SBR, for example, has practically no commercial use as an unfilled compound.

References

[1] Van Beilen & Poirier, 2007

[2] Brendan Rogers, *‘Rubber Compounding Chemistry and Applications’* – second edition, 2016

[3] MATADOR RUBBER s.r.o., *‘Rubber Chemistry’* – 2007

[4] International Rubber study Group, Worldwide rubber database, 2014

[5] Barbin W, Rodgers MB, *‘Science of rubber compounding’*. In: Mark JE, Erman B, Eirich FR. Eds., *‘Science and Technology of Rubber’*, 1994

[6] A.A. Basfar, M.M. Abdel-Aziz, F.A. Al-Harithy, *‘Mechanical Properties of Styrene-Butadiene Rubber Cured by Ionizing Radiation in the Presence of Sulfur and Polyfunctional Agent’*

[7] M. Galimberti, slides of the course "*Chemistry for elastomers and composite materials*", Politecnico di Milano.

[8] V.M. Il'in, A.K. Rezova, Kauchuk i Rezina, No. 2, (2015),pp. 36–43.

[9] J.E. Mark, B. Erman, F.R. Eirich, *'Science and technology of Rubber'* (1994).

[10] R. Ahmed, A. van de Klundert, I. Lardinois, '*Rubber Waste, Options for Small-scale Resource Recovery'*, 1996

[11] D. Kopeliovich, SubsTech

[12] M. J. Wang, S. Wolff, *'Rubber Chem. Technol.'*, 65, 715, 1992

[13] A. Blume, *Kautsch. Gummi Kunstst.*, 53, 338, 2000

[14] S. Wolff, *'Rubber Chem. Technol.'*, 69, 325, 1996

[15] W. Meon, A. Blume, H. –D. Luginsland, S. Uhrlandt, *'Rubber Compounding Chemistry and Applications'*, 2004

[16] J. Ramier, L. Chazeau, C. Gauthier, *'Rubber Chem. Technol.'*, 80, 183, 2007

CHAPTER 3

CARBON BLACK

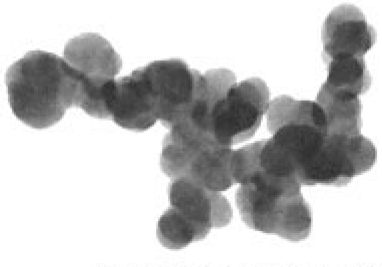
3.1 Introduction

Term “Carbon Black”, refers to a prime group of products, which has received much scientific and technological attention because of its wide-ranging applications [1]; in rubber reinforcement they are irreplaceable filler [2], on the other hand they are fascinating objects in electrically conductive materials [3]. Carbon Black is elemental carbon in the form of a fluffy fine powder with a large surface area; it is classified as a most widely used material with dimensions in nanometers (nm).

3.2 Structure of carbon black

Carbon black (CB) comprises of fine carbon particles (90-99% elemental carbon), as a result of incomplete combustion of ample and beefy petroleum artifacts. Carbon black at its smallest level consists of spherical primary particles, which quickly form aggregates. Primary carbon particles blend together permanently, in a randomly branched chain like structure, which is known as aggregate. The aggregate can have a small number or hundreds of primary spherical particles. Thermal black aggregates consist of single spheres rather than chains. These chains like structures are used to grip fluids and reinforce materials [4]. The aggregates can fix with each other through van der Waals forces to form feebly joined agglomerates [4, 5].

3.3 Properties



© Mitsubishi Chemical Corporation.

Figure 3.1 - Electron microscope image of carbon black

Carbon black particles have a complicated structure, with some spherical particles being fused together. The "particle size" is the size of spherical particles and the "structure" is the size of the particle chain. The hydroxyl or carboxyl group and other functional groups are found in the surface of carbon black, and their amount or composition is called "surface chemistry". These three - "particle size," "structure," and "surface chemistry" - are the basic properties of carbon black, and together are called the three main characteristics and they have a large effect on practical properties such as blackness and dispersibility when they are mixed with inks, paints, or resins.

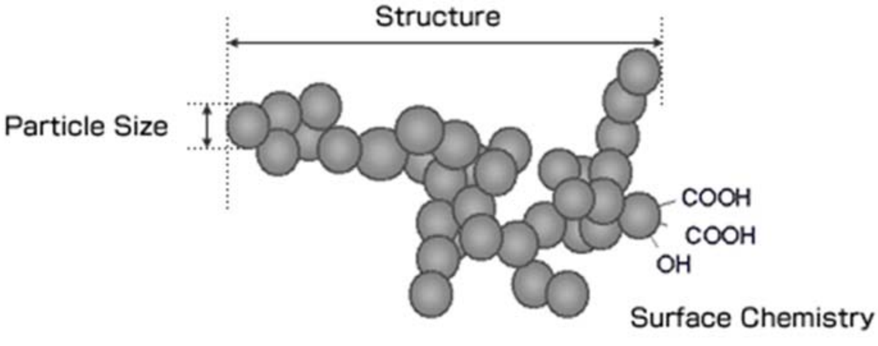


Figure 3.2 – Basic properties of carbon black

3.3. 1 Particle size

The diameter of spherical particles is the fundamental property which largely affects blackness and dispersibility when carbon black is mixed with resins or other vehicles [6]. In general, the smaller the particle size is, the higher the blackness of carbon black becomes. Dispersion, on the other hand, becomes difficult because of an increase in coagulation force.

3.3. 2 Structure

Like particle size, the size of the structure also affects the blackness and dispersibility of carbon black. Generally, the increase of structure size improves dispersibility but lowers blackness. Carbon black with a larger structure in particular shows an excellent conductive property [7].

3.3. 3 Surface chemistry

On carbon black's surface are present a variety of functional group. Depending on the type and amount of the functional groups, the affinity of carbon black with inks or paint varnishes will change.

Carbon black, with a large amount of hydroxyl group given with oxidation treatment, has a significantly improved affinity to print inks or varnishes, demostrating an excellent dispersibility.

3.4 Applications

Carbon black is a fundamental material with a long history, and it has been used as a coloring agent since the days before Christ. Carbon black is still being applied to new fields such as electronic equipment and devices because it has nano – particles with different functions such as ultra-violet absorption and conductivity. Some applications of CB are shown in following.

3.4.1 Coloring agent for ink and paints

Carbon black has higher tinting strength compared to iron black or organic pigments, and is commonly used for newspaper inks, printing inks, and paints. Carbon black is as well used as black pigment for inkjet ink or toners.

3.4.2 Resin and film coloring agents

As mentioned above carbon black has high tinting strength and is thermally stable, for that reason it is suitable for coloring resins and films that are heat – formed. Furthermore carbon black is excellent for absorbing ultraviolet light, providing a excellent resistance against ultraviolet rays and a coloring effect when only a small quantity is mixed with resins. Another use of carbon black is for general coloring for resins and films. Some applications of resins with carbon black are used in automobile bumpers, wire coverings and steel pipe linings which need weather resistance especially.

3.4.3 Electric conductive agent

The structure of carbon black particles is like the graphite – type crystalline, providing a very good electric conductivity. So, carbon black is generally used as conductive filler, being mixed in plastics, elastomers, paints, adhesives, films, and pastes. Fuel caps and fuel-introducing pipes of automobiles, are required of electric conductivity for preventing static. For that reason, carbon black is used as an superb antistatic agent.

3.4.4 Electronic equipment related material

Carbon black is also used as electronic equipment related material in different present components, magnetic recording materials because it provides constant resistance.

3.4.5 Rubber carbon blacks

The three properties of carbon black: primary particle size, the aggregate formation and the surface activity, have all led to the important application of Carbon Black as reinforcing filler in rubber applications. These Carbon Blacks are most usually referred to as Rubber Carbon Blacks. The reinforcing effect of Carbon Black was discovered accidentally rather than intentionally after the turn of the 19th century. Previously, the substance of choice for eliminating the inherent stickiness of rubber was zinc oxide. So this discovery of the reinforcing properties of Carbon Black represented a new light for the Carbon Black, tire and automotive industries. Nowadays, if Carbon Black is used as filler in the rubber compound instead of zinc oxide, tires with improved textile cord would have a long life.

3.4.6 Specialty carbon blacks

Some of carbon black advantages are listed below:

- Color stability
- Solvent resistance
- Acid and alkaline resistance
- Thermal stability
- High hiding power

These Carbon Blacks have a lot of applications in the printing, paints, coatings, plastics, fiber, paper and construction industries. The industry works with a widely accepted typology based on particle size. It serves as the key reference for most manufacturers.

3.5 Thermal – Oxidative processes

3.5.1 Furnace black processes

The Furnace Black method is the most recently developed process and has become the most widespread in large scale Carbon Black manufacturing. The Furnace Black method is continuous and uses liquid as feedstock and gaseous hydrocarbons as heat source. In the presence of natural gas, the liquid feedstock is sprayed into a heat source that is generated by the combustion of the natural gas and pre-heated air. Since it occurs at a very high temperature, the reaction is limited to a refractory – lined furnace, so the name. After the formation of Carbon Black, the process mixture is quenched by adding water. Furthermore this prevents any unwanted secondary reactions. The Carbon Black loaded gas after that passes throughout a heat exchanger for further cooling, while at the same time heating up the required process air. The Carbon Black particles are separated from the gas stream through a bag filter system. The gases produced by the reaction are combustible and, usually, are fed into an afterburning stage where the heat is used to dry the Carbon Black, or are burnt in a boiler to generate steam. The Carbon Black collected by the filter has a very low bulk density and, depending on the application, is usually pelletized or further densified to facilitate onward handling [8].

The wet – pelletizing process uses water and a binding agent in a specially designed wet pellet or "pin" mixer, which transforms the Carbon Black into spherical pellets. Next the Carbon Black

pellets are dried in rotary dryers. The binding agent ensures that the product is resistant to attrition and is easy to process and transport.
The incorporation of these pellets in a polymer matrix requires considerable shear forces, generally applied by internal mixers in the rubber industry. Specialty Carbon Blacks that are produced by the Furnace Black process are either loosely densified and packaged as powder Carbon Blacks or are transformed to easily dispersible pellets by application of the dry pelletizing process.

Oil – pelletized Carbon Blacks, used principally in the pigment industry, are an extra option that utilizes mineral oils in the pelletization process. Due to the light oil coating, these Carbon Blacks are characterized by even easier dispersion and virtually dust – free handling. This method offers environmental and work safety benefits. The fully closed installation keeps the emission of process gases and dust to a minimum. As well its environmental, economic and technical advantages furthermore it allows better flexibility since it is capable of manufacturing more different grades of Carbon Black than any other process being used nowadays. All raw materials are specifically specified in terms of quality, type and quantity. This makes it possible to produce a large range of Carbon Blacks, which are suitable for use in different applications without deeply changing the process for each product alternative. For instance, particle size or specific surface area can easily be defined at the outset by setting the appropriate process parameters. The Furnace Black process also permits the manufacturer to control particle aggregation, the so-called Carbon Black structure, by adding small quantities of an alkaline metal salt. The Furnace Black method creates Carbon Black with primary particle sizes ranging from 10 to 80 nm. The primary particle size is mentioned to point out the application properties of a given product. Free primary particles do not exist as they are strongly fused together and form so-called aggregates.


1) Powder Carbon Black

2) Dry-Pelletized Carbon Black

3) Wet-Pelletized Carbon Black

Figure 3.3 – The Furnace Black method

3.5.2 Degussa gas black processes

In the mid – 1030s Degussa developed the Gas Black method. This method is very much related to the Channel Black process developed in the US based on natural gas as the feedstock. Since this resource was much scarcer in Europe, the Degussa Gas Black method was developed to use coal tar distillates as raw material instead. Contrary to the Channel Black process, which poses a significant load on the environment, gas black plants are at the cutting edge of environmental technology.

The facilities are continuously vacuum – cleaned and the Carbon Black is collected in sealed filter systems that exceed official emission standards by a significant margin.

The oil is used in the Gas Black process uses instead of natural gas as the feedstock. The oil is heated in a vaporizer and the resultant vapors are carried by a hydrogen – rich gas into a gas tube that is fitted with a multiplicity of burners. The individual flames impose on the surface of a water-cooled drum. A portion of the Carbon Black that is generated is deposited on the roller while the rest enters the filter system. In the following stage the two Carbon Black streams are combined. Onward processing is then alike to the Furnace Black process. While it is possible to control the raw material fed by the carrier gas stream, the air has free access. However, while this restriction, the Gas Black method allows the production of Carbon Black with primary particle sizes ranging from 10 to 30 nm. The tradeoff is less flexibility in defining the structure. This cannot considered as disadvantage because Gas Blacks are inherently characterized by a loose structure and exceptional dispersibility.

These types of Carbon Black are currently used almost exclusively in pigment applications where the fine – particle Gas Blacks are of particular importance.

Because of contact with oxygen at high temperatures, acidic oxides form on the surface of the Carbon Black particle. Contrary to Furnace Blacks, Gas Blacks go through an acidic reaction when suspended in water. Oxidative post – treatment using nitrogen dioxide, ozone or other oxidants also make it possible to further increase the acidic surface groups significantly. These treated Carbon Blacks are used mostly in the Specialty Carbon Black sector, e.g. in the coating and ink industries. The majority of Gas Blacks are re – treated oxidatively.

3.5.3 Lamp black processes

The Lamp Black process is the oldest commercial Carbon Black production process. However, today's Lamp Black production units have a little in common with the olden Carbon Black ovens. Smoking chimneys and settlement chambers have long since given way to highly sophisticate filtering systems. The Lamp Black apparatus consists of a cast – iron pan that holds the liquid feedstock, which is surmounted by a fire – proof flue hood that is lined with refractory bricks. The air gap between the pan and the hood, as well as the vacuum present in the system, help regulate the air supply and hence enable the manufacturer to fine tune the Carbon Black’s definitive properties. Although the radiated heat from the hood causes the raw material to vaporize and partially combust, most of it is converted to Carbon Black.

In order to separate the solids, process gases containing Carbon Black are passed through a filter after the cooling stage.

3.5.4 Channel black processes (historical)

Channel Black process is developed in the United States in the middle of the last century, and this process is based on the incomplete combustion of natural gas. Similar to the Degussa Gas Black process, natural gas flames from a vast number of small burners impinge on water cooled channels. Since the 1950s, however, the Channel Black method constantly lost ground in the rubber industry. Following the oil crisis in the 1970s the process was discontinued in the US. The reasons were the limited yield of the raw material (3 – 6 %) and the environmental hazard posed by the emission of very fine Carbon Black particles. The thick black smoke billowing from Channel Black plants, called “hot houses,” could be spotted miles away.

3.6 Thermal decomposition processes

Thermal Blacks form quite slowly, resulting in coarse primary particle sizes ranging from 300 to 500 nm, referred to as medium thermal. However, formerly when using only natural gas as feedstock it was possible to dilute it with inert gases which would produce a Thermal Black composed of primary particles in the range from 120 to 200 nm. This was referred to as fine thermal, the latter has virtually disappeared from the market [8].

3.6.1 Thermal black processes

This method of producing Carbon Black is a non – continuous or cyclic process, with natural gas as the most frequently used feedstock, although higher grade hydrocarbon oils are also used. A Thermal Black plant delivers maximum efficiency when operated in a tandem mode and consists of two reactors operating alternately in cycles lasting five to eight minutes. One of which is heated with a natural gas or oil/air mixture while the other is fed with pure feedstock which undergoes thermal decomposition. One could also include the Thermal Black method in the group of thermal-oxidative processes, with the distinction that the energy generation and the decomposition reaction are not simultaneous. However, the fact that the actual Carbon Black formation occurs in the absence of oxygen and at decreasing temperature, results in Carbon Black properties that are markedly different from those achieved by thermal-oxidative processes.

3.6.2 Acetylene black processes

At higher temperatures, exothermic decomposition of acetylene yields carbon and hydrogen, forming the basis of the Acetylene Black process. Hydrocarbons are generally added to acetylene in order to avoid reactor temperatures from rising due to the exothermic reaction. The Carbon Black is separated from the hydrogen when the reaction mixture has cooled down,. The way Acetylene Blacks are created obviously distinguishes them from thermal – oxidative Carbon Blacks. Although the median primary particle size of Acetylene Black is in the same range as that of some Furnace Blacks (30 to 40 nm), the structure diverges clearly from the spherical form.

3.7 Health Information

Carbon black has been the focus of extensive scientific health studies during the past several decades. Carbon black is classified by the International Agency for Research on Cancer (IARC) as a Group 2B carcinogen (possibly carcinogenic to humans) based on "sufficient evidence" in animals and "inadequate evidence" in humans (IARC, 2010) [9]. Studies of carbon black manufacturing workers show no causative link between carbon black exposure and cancer risk in humans. However, results of carbon black production workers health studies suggest that cumulative exposure to carbon black may result in small decrements in lung function.

Carbon black is not a chemical irritant, but may cause mechanical irritation of the throat, eyes, and skin. It is not a skin sensitizer. Carbon black is not considered to be mutagenic.

Carbon Black has been investigated thoroughly in numerous toxicological and epidemiological studies, which demonstrate it is a substance of low toxicity. Following the CLP (EU regulation for Classification, Labelling and Packaging) criteria for identifying hazardous substances, Carbon Black has been determined to be non-hazardous under the EU REACH regulation by the CB4REACH Consortium.

References

[1] G. J. Perrott, R. Thiessen, *Carbon Black-Properties and uses*, 1920

[2] J. B. Donnet, A. Voet, *Carbon Black; Physics, chemistry and elastomeric Reinforcement,* 1976

[3] E. Enríquez, J. F. Fernández, M. A. Rubia, *Highly conductive coating of Carbon black/Silica composites obtained by a sol gel process*, 2012

[4] E. M Dannenberg, L. Paquin, H. Gwinnell, *Carbon black*, In: J. I. Kroschwitz, M. H. Grant and Kirk-Othmer, *Encyclopedia of Chemical Technology 4th Ed*, 1992.

[5] K. Gardiner, W. N. Trethowan, J. M. Harrington, *et.al., Occupational exposure to carbon black in its manufacture*, 1992

[6] L. Karásek, M. Sumita, *Characterization of dispersion state of filler and polymer-filler interactions in rubber-carbon black composites*, 1996

[7] F. Li, L. Qi, J. Yang, M. Xu, X. Luo, D. Ma, *Polyurethane/conducting carbon black composites: Structure, electric conductivity, strain recovery behavior, and their relationships*, 2000

[8] Orion, Engineered Carbons, 2015

[9] IARC, 2010

CHAPTER 4

TIRE

4.1 Introduction

The strong and flexible rubber covering attached to the rim of a wheel is called tire. Tires provide a gripping surface for traction and serve as a cushion for the wheels of a moving vehicle. Tires are found on automobiles, trucks, buses, aircraft landing gear, tractors and other farm equipment, industrial vehicles such as forklifts, and common conveyances such as baby carriages, shopping carts, wheel chairs, bicycles, and motorcycles.

For most vehicles tires are pneumatic; air is pressed inside the tire. In the past, pneumatic tires had an inner tube to hold the air pressure, but nowadays these tires are calculated to create a pressure seal with the rim of the wheel.

The performance requirements of tires are of a wide range. They have to bear the weight of the vehicle, must have enough grip on the road, have to transmit steering forces to guide the vehicle, to supply dampening between the road and the vehicle, have stability that enables their use at high speeds for long time periods, and have as low as possible impact on fuel consumption. As shown in Figure 3.1, tires are complex composites made of mixtures of rubber with metal and textile reinforcements [1].

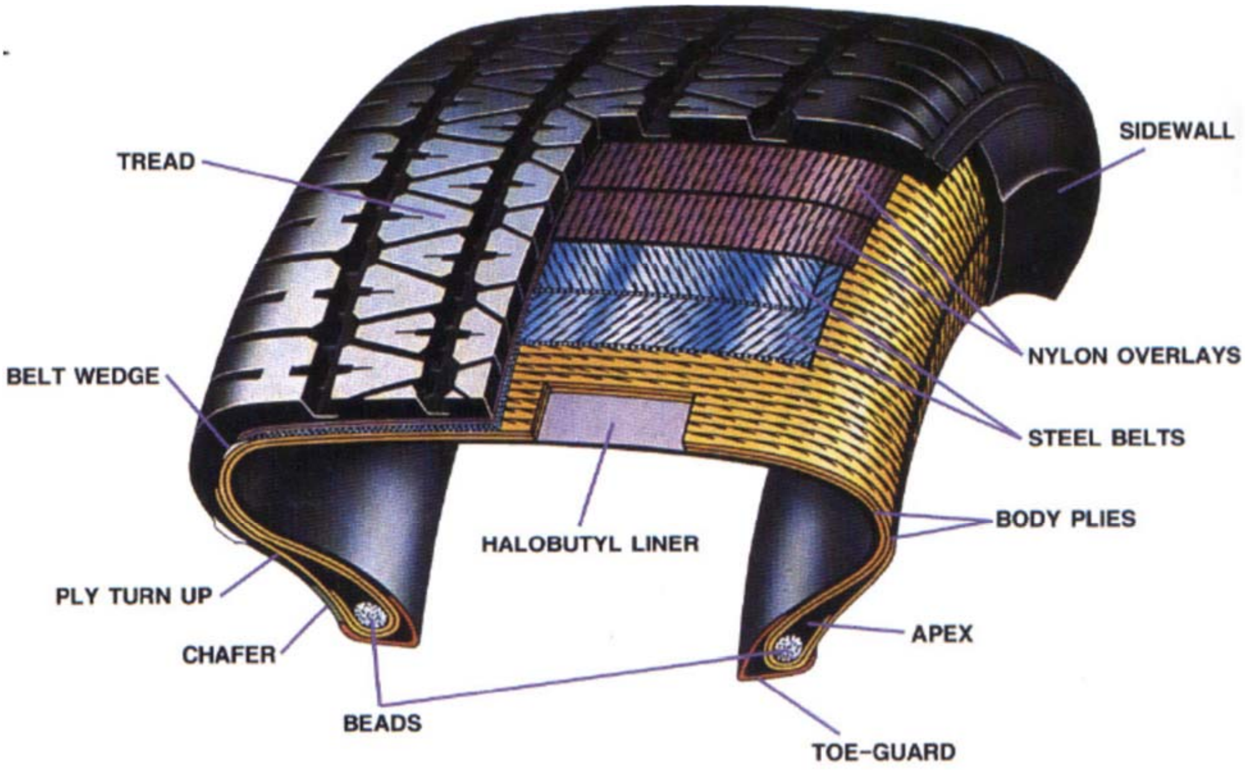


Figure 4.1 – Tire's construction

4. 2 Raw Materials

The main raw material used in manufacturing tires is rubber; both natural and synthetic rubber. To produce the raw rubber used in tire manufacturing is mixed the liquid latex with acids that cause the hardness of rubber. Excess water is squeezed out and the rubber is obtained into sheets. These sheets are dried in high chimneys, pressed into huge bales, and shipped to tire factories around the world. Synthetic rubber is produced from the polymers found in crude oil.

Carbon black is the other primary ingredient to be found in tire rubber. Carbon black is a fine, soft powder formed when crude oil or natural gas is burned with a limited quantity of oxygen, causing incomplete combustion and creating a large amount of fine soot. Carbon black is required too much for manufacturing tires that it is transported by rail cars and stored by huge silos at the tire factory until it is needed.

Other chemicals like sulphur are also used in tires. Specific chemicals, when mixed with rubber and then heated, produce specific tire characteristics such as high friction (but low mileage) for a racing tire or high mileage (but lower friction) for a passenger car tire [2]. Some chemicals keep the rubber flexible while it is being shaped into a tire while other chemicals protect the rubber from the ultraviolet radiation in sunshine [2].

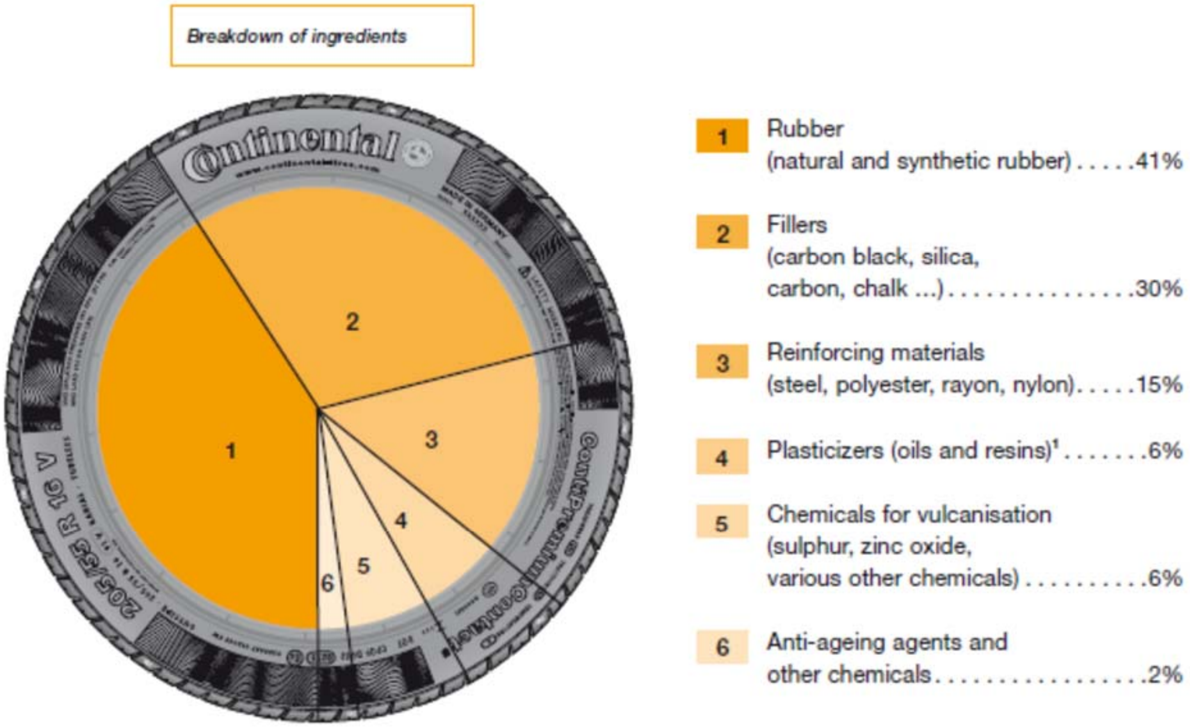


Figure 4.2 – Materials used in a tire

4. 3 Basic components/Tire construction

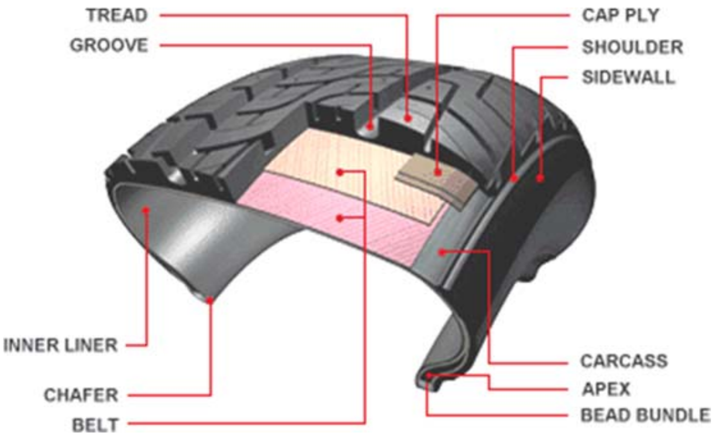


Figure 4.3 – Tire's construction

The construction of off – the – road depends, to a large extent, on the intended use of tires. However, common components to all off – the – road tires are the tread, carcass, beads, breakers, and sidewalls. Tubeless type tires also have an inner liner [2].

The tread covers the tire from the outside, and is the only part that directly comes in contact with the road surface. The tread has to be designed to protect the tire from cuts and wear. Depending on the intended use of the tire, the rubber compound applied to the tread will be changed to adapt cut tread pattern which also has a big impact on the performance of the tire. For different types of operations, are available, some tread patterns which feature very good cut resistance, traction and longer serviceability. All these factors must be taken into consideration before recommending a tire best suited for the function.

The sidewalls protect the carcass from damage. They are composed of flexible, crack resistant rubber. Tires with high cut resistant sidewalls can be used for jobs where chuck holes, large rocks, etc. are a problem. The sidewalls are designed to cushion the body plies from shock and cutting, while being able to flex and bend without cracking. The sidewall must also be able to withstand the ravages of the weather without deterioration.

Plies - A tire is composed of a number of layers or plies which are high tensile nylon cords loosely woven together and coated on both sides with a rubber compound. These layers of plies help contain the inflation pressure of the tire in supporting the load. The high-tensile nylon cords have a greater resistance to shock, cutting and heat. This improves the durability of the tire.

Carcass or Cord Body - The compressed air in a tire supports the load placed on the tire. The carcass forms a semi – rigid frame for the compressed air, but it is flexible enough to absorb some shocks and jolts. The carcass of the Bias tire consists of a number of rubber coated layers of fabric called - piles. The carcass determines the strength of the tire and the ability to flex.

The beads fix the tire to the rim to support the load.

Belts give extra protection to the radial plies underneath and determine the shape of the footprint.

Liner is composed of two or more layers of rubber and designed to keep air or liquid under pressure. The liner is made of an air-impermeable rubber compound and is similar to tubes used in tube-type tires. Tubeless tires normally have less weight with respect to tube type tires and are easier to maintain.

The breakers are rubber-coated layers of cord linking the tread and carcass, binding the two together. The breakers prevent cuts in the tread from reaching the carcass and absorb shocks.

The steel breaker tire has steel cord breaker that give it very high cut resistance. It is in particular of use where sharp rock is a problem, and is applicable at loader, dozer, dump truck, and rarely earthmover type tires. The adhesiveness between the steel cord and rubber is, however, more vulnerable to heat damage than that of nylon cord and rubber. As a result, steel breaker tires should not be subjected to conditions where heat generation is great. They should not be used for jobs where more easily retreaded tires can be used because of the complexity involved in retreading steel breaker tires. Steel breakers that extend to the sidewall are also available for jobs where high side cut resistance is required.

4. 4 End – of – Life Tires (ELT)

End – of – life tires are tires that can no longer be used on vehicles. All tires including passenger car, truck, airplane, two-wheel and off-road tires result in ELTs. However, the bulk of ELTs result from car and truck tires [3].

4.4.1 ELT Management

A predictable one billion tires worldwide reach the end of their useful lives every year. This number has been rising progressively and this tendency is probable to go on in the future. Different regional efforts by governmental authorities, the tire industry, and individual manufacturers are ongoing to manage ELTs and good progress is being made, though in many areas there is still a lot to be done.

When an ELT is taken off a vehicle, some markets exist to manage them, the most widespread including:

<u>Energy generation</u>: tire-derived fuel

<u>Material recycling:</u>

- e.g., civil engineering uses in which tires are shredded, cut or used whole
- e.g., ground rubber for rubber-modified asphalt, recreational surfaces including playground, synthetic field turf and athletic track applications, flooring, molded new rubber products.

ELTs that do not go into an end of use market normally follow one of two paths:

- Legally landfilled, in jurisdictions that allow landfilling of ELTs
- Dumped illegally into a stockpile or by the roadside

Uncontrolled landfilling is not favored because of health (e.g., potential malaria threat due to mosquito nesting) and environmental (e.g., fire risk) impacts. Moreover, landfilling leads to the loss of a resource that could be used beneficially somewhere else. The challenge and opportunity for all stakeholders in a given region where landfilling is still an alternative, including tire manufacturers, is to create an ELT system where ELTs are considered as a resource entering useful end-use markets.

In order to create this kind of system, a legal framework must deal with the collection, transport and storage of ELTs. The development of environmentally sound, economically viable, and self-sustaining end-use markets are also very important to the success of an ELT system.

Different ELT management systems exist in different countries worldwide. They have developed according to local cultural, political and industrial contexts. In many cases, ELT management is continually evolving, and existing systems have been adapted over time as learning about ELT management has increased [3].

Objectives for the industry to engage in ELT management

- To guarantee the industry accomplish its social and environmental responsibilities
- To guarantee ELTs are recognized as a potentially valuable secondary resource, in a global context of increasing resource scarcity and raw material costs
- To proactively manage cost and image threats to the industry of non-action
- To support the goal of 100% recovery rate, to treat ELTs generated annually and to treat existing stockpiles

Specific goals:

- To reduce the cost of the ELT chain by developing new markets
- To make sure ELT management is in line with legislative and environmental obligations in the countries in which this industry operates
- To develop new recovery routes
- To contribute in the process of creating or improving legislation concerning ELTs, in order to secure sustainable and economic treatment of ELTs

4.4. 2 ELT Management Systems in Europe

Today within the EU there are 3 different models for managing ELTs [4]:

- Extended Producer Responsibility (EPR)

- Liberal system (Free market)
- Tax system (Government responsibility, financed through a tax)

4.4. 3 Extended Producer Responsibility (EPR)

The producer's full or partial operational and/or financial responsibility for a product extended to the post-consumer state of a product's life cycle extended producer responsibility.

This means, under that system, the manufacturer has the responsibility of care to ensure that the waste coming from the products it has created is disposed in an environmentally sound manner. for Thus, for the waste that the consumer generates, the producer will be responsible.

The law defines the legal framework and assigns the responsibility to the producers (tire manufacturers and importers) to arrange the management of ELTs.

This Extended Producer Responsibility is followed through in different ways from a single ELT management company dealing with ELT collection and treatment in a country (such as in Portugal, the Netherlands or Sweden), through multiple ELT management companies (such as in Italy, France or Spain) or through individual producer responsibility (in Hungary).

A reporting responsibility of the ELT management companies towards the national authorities provides a good example of clear and reliable traceability.

Overall tire manufacturers have demonstrated a clear preference for this system and have taken the required steps to apply it. EPR is nowadays the most widespread system in Europe with 21 countries having adopted a legal framework assigning the responsibility to the producers (tire manufacturers and importers) to organize the management chain of ELTs.

4.4. 4 Liberal system (Free market)

Under this system, the legislation sets the objectives to be met but does not select those responsible. Thus, all the operators in the recovery chain deal under free market conditions and act in compliance with the legislation. This may be backed up by voluntary cooperation between companies to promote best practice.

Free market systems operate in Austria, Switzerland, Germany and the UK. The UK operates a "managed free market" system as ELT collectors and treatment operators have to report to national authorities.

4.4. 5 Government responsibility through a tax

The last model for managing ELTs is the tax system, applied in Denmark and Croatia. Under the tax system, each country is responsible for the management of ELTs. It is financed by a tax levied on tire producers and then passed on to the consumer.

In any market, the tire companies are ready to guarantee that their End-of-life tire arising are accounted for and dealt with in an environmentally sound way. The producer is responsible for ensuring that his products have a suitable recycling and recovery route.

The challenge is to collect and recover all tires and prevent them from depositing to illegal landfill, or to manage their export to ensure that their destination is acceptable to European requirements i.e. that they are being treated in corresponding environmental conditions as in Europe and fulfill the legal prescriptions of the EU Waste Shipment Directive. In Europe, the various management schemes have a obligation to ensure the required environmental standards are met and all do their maximum to ensure compliance. Though, when not managed by ELT management companies, ELTs leaving EU borders may not be fully traceable as to their final destination. This is a disadvantage that will need to be addressed by a global response to tire recycling.

The opportunity lies in the resources released by ELT recycling, whether in terms of energy or material recovery. Tires create opportunities to find new markets for new materials and new products [4]. Some of the opportunities are small, local solutions, others are high volume, high value solutions and others fall anywhere in between [4].

4.5 Scrap tires recycling

As all wastes, life-cycle analysis is the best approach to evaluate the alternatives between reuse, refabrication, recycling, recovering of used tyres and vulcanized scrap rubbers [5].

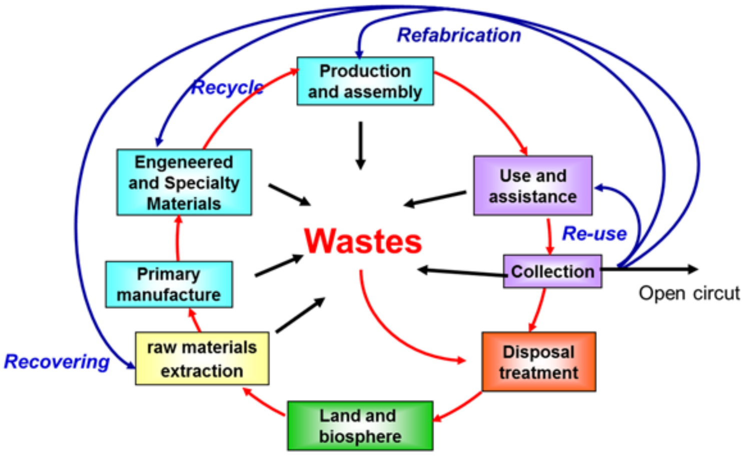


Figure 4.4 – Alternative in recovering matter/energy from end of life products

The alternatives are ranked for greenness by using the Lansink's ladder that shows how people should deal. The steps to take are listed:

- *prevention*
- *reuse:* to feed back the product to the market,
- *refabrication:* to disassemble the product to components which have a specific use
- *recycling:* to recover raw materials (or parts of raw materials, i.e. pyrolysis products)
- *energy recovery:* usually by combustion
- *landfill:* the least environmentally friendly alternative *deposit*.

The waste hierarchy of EU waste framework directive is shown in Figure 4.5. in the case of ELTs, the management of ELTs should start from the stage of preparing for re – use, which is the application for whole tires. And then, the stage of recycling comes next, which includes shredded tires and crumb and powdered rubber. Energy recovery is the last option for ELTs because of disposal of ELTs has already banned in EU [6].

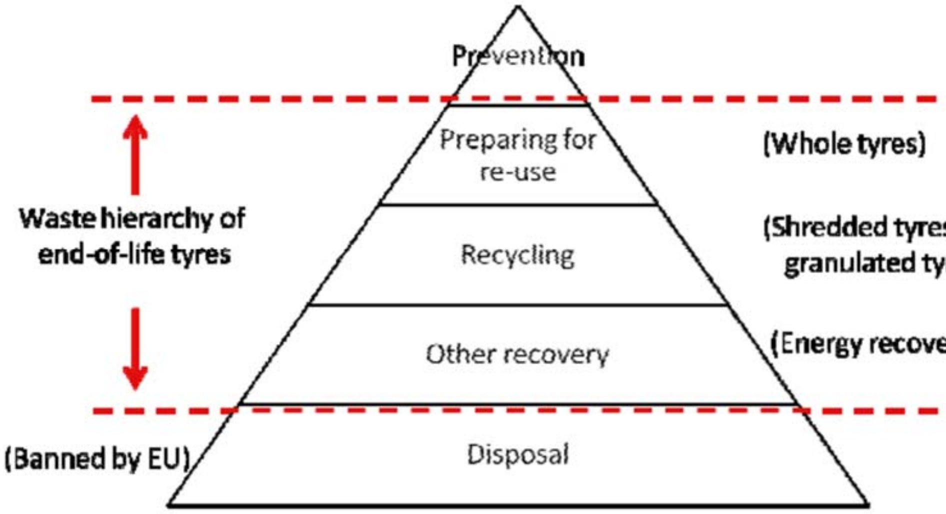


Figure 4.5 – Waste hierarchy of end – of – life tires

4.6 Technologies for material recycling

4.6.1 Shredding technologies

Mechanic shredder - The cut is performed with shearing crusher two or more parallel axes blades which spin at different speeds. The separation of the axes defines the final size, being able to find these fractions [7]:

- Shred small or 50x50 mm is mainly used as fuel in cement kilns.

- Shred medium or 100x100 mm is used as fuel or material recovery.
- Shred large or 150x150 mm has applications in civil engineering, for example, sealing of landfills, road construction, slope stabilization, road and railway embankments, drainage material (replacing sand and gravel), landfill construction, sound barriers, insulation, etc.

If not used for these applications, the shred material is used as previously to move to granulation later.

Cryogenic shredder - This technology uses liquid nitrogen to cool the tire to temperatures between -50 °C to -100 °C, in which the rubber enters the glass state, becoming very weak and is thus easier to shred. The semi-cryogenic shredder is a variation, where only liquid nitrogen is applied to certain parts of the tire.

Shredded tire allows making easy transport, the reduction of volume and the homogenization of the waste and for use in several applications. The disadvantages, there is considerable wear on the blades and its subsequent renewal requires a high cost. Moreover, all sizes shred have not real applications today, and there are not many studies to improve the technique [8].

4.6.2 Grinding technologies

Ambient grinding – It works by crushing against metal rings provided with holes. The equipment can be powered by shoveling into the hopper or directly by conveyor belt from the grinding process. It is important pre-shred for the feed with a material has a homogeneous size as possible. The rubber is classified in three fractions after grinding process:

- Granulation 2.5 - 4 mm has the most applications.
- Pulverization 0.8 - 2.5 mm has a great demand for artificial grass, as synthetic fiber filling with aggregate or as a base layer.
- Micronization < 0.8 mm its use is supported by Public Administration and when mixed with bitumen, asphalt can be manufactured.

Granulate have irregular shape with a significant surface roughness and the rubber is partially oxidized at the surface due to heat generated during the process.

Cryogenic grinding - The shredded rubber is cooled below the freezing point of -200 °C so that it becomes fragile and disappearing, its elasticity and thus it can be easily disintegrated. This process uses liquid nitrogen first, and then the rubber passes through an impact mill (similar to a hammer) where it is ground. This technology enables rapid separation of the three components of tires (rubber, steel and fibers) on drying [9].

The shape, size distribution and surface characteristics of grinding rubber obtained by cryogenic grinding are different from those obtained by ambient grinding. The granulate have a relatively smooth surface, a wide range of particle size and minimal surface oxidation [10].

Wet grinding - It is a not often used process that consists of a series of grinding wheels that inject into the surface of the tire high-pressure water spray for cooling of dust rubber. After, this process separates the water from dust and dried.

The advantages of grinding technologies are to get fine and regular particles with variable size distribution, as the granulate has greater scope in many applications [7]. The cryogenic grinding technology offers other advantages such as temperature monitoring, the existence of an inert atmosphere by avoiding the deterioration of rubber, it improves the surface morphology of the particles and smaller particles are obtained. Against, the grinding technologies have higher investment than shredding technologies. The wet and cryogenic grinding requires drying and can cause the leaching of ZnO, under certain environmental conditions (due to zinc compounds which are part of tire additives) [11].

4.6.3 Energy recovery

Cement industry - In Europe, the cement sector is the main use of tires as an alternative fuel source (Tire-Derived Fuels TDF) [20]. European legislation is adapted to permit and limit its use and emissions. ELT is an alternative fuel today, but it cannot exceed 20 % of total fossil fuel required in the manufacture of cement [4]. The 60 % of ELTs generated are used as fuel in cement kilns in Austria; while in Germany, France and Britain are used the 38 % and 8 % and 6 %, respectively. In Spain, there are several cement kilns using whole or shredded tires as TDF. The clinker obtained from TDF by 20 % substitution of conventional fuel is similar to that obtained using only pet coke [12]. At the moment, there are not scientific data showing a decline in the quality of the final product using this fuel.

Steel plants - Shredded tires can be used in electric arc furnaces as a substitute for anthracite (1.7 Kg ELT is equivalent to 1 Kg of anthracite [13] and part of the scrap. In addition to the use of the calorific value of the tire, all the steel contained in tires is recycled [13]. All without any appreciable changes in the levels of emissions of certain pollutants such as steelmaker dust and gases, and it may be even smaller, as in the case of heavy metals and CO2 [13]. The key is to introduce into the electric arc furnace a mixture of scrap and ELTs. The content carbon tire contributes to the decrease of iron, saving consumption of reducing agent, the iron in the tire joined the molten phase, improving metallurgical performance; and zinc in the tire, joins the steel powder.

Alternative fuel in thermal power stations and pulp and paper mills - At present, the use of ELTs as an alternative fuel in these industries is widespread in the U.S., and especially in Japan, but not in Europe [14]. U.S. consumed 39 million tons of ELTs in 24 paper mills in 2005, and Japan 32 % of ELTs generated in 2008, percentage which is much higher than that used in the cement industry, which was 13 % [14].

Other industrial boilers - This particular application is used mainly in Japan, which uses 2 % of ELTs for energy recovery in 8 of the 21 tire factories existing and 1 % in other industrial boilers [14].

The great advantage of the tire as TDF is its high energy content (Higher Heating Value 32KJ/Kg) and it is equal or better source of energy than other fuels [4]. ELTs can generate energy as heat, electricity or cogeneration and can be co-incinerated or used as the only source of energy in many processes. Furthermore ELTs can be used entire, shred or granulated.

Many studies shown that the use of ELTs reduces emissions, for example SO_x because tire contains less sulphur than conventional fuel, and emissions of greenhouse gases such as CO2 because the carbon content per unit of energy is lower than in coal and pet coke [15]. The ash produced generally contents fewer heavy metals than the ash coal combustion because in the cement kiln the rubber provides energy and iron and sulphur are incorporated into the cement.

The biggest disadvantage of ELTs energy recovery is its limited use as a 10 - 20 % alternative fuel. Moreover, its weight and volume, because it limits the distance from transport and the availability and the high temperatures reached in combustion, since it poses a high standard in terms of furnaces and refractory linings used (because of differences in burning rate of the different components, the difficulty of feeding the system and the presence of metals and metal oxides).

4.6.4 Emerging technologies

Road applications - One of the most important applications is the use of ELTs dust in the construction of roads. The production of bituminous mixtures with dust tire is a relatively old technology because it has been developed as in the U.S. since the 60s. Rubber asphalt is expanded in the U.S., and Europe is expected to grow in the future [4].

There are three types rubber-modified concrete:

- Rubber Modified Bitumen (BMC) has properties similar to polymer-modified bitumen and the amount of dust required is 12 - 15 % by weight. It can be used for the same applications as polymer-modified bitumen: a layer of rolling thin staple F and M, blends and mixes draining S intermediate layer with improved properties of fatigue and plastic deformations.

- Rubber Modified Bitumen with High Viscosity (BMAVC) is manufactured with a higher amount of dust rubber, between 15 - 22 % by weight and is used in applications where very high viscosity is needed.
- Rubber Improved Bitumen (BC) has better features than the conventional bitumen and the amount of dust rubber used is usually between 8 - 12 % by weight. It has intermediate properties between conventional and modified bitumen. Its main application is as basic and intermediate layers and as wearing courses with conventional mixtures of heavy traffic categories.

There are two main processes for producing rubber asphalt:

- Wet process: dust rubber is added to bitumen at high temperature (149 - 190 °C) absorb the lighter components of bitumen and swelling, and causes the rubber to soften, . The mixture should be in continuous agitation so as not to segregate.
- Dry process: dust rubber is added directly into the asphalt manufacturing plant, as if it were a mineral fraction. The dust acts partially as an aggregate, but the finest particles interact with bitumen changing its properties. There are two techniques depending on the maximum size of dust rubber. One uses high maximum sizes of up to 2 mm, and the other technique uses less dust rubber size < 0.5 mm and a lesser proportion.

The application in the road of recycled rubber has great advantages mostly because it saves nonrenewable raw materials, large volumes are needed in each project, and road construction takes place around the country. Also dust rubber improves the properties of conventional bitumen and governments encourage its use. However, it competes at a disadvantage with the low prices of petroleum products and aggregates and moreover, the cost of treatment for dust rubber is high.

4.6.5 Devulcanization

It is a process of decomposition that allows the recycling of rubber from ELTs based on chemical bond breaking cross monosulfide, disulfide and polysulfide (carbon-sulfur and sulfur-sulfur bonds) of vulcanized rubber [16]. The aim of the devulcanization of rubber is a product with properties similar to virgin rubber to return to revulcanize with or without the use of other compounds, and then to produce rubber mould applications. The devulcanization is an expensive technology but various applications have been developed and the investigation continues. Some of the existing processes are devulcanization chemical, bacterial, thermal, microwave, mechanical, ultrasonic, chemical-mechanical, thermo-mechanical and thermo-chemical and other [17]. They are only a small number of operating systems but with small capacity. The greatest potential for productive areas of research is to reduce processing costs and obtaining rubbers with properties identical to virgin rubber [17].

4.6.6 Pyrolysis

Pyrolysis is the thermal degradation process of shred or granulated tire in intermediate substances such as gas, oil, solid residue (char or carbonaceous solid residue) and steel. In the pyrolysis process, shred tire (1 - 3 cm), or granulated tire (0.5 - 4 mm) free from steel and textiles are heated at a moderate temperature (400 - 800 °C) in the absence of oxygen or a limited amount. The overall reaction which takes place in a reactor is described as follows:

- Organic material (rubber) is fed to the pyrolysis reactor and is subjected to thermal cracking, breaking up into a volatile fraction and a solid residue.
- Volatile fraction is cooled and thus resulting two fractions: a liquid fraction and a noncondensable gas fraction.
- Condensable liquid fraction is about 35 % of the initial weight. This fraction is commonly called tire-derived oil and it consists of organic compounds C_5 - C20.
- Non-condensable gas fraction is about 20 % by weight and is composed mostly of hydrogen (H_2), hydrogen sulfide (H_2S), carbon oxides (CO_x) and light hydrocarbons (C_1 - C_6), which can be used as fuel pyrolysis process or co-generation. It has a calorific value between 68 - 84 MJ m-3.
- Solid residue is a mixture of steel and char or black carbon and accounting for 45 % of initial weight.

Yields and composition depend on the temperature, pressure, residence time, particle size starting material, condensation temperature of the volatile fraction and the type of kilns used [18].

Although the scientific research, there are few industrial plants in operation. Now, researchers focus their efforts on analyzing the kinetics of pyrolysis with ELTs under different conditions of temperature (300 - 850 °C) and different proportions of oxygen (5 - 21 %) or nitrogen atmosphere, and to achieve cost-effective throughout different strategies for recovery.

The main advantage of pyrolysis technologies is to obtain products capable of recovery and a gas fraction that can be used as fuel in the process, as fuel in cement kilns or co-generation; tire-derived oils have characteristics similar to a gas-oil trade being able to use as fuel in conventional furnaces and combustion engines, and the pyrolytic carbon black has great potential because it can enhance fuel substitution (when mixed with coal), absorbing light, the manufacture of polymeric materials, or as feedstock in the manufacture of charcoal and tires.

The main drawback is the high cost of investment and process, and the price of the obtained products rarely justify a high-cost process because of competitive prices of the petroleum products.

4.6.7 Gasification

This is another thermal treatment technology which can use ELTs as well. The thermal degradation of organic matter is carried out in the reactor under low-oxygen atmosphere (1/3 - 1/5 stoichiometric for complete combustion) and a temperature about 600 °C.

The outcome is a synthesis gas or syngas with an estimated yield of 63 % by weight, and a solid phase representing about 37 % about total weight. Yield gasification process varies depending on the technology, fuel and gasifying agent used. The syngas has low calorific value (5 - 6 MJ Nm-3), and it is composed mainly of hydrogen (H_2) and carbon monoxide (CO) which energy value can be used to produce electricity under specially adapted internal combustion engine, with relatively high yields, and free emissions of dioxins and furans. The gas is cleaned of particulates, tars and other components, and it is cooled to about 40 ºC before entering the motor generator. Today there are motors specially designed for operation with poor gas, the motor can to achieve yields about 37 % [11]. The solid fraction is composed of carbon black and steel. These are easily separated for material recycling.

There are two technologies:

- Entrained bed reactor, is subdivided depending on the relative sense of the flow fuel and gasification agent in “downdraft” where the streams are parallel, and “updraft” when travelling in the opposite direction.
- Fluidized bed reactor, a gasification agent has an inert and waste in suspension until the particles of ELTs is gasified, becoming flying ash and then, these are washed away from the syngas.

This treatment obtains products capable of recovery and can be used as fuel for electrical or thermal energy. The disadvantages, the difficulty of predicting the composition of the gas due to the variation of parameters and low-electrical yield of 25 % compared with about 50 % that can be achieved with biomass waste such as agricultural or forest.

4.6.8 New plastic products

The development of plastic products is increasing. Shred tire with binder thermoplastic or polyurethane can produce different materials and objects such as shoe soles, casings, insulating sheets, backs, motorcycle helmets, etc. [4]. New products from recycled rubber are a enormous opportunity for new applications emerging in the market for ELTs rubber. The biggest doubt may come to object the quality and durability of the resulting materials, but it can be solved with the development of manuals and quality certificates.

References

[1] J. Mark, T. Erman, and B. Eirich, *Science and Technology of Rubber*, 1994

[2] Kovac, F. J. *Tire Technology,* Goodyear Tire and Rubber Co., 1978.

[3] World Business Council for Sustainable Development, 2018

[4] ETRMA, *END-OF-LIFE TYRE REPORT*, 2015

[5] A. Citterio, *Reclaiming of vulcanized rubbers / scrap tyres*, Polimi 2013

[6] European Union, 1999

[7] Basel Convention, *Revised technical guidelines on environmentally sound management of used tyres*, 2010

[8] S. Kromer, *Life Cycle Assesment of a car tyre*, 2002

[9] Secretariat of Basel Convention, *Technical guidelines on the identification and management of used tyres*, 2000

[10] D. A. Baeta, J. A. Zattera, M. G. Oliveira. P. J. Olivira, *Braz. J. Chem. Eng.*, 2009

[11] Juniper Consultancy Services Ltd., *Emerging solutions for managing scrap tyres. Technology solutions and market opportunities*, 2004

[12] M. A. Terezza, A. N. Scian, *Mater*, 2008

[13] M. Zaharia, V. Sahajwalla, B.C. Kim, R. Khanna, N. Saha-Chaudhury, P. O`Kane, J. Dicker, C. Skidmore and D. Knights, *Energy Fuels*, 2009

[14] T. Mino, *Tyre Industry of Japan*, 2009

[15] J.I. Reisan, *Air Emissions from Scrap Tire Combustion*, 1997

[16] M. Alexandre-Franco, C.C. Fernandez- Gonzalez, *Energy Fuels*, 2010

[17] M. Leary, *Evaluation of Waste Tire Devulcanization Technologies*, 2004

[18] S. Galvagno, S. Casu, T. Casablanca, A. Calabrese and G. Cornacchia, *Waste Management*, 2002.

CHAPTER 5

RECYCLING/RECLAIMING

5.1 Introduction

The rubber industry, in the beginning, could only rely on natural rubber which was scarce and expensive. Facing the natural rubber shortage forced the industry to find alternative resources to natural rubber in addition to finding a way to reclaim it. Reclaiming rubber from waste rubber products like tyres, tubes and any other rubber products is an appropriate approach to rubber recycling. In terms of scrap tyre management, not only can the rubber reclaiming process resolve the tyre disposal issue, but it could also reduce demands on finite petroleum resources. Reclaimed rubber from waste tyres is extensively used in polymeric blends. Reclaiming is the breaking of carbon bonds.

Through tyre rubber reclaiming, the rubber is softened and swollen due to the breaking of some cross-links as well as double bonds of three-dimensional strong thermoset polymers into two-dimensional thermoplastic products. The reclaimed rubber should have a soluble fraction with a high molecular weight to achieve better mechanical properties of the polymer. Nevertheless, the mechanical properties of reclaimed rubber are lower than that of the virgin rubber. On the other hand, there are some advantages in using reclaimed rubber in producing various rubber articles [1]. Lower energy consumption, lower heat generation, shorter mixing time, faster extrusion, and ultimately reducing the cost of the production are advantages of using reclaimed rubber. This process which is performed by applying an external source of energy is classified into different categories including physical, chemical, mechanical, cryogenic, microwave, and ultrasonic treatments [2, 3].

Table 5.1 – Characteristic of different devulcanization technologies [4]

Technology	**Basis of Processing**	**Zone of reactions**
Physical	Ultrasonic waves	Throughout particles
Physical	Microwaves	Throughout particles
Physical	Supercritical CO2	Throughout particles
Thermo – mechanical	Mechanical (squeezing) Thermal (steam)	Particles surface

Chemical	Chemicals/chemical reactions	Particles surface
Biological	Microorganisms	Particles surface

5.2 Types of reclaiming technologies

5.2.1 Ultrasound recycling

Ultrasonic energy is used for the devulcanization of cross linked rubber. Solid rubber articles are immersed into a liquid, and then ultrasonic energy is applied whereby the bulk rubber effectively disintegrates and dissolves into the liquid [5]. The devulcanization process requires a high energy level to break carbon–sulfur and sulfur–sulfur bonds. An ultrasonic field creates high frequency extension–contraction stresses in various media [6]. It is found that during ultrasound devulcanization molecular weight of sol fraction decreases from which it may be understood that during ultrasound treatment not only C–S or S–S bonds but also C–C bonds break. Levin et al [7] suggested a revulcanization scheme. They concluded that devulcanized rubber contained a larger amount of sulfidized molecules which were responsible for crosslinking during revulcanization.

5.2.2 Microwave recycling

In the microwave recycling method, a controlled dose of microwave electromagnetic energy at specified frequency is used to break the sulfur – sulfur or carbon – carbon bonds in the crosslinked rubber powder [8]. Thus in this process elastomer waste can be reclaimed without depolymerization to a material capable of being recompounded and re-vulcanized having physical properties essentially equivalent to the original vulcanizate. By using microwaves, the temperature of the material increases very fast to reach finally 260–350ºC. A pre-condition to arrive at this temperature level for devulcanization is that the vulcanizates should contain carbon black, making them suitable for this method. The waste material for reclamation must have some polarity so that the microwave energy will generate the heat necessary to devulcanize. The devulcanized rubber is not degraded when the material being recycled [9] which normally take place in the usual commercial processes currently being practiced. In this process sulfur vulcanized elastomer containing polar groups is suitable for microwave devulcanization. Tyler et al [10] have claimed their microwave devulcanization process as a method of pollution controlled reclaiming of sulfur vulcanized elastomer containing polar groups. Carbon black containing rubber is susceptible to ultra high frequency in a microwave chamber due to interface or ion polarization: accumulation of free electrons at the interface of different phases with a different conductivity and dielectric constant. Therefore, it appears that this microwave technique is a unique method of reclaiming in terms of properties and fastness of the process. This method is very much useful because it provides an economical, ecologically sound method of reusing elastomeric waste to return it to the same process and products in which it was originally generated and it produces a similar product with equivalent physical properties. The process has the disadvantage that it is difficult to control.

5.2.3 *Supercritical carbon dioxide*

The use of Supercritical Fluids (SCF) as solvents lets, in many cases, to reduce time, cost and hazard with respect to traditional techniques with solvents [11]. The supercritical state is a particular state of aggregation in which exists no separation between liquid and gas phases exist. The supercritical fluid system consists in two phases in equilibrium, a low density gas and a dense liquid. As the critical temperature (300 K) is reached, the liquid became more fluid, while the gas at equilibrium becomes denser. At the critical point the density does not show any longer differences and the two phases become one fluid phase. Compared to a classical liquid extraction with solvent, the use of a supercritical fluid with similar solvating power will be performed in a shorter time, thanks to better transport properties. Moreover it is easier to remove carbon dioxide since it is a gas at room temperature (the critical parameters are 304,1 K and 72,8 bar), and it is chemically inactive, nontoxic, inflammable, inexpensive and widely available. It is noteworthy that this type of fluids shows the ability of permeating into polymers.

5.2.4 *Thermo-mechanical reclaiming process*

During most mechanical processes a strong rise in temperature occurs that aids in degrading the rubber network. Thermo-mechanical recycling of rubber is assumed to be a combination of sulfur cross links and breaking carbon-to-carbon bonds. This leads to the formation of soluble branched structures and fragments of gel. The recent material recycling processes all use thermo-mechanical regeneration methods. Recycling chemicals and oils are frequently used in addition to the thermal and mechanical breakdown: disulfides, thiols, amines and unsaturated compounds are the most common recycling chemicals. Softeners lower the thermal degradation resistance of a vulcanizate by deteriorating the interaction between filler and rubber chains.

5.2.5 *Chemical treatment*

Different chemical compounds are used in order to promote the breaking of S-S bridges and C-S bonds. Normally a process requires mixing of the small size rubber particles and devulcanizing agents in controlled conditions of temperature and pressure. These chemical approaches result usually in high efficiency devulcanization.

Unfortunately, chemical methods are considered and also reported to attack only the surface layer of dust. Thus, is it possible to compatibilize the rubber powder well, but not to use it to its fullest. Apparently this is true when a good solvent for the swelling is not engaged. With the powder puffed from a good solvent, pervasive reactions around the rubber powder, on the contrary, can be accomplished but rubber industry do not accept the use of organic solvents.

Most of the industrial reclaiming processes make use of chemical agents such as mercaptans, disulfides, phenols, amines and metal chlorides. The function of these reagents is to initiate the cleavage of sulfur crosslinks or to terminate the chemical chains induced as a result of C–S, S–S, and C–C bond cleavage. Two different mechanisms are followed: radical or nucleophilic mechanism.

5.2.6 Microorganisms

One possible way of getting rid of spent rubber could be to degrade it using microorganisms. Biological attack of natural rubber latex is quite facile. Man has tried time and again to consider elastomeric articles as source for microbial attack. Obviously nature is able to take care of its own waste problems but as soon as man become involved and convert the natural rubber polymer into a technical material by sulfur and numerous other ingredients, biological attack is minimized. Spent rubber could be used as substrate for microorganisms provided the structure can be efficiently degraded [12]. The biological process represents the more environmental friendly devulcanization technique with low-energy consumption.

5. 3 Advantages of reclaimed rubber

Rubber recovery can be a difficult process. There are many reasons, however why rubber should be reclaimed or recovered [13]:

- Recovered rubber can cost half that of natural or synthetic rubber.
- Recovered rubber has some properties that are better than those of virgin rubber.
- Producing rubber from reclaim requires less energy in the total production process than does virgin material.
- It is an excellent way to dispose of unwanted rubber products, which is often difficult.
- It conserves non-renewable petroleum products, which are used to produce synthetic rubbers.
- Recycling activities can generate work in developing countries.

- Many useful products are derived from reused tyres and other rubber products.
- If tyres are incinerated to reclaim embodied energy then they can yield substantial quantities of useful power. In Australia, some cement factories use waste tyres as a fuel source.

5.3.1 Environmental effects of rubber recovery

There are three types of environmental effects related to rubber tires: first, the environmental effects (primarily neutral or negative) of disposal; secondly, the environmental impacts (both negative and positive) associated with recovery and recycling of waste tires; and third, the effects on worker health and safety for those working in recycling enterprises.

5.3.2 Environmental Benefits of Recovery

Conservation of Value Added

The process of manufacturing and giving value to materials has environmental effects at each step in the production process. By conserving the value added of a particular step, recycling makes the material available while avoiding the environmental effects associated with production.

Raw Material Conservation

The raw material of natural rubber is latex sap from rubber trees. Rubber plantations are a form of monoculture in much of the tropical developing world, where they frequently displace diverse virgin or regenerated rainforest. The flora and fauna of plantations is greatly impoverished, and they are artificial ecosystems vulnerable to outbreaks of pests and to changes in weather patterns. To the extent that rubber is a necessary and valued substance in modern life, the availability of rubber from secondary sources limits the need for new rubber plantations and thus their negative environmental consequences.

Furthermore, synthetic tires are made from petroleum products. The extraction of oil and other petroleum products is also environmentally damaging, and the supplies of these materials are limited. Thus recycling has benefits to the global material supply.

Limitation of Disposal.

Although tires are almost inert, they are difficult to dispose of, unsightly, and may provide a breeding ground for mosquitoes. To the extent that prevention, reuse, repair, and retreading reduce disposal, this is also an environmental benefit.

Conservation of Energy

The production or repair of tires from the waste stream, conserves energy and materials, since there is less energy used in recycling than in new manufacture of tires, rubber, or formal sector consumer products that would compete with the recycled ones. Also, the environmental effects of most operations, from retreading to secondary manufacture, are qualitatively similar to those from the use of virgin materials, but far lower in quantity, giving a net benefit. Thus there is a net resource and energy benefit to the use of secondary rubber.

Risk Reduction

One of the environmental dangers associated with tires is the danger of fire from stockpiled tires. Recovery projects have a two-way effect on this risk. On the one hand, recovery enterprises may stimulate the stockpiling of tires as part of building up an inventory of raw materials, although these are usually more carefully managed than piles of tires that are not destined for use. On the other, recovery projects may regularly use stockpiled tires, with the result that there are fewer piles at risk.

5.4 Negative Environmental Impacts

Smoke and Hydrocarbons from Burning of Rubber in Recycling Operations

Most recovery operations involve burning of tires or rubber at some stage of processing. The ash from burning of tires may also be a hazardous substance. Given the fact that most burning operations are manual and small, there seems to be no available strategy to mitigate this effect. With adequate resources, the substitution of mechanical processes for burning could reduce smoke generation in certain circumstances.

Release of Rejected Tires, Buffings and Dust to the Environment

Most types of reclamation, from puncture repair to remoulding, involve a pre-selection of usable tires and/or tubes, with the unusable ones to be discarded. At this point, a quantity of tires must be disposed of, and this may occur through dumping, the hazards of which have been discussed above. Re-grooving, retreading, and certain kinds of manual production involve rasping, buffing, sanding, shaving, or other cutting processes which produce small fragments, buffings, and dust. Mechanical grinding, milling, and rasping also produce dust and buffings, which create a strong odour of rubber, and may contaminate the immediate surroundings. Avoidance of release of these items and substances will generally require an alteration not only in the operations involved, but also in the mentality of the workers.

Use and Discharge of Hazardous Substances

Reclamation processes also produce waste in the form of residues and by-products, many of which may also be hazardous. The production of reclaim has a large potential for emissions to water, air, and soil, as there are a great many petroleum-based additives and other substances which are both used and generated in the process. Retreading involves the use of certain petroleum products, which are vaporized during the revulcanization process.

The capital-intensive process for producing rubber reclaim has potentially detrimental environmental effects, depending in part on the process used. Wet processes produce a highly contaminated waste water containing sulphur derivatives, organic oils, softeners and suspended solids. The effluent has a high chemical oxygen demand and is often acidic or alkaline. When the wet digester process is used there are considerable amounts of metal chlorides, and a sludge of hydrolyzed fiber and fine rubber particles in the effluent. The process also produces an unpleasant odor.

The environmental risks from improper use or release of these substances to the environment are difficult to assess. Mitigation measures include training and education, as well as providing appropriate receptacles and collection systems for these substances and materials. Over the longer term, research into less hazardous equivalents (either less hazardous substances or the same substances in a less hazardous form) might prove helpful.

Hazards of Recycled Tires or Recovered Products

In certain cases, the tires, tubes, and secondary products which are produced by small-scale manufacturers, retreaders, regroovers, and the like, may themselves form an environmental hazard.

In the larger picture, the environmental hazard represented by these products is relatively small. Still, their effects can be constrained by introducing measures of quality control, as well as by providing free disposal for tires and casings that are inappropriate for reuse.

Environmental Losses Due to Pre-Emption of a More Environmentally Beneficial Recovery Strategy by a Less Beneficial One

This is the situation that results when one recovery strategy -- for example regrooving – preempts retreading or secondary manufacture whose net environmental benefit might be higher. Given that the local marketplace determines, in part, which products are marketable, and which aspects of retained value are most commercially viable, this risk seems unavoidable.

5.5 Risks to Worker Health and Safety

A third category of risks and problems is threats to worker health and safety.

Danger from Dusts, Buffings, and Powders

The danger for workers from dusts, buffings and powders varies by type of exposure. Both inhalation and contact with skin can be dangerous, causing illness or cancer. In addition, ingestion through eating or drinking in a dusty area can cause particles to be absorbed into the stomach, causing poisoning and stomach cancer.

Adequate ventilation and strict industrial hygiene is the most commonly deployed mitigation strategy. Providing workers with gloves, masks, and protective clothing and footwear may also mitigate the problem, but only when accompanied by a policy of ensuring that these become a part of normal everyday operations. The providing of a separate area for eating and/or protected storage for foodstuffs would also be useful. Technical innovations that can be helpful include installing blowing systems in the machinery itself, and orienting vacuum blowers right over the process. In certain cases, it is recommended to substitute liquid additives in place of those in powder form.

Danger from Fumes or Vapours Containing Carcinogenic or Hazardous Substances

These dangers, like those of dust exposure, may occur from inhalation, ingestion, or skin contact. Vapours from rubber production include carcinogenic substances, as well as enbrytoxins, which are harmful to fetuses. Exhaust ventilation is a key ingredient of almost any strategy for control of vapours. The exclusion of pregnant women from locations where vapours are formed is also advisable. Masks and protective equipment, especially gloves, can assist in the protection of individuals, but only if these are regularly and properly used.

In certain cases changes in the process may be useful as well. In relation to both retreading and moulding, the choice of certain compounding ingredients may have the effect of reducing vapour formation. A fairly high level of technical sophistication is necessary to precisely identify the problems and propose and implement solutions, and would probably require not only external financing, but also external expertise. Even then, there is no guarantee that the proposed changes could be implemented at the informal sector micro-enterprise level.

Injury from Physical Processes, Including Cutting Tools or Processing Machinery

There are three sorts of risks to workers under this category. First, there is the risk of cutting with cutting tools. Secondly, there is a risk of injury through improper use of machinery. Third, there is the risk to workers of excessive lifting, that can result in back strain.

All three of these risks are mitigated by a relatively long period of apprenticeship before workers are allowed to use sharp tools or operate the machines on their own. Careful maintenance of tools and equipment is also a factor in injury reduction. In terms of lifting, the use of pallet jacks or other leverage tools can reduce the burden on individual workers. The specific relevance of these measures must of course be assessed for each individual case.

Dangers from Smoke from Burning Rubber

Both smoke from burning rubber and the dust from buffings can be dangerous to the health of workers. Smoke inhalation, particularly when the smoke contains products of combustion from complex polymers, as is the case with tires can cause various lung ailments and can be carcinogenic. It can also cause eye and throat irritation.

Good ventilation is one generally recommended mitigation strategy. Protective masks, goggles, or clothing could be helpful, as long as these become a part of regular operations. These risks can be significantly reduced through careful project planning and design. The location of most small workshops in partially open-air buildings or out of doors minimizes direct risks to workers, although it disperses potential contaminants more quickly into the environment.

Health and Safety Risks of Scavenging and Collection of Tires

Health and safety risks in the scavenging of tires can range from back and muscle strain to contact with septic or contaminated substances. Scavengers frequently lack any protective equipment, such as gloves or shoes that would make scavenging safer. Also, tires are quite heavy for a child to lift, and truck or bus tires can easily strain an adult's back.

The dangers from lifting and carrying can be significantly reduced by providing scavengers with pallet jacks, lifting hooks, and carts. These come under the general category of collection and transportation improvements, and are usually associated with some type of formal recognition of the collectors. In some cases, set-up of collection points can make the acquisition of equipment for these points worthwhile.

5.6 Uses of Reclaimed Rubber

Recycled rubber is being used by manufacturers in a wide variety of applications today. Manufacturers prize scrap tires and rubber as a raw material input due in part to cost and energy savings.

Here are a number of settings where the recycled rubber is used most:

1. Used as cushioning in parks, schools etc. so that if children fall, they are not hurt much.
2. Used in sport shoes, working shoes and raincoats in clothing industries.

3. Rubber along with other strengthening material is used in making sidewalk panels which are more resistant to be damaged by roots and also serve as a more comfortable pavement.
4. Use in landfills as a protective covering.
5. Serve as a coal fuel source.
6. Hospital floors and surgical gloves
7. Vegetation protectors and windbreaks, sheds, livestock mats, bumpers, and feeders

References

[1] De, S.K. Isayev, A. Khait, K. *Rubber Recycling*, 2005.

[2] S. Bandyopadhyay, S.L. Agrawal, R. Ameta, R.; Dasgupta, R. Mukhopadhyay, A.S. Deuri, S.C. Ameta, S.C., *An overview of rubber recycling. Prog. Rubber Plast. Recycl. Technol,*. 2008

[3] Rajan, V.V.; Dierkes,W.K.; Joseph, R.; Noordermeer, J.W.M. *Science and technology of rubber reclamation with special attention to NR-based waste latex products. Prog. Polym. Sci.,* 2006

[4] A. Citterio, *Reclaiming of vulcanized rubbers / scrap tyres*, Polimi 2013

[5] Pelofsky, A.H., *Rubber reclamation using ultrasonic energy*, USA: Cities Service Oil Co., [US: 3725314], 1973

[6] Warner, W.C., *Rubber Chem. Technol*., 1994

[7] Levin, V.Yu., Kim, S.H., and Isayev, A.I., *Rubber Chem. Technol*., 1997

[8] Novotny, D.S., Marsh, R.L., Masters, F.C., Tally, D.N., USA: *Goodyear Tire and Rubber*; [US: 4104205], 1978

[9] Clifford, M.L., US Patent, 4,130,616, 1978

[10] Tyler, K.A., and Cerny, G.L., USA: *Goodyear Tire and Rubber*; [US: 4459450], 1984

[11] M. Kojima, K. Ogawa, H. Mizoshima, M. Tosaka, S. Kohjiya, and Y. Ikeda, *RUBBER CHEM. TECHNOL*., 2003

[12] Kawai, F., *Breakdown of plastics and polymers by microorganisms*, In: Fiechter A (Ed) Adv. *Biochem. Eng. Biotechnol*., 1994

[13] Practical Action Technology challenging poverty

[14] R. Ahmed, A. van de Klundert, I. Lardinois. (editors) *For Small-scale Resource Recovery Urban Solid Waste Series 3*

SECTION II

RESULTS AND DISCUTION

CHAPTER 6

PREPARATION OF PYRROLE COMPOUNDS

6.1 Introduction

In this chapter is reported the preparation and characterization of different pyrrole compounds is. Aim of the research activity was to apply experimental conditions compatible with the so called sustainable chemistry: the Paal Knorr reaction for the synthesis of pyrrole compounds was done in the absence of solvents(s) and catalyst(s).

Yield and atom economy of the reactions were calculated. The characterization of pyrrole compounds was performed by ^{1}H-NMR Spectroscopy.

6. 2 Paal Knorr reaction

The Paal – Knorr synthesis has been applied in the synthesis of pyrroles.

The Paal – Knorr synthesis is a synthetically valuable method for obtaining substituted furans and pyrroles, common structural components of many natural products. The research of pyrroles and pyrrole derivatives began in 1985 when Paal and Knorr individually published effective synthetic routes to pyrrole and its derivatives [1, 2]. Both chemists described the initial examples of condensation reactions between 1,4 – diketones and primary amines, which become known as the Paal – Knorr pyrrole synthesis [3].

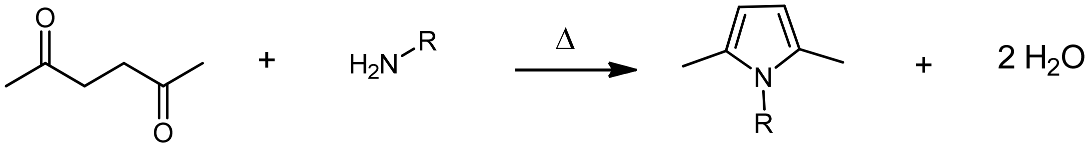


Figure 6.1 – General Paal – Knorr synthesis of pyrrols

In 1991 V. Amarnath et al. [4] suggest the mechanism of Paal-Knorr reaction based on the attack of the amine to the protonated carbonyl, forming hemiaminal. Further the amine attacks the other carbonyl and forms 2,5-dihydroxytetrahydropyrrole derivative, which is further dehydrated to form the corresponding substituted pyrrole [5]. The proposed mechanism is presented on Figure 6.2.

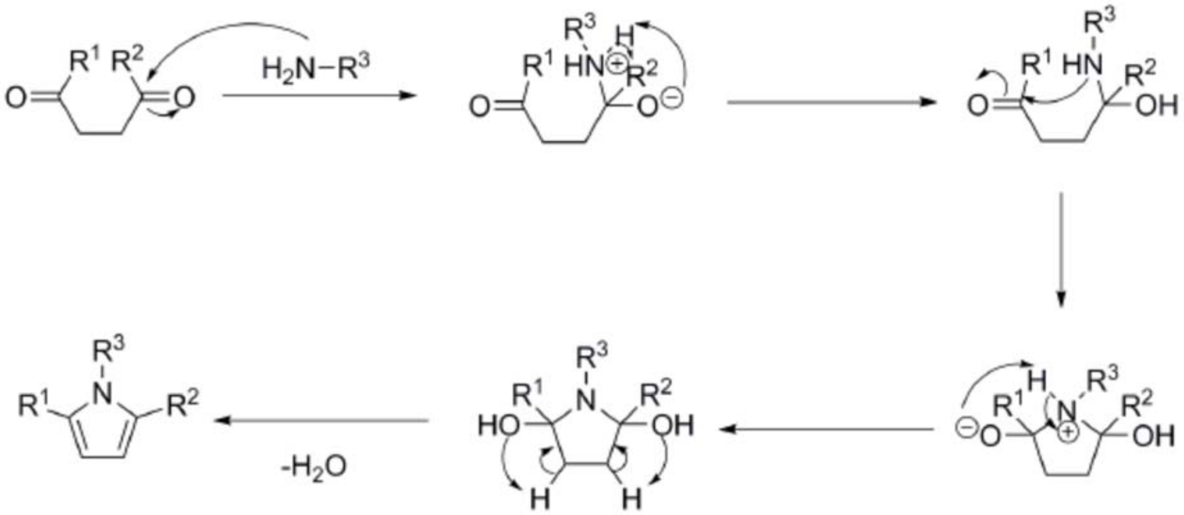
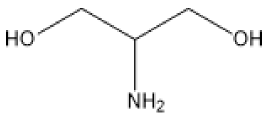
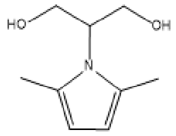
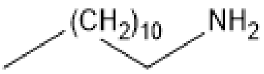
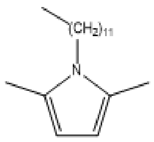
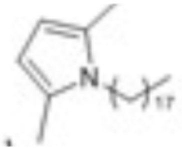
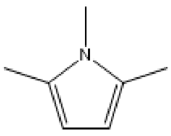
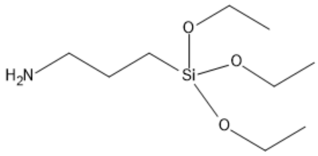
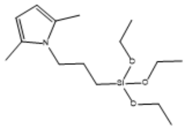
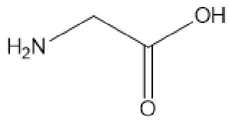
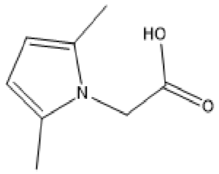


Figure 6.2 – Mechanism of Paal – Knorr reaction

Each amine and 2,5-hexanedione were used in equimolar amount and the aromatic pyrrole compounds were obtained at high temperature. Experimental conditions are shown in Table 6.1. It is worth underlying that reactions were performed in neat conditions without any solvent or catalyst and in a range of temperature between 130 °C and 150 °C. The by-product of the reaction was only water.

Table 6.1 – Summary of synthetized pyrrole compounds

Amine	Reaction time	Temperature	Acronym	Product	Yield [%]
	3 h	150 °C	SP		96
	4 h	130 °C	DDcP		86
	3 h	130 °C	ODcP		90
	3 h	130 °C	TMP		89

	3 h	130 °C	APTESP		80
	3 h	130 °C	GlyP		95

6. 3 2-(2,5-dimethyl-1H-pyrrol-1-yl) propane-1,3-diol (SP) – Preparation and characterization

Chemical structure of SP is shown in Figure 6.4.

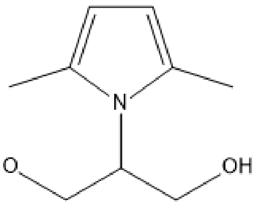


Figure 6.3 - Serinol pyrrole (SP)

SP was synthetized from the reaction between 2-amino-1,3-propanediol (serinol) and 2,5-hexandione at 150 °C. The details of the reaction were reported in the experimental part. The reaction was done without any catalyst or solvent.

The SP is considered as a Janus molecule that means it has a dual reactivity.

Actually, the aromatic ring could give rise to π---π stacking with aromatic compounds; otherwise, the moiety coming from the hydroxy groups, can establish interactions with polar environments.

n addition, hydroxy groups can be functional groups suitable for the preparation of the step growth polymers. SP was obtained as a colorless/light yellow liquid (at room temperature and atmospheric pressure) with high solubility in water. The yield obtained by pure product was 96 %.

^{1}H NMR was used to characterize SP, and the signals and also the integrations, reported in the experimental part, have confirmed the production of SP during the reaction between 2-amino-1,3-propanediol and 2,5-hexanedione at 150 °C.

6. 4 1-dodecyl-2,5-dimethyl-1H-pyrrole (DDcP) – Preparation and characterization

Chemical structure is shown in Figure 6.5.

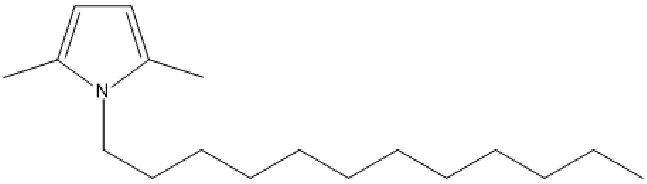


Figure 6.4 – Dodecyl pyrrole (DDcP)

DDcP was synthetized from the reaction between dodecan-1-amine and 2,5-hexanedione at 130 °C. The details of the reaction were reported in the experimental part. The reaction was done without any catalyst or solvent. The yield obtained by pure product was 86 %.

The DDcP was obtained as an amber viscous liquid at room temperature and atmospheric pressure. DDcP was characterized by ^{1}H NMR spectroscopy.

6. 5 Synthesis of 2,5-dimethyl-1-octadecyl-1H-pyrrole (ODcP)

ODcP was synthetized from the reaction between octadecamine and 2,5-hexanedione at 130 °C. The details of the reaction were reported in the experimental part. The reaction was done without any catalyst or solvent.

ODcP is a pyrrole compound with a long aliphatic chain attached to the nitrogen atom. It is considered as an aromatic molecule, so it could give rise π---π stacking with aromatic compounds, instead the aliphatic chain could interact with other aliphatic components as for instance hexane, etc.

The ODcP was obtained as an yellow viscous liquid at room temperature and atmospheric pressure. The yield obtained by pure product was 90 %. ODcP was characterized by ^{1}H NMR spectroscopy.

6. 6 1,2,5-trimethyl-1H-pyrrole (TMP) – Synthesis and characterization

Chemical structure of TMP is shown in Figure 6.6.

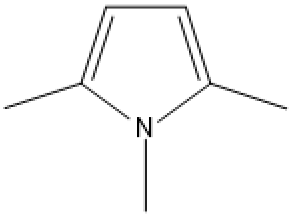


Figure 6.5 – Trimethyl pyrrole (TMP)

TMP was synthetized from the reaction between methanamine and 2,5-hexanedione at 130 °C. The details of the reaction were reported in experimental part. The reaction was done without any catalyst or solvent.

TMP is a pyrrole compound with only one methyl group (CH_3) attached to the aromatic ring. For this reason, the behavior of trimethyl pyrrole is similar to the aromatic molecules as toluene, xylene, etc. The TMP obtained from the reaction synthesis between methanamine and 2,5-hexanedione, was a dark viscous liquid at room temperature and atmospheric pressure. The yield obtained by pure product was 89 %.

The pyrrole compound was analyzed by ^{1}H NMR spectroscopy. All the integrations reported in the experimental section have been satisfied.

6. 7 2,5-dimethyl-1-(3-(triethoxysilyl)propyl)-1H-pyrrole (APTESP) – Preparation and characterization

Chemical structure of APTESP is shown in Figure 6.7.

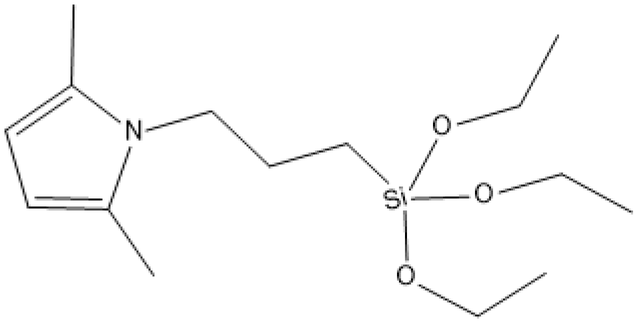


Figure 6.6 - 2,5-dimethyl-1-(3-(triethoxysilyl) propyl)-1H-pyrrole (APTESP)

APTESP was synthetized from the reaction between 3-(triethoxysilyl) propan-1-amine and 2,5-hexanedione at 130 °C. The details of the reaction were reported in experimental part. The reaction was done without any catalyst or solvent.

The obtained product was a light yellow solid at room temperature and atmospheric pressure. The yield obtained by pure product was 80 %.

To characterize the APTESP it was used ^{1}H NMR. All the signals and the integrations confirmed the reaction was occurred.

6. 8 2-(2,5-dimethyl-1H-pyrrol-1-yl) acetic acid (GlyP) – Preparation and characterization

Chemical structure of GlyP is shown in Figure 6.8.

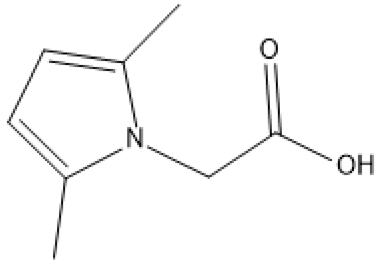


Figure 6.7 - Glycil pyrrole (GlyP)

GlyP was synthetized from the reaction between 3-(triethoxysilyl) propan-1-amine and 2,5-hexanedione at 130 °C. The details of the reaction were reported in experimental part. The reaction was done without any catalyst or solvent. The obtained product was crystalized at room temperature and atmospheric pressure. The yield obtained by pure product was 95 %.

The GlyP shows two different behaviors because of carboxyl group attached to the nitrogen atom: the aromatic ring could give rise π---π interactions, while the carboxyl group could interact with other kind of molecules as for instance carboxylic acids.

A structural characterization of GlyP was performed by means of 1H NMR.

6. 9 Conclusions

As mentioned above the pyrrole compounds were prepared using a simple and adaptable reaction without using any solvents or catalysts.

The yield obtained for each pyrrole compound was very high, it goes at a range of 80 – 96%.

The process could be thus considered “green” and “sustainable”.

All the pyrrole compounds were analyzed by ^{1}H NMR and ^{13}C NMR.

The synthesized pyrrole compounds were suitable for the preparation of adducts with carbon black described in the following chapter.

References

[1] L. Knorr, *Chem. Ber.*, 1885

[2] C. Paal., *Chem. Ber.*,1885

[3] Z. Wang, *Comprehensive Organic Name Reactions and Reagents*, 2010

[4] V. Amarnath, D.C. Anthony, K. Amarnath, W.M. Valentine, L.A. Wetterau, D.G. Graham, *Intermediates in the Paal-Knorr synthesis of pyrroles*, 1991

[5] A. Wollrab, *Organ. Chem.*, 1999

CHAPTER 7

FUNCTIONALIZATION OF CARBON BLACK WITH PYRROLE COMPOUNDS

7.1 Introduction

In this chapter was represented the functionalization of carbon black (CB) with different pyrrole compounds (PyC). The synthesis of PyC is described in the previous chapter. An important aim of this research was to represent the stability of the interaction between CB and PyC with different properties.

In this chapter are discussed preparation procedure, yield of functionalization and the characterization of adducts.

In particular, characterization of CB-PyC adducts was done by FT-IR Spectroscopy and TGA. After the reaction, each product was thoroughly washed, and the extracted residue was analyzed by ^{1}H Nuclear Magnetic Resonance Spectroscopy.

7.2 Preparation of CB-PyC adducts

The preparation of CB – PyC adducts is well described in the experimental part. The ratio used between the mass of the pyrrole compound and the mass of CB is 1/10. The carbon black used is Carbon Black N234 (CB234) which, has high structure, high abrasion. Its iodine adsorption value is 120g/kg, and DBP adsorption is 125cm^3/100g.

TGA analyses were conducted on such adducts which were also characterized with Attenuated Total Reflectance Infrared spectroscopy (ATR).

In Figure 7.1 is shown the schematic procedure used for functionalization of carbon black with pyrrole compounds.

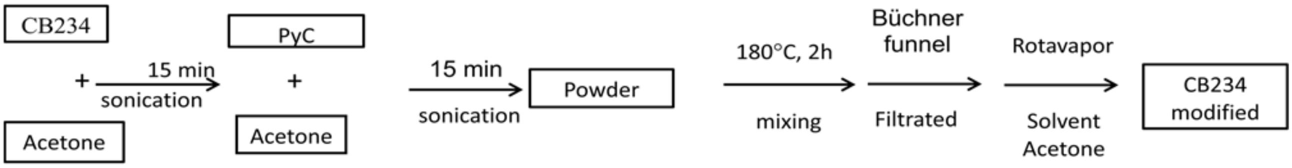


Figure 7.1 – Procedure of functionalization of CB - PyC

As it can be seen in the Figure 7.1 in this procedure acetone is used as solvent for the sonication step. In the following paragraph the yield of functionalization of CB-PyC will be discussed. Adducts were obtained as a black powder. The same procedure was adopted for the preparations of all the adducts presented in the experimental section.

7.3 Yield of functionalization of CB-PyC

The efficiency of interaction was investigated by calculating the yield of functionalization, comparing the amount of PyC in the adduct before and after acetone extraction. Functionalization yield was determined through the following equation:

$$Functionalization\ yield\ (\%) = 100 * \frac{PyC\ mass\ \%\ in\ (CB - PyC\ adduct) after\ acetone\ washing}{PyC\ mass\ \%\ in\ (CB - PyC\ adduct) before\ acetone\ washing}$$

% mass of PyC in CB – PyC adduct (before and after acetone washing) were obtained from TGA analysis, as the mass loss in the temperature range from 150°C – 700°C. All the data are shown on the Table 7.1.

Table 7.1 – Mass loss for CB234, CB234 – PyC adducts, from TGA analysis

Sample **Mass loss (%)**			
	T < 150°C	**150°C < T < 700°C**	**T > 700°C**
CB234-ODcP	0	9.8	90.2
CB234-SP	1	7.7	91.3
CB234-APTESP	1	7.8	91.2
CB234-GlyP	0	8.2	91.8
CB234-TMP	0	6.5	93.5

As it can be read in Table 7.1, larger functionalization yield, 98%, was obtained with ODcP as the pyrrole compound. The yield was about 82% for PyC based on GlyP as primary amine, almost 78% for PyC based on APTESP as the primary amine, 77% for PyC based on SP as primary amine and was about 65% with TMP as the PyC. Briefly very good values of functionalization yield were obtained, thus demonstrating that new materials were prepared.

7.4 Characterization of CB/PyC Adducts

In the following the characterization of adducts CB-PyC will be described. For this characterization different techniques were used: Thermogravimetric analysis (TGA), Fourier Transformed Infrared Spectroscopy (FTIR), UV – Vis spectroscopy, Brunner-Emmett-Teller analysis (BET).

Thermogravimetric analyses were conducted to estimate the yield of functionalization, which was related to the mass loss at different temperatures.

FT-IR analyses were used to detect the presence of the characteristic spectral features of the functional groups of the pyrrole compounds, physically or chemically adsorbed on carbon black. Differences between the spectra of the initial reagents (carbon black and pyrrole compounds separately) and the spectra of adducts are pointed out.

Indeed, FT-IR gave several qualitative data about the presence of specific functional group, but it was not able to give any quantitative information. Thermogravimetric analysis instead was a technique was able to give quantitative information about adducts.

The UV – Vis spectra was used to show the absorbance and stability of dispersion of adducts.

The BET theory (abbreviated from Brunner-Emmett-Teller theory) is used to measure the surface area of modified carbon black. Surface area analysis is one of the most widely used methods in material characterization.

7.4.1 Thermogravimetric analyses (TGA)

In this paragraph, the thermogravimetric analyses for the pristine Carbon Black N234 and for each adduct CB/PyC sample are reported.

A thermogravimetric analysis is an analitycal method of thermal analysis in which the mass of a defined sample is measured over time as the temperature increases. The result is a plot that represents the dependence between the mass loss and the temperature.

Data from TGA of CB/PyC adducts are reported in Table 7.1 and the thermograph of the CB-PyC adducts will be demonstrated below.

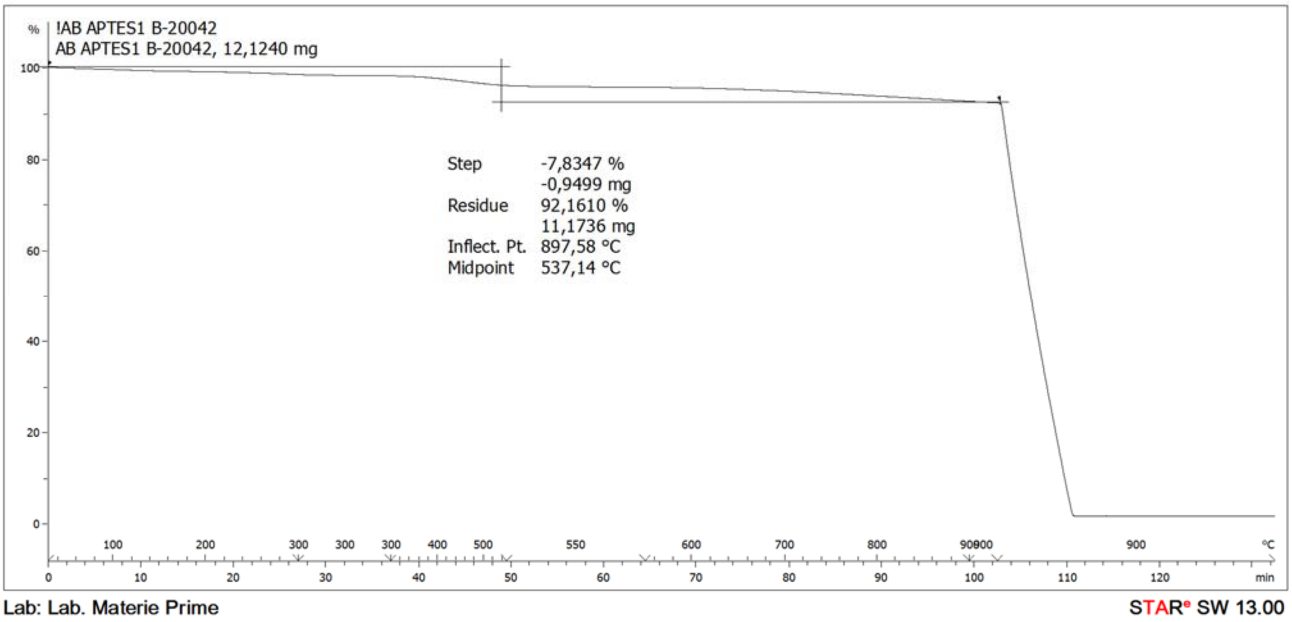


Figure 7.2 – TGA analysis of the adduct CB-APTESP (10% mass)

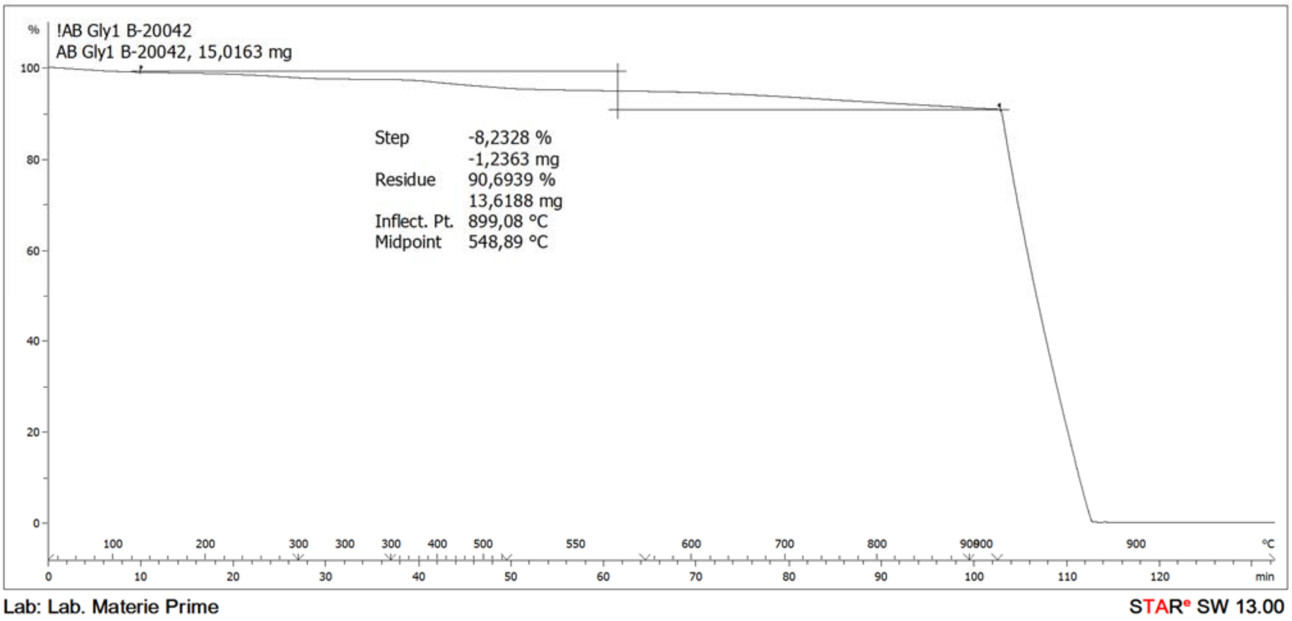


Figure 7.3 – TGA analysis of the adduct CB-GlyP (10% mass)

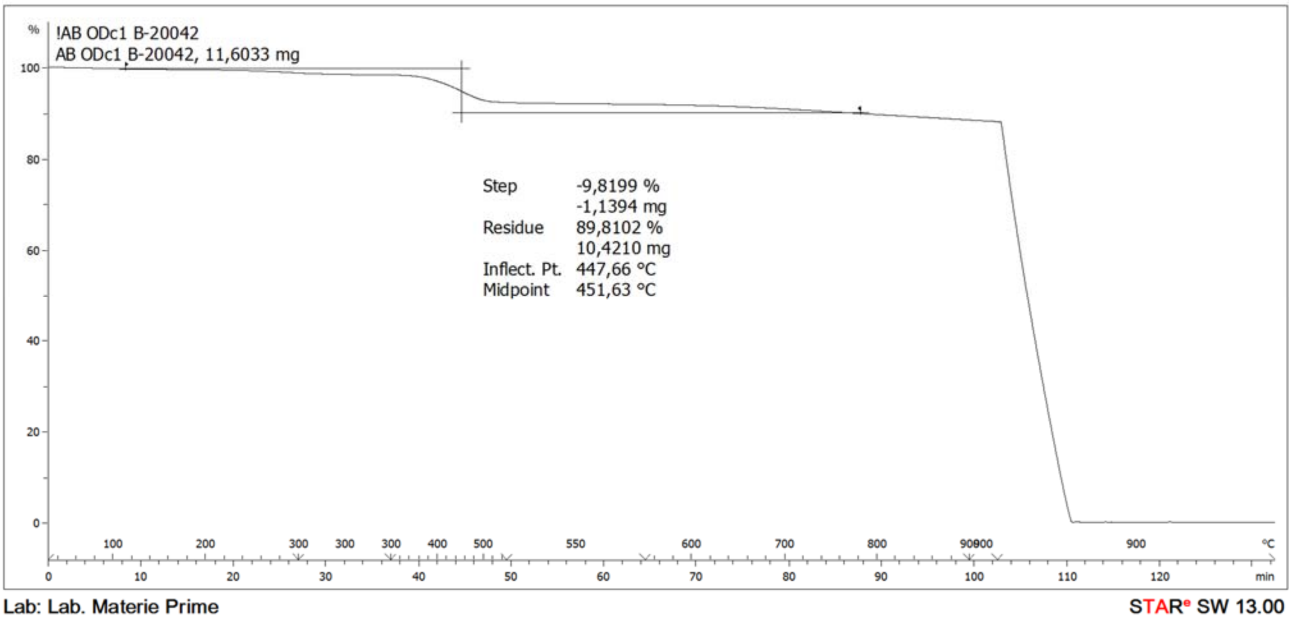


Figure 7.4 – TGA analysis of the adduct CB-ODcP (10% mass)

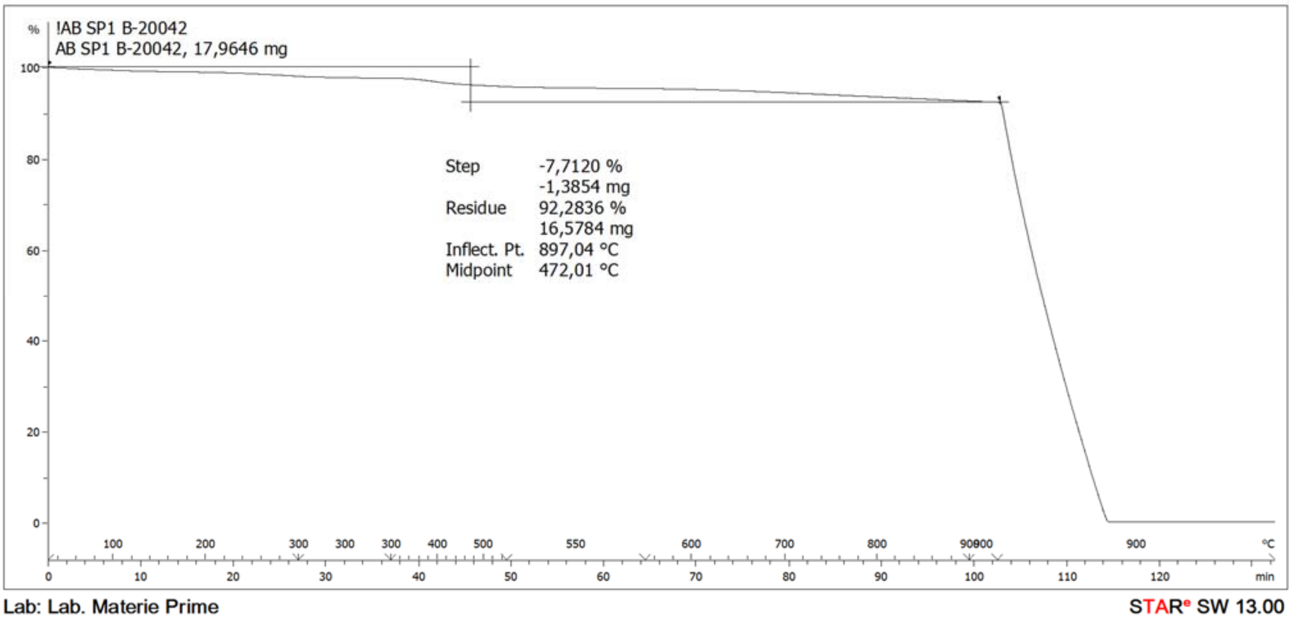


Figure 7.5 – TGA analysis of the adduct CB-SP (10% mass)

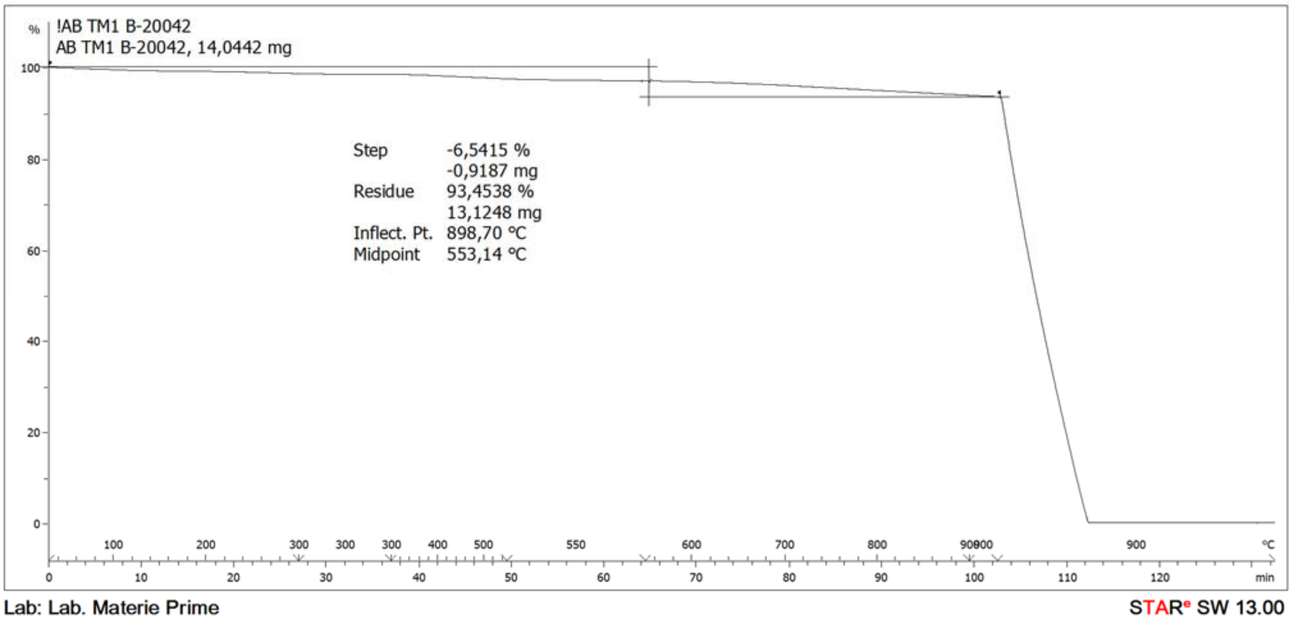


Figure 7.6 – TGA analysis of the adduct CB-TMP (10% mass)

The decomposition profile for CB/PyC adducts reveals three main steps, in the following temperature ranges: below 150°C, from 150°C to 700°C and above 700°C. Analyzing the Figure 7.2 to Figure 7.6 it was possible to estimate the amount of PyC present in the adduct. The values of mass loss of CB-PyC are shown on Table 7.1, from where it is possible to notice that the mass loss of CB-PyC is in line with the mass loss of pristine carbon black. For the temperature lower than 150°C the mass loss is insignificant, around 0 to 1%. Second step, 150°C < T < 700°C, shows a mass loss of the range of 6,5 to 9,8%. From these TGA analyses, it can be said that the functionalization of carbon black with pyrrole compounds occurred.

Equation for calculating the functionalization yield and yield data for all CB-PyC adducts are reported in the experimental part and the largest functionalization yield, 98%, was obtained with ODcP.

7.4.2 Fourier Transformed Infrared Spectroscopy (FTIR)

IR of CB-PyC was performed in order to detect the functionalities arising from the PyC bonded to CB. For the tested adducts, 10 % mass of PyC was introduced. In Figure 7.7 the IR spectra of CB-PyC adduct are reported:

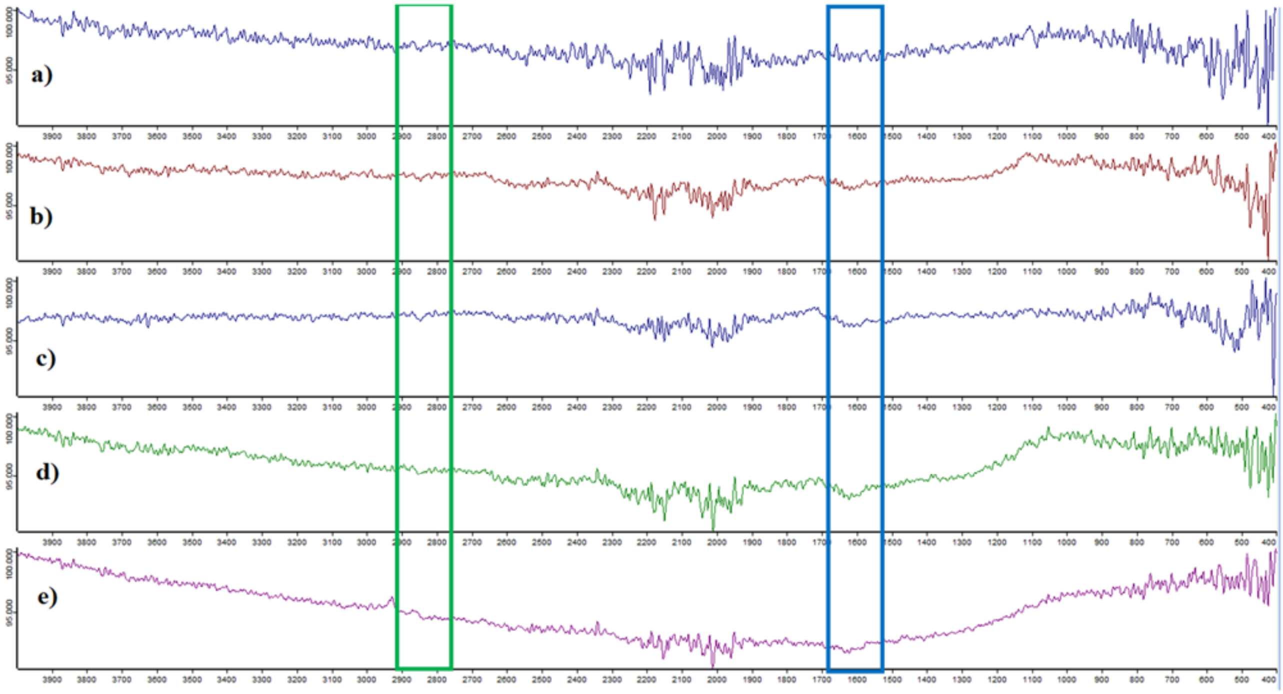


Figure 7.7 – IR spectra of CB-PyC adducts: a) CB-TMP, b) CB-APTESP, c) CB-GlyP, d) CB-SP, e) CB-ODcP.

At around 2900 cm^{-1} the most pronounced signals could be seen. At this wavenumber, were detected the stretching of the alkyl chains, bonded to the nitrogen atom of the pyrrole ring. In fact, best signal was obtained for CB-ODcP adduct, but also for the other adducts a peak could be noticed, as highlighted by the green frame in Figure 7.7.

At around 1600 cm^{-1}, the region marked by a blue frame, some changes are identified. These signals identify the stretching of C=O groups deriving from the oxidation of the PyC before the formation of adducts.

The spectra in Figure 7.7 verifies that the reaction of formation of the stable CB-PyC adduct has correctly occurred.

7.4.3 UV – Vis spectroscopy

In this paragraph UV – Vis analysis on dispersions of CB-PyC adducts with different concentrations: 1 mg/mL; 0.5 mg/mL; 0.25 mg/mL; 0.1 mg/mL, was discussed. The solvent used was ethyl acetate, which was able to form stable suspensions with all the adducts tested. The procedure is well described on experimental part.

The stability of dispersion, with 1 mg/mL as the adduct concentration, was investigated by taking UV-Vis spectra on samples stored for 2 weeks, on samples centrifugated at 6000 rpm for 30 min and on samples centrifugated at 6000 rpm for 30 min after 1 week storage.

These UV-Vis analyses permitted to obtain a calibration curve for every adduct tested, considering UV absorption at 300 nm. Calibration curves are shown below.

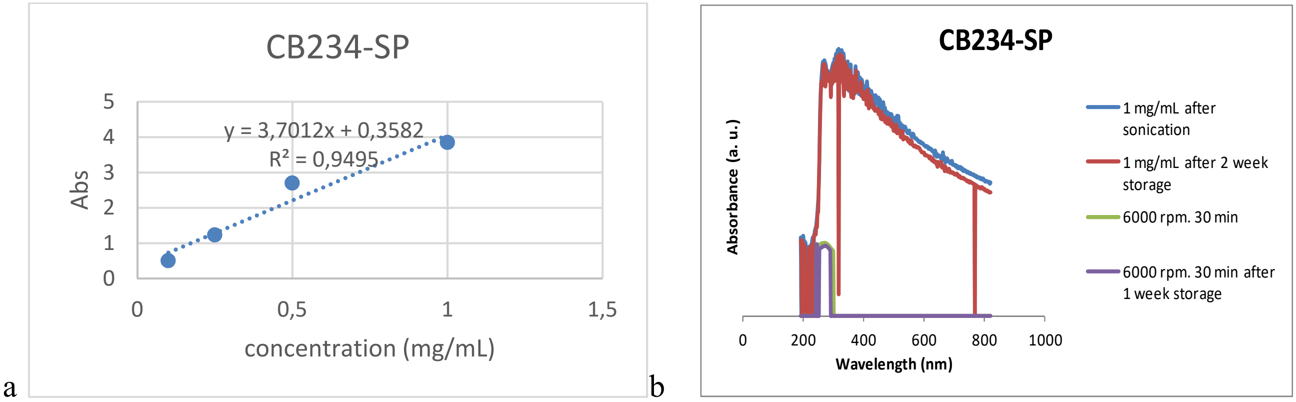


Figure 7.8 – (a) Linear relationship between the absorbance at 300 nm and the concentration of CB234/SP adduct in ethyl acetate; (b) UV – Vis traces of the same sample after sonication, 1 week storage, centrifugation and two week storage

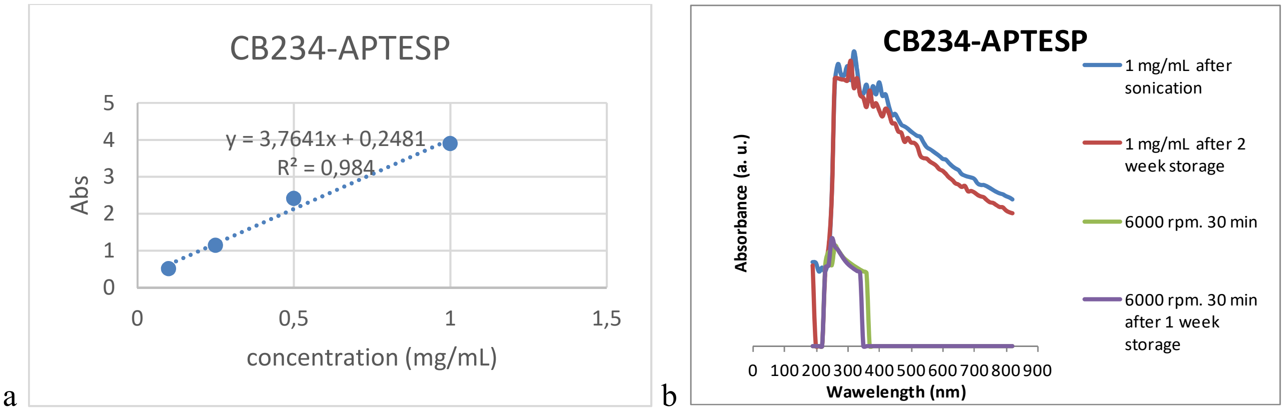


Figure 7.9 – (a) Linear relationship between the absorbance at 300 nm and the concentration of CB234/APTESP adduct in ethyl acetate; (b) UV – Vis traces of the same sample after sonication, 1 week storage, centrifugation and two week storage

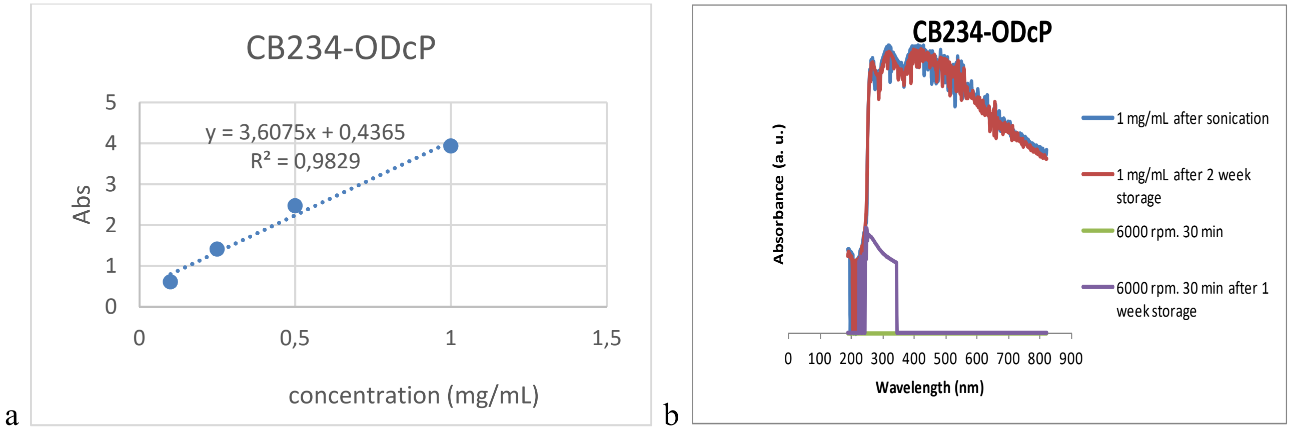


Figure 7.10 – (a) Linear relationship between the absorbance at 300 nm and the concentration of CB234/ODcP adduct in ethyl acetate; (b) UV – Vis traces of the same sample after sonication, 1 week storage, centrifugation and two week storage

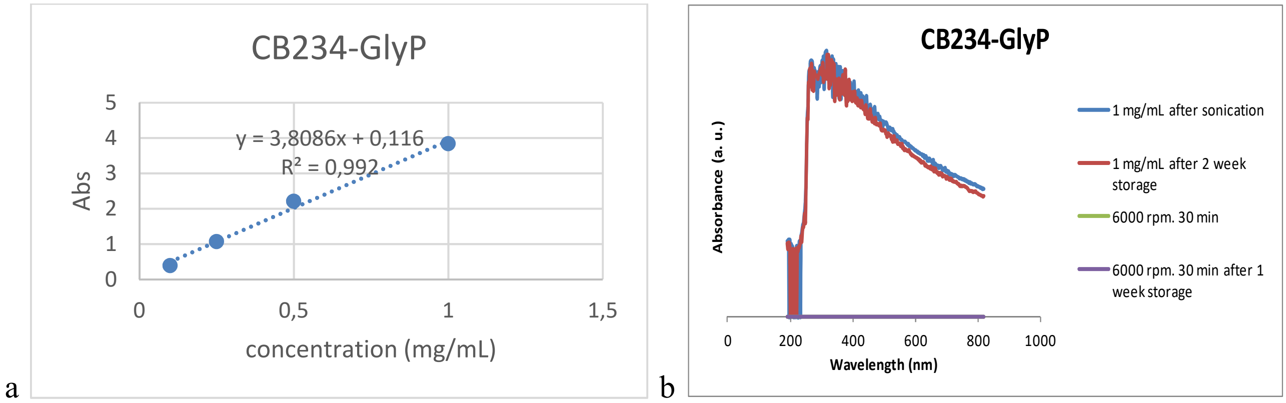


Figure 7.11 – (a) Linear relationship between the absorbance at 300 nm and the concentration of CB234/GlyP adduct in ethyl acetate; (b) UV – Vis traces of the same sample after sonication, 1 week storage, centrifugation and two week storage

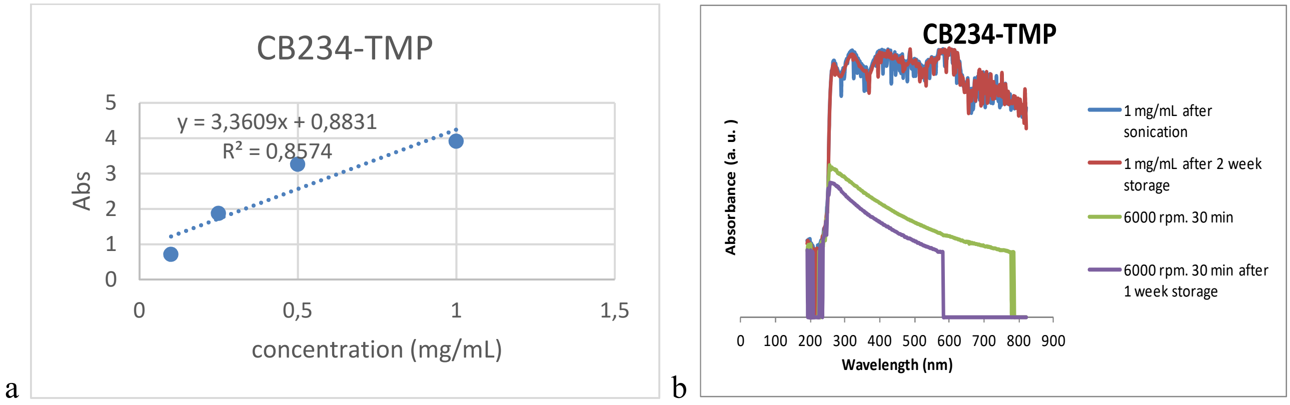


Figure 7.12 – (a) Linear relationship between the absorbance at 300 nm and the concentration of CB234/TMP adduct in ethyl acetate; (b) UV – Vis traces of the same sample after sonication, 1 week storage, centrifugation and two week storage

With the help of calibration curves is estimated the amount of adduct left in the suspension after 1 week storage. It is clearly showed that very good results were obtained. Graphs above clearly show that the absorbance, taken immediately after sonication, monotonously increases with the adduct concentration. This means that ethyl acetate was able to form good suspensions with all CB234-PyC adducts.

7.4.4 Brunauer – Emmett – Teller (BET) analysis

Brunauer – Emmett – Teller (BET) analysis were performed to determine the surface area of CB – PyC adducts, and to show how the modification affects the surface properties of the material. The specific surface area of the carbons was determined from the N_2 adsorption isotherms by applying the (BET) equation at a relative pressure of 0.35 and an average area per molecule of N_2 in a completed monolayer of 16.2Å.

In Table 7.2 the values of BET surface areas, the external surface area and the area of the micropores are reported. Also, the percentage of moles of PyC on CB, for CB- PyC adducts is reported (calculated through TGA data).

Table 7.2 – Percentage of moles of PyC on CB, BET surface area, external surface area and area of the micropores for the tested CB- PyC adducts.

CB-	n (PyC)/n (CB) [%]	BET surface area [m^2/g]	External surface area [m^2/g]	Area of micropores [m^2/g]
N234	0	112.4	108.2	4.1
TMP	0.734	99.4	92.3	7.0
APTESP	0.333	91.5	86.6	6.6
GlyP	0.624	96.1	82.0	14.2
SP	0.648	53.3	44.3	9.0
ODcP	0.369	23.6	21.2	1.9

From Table 7.2 a decrease of both the BET surface area and the external surface area could be seen, for all the tested CB-PyC adducts. This result could be explained by the agglomeration of the carbon particles, resulting from the interaction of the surface oxidized functional groups of the pyrrole derivatives. The measured area of the micropores is increased for every tested adducts, except for ODcP.

In **Figure 7.13** and **Figure 7.14** the adsorption potential distributions and the differential pore size distribution for CB N234 and CB-PyC adducts are reported respectively.

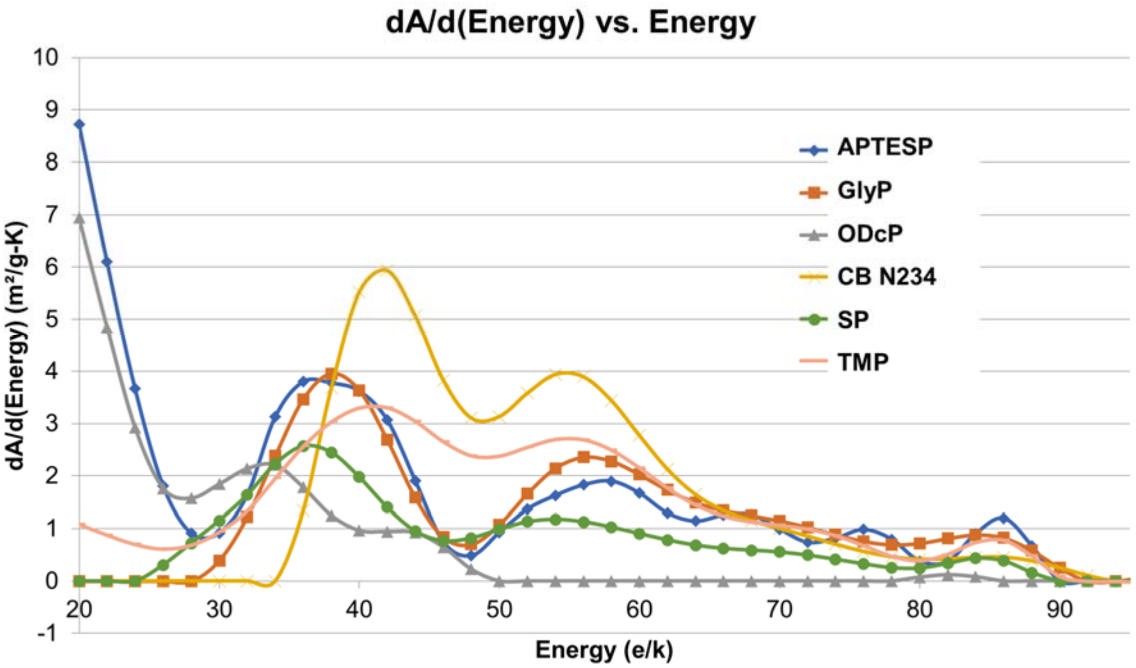


Figure 7.13 – Adsorption potential distributions for CB N234 and CB-PyC adducts

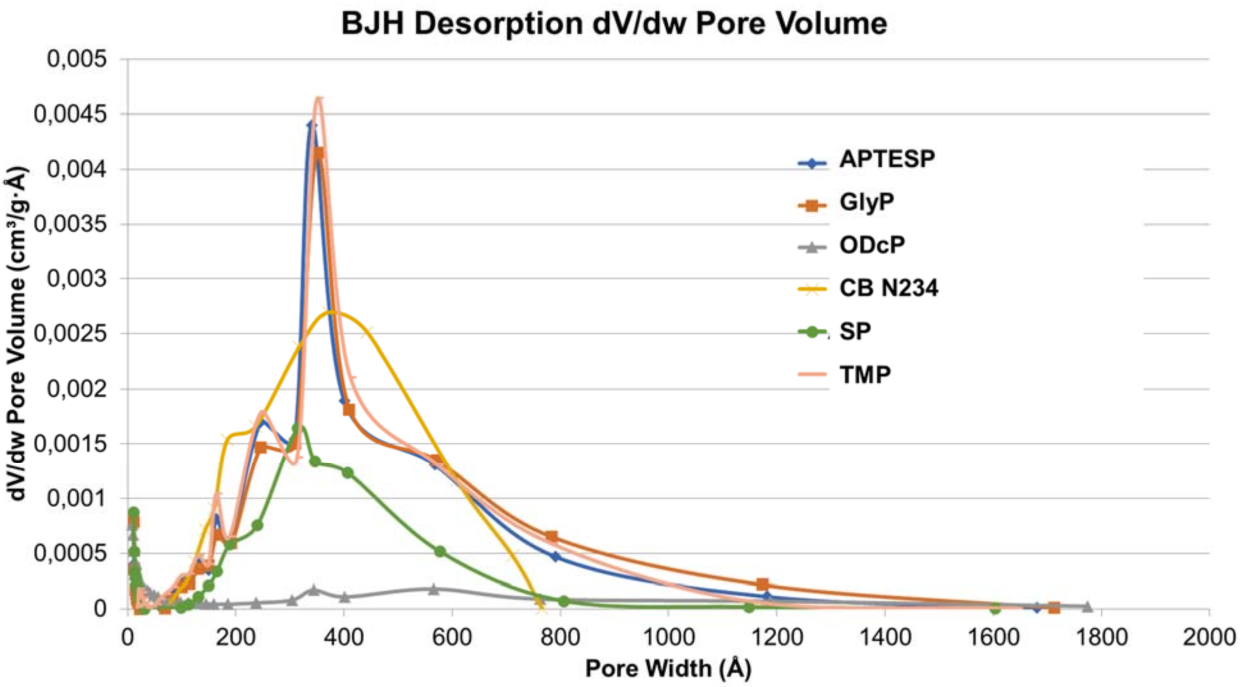


Figure 7.14 – Differential pore size distribution for CB N234 and CB-PyC adducts

From these graphs very different curves of the CB – PyC adducts, with respect to pristine CB N234, could be seen. This means that the surface area is significantly changed.

The pore size distribution is totally changed for the functionalized carbon blacks, with respect to pristine CB N234. For CB – APTESP, CB – GlyP and CB – TMP, the majority of the pores has a width of about 400 Å, and an increased volume, with respect the pores of CB N234. This data are in line with the values in Table 7.2. For CB – SP adduct the majority of the pores has a width between 300 and 800 Å. Instead, the surface of CB – ODcP adduct seems to be almost non-porous, and the roughness is drastically decreased.

7.5 Conclusions

CB234-PyC adducts were prepared by heating a mixture of carbon black with PyC presented in Chapter 6.

The yield obtained for each CB-PyC was high, it goes at a range of 65– 98%.

For the characterization of CB-PyC different techniques were used: Thermogravimetric analysis (TGA), Fourier Transformed Infrared Spectroscopy (FTIR), UV – Vis spectroscopy, BET analysis.

These analysis clearly revealed the presence of PyC and thus confirmed the formation of adducts.

In this chapter was also shown that CB-PyC adducts were well suspended on ethyl acetate. And the surface area is significantly changed.

CHAPTER 8
SOLUBILITY PARAMETER OF CARBON BLACK

8.1 Introduction

As reported in the Introduction of this thesis, studying the dispersion of CB/PyC adducts in different solvents was one of the objectives of this work. Thus in this Chapter the ability of PyC to modify the solubility parameter of carbon black will be discussed. The whole procedure is well described in the experimental part. On this study 10 solvents were used, which will be classified as good or bad after 30 minutes and 1 week storage as shown in the Table 8.3.

8.2 Hildebrand and Hansen solubility parameter

The solubility parameter indicates the corresponding solvency behavior of a specific solvent. Was **Hildebrand,** who first presented the solubility parameter term, and he defined it as the square root of the cohesive energy density:

$$\delta = (\frac{E}{V})^{1/2}$$

Where E is the energy of vaporization of the pure solvent, and V is its molar volume.

Solvents with smaller molecular volumes will be thermodynamically better than larger ones having identical solubility parameters [1]. A practical aspect of this is that solvents with relatively low molecular volumes, such methanol and acetone, can dissolve a polymer at larger solubility parameter differences than might be expected from comparisons with other solvents with larger molecular volumes [1].

In 1996, **Charles M. Hansen** extended the Hildebrand parameter to estimate the relative miscibility of polar and hydrogen bonding systems:

$$\delta^2 = {\delta_D}^2 + {\delta_P}^2 + {\delta_H}^2$$

There are three major types of interactions. The most general are the non polar interactions also called *dispersion interactions* E_D. As molecules are built up from atoms, all molecules contain those types of attractive forces.

The second type of cohesion energy is *the polar cohesive energy*, E_P. These are inherently molecular interactions and are found in most molecules to one extent or another. The dipole moment is the primary parameter used to calculate these interactions.

The third major cohesive energy source is hydrogen bonding, E_H also called an *electron exchange parameter*. The basis of this type of cohesive energy is attraction among molecules because of the hydrogen bonds. The hydrogen bonding parameter has been used to more or less collect the energies from interactions not included in the other two parameters. Alcohols, glycols, carboxylic acids, and other hydrophilic materials have high-hydrogen-bonding parameters.

The basic equation governing the assignment of Hansen parameters is that the total cohesion energy, E, must be the sum of the individual energies that make it up.

$$E = E_D + E_P + E_H$$

Dividing this by the molar volume gives the square of the total (or Hildebrand) solubility parameter as the sum of the squares of the Hansen D, P, and H components.

$$E/V = E_D/V + E_P/V + E_H/V$$

$$\delta^2 = {\delta_D}^2 + {\delta_P}^2 + {\delta_H}^2$$

Where δ_d, δ_p, and δ_h are the dispersion, polar, and hydrogen bond components of δ, respectively. Division of the Hildebrand parameter into the three-component Hansen parameters (dispersion force, polar force, and hydrogen bonding force) considerably increases the accuracy with which non-ionic molecular interactions can be predicted and described.

8.2.1 Solubility parameter of solvents

As mentioned in the Introduction 10 solvents with different polarity were used to define the solubility parameter of CB-PyC adducts. In the Table 8.1, the solubility parameter of these solvents will be demonstrated. For calculating the solubility parameter the above equations were used, the data were taken from literature.

Table 8.1 – Solubility parameter of solvents

Solvent	δd	δp	δH	Δav
Water	15,5	16	18,6	16,7
Hexane	14,9	0	0	4,966667
2-propanol	15,8	6,1	16,4	12,76667
Toluene	18	1,4	2	7,133333
Ethyl acetate	15,8	5,3	7,2	9,433333
Acetone	15,5	10,4	7	10,96667
Chloroform	17,8	3,1	5,7	8,866667
Methanol	15,1	12,3	22,2	16,53333
Glycerol	17,4	12,1	29,3	19,6
Xylene	17,6	1	3,1	7,233333

These values were inserted also in the following graph:

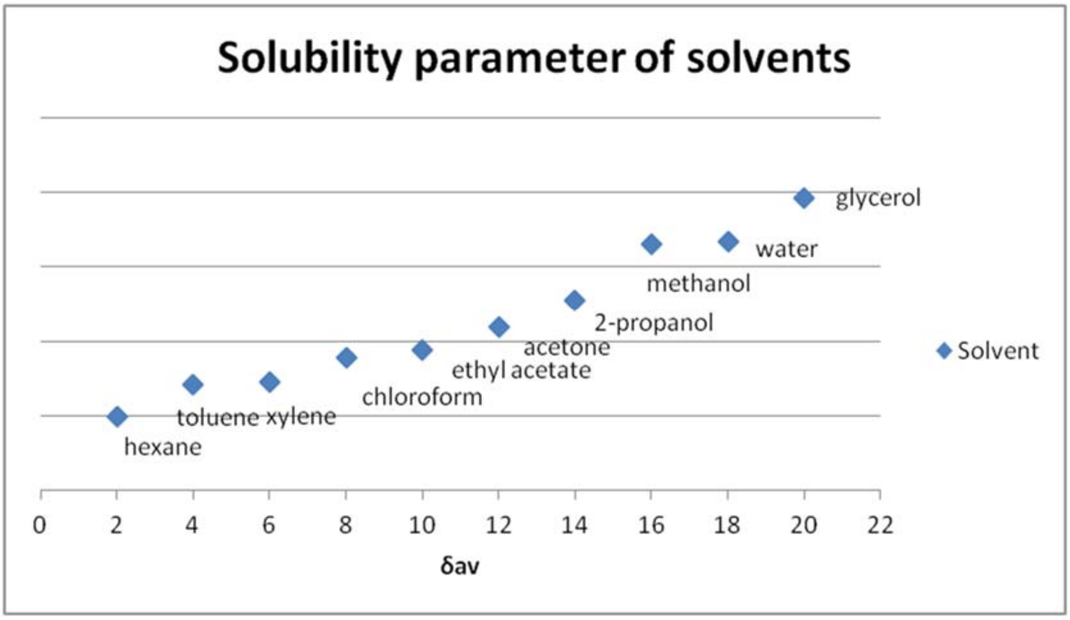


Figure 8.1 – Solubility parameter of solvents

8.3 Solubility parameter of CB-PyC adducts

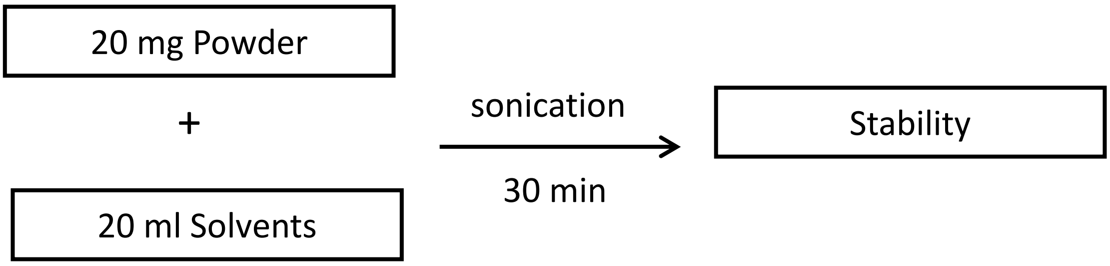


Figure 8.2 – Scheme of the procedure adopted for the solubility tests

The procedure for the preparations, shown in Figure 8.2, is reported in detail in the experimental part. In brief, the adduct was mixed together with the solvent and sonicated for 30 minutes.

The solvents used have different characteristics: for example, water is the most common polar solvent, hexane is a well-known apolar solvent, and toluene was chosen as an example of aromatic solvent. They all have different values of Hansen solubility parameter.

The solvent was considered as a “good” solvent, in the presence of stable dispersion as “bad” solvent in the presence of unstable dispersion.

The results of dispersion test are shown below in Table 8.3.

Table 8.2 - Results of the dispersion tests of CB/PyC adducts in different solvents

Adduct		***Solvents***											
		Hexane	**Heptane**	**Cyclohexane**	**Toluene**	**Xylene**	**Chloroform**	**Ethyl acetate**	**Acetone**	**2-propanol**	**Methanol**	**H_2O**	**Glycerol**
CB234 +SP	***After sonication***	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
	After 30 min	Bad	Bad	Bad	Good	Good	Good	Good	Good	Good	Good	Good	Good
	After 1 week	Bad	Bad	Bad	Bad	Good	Good	Good	Good	Good	Bad	Good	Good
CB234 + ODCP	***After sonication***	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Bad	Bad
	After 30 min	Good	Good	Good	Good	Good	Good	Good	Good	Good	Bad	Bad	Bad
	After 1 week	Good	Bad	Good	Good	Good	Good	Good	Good	Bad	Bad	Bad	Bad
CB234 + GlyP	***After sonication***	Good	Good	Bad	Good	Good	Good	Good	Good	Good	Bad	Good	Good
	After 30 min	Bad	Bad	Bad	Bad	Good/Bad	Good	Good	Good	Good	Bad	Good	Good
	After 1 week	Bad	Bad	Bad	Bad	Bad	Good	Good	Good	Good	Bad	Good	Good
CB234 + APTESP	***After sonication***	Good	Good	Bad	Good	Good	Good	Good	Good	Bad	Bad	Good	Good
	After 30 min	Bad	Bad	Bad	Good	Good	Good	Good	Good	Bad	Bad	Good -	Good
	After 1 week	Bad	Bad	Bad	Good	Good	Good	Good	Good	Bad	Bad	Bad	Good
CB234 + TMP	***After sonication***	Good	Good	Good	Good	Good	Good	Good	Bad	Bad	Good	Good	Good
	After 30 min	Bad	Bad	Bad	Good	Good	Good	Good	Bad	Bad	Good	Bad	Good
	After 1 week	Bad	Bad	Bad	Good/Bad	Bad	Good	Good	Bad	Bad	Bad	Bad	Good

Figure 8.3 to Figure 8.7 show pictures of solubility test taken in the laborator 30 minutes after the sonication. These pictures verify the results shown in Table 8.2, and demonstrate the stability of CB-PyC adducts in different solvents

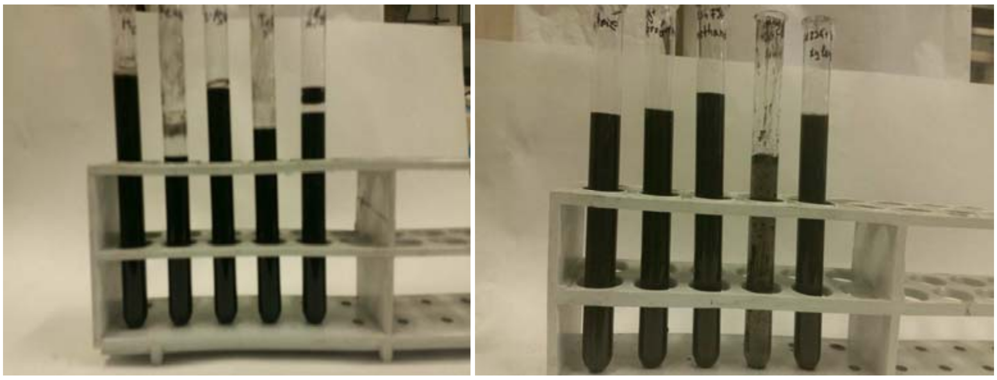


Figure 8.3 – Solubility test CB-SP. From left to right: H2O, Hexane, 2-propanol, Toluene, Ethyl acetate, Acetone, Chloroform, Methanol, Glycerol, Xylene

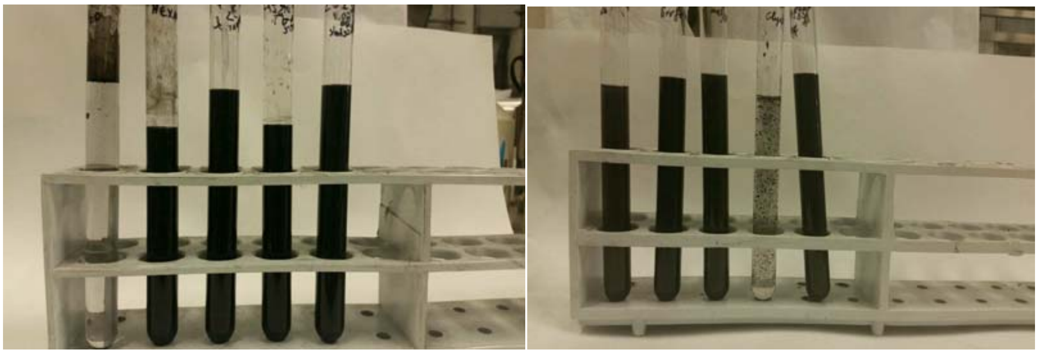


Figure 8.4 – Solubility test CB-ODcP. From left to right: H2O, Hexane, 2-propanol, Toluene, Ethyl acetate, Acetone, Chloroform, Methanol, Glycerol, Xylene

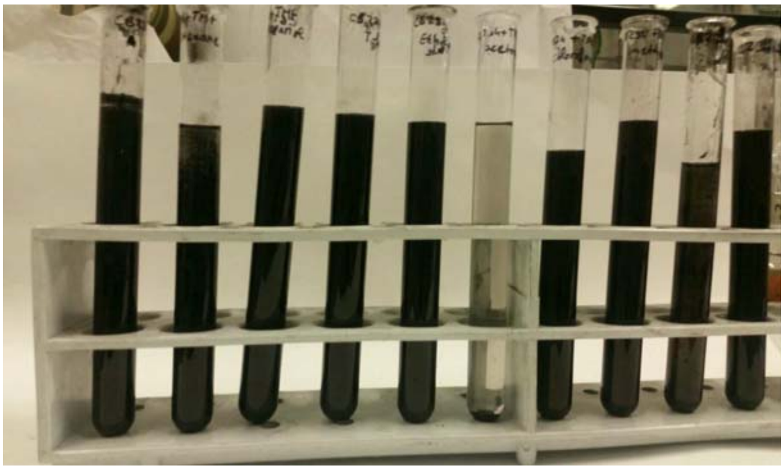


Figure 8.5 – Solubility test CB-TMP. From left to right: H2O, Hexane, 2-propanol, Toluene, Ethyl acetate, Acetone, Chloroform, Methanol, Glycerol, Xylene

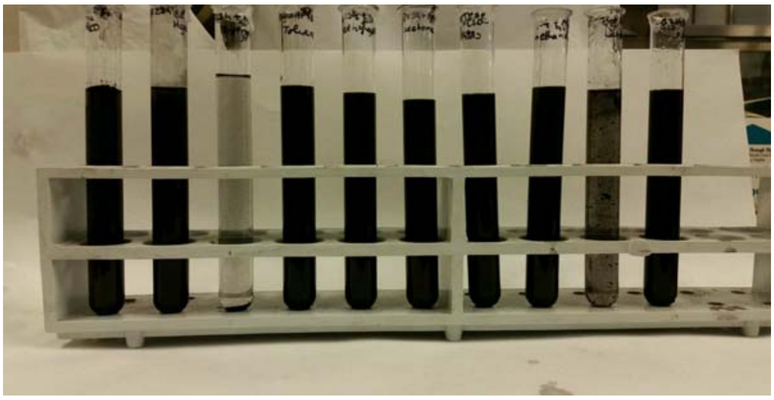


Figure 8.6 – Solubility test CB-APTESP. From left to right: H2O, Hexane, 2-propanol, Toluene, Ethyl acetate, Acetone, Chloroform, Methanol, Glycerol, Xylene

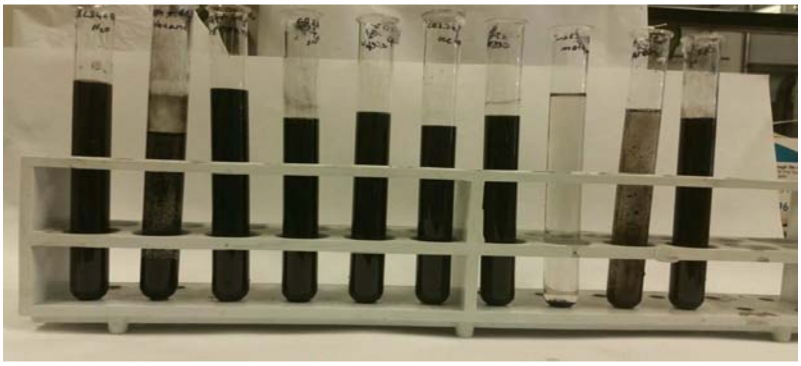


Figure 8.7 – Solubility test CB-APTESP. From left to right: H2O, Hexane, 2-propanol, Toluene, Ethyl acetate, Acetone, Chloroform, Methanol, Glycerol, Xylene

The results of the Table 8.3 were put also on the graph below:

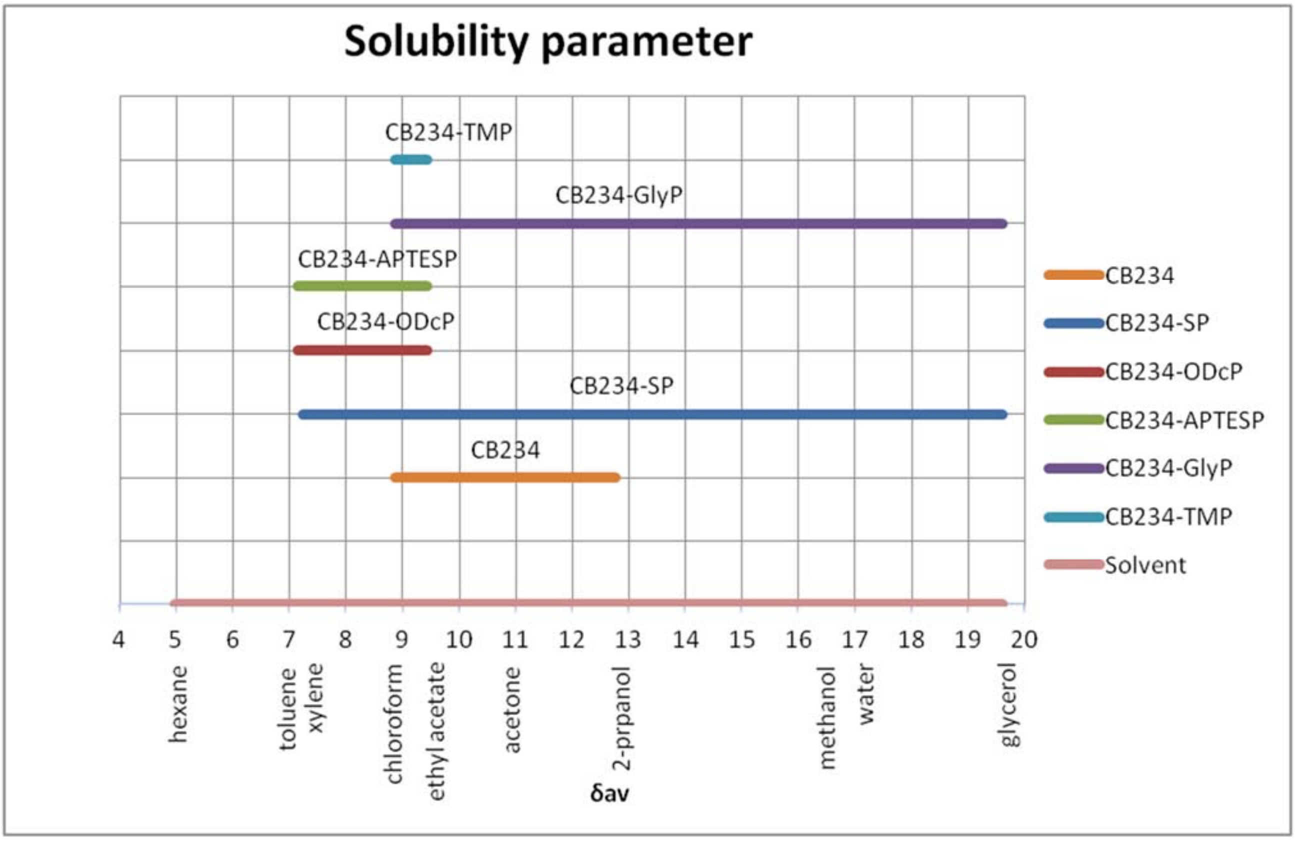


Figure 8.8 - Results of the dispersion tests of CB/PyC adducts in different solvents

From the Table 8.2 and Figure 8.8, very good dispersion can be seen. Toluene, Ethyl Acetate, Chloroform and Xylene were classified mostly as "good" solvents for CB/PyC adducts. Best results were achieved with CB/SP and CB/GlyP adducts which were well dispersed almost in all solvents. All adducts were able to be well suspended in chloroform and athyl acetate. All adducts were able to create stable suspensions with the media which could theoretically create an interaction between them and the substituents on the nitrogen atom of the pyrrole compound.

8.4 Hansen solubility sphere

The CB/PyC adducts solubility parameter was calculated using the Equation n…. The values are shown in Table 8.4.

Table 8.3 – Solubility sphere coordinates of CB/PyC

Adduct	**δ_D**	**δ_P**	**δ_H**
CB N234	21.1	12.3	11.3
CB/APTESP	14.9	6.0	8.5

CB/GlyP	12.1	8.6	12.8
CB/ODcP	6.4	5.7	7.9
CB/SP	11.8	11.1	11.5
CB/TMP	18.1	3.5	4.9

Given the parameters (coordinates) of the solvents, it is possible to define a sphere, centered on the solubility parameters of the solute, which encompasses the good solvents points and excludes the non-solvents.

The sphere radius is defined as R_0, the radius of interaction, while the distance between the solute and the solvent is Ra, calculated as in Equation below.

$$R_{a,ij}^{\ 2} = 4(\delta_{D,i} - \delta_{D,j})^2 + (\delta_{P,i} - \delta_{\mathrm{P},j})^2 + (\delta_{H,i} - \delta_{H,j})^2$$

The ratio between Ra,*ij* and R_0 is defined in following Equation as RED, relative energy difference. Solutes and solvents with good affinity have relative energy difference lower than.

$$RED = \frac{R_{a,ij}}{R_o}$$

An optimization problem is therefore defined: the center coordinates of the Hansen solubility sphere are calculated by minimizing the radius of interaction (i.e. the distance from the coordinates of the good solvents), including the good solvents (RED<1) and excluding the bad ones. The sphere center coordinates correspond to the three unknown HSP of the solute.

The fitting sphere program was adapted from and solved in Matlab environment using the Nelder-Mead simplex algorithm.

The spheres shown below were generated to encompass the good solvents point and to exclude the bad solvent, being centered on the solubility parameters of CB/PyC adducts. Solubility parameters of adducts are presented in Table 8.4, while solubility parameter of solvents are presented in Table 8.1.

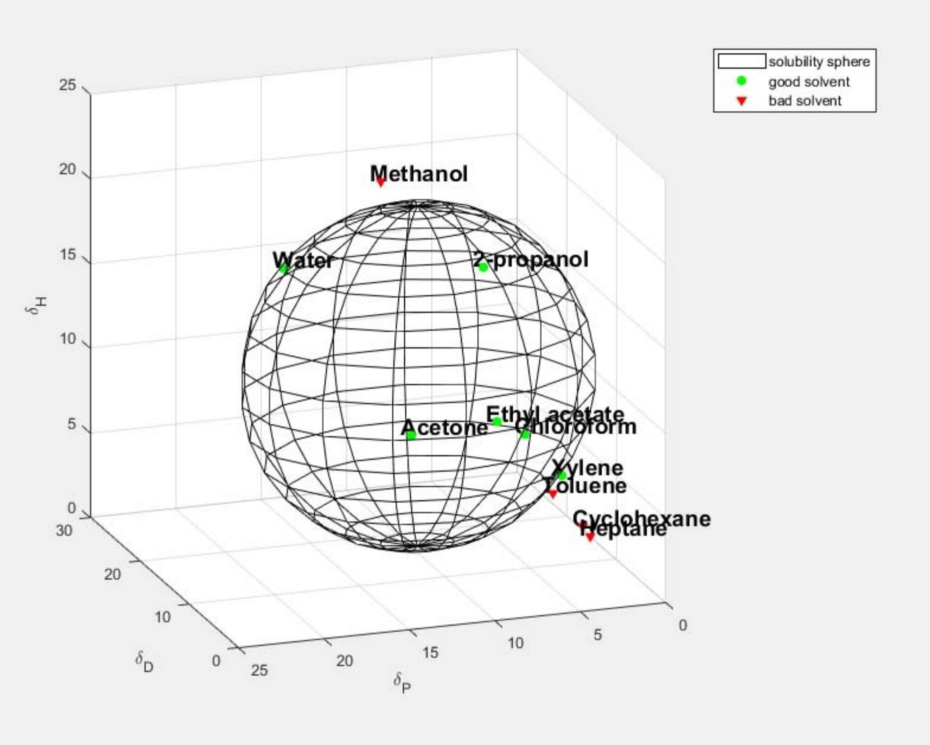


Figure 8.9 – Solubility sphere of CB-SP adduct

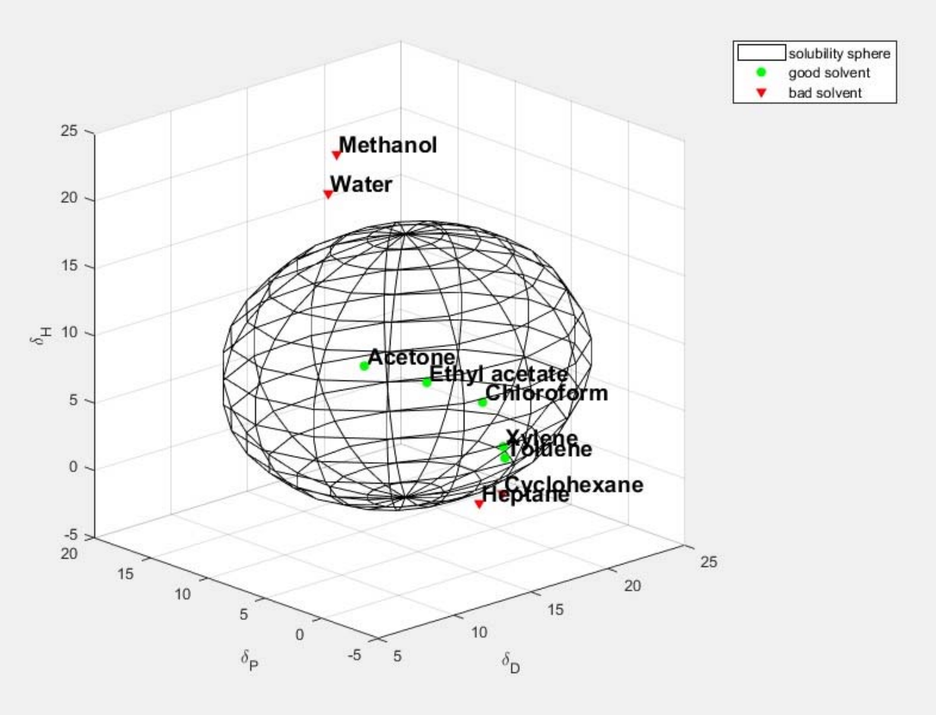


Figure 8.10 – Solubility sphere of CB-APTESP adduct

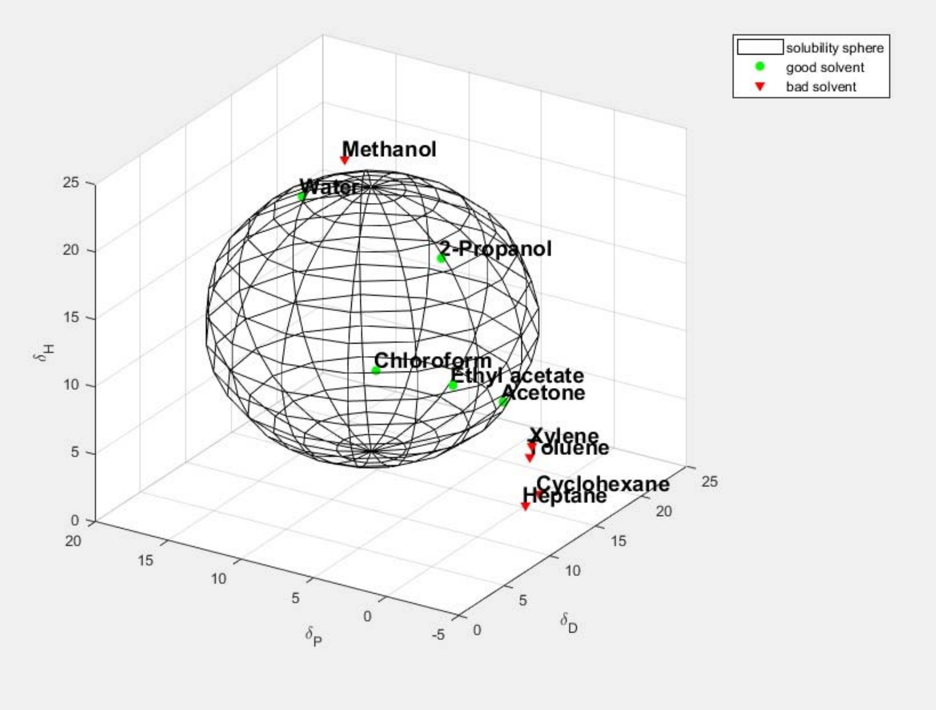


Figure 8.11 – Solubility sphere of CB-GlyP adduct

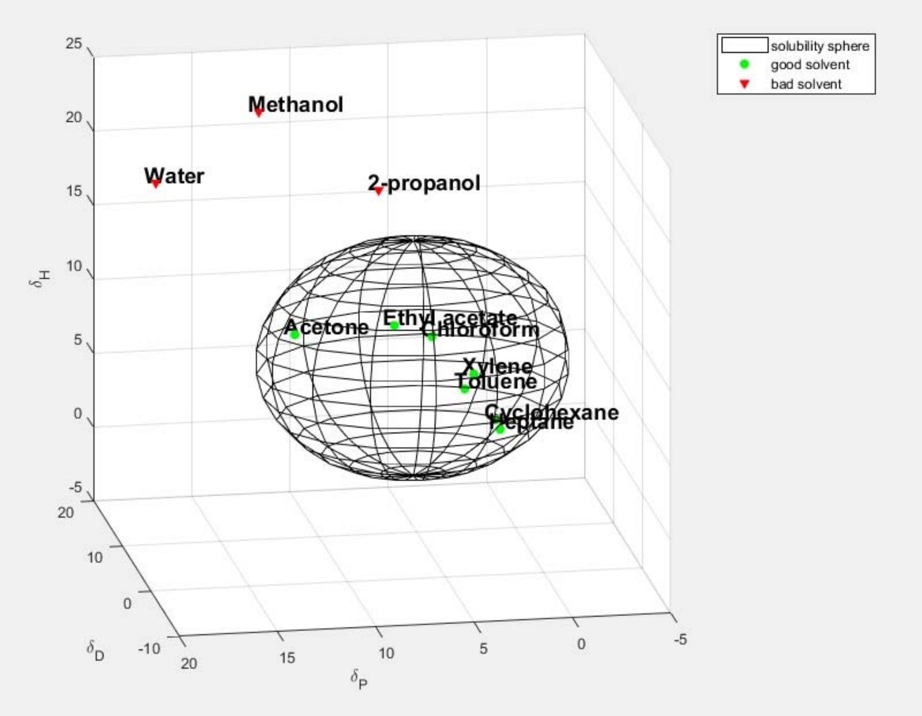


Figure 8.12 – Solubility sphere of CB-ODcP adduct

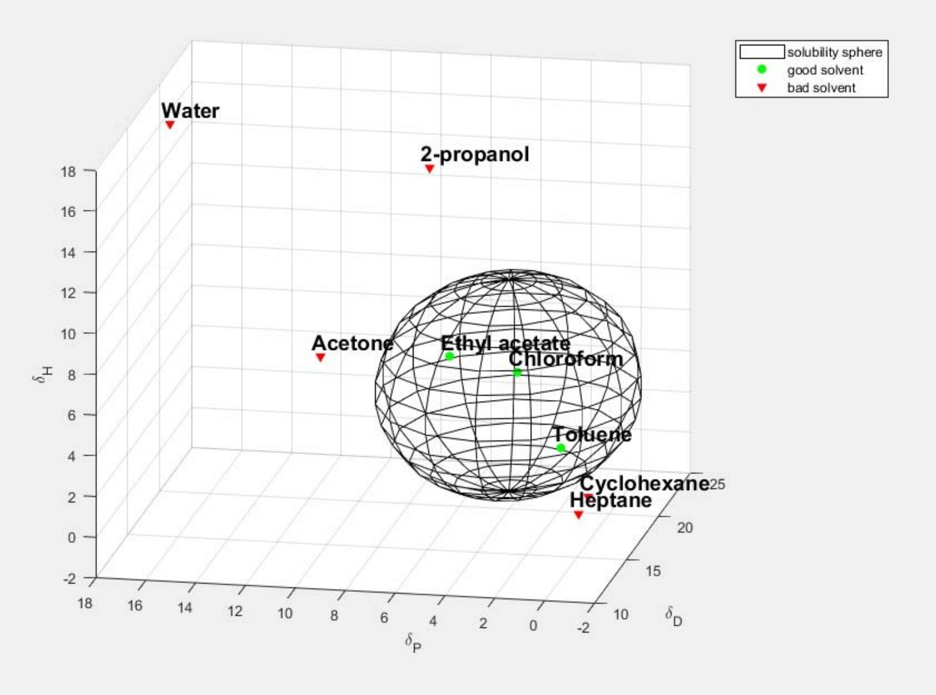


Figure 8.13 – Solubility sphere of CB-TMP adduct

These results show the ability of solvents to modify the solubility parameter of carbon black. Green points correspond to “good” solvents, while red points correspond to “bad” solvents, respectively.

8.5 Conclusions

Stable dispersions of CB-PyC adducts were prepared in solvents with different solubility parameters. CB-PyC were those prepared on Chapter 7. Qualitative results of dispersion tests were used to calculate the Hansen spheres for CB-PyC adducts.

In this Chapter the modification of solubility parameter of CB-PyC adducts were demonstrated.

References:

[1] Charles M. Hansen, *“Hansen Solubility Parameter”*, A User’s Handbook second edition, 2007.

CHAPTER 9

FUNCTIONALIZATION OF RUBBER POWDER WITH PYRROLE COMPOUNDS

9. 1 Introduction

Functionalization of rubber powder with pyrrole compounds was an important goal of this thesis. In this chapter the preparation and characterization of RP-PyC adducts is discussed.

Three different rubber’s samples were used, coming from three different commercial sources:

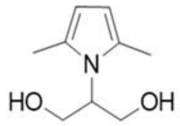
(i) Austin Rubber: rubber compound is reclaimed by means of grinding and use of terpenes

(ii) Lehigh: rubber compound is reclaimed by cryogrinding

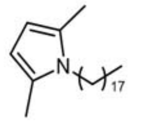
(iii) FKM rubber waste, coming from the production process of rubber goods such as O-rings and gaskets, underwent cryogrinding. Intention was only to reduce the average size of the rubber particles and not the reclaim. Unfortunately, due to confidentiality reasons, information about the rubber sample was not provided.

Their main properties will be shown in the following paragraphs.

The pyrrole compounds used for the functionalization of rubber powder are the following:



serinol pyrrole
(SP)



octadecyl pyrrole
(ODcP)

They were described in Chapter 6.

In this chapter preparation and characterization of the adducts is discussed.

9.1.1 Powder rubber sample from Austin Rubber

An Austin Rubber sample has been used in a previous thesis [1]. Thus information about this type of rubber is taken from this thesis. According to Patent N. 7767722 [2], the devulcanization process of Austin Rubber requires the use of terpene. The devulcanization reagent is a mixture of α or β-Turpineol and 1-butanol or propanol that is claimed to cleave the S – S and C – S bonds. The process is carried out at a temperature of 70-90°C and requires 3 grams of this agent for every gram of rubber. The rubber powder is not washed after the devulcanization and the mixture of turpentine oil and solvent is recycled. Due to this treatment the rubber powder tends to aggregate.

In Figure 9.1 is reported the scheme of production of this material.

Figure 9.1 – Scheme of production of the rubber powder produced by Austin Rubber

Preparation of reclaimed rubber with Austin Rubber technology entails grinding which is carried out at room temperature that means it consumes less energy than a cryo-grinding. In this process, the burden of devulcanization is on terpenes. They can promote further devulcanization and compatibilization in the new mixing process, can favour kinetics of vulcanization and can reduce hysteresis, breaking long sulphur bridges.

In conclusion, good points of the Austin Rubber process appear to be:

(i) grinding at room temperature
(ii) devulcanization with biosourced chemicals such as terpenes
(iii) chance of using terpenes which remain in reclaimed rubber.

9.1.2 Lehigh's Rubber: Polydine 140

Lehigh's rubber was also used in the same previous thesis [1] and the information about this rubber is taken from there.

Lehigh's technology is one of the leaders in the cryogenic grinding.

Main phases of the cryogenic Lehigh process are summarized in Figure 9.2.

Figure 9.2 – Production scheme of rubber production by Lehigh

Some applications are: new tires (tread and sidewall), conveyor belts, general rubber goods, plastics, polyurethane foams, oil field applications (basically perforation), adhesives, coatings, and construction.

According to their internal study, 1 ton of Micronized Rubber Powder saves about 22 MWh of energy and 40% the CO2 emission of oil-derived resins. The powder is very fine and slide.

Lehigh's rubber powder technology appears to prepare a good product. One drawback of this type of rubber can be the use of high amount of energy for cryo-grinding.

9.1.3 Powder sample from Waste of FKM compound

FKM rubber waste, coming from the production process of rubber goods such as O-rings and gaskets, underwent cryogrinding and was reduced to 0.5 micron size. Further information was not available. TGA analysis was performed in the frame of this Thesis, to assess the amount of rubber and the amount of filler. The FKM rubbers are mixtures of fluorinated monomers, whose fluorine content ranges from about 60% to about 76% by mass.

9. 2 Preparation of RP-PyC adducts

The preparation of RP – PyC adducts is well described in the experimental part. The ratio used between the mass of the pyrrole compounds and the mass of RP is 1/10. The properties of rubber compounds used for the functionalization are described in the previous paragraphs.

TGA analyses were conducted on such adducts which were also characterized with Attenuated Total Reflectance Infrared spectroscopy (ATR).

In Figure 9.3 is shown the schematic procedure used for functionalization of rubber powder with pyrrole compounds.

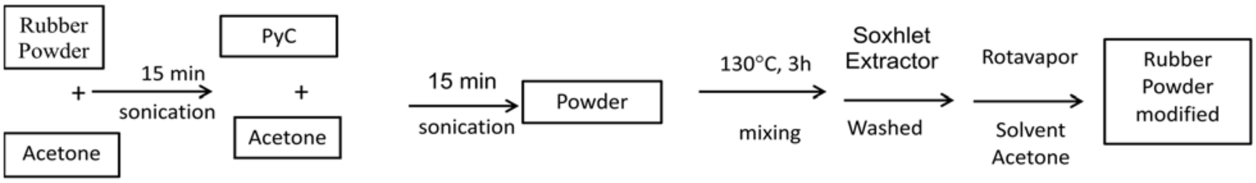


Figure 9.3 – Procedure of functionalization of RP - PyC

After the reaction RP - PyC adducts were washed for at least 12 hours using a soxhlet extractor, to remove impurities and the pyrrole that didn't react with rubber powder.

9. 3 Characterization of RP- PyC adducts

In this paragraph the characterization of RP - PyC adducts will be described. As we have previously seen for CB - PyC adducts, also for RP - PyC adducts characterization, different techniques were used, like: Thermogravimetric analysis (TGA), Fourier Transformed Infrared Spectroscopy (FTIR) and Contact Angle.

Thermogravimetric analyses were conducted to estimate the yield of functionalization, which was related to the mass loss at different temperatures.

FT-IR analyses were used to detect the presence of the characteristic spectral features of the functional groups of the pyrrole compounds, physically or chemically adsorbed on rubber powder.

9.3.1 Thermogravimetric analysis (TGA)

In this paragraph, the thermogravimetric analyses for the unmodified Rubber Powder, for RP/SP and for RP – ODcP sample are reported.

TGA traces for sample RP1, RP2 and RP3 unmodified are reported in Figure 9.4, Figure 9.5, and Figure 9.6, respectively:

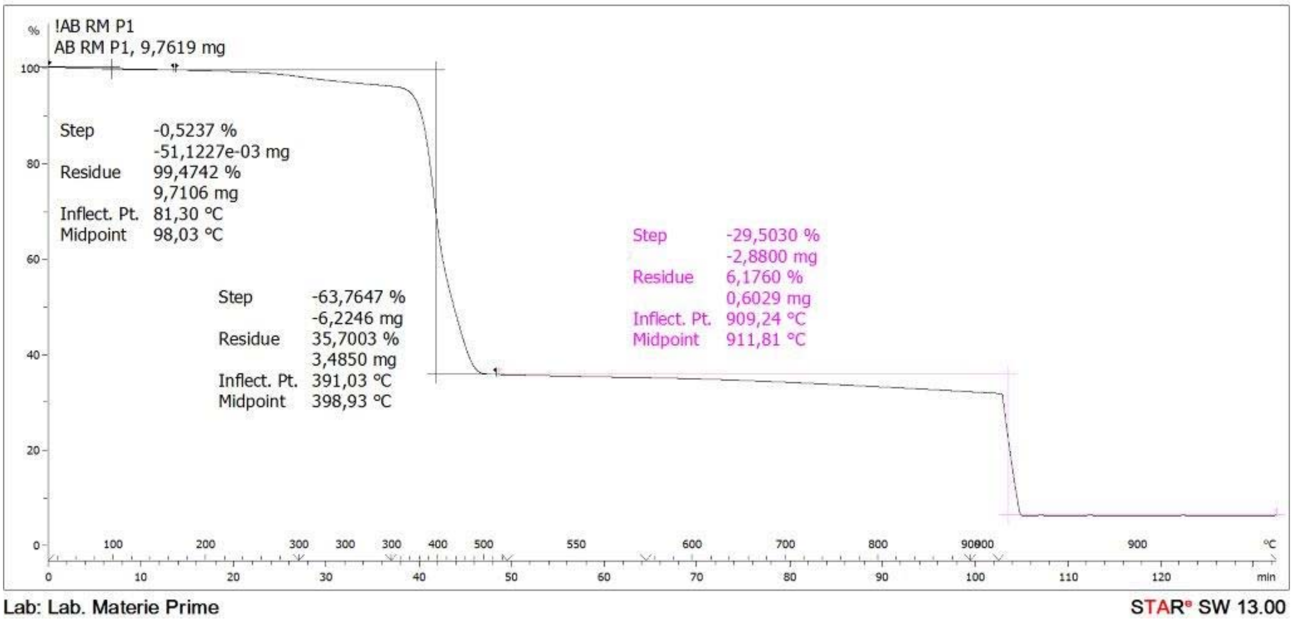


Figure 9.4 – TGA of Austin's Rubber (RP1) sample

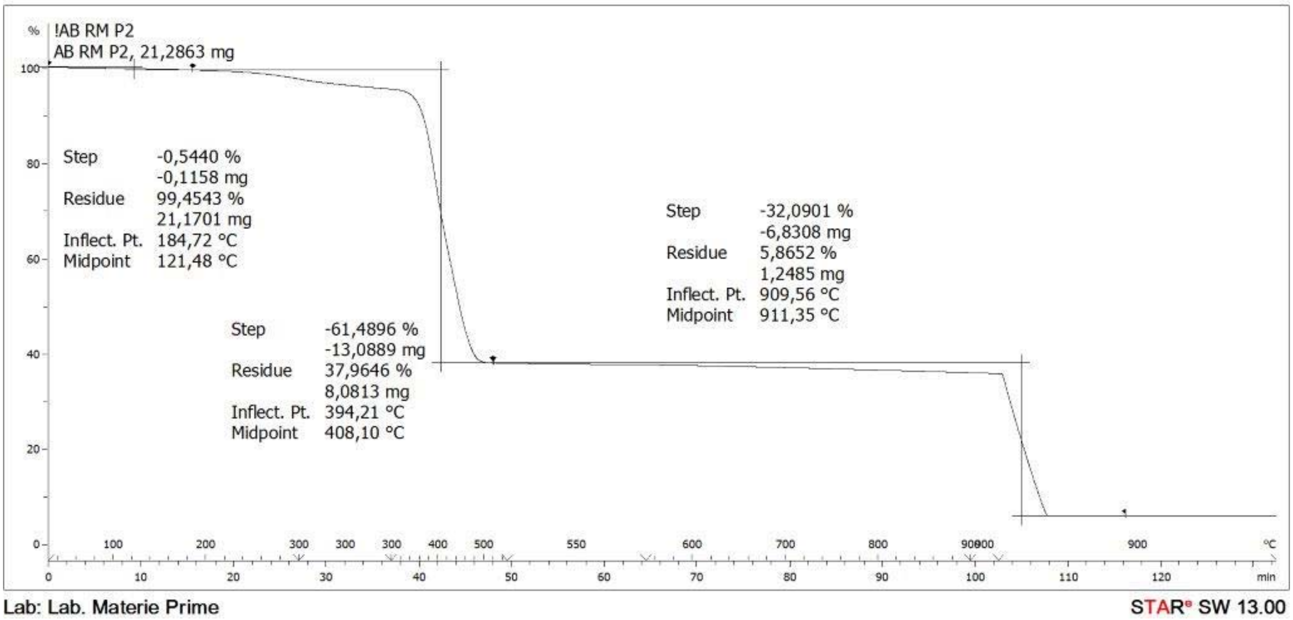


Figure 9.5 – TGA of Lehigh's Rubber (RP2) sample

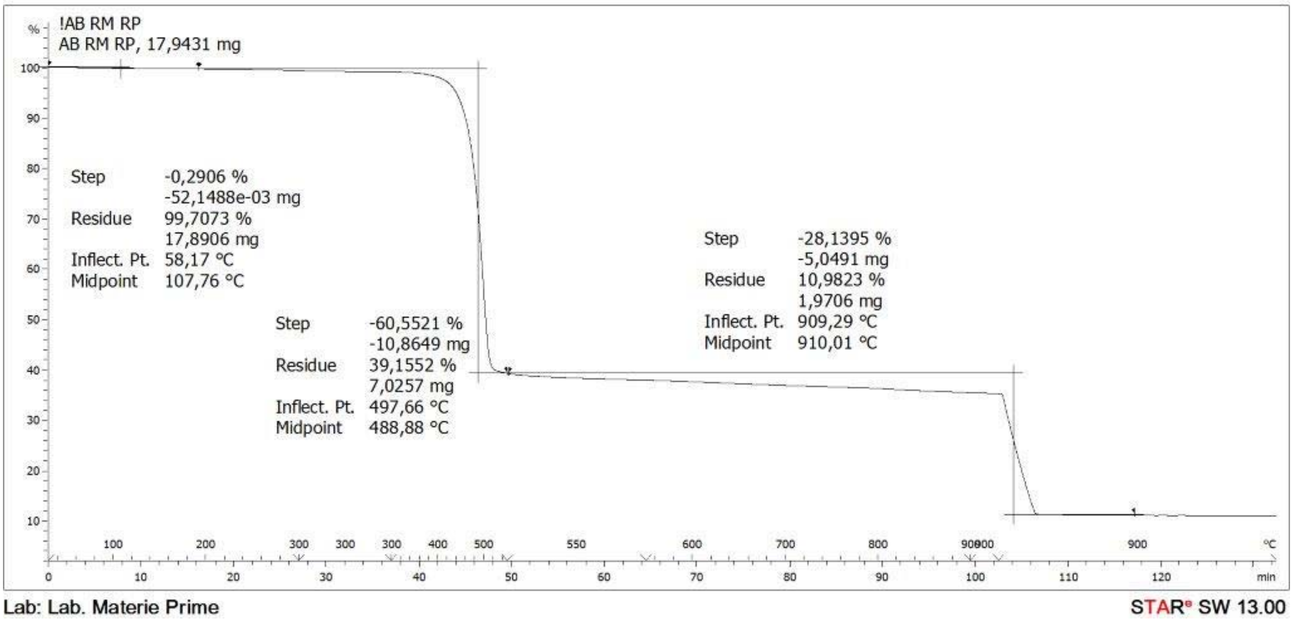


Figure 9.6 – TGA of FKM compound waste (RP3)

The quantity of chemicals presents in the rubber is given by the first decomposition in the temperature range from 0°C to 300°C: it can be estimated as 0,5 % for RP1 and RP2 and as 0,2 % for RP3. Second step gives the rubber content and the last step shows the CB content.

TGA and solvent extraction give the indication that RP3 (FKM compound waste) sample has lower content of non rubber components.

TGA of RP1, RP2 and RP3 with SP are reported in Figure 9.7 – Figure 9.9.

TGA of RP1, RP2 and RP3 with ODcP are reported in Figure 9.10 – Figure 9.12.

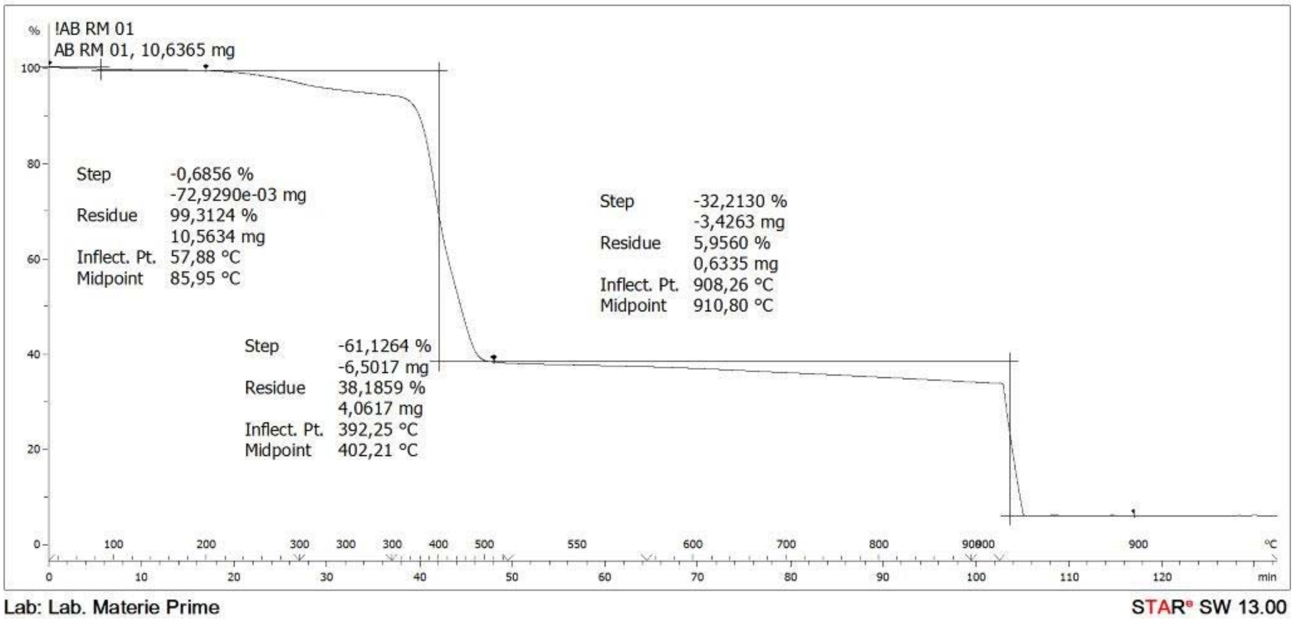


Figure 9.7 – TGA of RP1-SP adduct

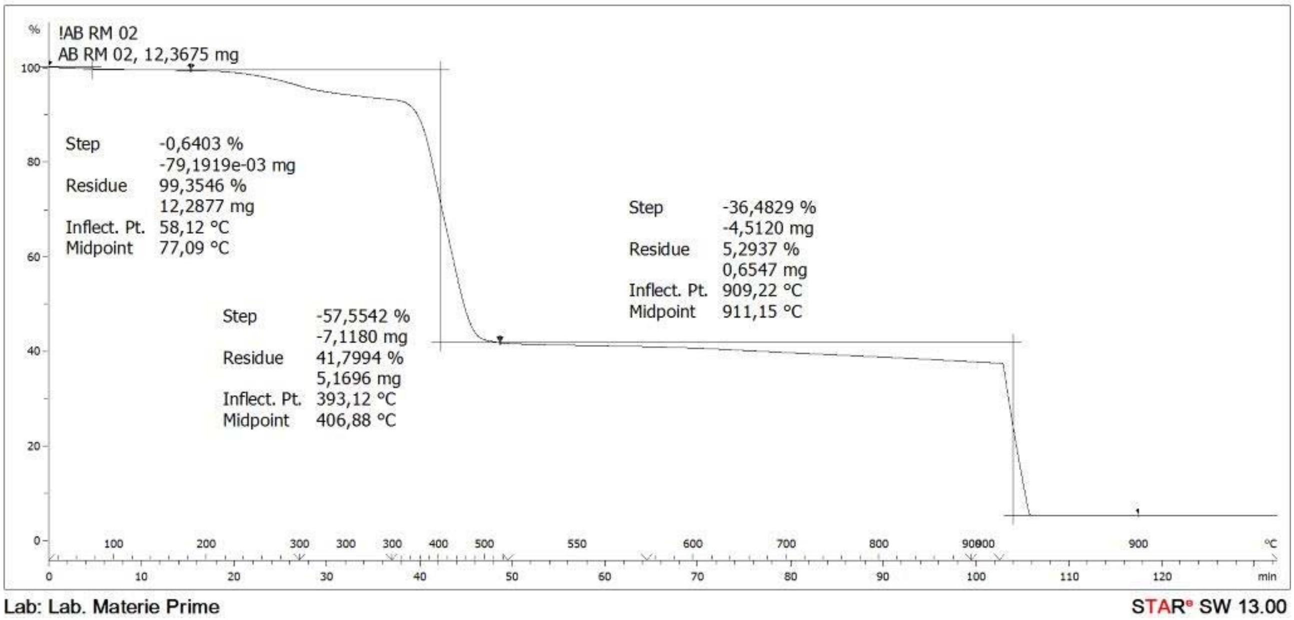


Figure 9.8 – TGA of RP2-SP adduct

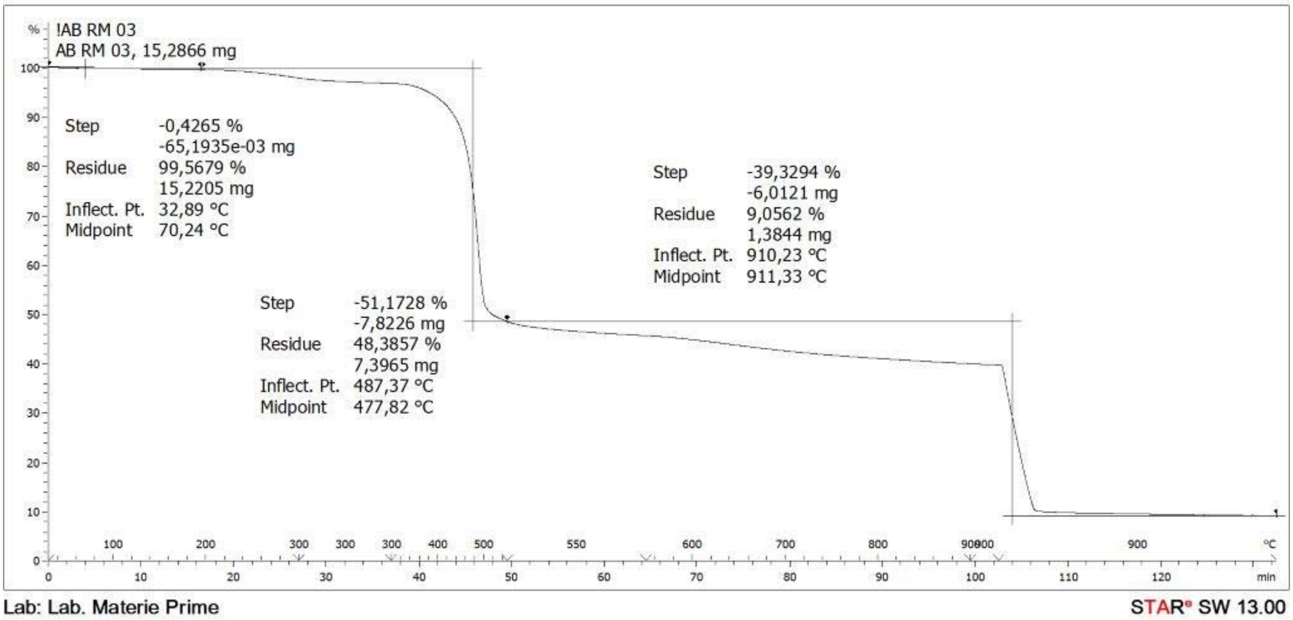


Figure 9.9 – TGA of RP3-SP adduct

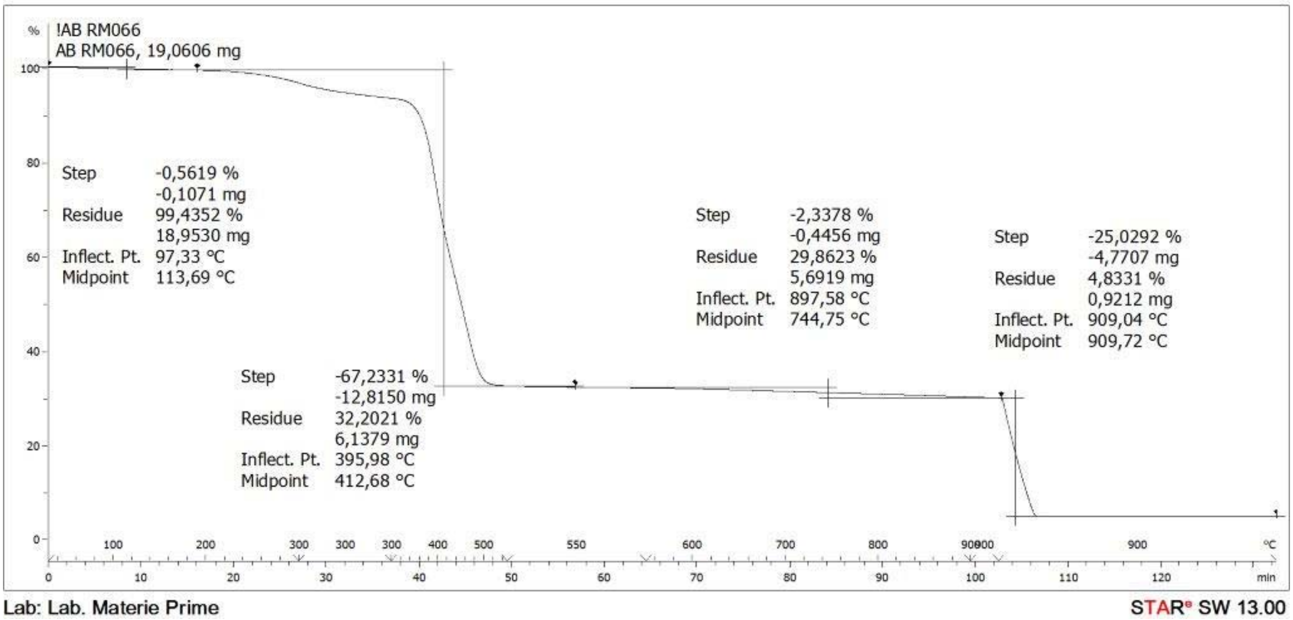


Figure 9.10 – TGA of RP1-ODcP adduct

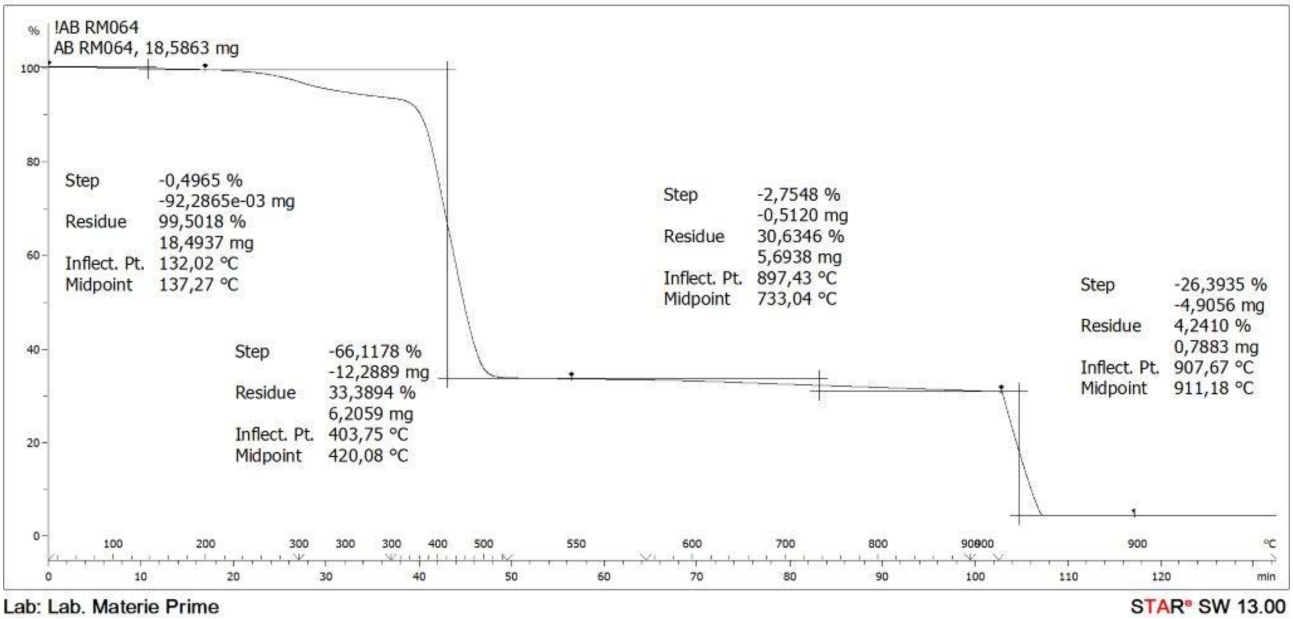


Figure 9.11 – TGA of RP2-ODcP adduct

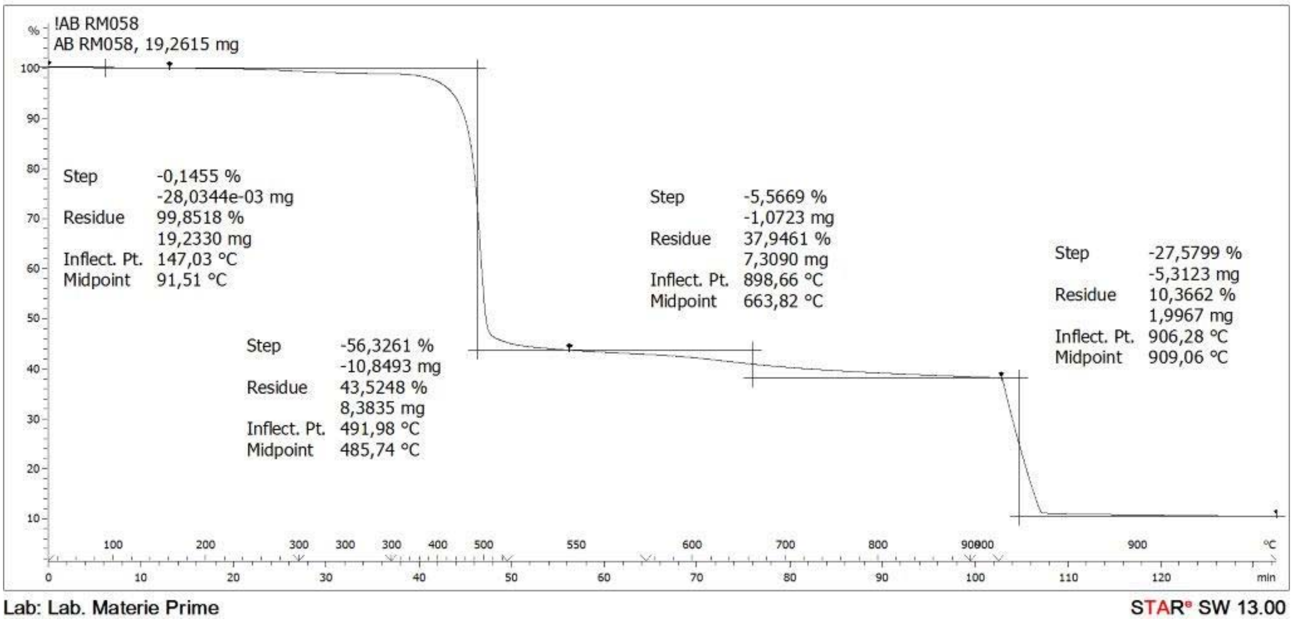


Figure 9.12 – TGA of RP3-ODcP adduct

In Table 9.1 are reported the data arising from TGA analysis.

From the data in Table 9.1 it is possible to notice that in the temperature <150°C all adducts reveal a higher mass loss with respect to RP, with the exception of RP2-ODcP which remains the same and RP3-ODcP which has a lower mass loss than RP3: 0,1 % instead of 0,3 %.

Analyzing the second step, between 150 °C and 500 °C it was possible to estimate the amount of SP and ODcP compound present in the adduct. The RP-SP adducts reveal mass loss in this temperature range. The ODcP revealed a mass loss only with RP3. Taking into account that PyC adducts' samples were thoroughly washed before undergoing TGA analysis, it can be said that the functionalization of RP with pyrrole compounds occurred. Similar values of mass loss were obtained with APTESP, TMP and GlyP.

Table 9.1 – TGA data of RP-PyC

sample	**mass loss%**		
	T < 150°C	NR (150<T<500°C)	CB (T>500°C)
RP1	0.5	63.8	29.5
RP2	0.5	61.5	32.1
RP3	0.3	61.1	28.1
RP1/SP	0.7	61.1	32.2
RP2/SP	0.6	57.6	36.5
RP3/SP	0.4	51.2	39.0
RP1/ODcP	0.6	67.2	27.4
RP2/ODcP	0.5	66.1	29.1
RP3/ODcP	0.1	56.3	33.2

9.3.2 Fourier Transformed Infrared Spectroscopy (FTIR)

By using infrared spectroscopy (IR) it is possible to detect the functional groups in a molecule from vibrations and bending of bonds between the connected atoms [3, 4].

FT-IR has given the absorbance of each functional group present in the RP3-PyC adducts with respect to the wavelength of the light source.

The light source used for the FTIR spectra was in the range between 450 cm^{-1} to 4000 cm^{-1}. The details of the process were reported in the experimental section.

Firstly will be analyzed Fourier Transform Infrared Spectroscopy of the pristine Rubber Powder (RP3) presented in the Figure 9.13.

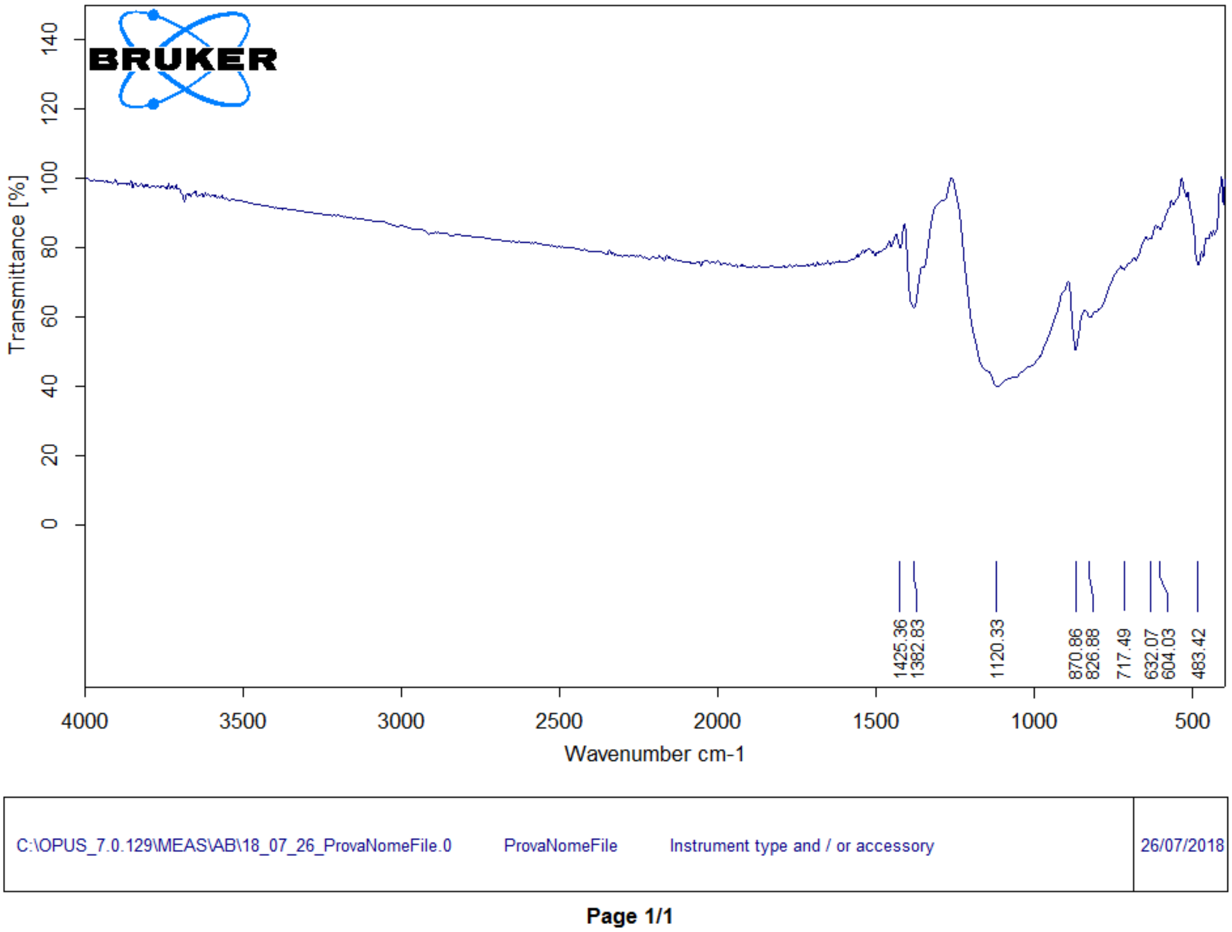


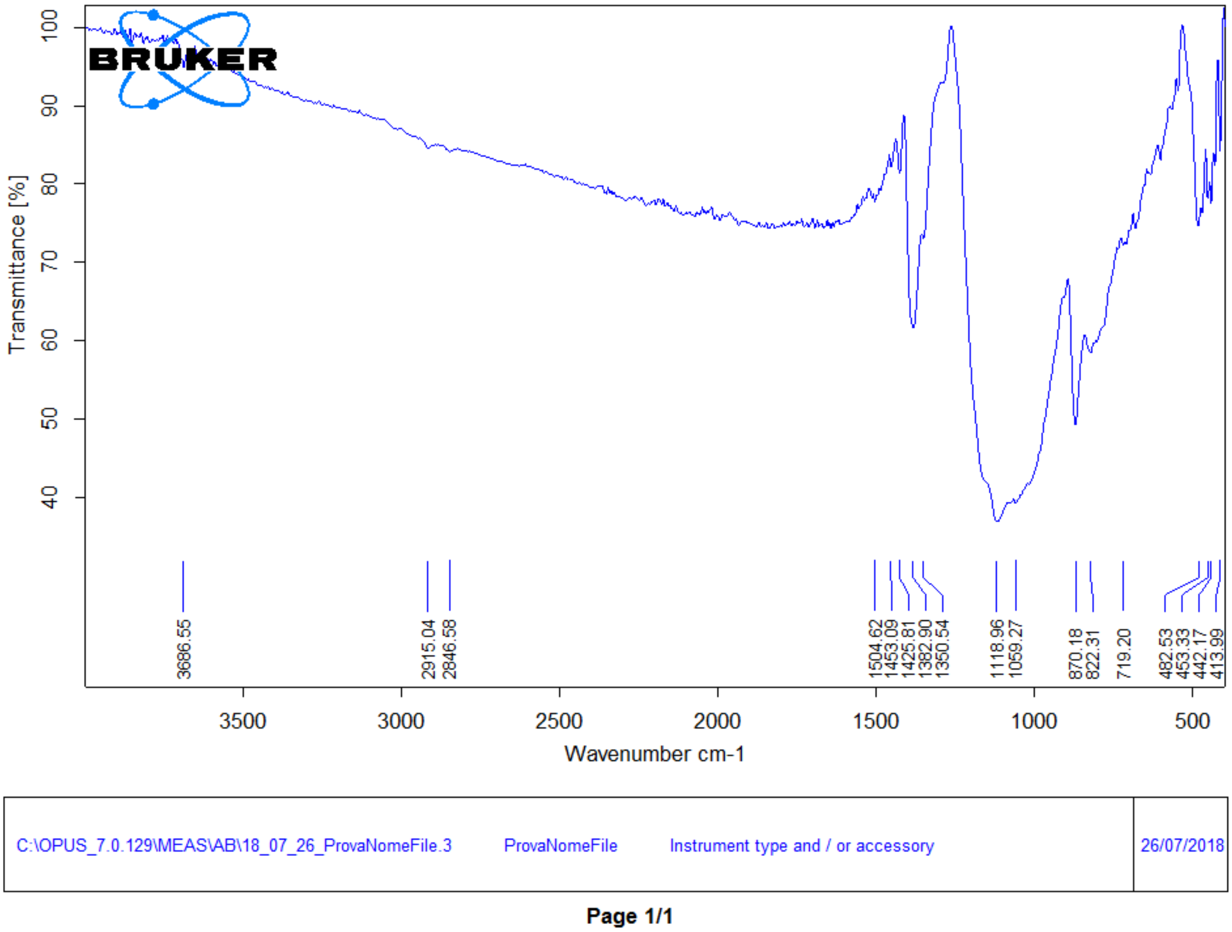
Figure 9.13 – Infrared spectroscopy of RP3 (FKM compound waste)

Literature reported the characteristic pyrrole signals at different wavelength [5].

IR traces for FKM compound waste powder could be detected at the following wavelength:

- 632 cm^{-1}: [=C-Br] bending
- 717 cm^{-1}: [=C-H] bending
- 826 cm^{-1}: [=C-H] bending
- 870 cm^{-1}: [=C-H] bending
- 1120 cm^{-1}: [=C-O] stretching
- 1382 cm^{-1}: [=C-H] bending
- 1425 cm^{-1}: [O-H] bending

In following figures are represented the IR spectroscopy of RP3-PyC adduct.



C:\OPUS_7.0.129\MEAS\AB\18_07_26_ProvaNomeFile.3 ProvaNomeFile Instrument type and / or accessory 26/07/2018

Page 1/1

Figure 9.14 – Infrared spectroscopy of RP3-APTESP

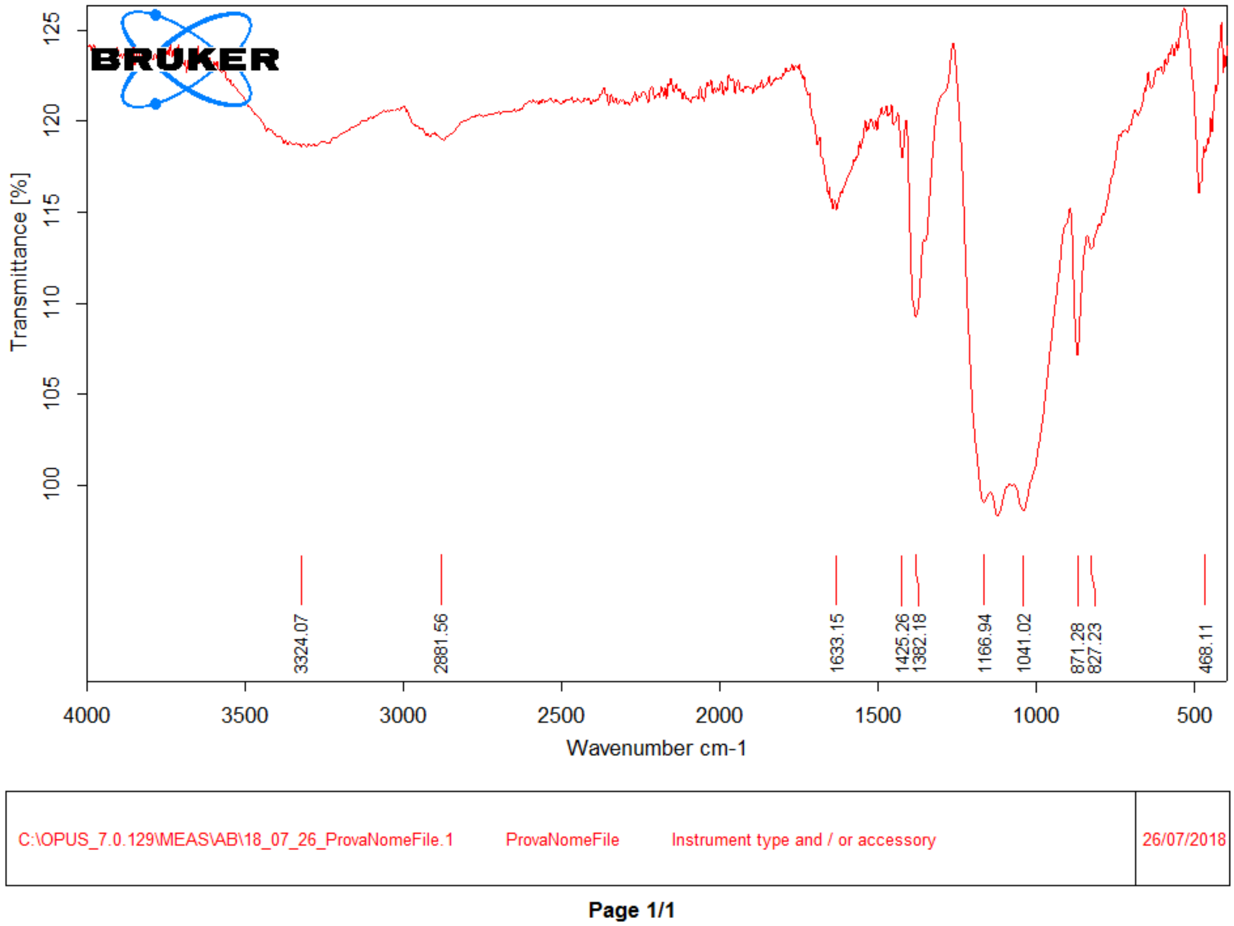
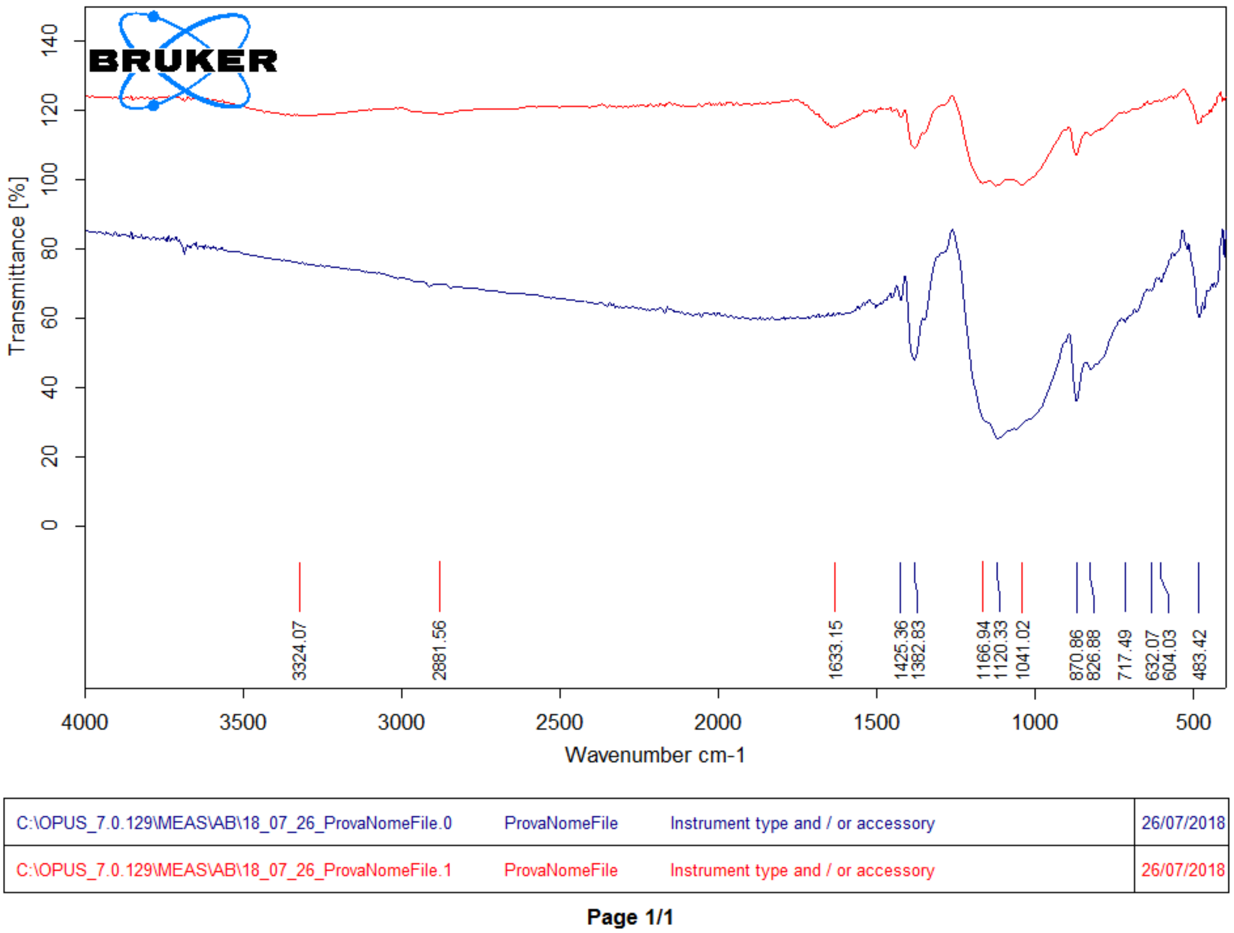


Figure 9.15 – Infrared spectroscopy of RP3-SP



C:\OPUS_7.0.129\MEAS\AB\18_07_26_ProvaNomeFile.0	ProvaNomeFile	Instrument type and / or accessory	26/07/2018
C:\OPUS_7.0.129\MEAS\AB\18_07_26_ProvaNomeFile.1	ProvaNomeFile	Instrument type and / or accessory	26/07/2018

Page 1/1

Figure 9.16 – Comparison of RP3 and RP3-SP spectra

Figure 9.17 and Figure 9.18 compare the IR spectra of rubber powder, of the pyrrole compound (SP and ODcP) and of the RP3/PyC adducts, to verify the presence of these molecules in the sample.

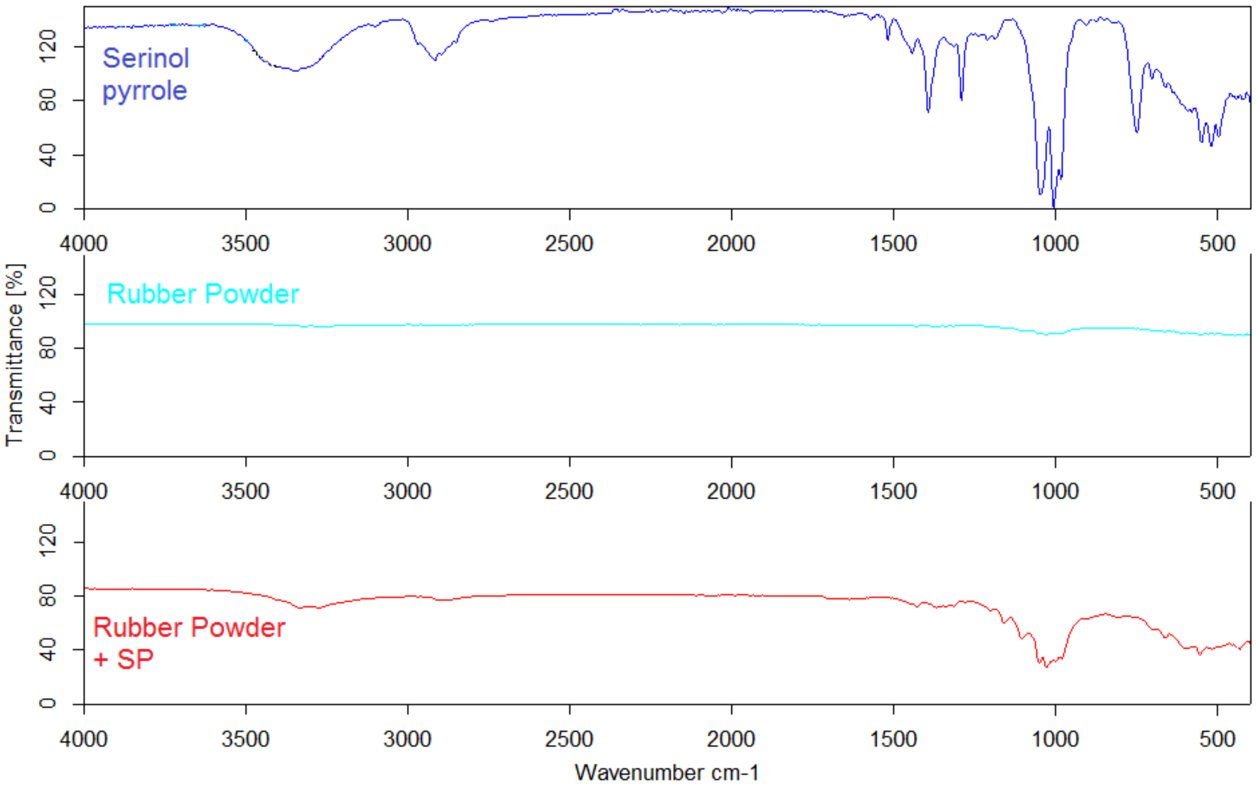


Figure 9.17 – Comparison of RP3, SP and RP3-SP spectra

Figure 9.17 shows an interesting profile. The spectrum of Rubber Powder + SP is different from the one of SP. The signal of -OH groups at 3300 cm^{-1} is shifted. The absence of the signal at 1400 cm^{-1} suggests that the =C-H bond established an interaction with the rubber powder. Another signal (due to C=C bond) is absent at 750 cm^{-1}.

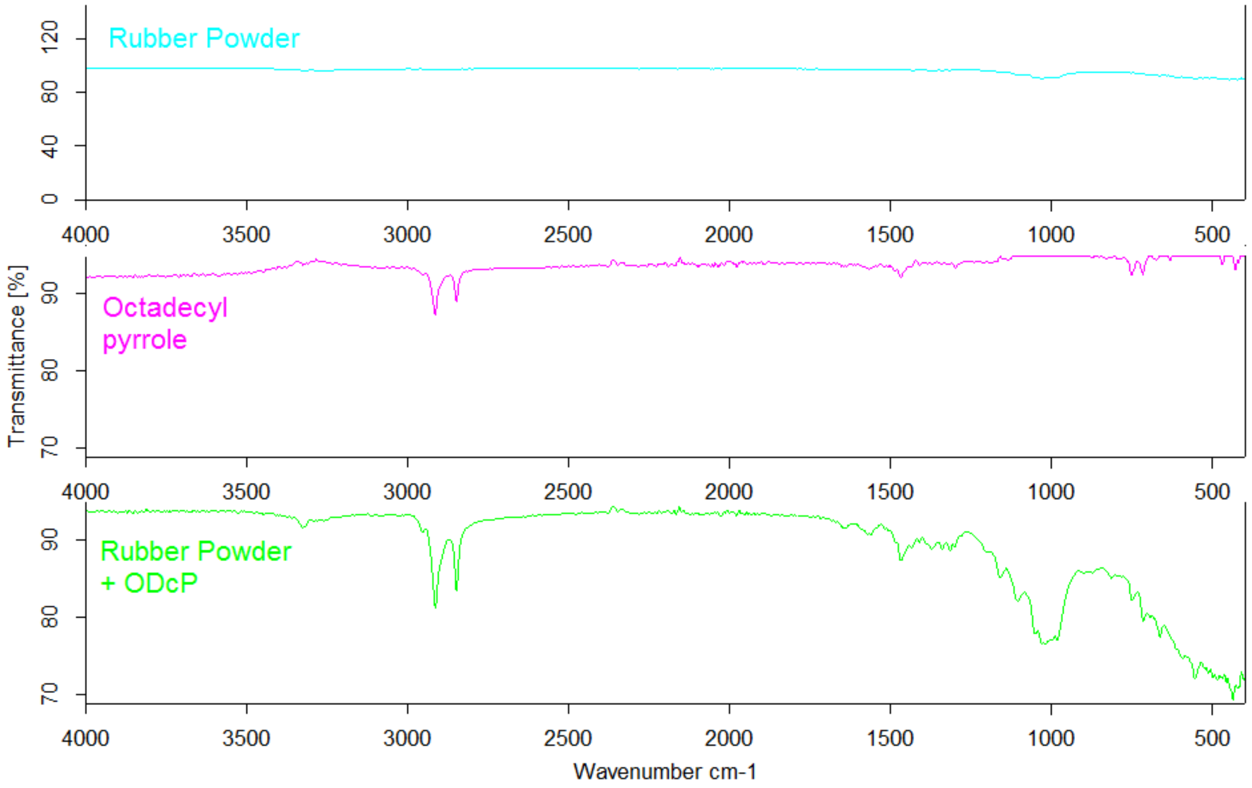


Figure 9.18 – Comparison of RP3, ODcP and RP3-ODcP spectra

Figure 9.18 shows interesting profiles as well. The IR spectrum of Rubber Powder + ODcP shows the presence of new peaks with respect to the spectra of Rubber Powder. It can be seen the presence of =C-O at 1050 cm^{-1}, O-H at 3300 cm^{-1}.

The IR spectra of RP3/PyC suggest that the pyrrole compounds were able to interact with rubber powder.

9. 4 Conclusions

RP-PyC adducts were prepared by heating a mixture of rubber powder and a PyC. PyCs were those presented in Chapter 6.

TGA and IR analysis allowed us to understand the functionalization of the rubber powder with pyrrole compounds. From these analyses we can say that PyC and the rubber powder interacted with each – other, thus the functionalization of rubber powder with pyrrole compounds occurred.

References

[1] Ghilardi M., Thesis at Politecnico Milano, 2015/2016

[2] Liang-tse Fan, Mohammad Reza Shafie, "Patent N. 7767722", Green Source Energy

[3] W.D. Callister, D.G. Rethwisch “scienza dei materiali”, 2012, Edises

[4] R.T. Morrison & R.N. Boyd – Chimica organica - CEA

[5] J. Abelard, R.A. Wilmsmeyer, A.C. Edwards, W.O. Gordon, E.M. Durke, J.C. Karwacki, D. Troya, J.R. Morris, *J of Physical Chem*, 2016

CHAPTER 10

RUBBER COMPOSITES

10. 1 Introduction

This chapter regards the production of two different kinds of rubber composites: containing a rubber waste and containing functionalized carbon black. The rubber waste was a crosslinked rubber composite containing fluorinated rubber (FKM) and carbon black, coming from the process for the production of rubber goods, such as O-rings and gaskets.

Thermogravimetric analysis allowed to determine that RP was essentially made of FKM and CB, in 2 : 1 mass ratio.

The composites discussed in this chapter were based on NR and BR as the rubbers, silica, and carbon black as the fillers.

The waste of FKM compound, here below named as RP (Rubber Powder) was used in place of a minor part of:

(i) natural rubber

(ii) silica.

The waste of FKM compound:

(i) was used as such: pristine RP

(ii) or was functionalized with serinol pyrrole (RP-SP) or with octadecyl pyrrole (RP-ODcP).

Objectives of this activity were thus to study the ability of a crosslinked polar rubber waste:

(i) to act as a rubber

(ii) to replace a polar filler.

In the light of the latter objective, aim of this part of the research was thus to study the effect of functionalization of RP with SP to promote the interaction of RP with silica.

In addition, rubber compounds based on NR and BR were produced using CB functionalized with two different PyC (SP and ODcP), in partial replacement of pristine CB. CB grade was N 234. Mass percentage of PyC on CB was equal to 10%. Dynamic-mechanical properties were tested. The objective of this last study was to investigate the effect of CB modification with different PyC, especially in terms of Payne effect and hysteresis.

10. 2 Rubber composites filled with CB-PyC in replacement of pristine CB

As mentioned above, rubber compounds based on NR and BR were produced using CB functionalized with two different PyC (SP and ODcP), in partial replacement of pristine CB.

10.2.1 Formulations and preparation of rubber composites

Recipes of composites are reported in **Table 10.1.**

Table 10.1 – Recipes for rubber composites.

Ingredients [a]	**density**	**Reference (CB)**	**CB-SP**	**CB-ODcP**
	gr/cm^3	phr	phr	phr
BR Neocis	0.91	50.00	50.00	50.00
NR - SIR20	0.92	50.00	50.00	50.00
CB-PyC	1.80	0.00	22.00	22.00
CB N234	1.80	25.00	5.00	5.00
PyC			2.00	2.00
Silica Zeosil 1165	2.10	25.00	25.00	25.00
TESPT	1.08	2.00	2.00	2.00
Stearic acid	0.85	2.00	2.00	2.00
ZnO	5.55	4.00	4.00	4.00
6PPD	1.00	2.00	2.00	2.00
TBBS	1.32	1.80	1.80	1.80
Sulphur	2.00	1.50	1.50	1.50
Total		163.30	165.30	165.30

[a] for further details on the ingredients see the experimental part.

In **Table 10.1** are shown the recipes of rubber compounds produced using the functionalized CB, CB – SP and CB – ODcP adducts, in partial replacement of pristine CB. 25 phr of CB were replaced by CB-PyC. The amount og

22 phr of each CB modified with PyC (SP or ODcP).

A standard two-step procedure was used for the preparation of the composites of **Table 10.1**.

It is schematically described in **Figure 10.1**.

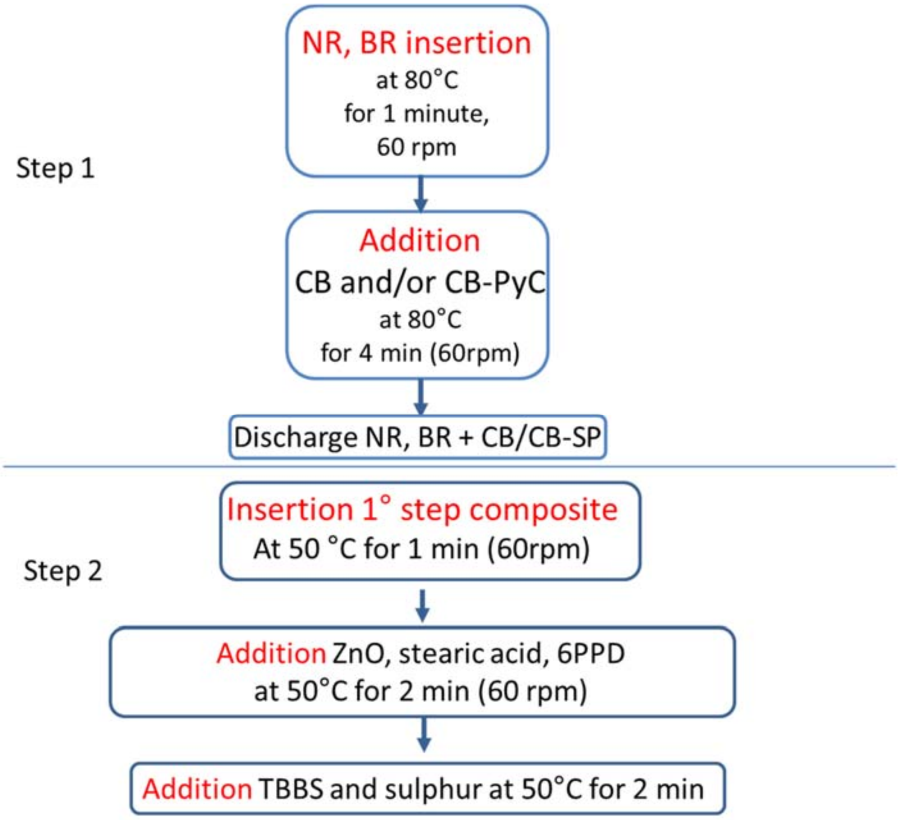


Figure 10.1 – Block scheme for the preparation of rubber composites of **Table 10.1**.

10.2.2 Vulcanization

Crosslinking was performed with a sulphur-based system. Rheometric curves were taken at 170°C. They are shown in **Figure 10.2**, and data are in **Table 10.2**.

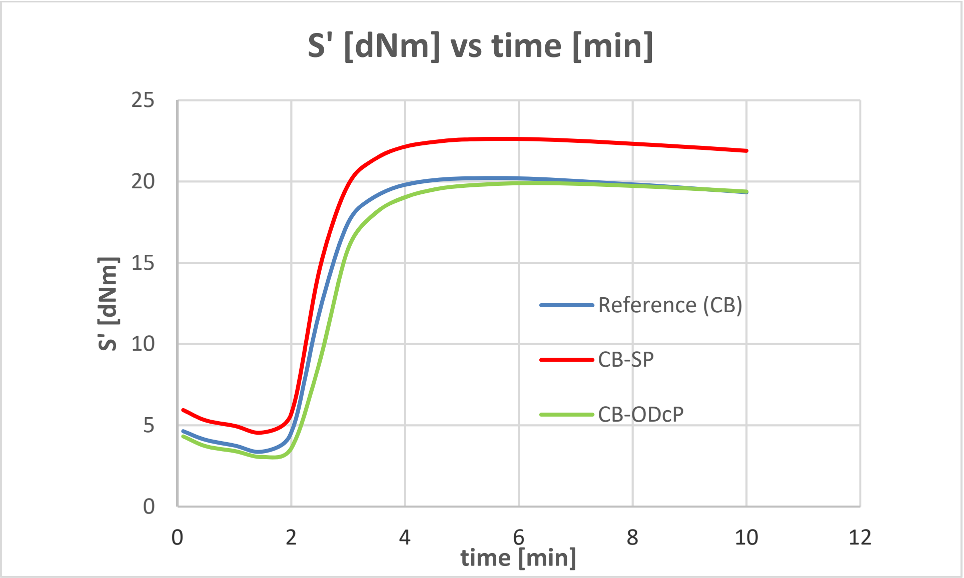


Figure 10.2 – Rheometric curves obtained at 170°C for rubber compounds containing: pristine CB N234 (blue curve); 22 phr of CB-SP (10 mass%) (red curve); 22 phr CB-ODcP (10 mass%) (green curve).

Table 10.2 – Torque values, induction times (t_{s1}) and times to achieve the optimum level of vulcanization (t_{90}) obtained for rubber composites of **Table 10.1.**

	Reference (CB)	**CB-SP**	**CB-ODcP**
M_L [a]	3.76	4,56	3,05
M_H [a]	20,20	22,62	19,90
$M_H – M_L$ [a]	16,44	18,06	16,85
t_{s1} [b]	2,18	2,78	2,73
t_{90} [b]	3,30	3,20	3,40

[a] in dNm; [b] in minutes.

CB – SP caused an increase on both M_L and M_H modulus, whereas the behaviour in vulcanization of the composites with CB and with CB-ODcP are very similar.

10.2.3 Dynamic-mechanical properties

Strain sweep experiments were performed by applying the stress in the shear mode. Curves and data are reported in the following Figures and Table.

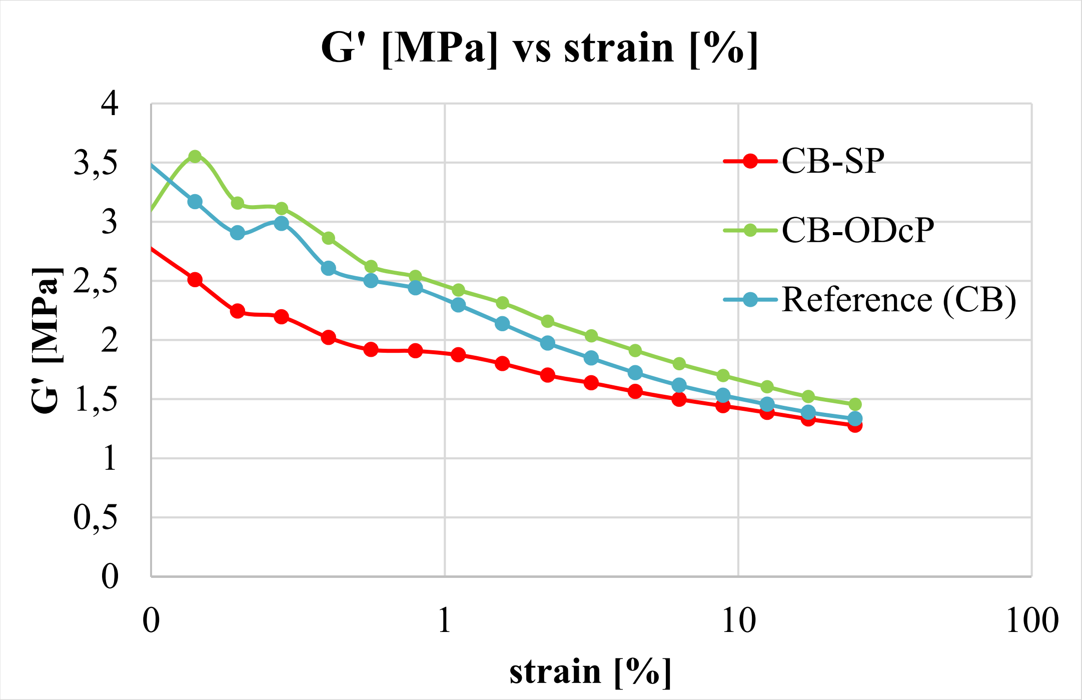


Figure 10.3 – G’ curves for CB (blue curve), CB-SP (red curve) and CB-ODcP (green curve).

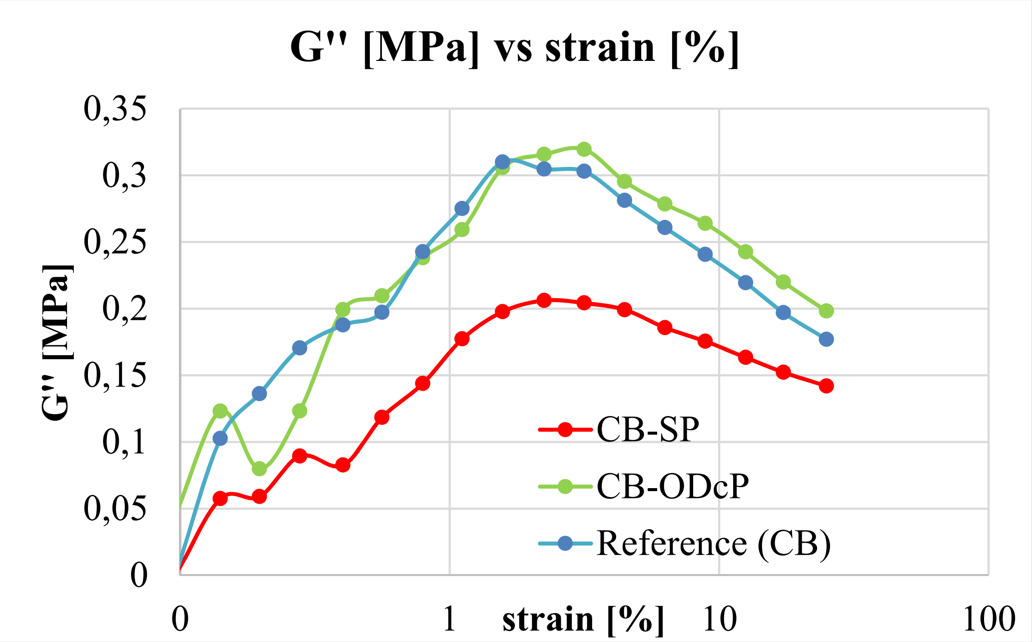


Figure 10.4 – G” curves for CB (blue curve), CB-SP (red curve) and CB-ODcP (green curve).

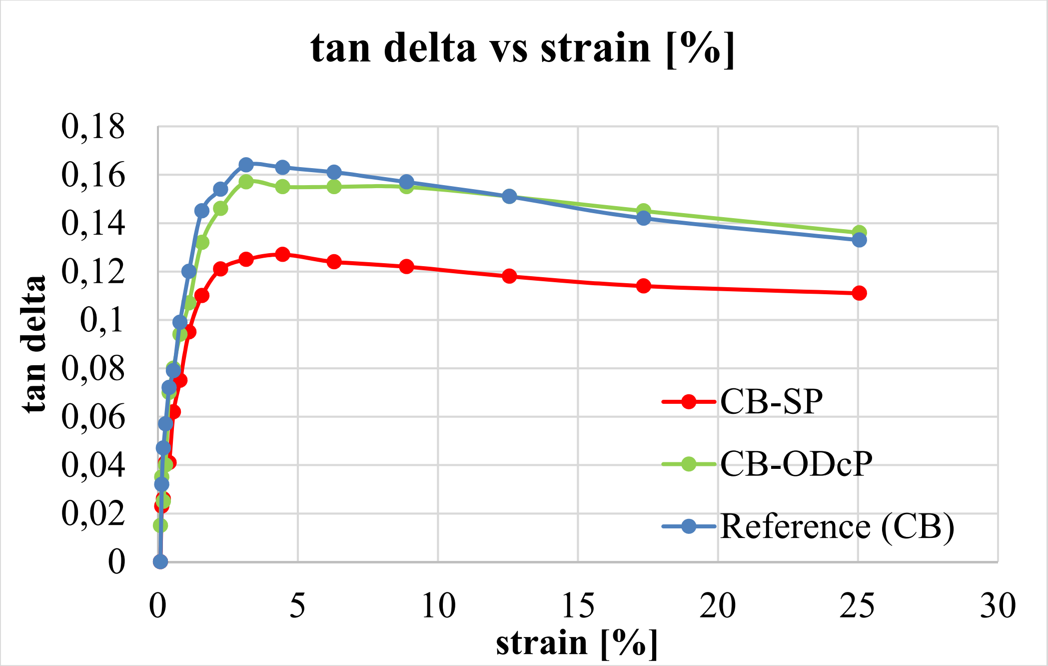


Figure 10.5 – Tan Delta curves for CB (blue curve), CB-SP (red curve) and CB-ODcP (green curve).

Table 10.3 – Main dynamic-mechanical results for composites of **Table 10.1**.

Parameter	**CB**	**CB-SP**	**CB-ODcP**	**Silica**
G’ min	1,27	1,45	1,33	6,56
G’ max	2,80	3,55	3,51	8,14
ΔG’	1,53	2,10	2,18	1,58
G” max	0,20	0,31	0,30	0,94
Tan Delta max	0,12	0,15	0,16	0,16

CB-SP caused a decrease of both Payne effect and hysteresis (Tan Delta). CB and CB-ODcP give rise to almost the same behaviour.

Data shown in this paragraph reveal that functionalization of CB with SP leads to reduction of dissipation of energy. SP appears to be a functionalizing agent to be investigated also in the case of powder rubber.

10. 3 Composites with fluorinated rubber waste in place of natural rubber

As mentioned above, the rubber matrices selected for the composites described in this chapter were NR and BR, while both carbon black and silica were used as fillers.

In this study, rubber waste was used in place of natural rubber. As previously discussed, rubber waste (RP) contains also CB (mass percentage equal to 33%), then a part of pristine CB was replaced by the CB contained into the rubber waste.

In the following paragraph, composites with RP (either pristine or functionalized) are compared with the composite with CB, without any functionalization.

10.3.1 Formulations and preparation of rubber composites

Recipes of the composites are reported in **Table 10.4**.

Table 10.4 – Recipes for rubber composites.

Ingredients [a]	**density**	**Ref CB**	**Ref RP**	**RP-SP**	**RP-ODcP**
	gr/cm^3	phr	phr	phr	phr
BR	0.91	50.00	50.00	50.00	50.00
NR	0.92	50.00	38.00	38.00	38.00
RP (μ=0.5)	2.02	0	18.00	0.00	0.00
RP-PyC (10%wt), containing:	2.02	0	18.00	20.00	20.00
FKM			12.00	12.00	12.00
CB			6.00	6.00	6.00
PyC			0.00	2.00	2.00
CB N234	1.80	25.00	19.00	19.00	19.00
Silica Zeosil 1165	2.10	25.00	25.00	25.00	25.00
TESPT	1.08	2.00	2.00	2.00	2.00
Stearic acid	0.85	2.00	2.00	2.00	2.00
ZnO	5.55	4.00	4.00	4.00	4.00
6PPD	1.00	2.00	2.00	2.00	2.00
TBBS	1.32	1.80	1.80	1.80	1.80
Sulphur	2.00	1.50	1.50	1.50	1.50
Total		163.30	163.30	165.30	165.30

[a] for details on the ingredients see the experimental part.

12 phr of NR and 6 phr of CB N234 were replaced by 18 phr of pristine RP or 18 phr of RP modified with 2 phr of PyC (SP or ODcP). SP and ODcP were thus considered as an extra ingredient, without modifying the recipe of the reference composite with pristine RP. Indeed, they

were present in a very low amount. As the density of RP (either pristine or functionalized) is much larger than the density of NR, 12 phr of NR were replaced with 18 phr of RP (either pristine or functionalized). In consideration of the chemical composition of RP, FKM was 12 phr and CB was 6 phr.

A standard three-step procedure was used for the preparation of the composites of **Table 10.4**.

It is schematically described in **Figure 10.6**.

A Brabender® type internal mixer was used, with a 50-cc chamber and a fill factor of 0.8 (80%).

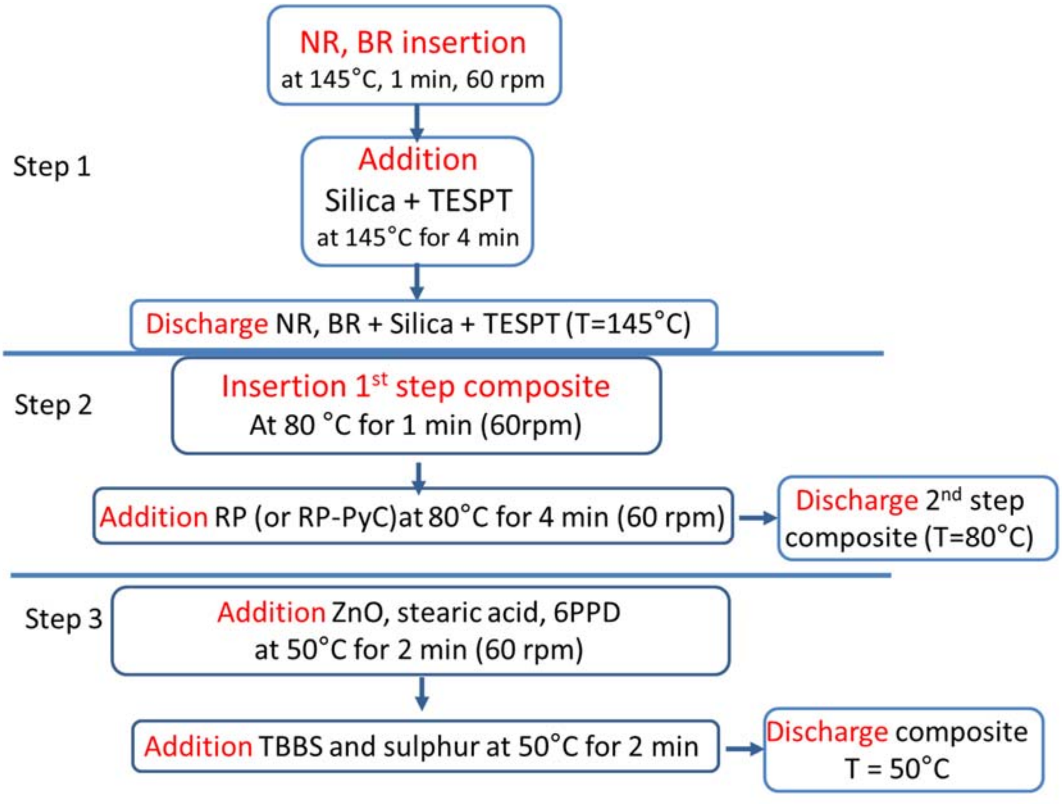


Figure 10.6 – Block scheme for the preparation of rubber composites of **Table 10.4.**

10.3.2 Vulcanization

Crosslinking was performed with a sulphur-based system. Rheometric curves were taken at 170°C. They are shown in **Figure 10.7**, and data are in **Table 10.5**.

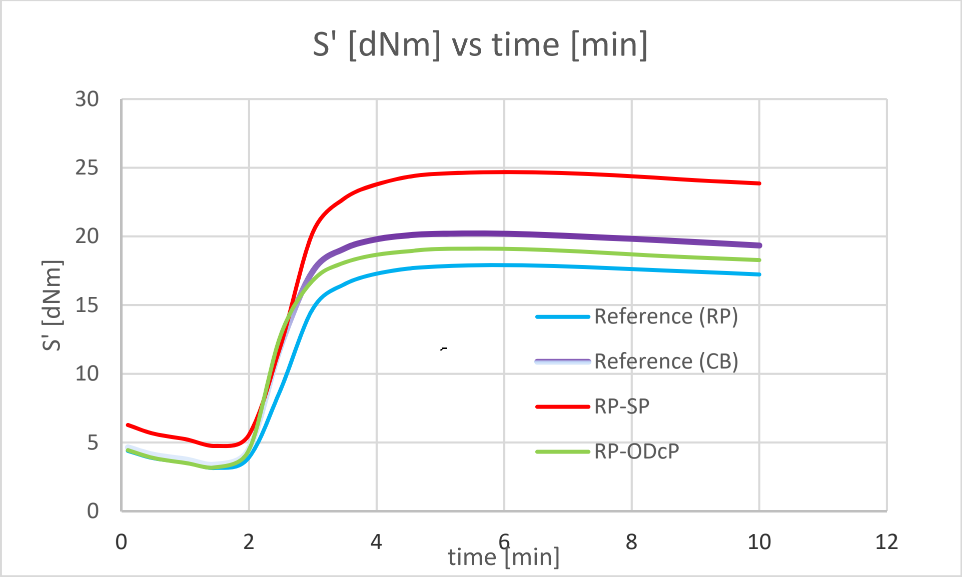


Figure 10.7 – Rheometric curves obtained at 170°C for rubber compounds containing: 20 phr of pristine RP (blue curve); 25 phr of pristine CB (purple curve); 22 phr of RP-SP (10 mass%) (red curve); 22 phr RP-ODcP (10 mass%) (grey curve)

Table 10.5 – Torque values, induction times (t_{s1}) and times to achieve the optimum level of vulcanization (t_{90}) obtained for rubber composites of **Table 10.3** and **10.4**.

	Reference (CB)	**Reference (RP)**	**RP-SP**	**RP-ODcP**
M_L ^{a}	3.76	3,14	4,74	3,20
M_H ^{a}	20,20	17,92	24,69	19,09
$M_H - M_L$ ^{a}	16,44	14,78	19,95	15,89
t_{s1} ^{b}	2,18	2.70	2,70	2,70
t_{90} ^{b}	3,30	3,52	3,40	3,25

^{a} in dNm; ^{b} in minutes.

From Table 10.5 and Figure 10.7, it appears that:

- the replacement of NR and CB with RP, either pristine or functionalized with ODcP, does not appreciably affect the vulcanization behaviour. ODcP leads to larger M_H value, but the differences with the curve of the composite with RP are subtle

- functionalization of RP with SP brings about appreciable modification of the vulcanization behaviour. As already observed in the case of composites with CB and CB-SP, SP leads to larger values of M_L and M_H.

10.3.3 Dynamic-mechanical properties

To investigate dynamic-mechanical properties, strain-sweep tests were performed at 50°C on crosslinked samples. Results are shown as curves in **Figure 10.8**, **Figure 10.9** and **Figure 10.10**, and reported as data in **Table 10.6**. Blank refers to the composite with RP.

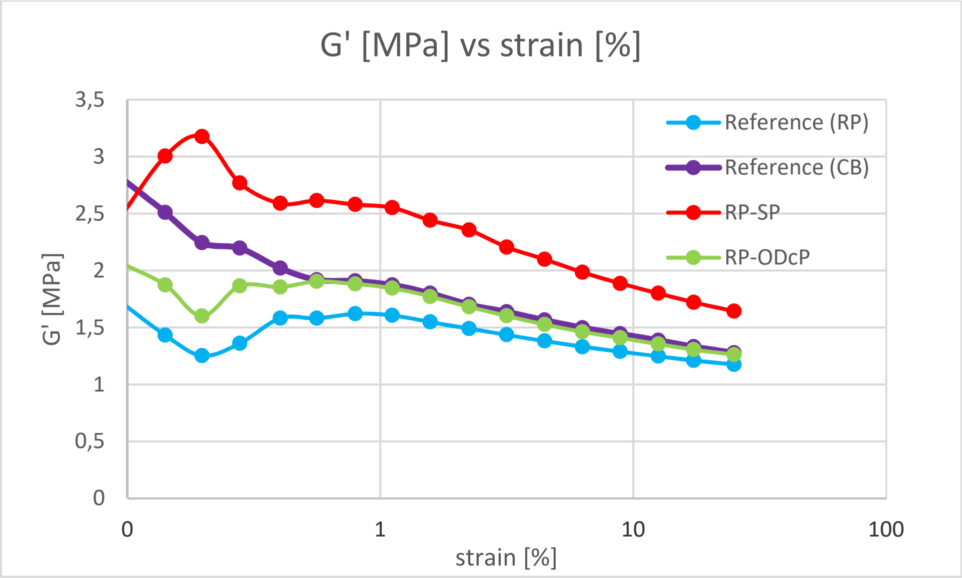


Figure 10.8 – Dynamic storage modulus G’ [MPa] versus strain amplitude [%] for rubber compounds containing: 20 phr of pristine RP (blue curve); 25 phr of pristine CB (purple curve); 22 phr of RP-SP (10 mass%) (red curve); 22 phr RP-ODcP (10 mass%) (grey curve).

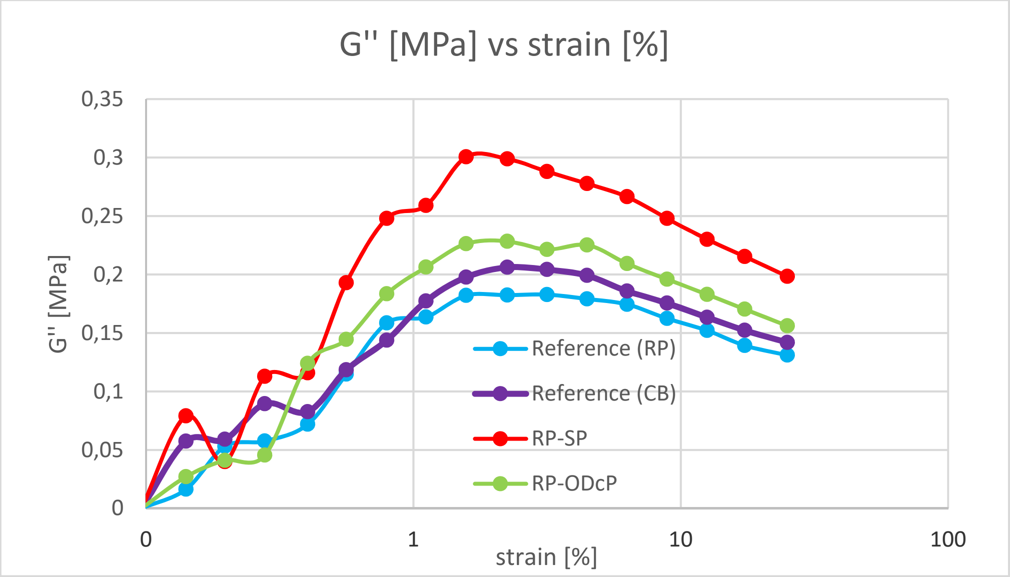


Figure 10.9 – Loss modulus G" [MPa] versus strain amplitude [%] for rubber compounds containing: 20 phr of pristine RP (blue curve); 25 phr of pristine CB (purple curve); 22 phr of RP-SP (10 mass%) (red curve); 22 phr RP-ODcP (10 mass%) (grey curve).

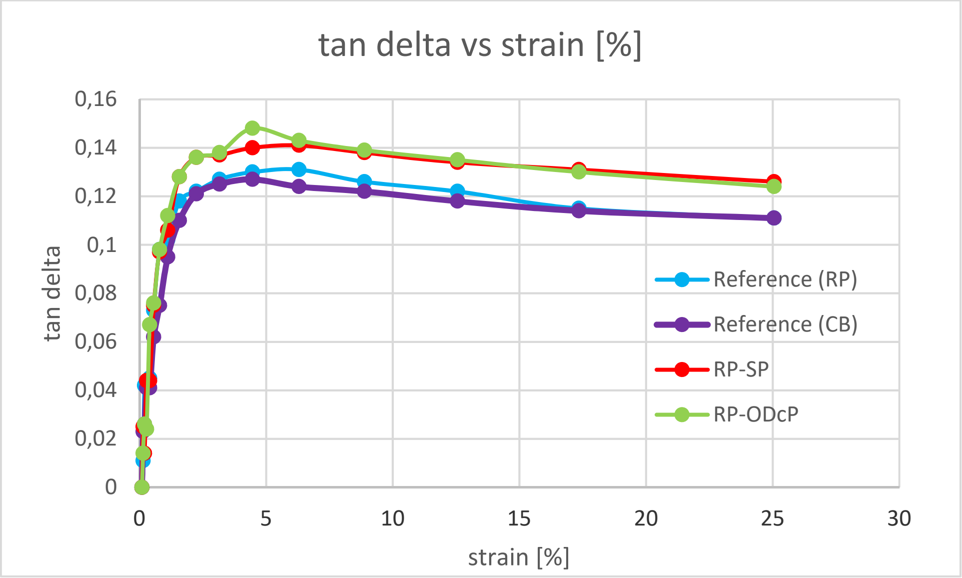


Figure 10.10 – Tan delta versus strain amplitude [%] for crosslinked composites of **Table 10.4.**

Table 10.6 – Dynamic-mechanical properties of rubber compounds obtained through strain sweep experiments.

Parameter	**CB**	**RP**	**RP-SP**	**RP-ODcP**
G’ $_{min}$	1,27	1.17	1.64	1.26
G’ $_{max}$	2,80	1.70	3.17	2.05
ΔG’	1,53	0.53	2.07	0.79
G” $_{max}$	0,20	0.18	0.30	0.22
Tan Delta $_{max}$	0,12	0.13	0.14	0.14

Figures 10.8 – 10.10 and Table 10.6 show that:

- the replacement of NR and CB with RP, either pristine or functionalized with ODcP, leads to lower Payne effect and to similar tan delta

- the replacement of NR and CB with RP functionalized with SP leads to larger Payne effect and to similar tan delta

- RP-SP and RP-ODcP lead to larger values of G’, G” and Tan Delta with respect to Reference RP. In particular, compound with RP-SP shows larger values of G’ modulus at minimum and low strains, larger ΔG’ values, larger values of G’’ at all strains and larger G’’ values for a given G’ value.

To account for these results, the following hypotheses can be elaborated:

(i) the replacement of NR and CB with RP and functionalized RP reduces the filler networking

(ii) the functionalized RP (in particular functionalized with SP) leads to larger filler networking because of the interaction with silica.

10.3.4 Conclusions

It seems reasonable to conclude that pristine waste crosslinked fluorinated rubber leads to interesting properties (in particular lower Payne effect) when used in place of part of a rubber (NR) and CB.

The functionalization of RP could lead to undesired increase of hysteresis.

10. 4 Composites with fluorinated rubber waste in place of silica

RP is made of a polar rubber and in vulcanized. It appeared reasonable to use it in place of a polar filler, such as silica.

In following paragraphs, formulations and preparation of rubber composites, vulcanization reaction, dynamic compression tests and stress – strain tests are reported.

10.4.1 Formulations and preparation of rubber composites

Recipes of the composites are reported in **Table 10.7.**

Table 10.7 – Recipes for rubber composites.

Ingredients [a]	**Density**	**Silica**	**RP**	**RP-SP**
	[g/cm^3]	[phr]	[phr]	[phr]
BR Neocis	0.91	50	50	50
NR (SIR20)	0.92	50	50	50
CB N234	1.80	25	25	25
Silica (Zeosil 1165 MP)	2.1	25	15	15
Rubber Powder (RP) (µ = 0.5)	2.02	0	10	0
RP-SP	2.02	0	0	10
TESPT	1.08	2	2	2
Stearic Acid	0.85	2	2	2
ZnO	5.55	4	4	4
6PPD	1	2	2	2
TBBS	1.32	1.8	1.8	1.8
Sulphur	2	1.5	1.5	1.5

[a] for further details on the ingredients see the experimental part.

Composites were based on:

- 25 phr of pristine silica Zeosil 1165 MP,

- pristine RP
- 10 phr of pristine silica and 15 phr of RP-SP.

A standard three-step procedure was used for the preparation of the composites of **Table 10.7**, the same already reported in Figure 10.6

Again, a Brabender® type internal mixer was used, with a 50-cc chamber and a fill factor of 0.8 (80%).

10.4.2 Vulcanization reaction

Crosslinking was performed with a sulphur-based system. Rheometric curves were taken at 170°C. They are shown in **Figure 10.11**, and data are in **Table 10.8**.

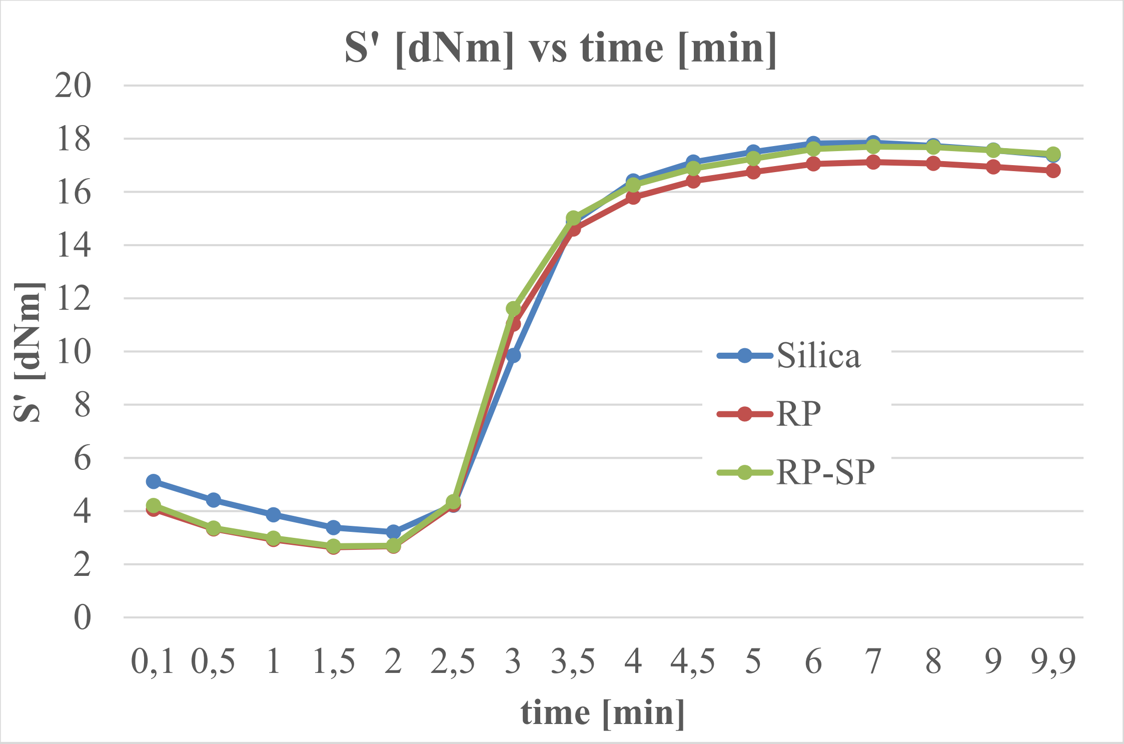


Figure 10.11 – Rheometric curves obtained at 170°C for rubber compounds containing: 25 phr of pristine silica Zeosil 1165 MP (blue curve); 10 phr of pristine silica + 15 phr of pristine RP (red curve); 10 phr of pristine silica + 15 phr of RP-SP (grey curve).

Table 10.8 – Torque values, induction times (t_{s1}) and times to achieve the optimum level of vulcanization (t_{90}) obtained for rubber composites of **Table 10.7**.

	Silica	RP	RP-SP

M_L [a]	3,21	2.70	2,70
M_H [a]	17,70	17,12	17,70
$M_H - M_L$ [a]	14,49	14,42	15,00
t_{s1} [b]	2,79	3.30	2,79
t_{90} [b]	3,80	3,80	3,80

[a] in dNm; [b] in minutes.

Vulcanization curves appear pretty similar. Curve of Silica compound achieves higher M_L value, whereas the curve of RP achieves slightly lower M_H with respect to the other two compounds. Hence, kinetics of vulcanization is not appreciably affected by the replacement of silica with RP, either pristine or functionalized with SP.

10.4.3 Dynamic compression tests

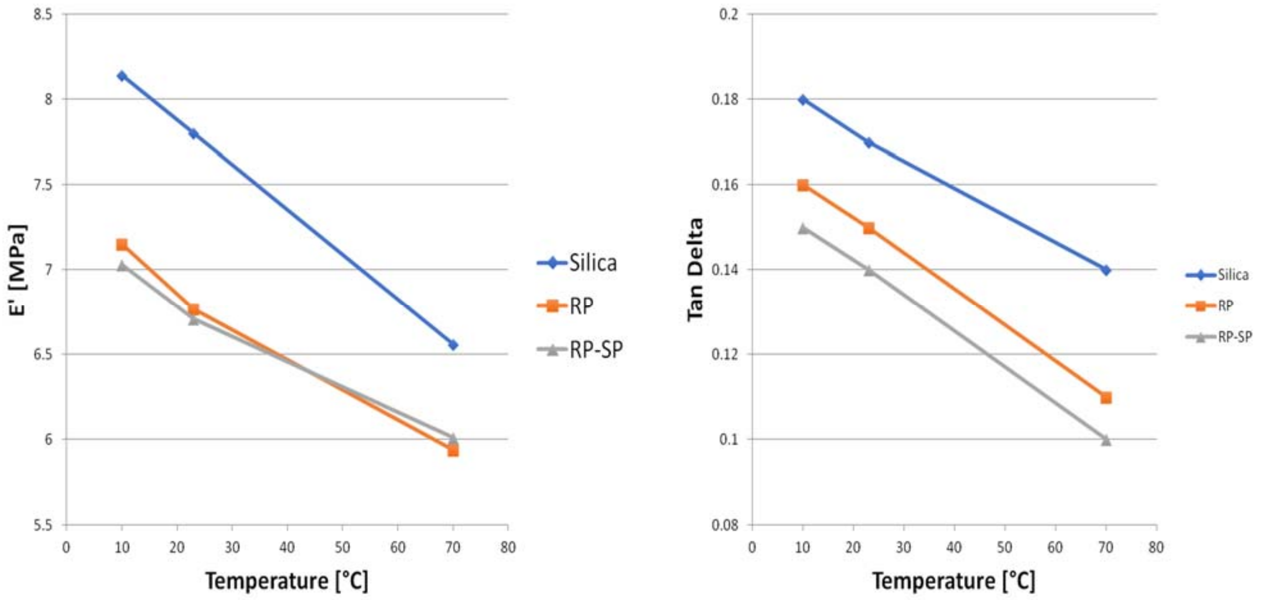


Figure 10.12 – Dynamic compression tests. In the left: E' [MPa] vs temperature [°C]; In the right: tan delta vs temperature [°C] for rubber composites of **Table 10.7**.

Table 10.9 – Main results of dynamic compression tests of composites of **Table 10.7**.

	Silica	**RP**	**RP-SP**
E’@10°C	8.14	7.15	7.03
E’’@10°C	1.47	1.14	1.06
Tan Delta@10°C	0.18	0.16	0.15
E’@23°C	7.80	6.77	6.71
E’’@23°C	1.32	1	0.92
Tan Delta@23°C	0.17	0.15	0.14
E’@70°C	6.56	5.94	6.01
E’’@70°C	0.94	0.63	0.62
Tan Delta@70°C	0.14	0.11	0.10
ΔE’ (E’@10°C - E’@70°C)	1.58	1.21	1.02

Results appear indeed interesting. RP (pristine or functionalized) in place of silica give rise to lower dynamic rigidity. Most interesting results come from hysteresis values. RP in place of silica leads to lower hysteresis. The lowest hysteresis was obtained with RP-SP.

10.4.4 Stress strain tests

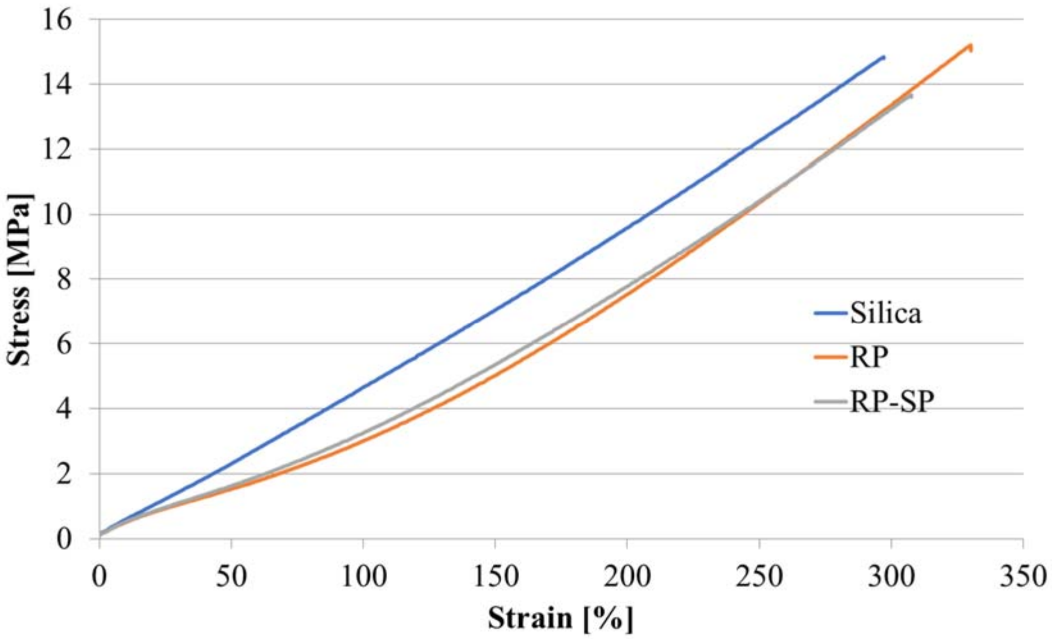


Figure 10.13 – Stress [MPa] vs strain amplitude [%] for composites of **Table 10.7**.

Table 10.10 – Results of strain sweep tests for composites of **Table 10.7**.

	Silica	**RP**	**RP-SP**
σ_{100} (MPa)	4.66	3	3.25
σ_{200} (MPa)	9.59	7.54	7.78
σ_{300} (MPa)	/	13.34	13.24
σ_{300} / σ_{200}	/	1.76	1.70
σ_B (MPa)	14.80	15.04	13.61
ε_B (%)	297.14	330.16	307.63
Energy (J/cm^3)	21.26	21.37	18.56

Stress-strain data and curves show that RP and RP-SP lead to lower stresses at all elongations and to larger elongations at break.

10. 5 Conclusions

Rubber composites based on NR, BR, silica and CB were prepared.

The following comments refer in particular to the effect of functionalization on tensile and dynamic-mechanical properties.

Functionalization of CB with SP led to lower Payne Effect and hysteresis, with respect to the composite with pristine CB..

Fluorinated rubber (FKM) waste, either pristine or functionalized with serinol pyrrole (RP-SP) and octadecyl pyrrole (RP-ODcP), was used in place of either NR and CB or silica.

The use in place of NR/CB led to interesting properties when pristine RP was used, whereas the functionalization of RP led to worse hysteretic properties.

The use in place of silica of RP, either pristine or functionalized, led to good tensile properties, with longer elongation at break, and to lower hysteresis, in particular when RP was functionalized with SP.

All these experimental findings seem to suggest that:

RP (polar rubber (FKM) waste, crosslinked):

(i) can be used to replace NR and CB in a NR/BR, CB/silica compound. Functionalized RP seems to lead to worse results.

(ii) give good tensile and hysteretic properties when used in place of silica. In particular, functionalization with serinol pyrrole further reduces the hysteresis.

SECTION III

EXPERIMENTAL

CHAPTER 11

11.1 Materials

11.1.1 Chemicals

All the following reagents and solvents were purchased by Sigma-Aldrich and were used without further purification: 2,5-hexandione; 2-amino-1,3-propanediol; octadecanamine; methanamine (40% V/V in H_2O; $\rho = 0.897$ g/ cm^3); 3(triothoxysilyl)propan–1-amine; 2-amminoacetic acid.

Deuterated choloform ($CDCl_3$) and dimethylsulfuxide (DMSO-d6) were used to perform ^1H NMR and ^{13}C NMR tests.

Hexane, heptane, cyclohexane, xylene, chloroform, ethyl acetate, acetone, 2-propanol, methanol, glycerol and water (all from Sigma-Aldrich, used as received) were the solvent used for the solubility test.

11.1.2 Carbon blacks

Carbon Black N326

Technical data sheet of Carbon Black N326 (from Cabot) reports:

- BET surface area = 78 m^2/g
- External surface area = 76 m^2/g
- Oil adsorption number = 72 $cm^3/100g$
- Heating loss <= 1.0 %
- Sieve residue 45µm <= 0.05
- Sieve residue 180µm <= 0.01.

Carbon Black N234

Technical data sheet of Carbon Black N234 (from Cabot) reports:

- BET surface area = 112 m^2/g
- External surface area = 110 m^2/g
- Oil adsorption number = 125 $cm^3/100g$
- Heating loss <= 2.5 %
- Sieve residue 45µm <= 0.100
- Sieve residue 180µm <= 0.001.

11.1.3 Fluorinated rubber powder

11.1.4 *Silica Zeosil 1165*

The chemical composition of silica Zeosil 1165 is defined by the ratio 10/1 of SiO_2/H_2O. The product is used in the white micropearl phase. Technical data sheet reports:

- Specific Surface Area = 140 – 180 m^2/g;
- Loss on Drying (2 hours @ 105 °C) <= 8.0 %;
- Soluble Salts (as Na_2SO_4) <= 2.0 %.

11.1.5 Rubbers

Natural poly(1,4-cis-isoprene) (NR) (EQR–E.Q. Rubber, BR-THAI, Eatern GR. Thailandia – Chonburi) had trade name STR20 and 73 Mooney Units (MU) as Mooney viscosity (ML(1+4)100°C).

Butadiene rubber europrene neocis 40 (BR) (Eni) Mooney Viscosity ML 1+4(100 °C) unmassed ASTM D 1646 MU 43 Cis - 1:4 Content Internal Method % 97 min Volatile matter.

11.1.6 Chemicals for elastomeric compounds preparation

The following chemicals have been used for the elastomeric compounds preparation: bis(3-triethoxysilylpropyl) tetrasulfide (TESPT), ZnO (Zinc Oxide), Stearic acid (Sogis), 6PPD ((1,3-dimethyl butyl)-N'-Phenyl-p-phenylenediamine from Crompton), S (sulfur from Solfotecnica), TBBS (N-tert-butyl-2-benzothiazyl) sulfonamide, from Flexsys).

11.2 Synthesis of pyrrole compounds

11.2.1 Synthesis of 2,5-dimethyl-1-octadecyl-1H-pyrrole (ODcP)

0.55 g of octadecanamine (2 mmol) and 0.23 g of 2,5-hexanedione (2 mmol) were poured in a 50 ml round bottom flask equipped with magnetic stirrer. The mixture was left to stir at 130°C for 3 hours. After this time, the reaction mixture was cooled to room temperature. Pure product was obtained yielding 0.5 g (64%).

^1H NMR ($CDCl_3$, 400 MHz); δ (ppm) = 5.81 (s, 2H, $C\underline{H}$), 3.78-3.74 (t, 2H, N-$C\underline{H}_2$-$C\underline{H}_2$), 2.27 (s, 6H, $C\underline{H}_3$), 1.66 (m, 2H, $C\underline{H}_2$-$C\underline{H}_2$-R), 1.37 (m, 2H, $C\underline{H}_2$-CH_3), 1.33 (m, 12H, $C\underline{H}_2$), 0.95 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100MHz); δ (ppm) = 127.27, 105.03, 43.72, 32.01, 31.10, 29.78, 27.05, 22.76, 14.16, 12.51.

11.2.2 Synthesis of 1-(triethoxysilyl)propyl)-2,5-dimethyl-1H-pyrrole (APTESP)

1 g of 3(triothoxysilyl)propan–1-amine (4.82 mmol) and 0.55 g of 2,5-hexanedione (4.88 mmol) were poured in a 50 ml round bottom flask equipped with magnetic stirrer. The mixture was left to

stir at 130°C for 3 hours. After this time, the reaction mixture was cooled to room temperature. Pure product was obtained yielding 0.67 g (43%).

^{1}H NMR ($CDCl_3$, 400 MHz); δ (ppm) = 5.73 (s, 2H, C$\underline{H}$), 3.80 (m, 6H, O-C$\underline{H}_2$), 3.70 (m, 2H, N-C$\underline{H}_2$), 2.20 (s, 6H, C$\underline{H}_3$), 1.71 (m, 2H, CH_2), 1.22 (m, 2H, C$\underline{H}_2$), 0.62 (m, 3H, C$\underline{H}_3$). ^{13}C NMR ($CDCl_3$, 100MHz); δ (ppm) = 127.6, 105.6, 56.1, 51.05, 27.01, 19.2, 13.01, 12.51.

11.2.3 Synthesis of 2-(2,5-dimethyl-1H-pyrrol-1-yl)acetic acid (GlyP)

1 g of 2-aminoacetic acid (0.013 mol) and 1.52 g of 2,5-hexanedione (0.013 mol) were poured in a 50 ml round bottom flask equipped with magnetic stirrer. The mixture was left to stir at 130°C for 3 hours. After this time, the reaction mixture was cooled to room temperature. Pure product was obtained yielding 1.64 g (65%).

^{1}H NMR ($CDCl_3$, 400 MHz); δ (ppm) = 9.68 (1H, COO$\underline{H}$), 5.76(s, 2H, C$\underline{H}$), 4.47 (s, 2H, C$\underline{H}_2$), 2.14 (s, 6H, C$\underline{H}_3$). ^{13}C NMR ($CDCl_3$, 100MHz); δ (ppm) = 173.16, 128.02, 105.50, 45.20, 12.28.

11.2.4 Synthesis of 1,2,5-trimethyl-1H-pyrrole (TMP)

5.51 g of 2,5-hexandione (0.0483 mol) and 3.75 g of methanamine 40% V/V in water (0.0483 mol) were poured in a 100 mL round bottomed flask equipped with magnetic stirrer. The mixture was then stirred (300 rpm), at 130 °C for 4 hours. At the end of the reaction, the mixture was cooled down at room temperature. After the removal of the water, it was obtained 4.3 g of dark amber viscous oil.

^{1}H NMR (CDCl3, 400 MHz); δ (ppm) = 5.80 (s, 2H, CH), 2.24 (s, 6H, CH3), 3.41 (s, 3H, CH3). ^{13}C NMR (CDCl3, 100 MHz); δ (ppm) = 127.6, 105.6, 32.4, 12.8.

11.2.5 Synthesis of 2-(2,5-dimethyl-1H-pyrrol-1-yl)propane-1,3-diol (SP)

5 g of serinol (0.055 mol) and 6.27 g of 2,5-hexanedione (0.055 mol) were poured in a 50 ml round bottom flask equipped with magnetic stirrer. The mixture was left to stir at 150°C for 3 hours. After this time, the reaction mixture was cooled to room temperature. Pure product was obtained yielding 6.55g (58 %).

^{1}H NMR ($CDCl_3$, 400 MHz); δ (ppm) = 2.27 (s, 6H), 3.99 (m, 4H); 4.42 (quintet, 1H); 5.79 (s, 2H). ^{13}C NMR (DMSO-*d*6, 100MHz); δ (ppm) = 127.7, 105.9, 43.72, 71.6, 61.2, 13.9.

11.3 Functionalization procedures

11.3.1 Synthesis of adducts between Carbon Black (CB, N234 or N326) and pyrrole compounds

General procedure

In a round bottom flask there were put in sequence CB (N234 or N326) and acetone. The suspension was sonicated for 15 min, using a 2 L ultrasonic bath. Then the pyrrole compound (PyC) was added (1:10 mass with respect to CB). The resulting suspension was sonicated for 15 min. The solvent was removed under reduced pressure. The black powder of CB/SP was poured into a round bottom flask equipped with magnetic stirrer and was heated at 180°C for 4 h. After this time, the mixture was placed in a Soxhlet extractor and washed with acetone for at least 12 h., then recovered and weighted.

Table 11.1 – Yield of CB-PyC after washed with acetone

Adduct	Yield (%)
CB-ODcP	98
CB-SP	77
CB-APTESP	78
CB-GlyP	82
CB-TMP	65

$$Functionalization\ Yield\ (\%) = \frac{PyC_{after\ washing}}{PyC_{initially\ mixed\ with\ CB}} \times 100 \qquad \text{(Eq.1)}$$

% mass of PyC in CB234-PyC adduct were obtained from TGA analysis, as the mass loss in temperature range from 150°C to 700°C. Data are shown in Table 11.2 below in the text.

Table 11.2 – Mass loss for CB234-PyC adducts, from TGA analysis

Sample Mass loss (%)			
	T < 150°C	**150°C < T < 700°C**	**T > 700°C**
CB234-ODcP	0	9.8	90.2
CB234-SP	1	7.7	91.3
CB234-APTESP	1	7.8	91.2
CB234-GlyP	0	8.2	91.8
CB234-TMP	0	6.5	93.5

11.3.2 Reaction between recycled rubber powder (RRP) and pyrrole compounds

5g of RRP were dispersed with 120 ml of acetone in a 250 ml one-neck round-bottomed flask and sonicated in an ultrasonic bath for 15 minutes. A solution of SP in acetone (0.36 g in 30 ml of acetone) was added and the resulting suspension was sonicated again for 15 minutes. After removing the solvent under reduced pressure, the reaction mixture was heated at 130°C for 3 hours under stirring (350 rpm) and then cooled to room temperature. After this time, the mixture was placed in a Soxhlet extractor and washed with acetone for at least 12 h., then recovered and weighted.

IR spectrum of the product was recorded using ATR technique.

IR (ATR), λ(cm^{-1}): 3370-3330, 2970, 1638, 1579, 1444, 1153, 1045, 1008, 978, 750.

11.4 Tire compounds

11.4.1 Standard procedure for the preparation of elastomeric compounds

Natural rubber and butadiene rubber were fed into a Brabender® internal mixer and masticated at 145 °C for 1 minute. Then silica and silane TESPT were added at T=145°C and mixed for 4 minutes. The obtained composite was discharged at T=145°C. The temperature of the internal mixer was then set to 80°C, and the composite obtained in the first step was charged and mixed for 1 minute. At that point, CB (as it was or modified with PyCs) or RRP (as it was or modified with PyCs) were fed and mixed for further 4 minutes, then the composite was discharged at T=80°C. The composite thus prepared was then fed into the internal mixer at 50 °C, masticated for 1 minute, then stearic acid, zinc oxide and 6PPD were added and mixed for 2 minutes. Finally, TBBS and sulfur were added and mixed for 2 minutes.
The composite was then unloaded at 50 °C.

Table 11.3 – Recipe of composite with CB

Ingredients [a]	**Density**	**Blank test**	**CB-SP**	**CB-ODcP**
	[g/cm^3]	[phr]	[phr]	[phr]
Natural rubber [SIR20]	0.92	50.0	50.0	50.0
Butadiene rubber [Neocis 40]	0.91	50.0	50.0	50.0
Carbon Black N234	1.80	25.0	5.0	5.0
CB N234-PyC (10 mass%)	1.80	0.0	22.0	22.0
CB		*25.0*	*20.0*	*20.0*
PyC		*0.0*	*2.0*	*2.0*
TESPT	1.08	2.0	2.0	2.0
SiO_2 Zeosil 1165	2.10	25.0	25.0	25.0

[a] Other ingredients for all composites in phr: zinc oxide 4.0, stearic acid 2.0, 6PPD 2.0, sulfur 1.5, TBBS 1.8.

Table 11.4 – Recipe of composite with RP

Ingredients [a]	**Density**	**Blank test**	**RP-SP**	**RP-ODcP**
	[g/cm^3]	[phr]	[phr]	[phr]
Natural rubber [SIR20]	0.92	50.0	50.0	50.0

Butadiene rubber [Neocis 40]	0.91	38.0	38.0	38.0
Recycled Rubber Powder	2.02	18.0	0.0	0.0
RRP-PyC (10 mass%)	2.02	0.0	20.0	20.0
NR		*12.0*	*12.0*	*12.0*
CB		*6.0*	*6.0*	*6.0*
PyC		*0.0*	*2.0*	*2.0*
CB N326	1.80	19.0	19.0	19.0
TESPT	1.08	2.0	2.0	2.0
SiO_2 Zeosil 1165	2.10	25.0	25.0	25.0

[a] Other ingredients for all composites in phr: zinc oxide 4.0, stearic acid 2.0, 6PPD 2.0, sulfur 1.5, TBBS 1.8.

Table 11.5 – Recipe of composite with Silica

Ingredients [a]	**Density**	**Silica**	**RP**	**RP-SP**
	[g/cm^3]	[phr]	[phr]	[phr]
BR Neocis	0.91	50	50	50
NR (SIR20)	0.92	50	50	50
CB N234	1.80	25	25	25
Silica (Zeosil 1165 MP)	2.1	25	15	15
Rubber Powder (RP) (μ = 0.5)	2.02	0	10	0
RP-SP	2.02	0	0	10
TESPT	1.08	2	2	2
Stearic Acid	0.85	2	2	2
ZnO	5.55	4	4	4
6PPD	1	2	2	2
TBBS	1.32	1.8	1.8	1.8
Sulphur	2	1.5	1.5	1.5

11.5 Characterization techniques

11.5.1 Thermo-gravimetric analysis

TGA test under flowing N_2 (60mL/min) were performed with a Mettler TGA SDTA/851 instrument according to the standard method ISO9924-1. Samples (10 mg) were heated from 30 to 300°C at 10°C/min, kept at 300°C for 10 min, and then heated up to 550°C at 20°C/min. After being maintained at 550°C for 15 min, they were further heated up to 700°C and kept at 700°C for 30 min under flowing air (60 mL/min).

11.5.2 *Attenuated Total Reflectance (ATR)*

The IR spectra were recorded in transmission mode (128 scan and 4 cm−1 resolution) placing a small amount of powder sample in a Diamond Anvil Cell (DAC) using a ThermoElectron Continuμm IR microscope coupled with a FT-IR Nicolet Nexus spectrometer.

11.5.3 Nuclear Magnetic Resonance (NMR)

11.5.3.1 ^1H NMR

The NMR spectra were recorded on a Bruker AV 400 (400MHz). To record ^1H NMR spectra it was used a 5 mm multinuclear probe with reverse detection. 64 scans were used with an acquiring time of 6 minutes. Chemical shifts were reported in ppm with the solvent residual peak as internal standard (DMSO-d6: $\delta_H = 2.50$ ppm, $CDCl_3$: $\delta_H = 7.26$ ppm)

11.5.3.2 ^{13}C NMR

The NMR spectra were recorded on a Bruker AV 400 (400MHz) equipped with a 5 mm multinuclear probe with reverse detection was used to record ^{13}C NMR spectra, 1400 scans and an acquiring time of 15 minutes.

11.5.4 Sonication

A 2L ultrasonic bath (power 260 W) from Soltec Ultrasonic Cleaner was used.

11.5.5 Soxhlet extraction

Every adduct between pyrrole compounds and both CB and RRP was washed using a Soxhlet extractor. In this discontinuous process, acetone (used as solvent) was put into the boiling flask, and it was evaporated and re-condensed thanks to the distillation column above. The condensed acetone flows through a thimble (made of thick filter paper) where the solid powder is. The chamber containing the solid material which requires extraction, is connected to the boiling flask below by a syphoning mechanism, which allows the chamber to fill to a point, at which it will empty its contents and start to fill again, and the extracted compounds will accumulate in the boiling flask below. This process was applied to every adduct for at least 12 hours.

11.5.6 UV-Vis analysis – Sample's preparation and characterization

Dispersions of CB-PyC adducts were prepared at different concentrations: 1 mg/mL; 0.5 mg/mL; 0.25 mg/mL; 0.1 mg/mL. Each dispersion was sonicated for 30 min using an ultrasonic bath (260 W) and subsequently UV-Vis absorption was measured.

Suspension of adduct (3 mL) was placed by pipette Pasteur, in quartz cuvettes of 1 cm optical path (volume 1 or 3 mL) and analyzed by a Hewlett Packard 8452A diode array spectrophotometer, firstly resetting the instrument with the pure solvent (as background) and then acquiring the UV spectrum from 200 to 900 nm. The UV-visible spectrum reported intensity of the absorption as a function of the wavelength of the radiation between 200 and 750 nm, with a typical maximum peak at 300 nm.

UV-Vis absorption analysis was performed on dispersions of CB-PyC adducts with 0.1, 0.25, 0.5 and 1 mg/mL as adduct concentrations. The solvent used was ethyl acetate, which was able to form stable suspensions with all the adducts tested.

These UV-Vis analyses permitted to obtain a calibration curve for every adduct tested, considering UV absorption at 300 nm.

11.6 Calculation of Hansen solubility sphere and Hansen solubility parameters

The calculation of the Hansen solubility parameters (HSP) for carbon black was performed applying the Hansen solubility sphere representation of miscibility. The idea at the basis of this geometrical approach is the calculation of the cohesive energy density (UT/V) of a compound as the sum of three interaction contributions, as given by equation 2; dispersion (non-polar van der Waals forces) (δ_D), polar (δ_P), and hydrogen bonding (δ_H).

$$\frac{U_T}{V} = \delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \qquad \text{Eq. (2)}$$

The compound is therefore identified by three coordinates (δ_D, δ_P, and δ_H) in the Hansen parameters space. The distance between points (e.g a solute and its solvent) is related to their cohesive energy density difference, which is related to the enthalpy of mixing. As the enthalpy of mixing is minimal for miscible substances, two points close to each other in the Hansen space correspond to miscible compounds.

To estimate the HSP of a solute i, a dispersion test is performed on different solvents j, distinguishing good solvents (providing stable solutions/dispersions) and bad solvents, which are not able to give stable dispersions. Given the parameters (coordinates) of the solvents, it is possible to define a sphere, centered on the solubility parameters of the solute, which encompasses the good solvents points and excludes the non-solvents.

The sphere radius is defined as R_0, the radius of interaction, while the distance between the solute and the solvent is Ra, calculated as in Equation 3.

$$R_{a,ij}{}^2 = 4(\delta_{D,i} - \delta_{D,j})^2 + (\delta_{P,i} - \delta_{\mathrm{P},j})^2 + (\delta_{H,i} - \delta_{H,j})^2 \qquad \text{Eq (3)}$$

The ratio between Ra,*ij* and R_0 is defined in Equation 4 as RED, relative energy difference. Solutes and solvents with good affinity have relative energy difference lower than 1.

$$RED = \frac{R_{a,ij}}{R_o} \qquad \text{Eq (4)}$$

An optimization problem is therefore defined: the center coordinates of the Hansen solubility sphere are calculated by minimizing the radius of interaction (i.e. the distance from the coordinates of the good solvents), including the good solvents (RED<1) and excluding the bad ones. The sphere center coordinates correspond to the three unknown HSP of the solute.

The fitting sphere program was adapted from and solved in Matlab environment using the Nelder-Mead simplex algorithm.

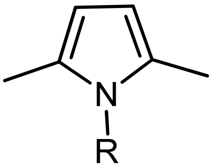
SECTION IV

CONCLUSIONS

CONCLUSIONS

The present thesis was focused on “circular economy”, in particular on rubber products and, in particular, on wastes coming from the industrial production of fluorinated rubbers.

An innovative approach was studied for building a new cradle for rubber products at the end of the first life, named in this thesis “Powder Rubber” (RP). This approach was based on the functionalization of the carbon black contained in RP with an innovative class of chemicals, pyrrole compounds (Py) coming from the Paal Knorr reaction of a primary amine with 2,5-hexanedione, whose chemical structure is reported as follows.



Functionalization was aimed at achieving a better compatibilization of RP, used as ingredient in new rubber composites.

In the first part of the research activity, carbon black was succesfully functionalized with various PyC, obtaining high functionalization yield.

The Hansen solubility parameters of the CB/PyC adducts were estimated by assessing the compatibility of the adducts in a series of solvents and applying an elaboration method. It was found that functionalization led to the substantial modification of the solubility parameters of the carbon allotrope.

Functionalization was then performed of different samples of rubber powder: (i) two samples of reclaimed rubbers, coming from milling in the presence of terpenes and from cryomilling (ii) the sample of industrial waste of fluorinated rubber. Functionalization was successful.

The waste of FKM was used in rubber composites based on diene rubbers, CB and silica, either in place of NR/CB or in place of silica. It was found that this RP based on FKM give positive results in both types of compounds, that means by applying both types of replacements. For the replacement of NR/CB, best results were obtained with RP without functionalization. In particular, lower Payne effect was obtained for the rubber composite. For the replacement of silica, best results were achieved with RP functionalized with serinol pyrrole. In particular, lower hysteresis was obtained in the presence of good tensile properties. It seems that the compatibilization of the RP based on FKM compound, thanks to the functionalization with a polar molecule, gives the best performances when RP is used in place of a polar filler such as silica.

Main objectives of the present thesis were:

☞ to use the fluorinated rubber waste in place of either a rubber (natural rubber) or in place of silica in a rubber composites based on diene rubbers

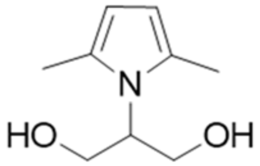
☞ to functionalize the rubber powder, to improve its compatibility in the rubber composite, replacing either a rubber (natural rubber) or silica also with the functionalized rubber waste.

In previous studies performed by the research Group where I made my thesis, functionalization of sp^2 carbon allotropes was performed with pyrrole compound (PyC) prepared from a primary amine and 2,5-hexanedione [1, 2]. The chemical structure of the pyrrole compound is shown in the Figure below.

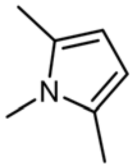
The functionalization method was found to be indeed sustainable: no solvent or catalysts were used, reagent and the carbon allotrope were simply mixed and energy (thermal or mechanical) was given. Functionalization yield was very high. Solubility parameters of the carbon allotropes were modified.

In a previous thesis [3], promising results were obtained by functionalizing the rubber powder coming from ground tyre rubber.

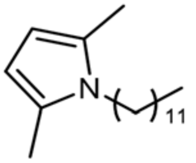
In this thesis, the first step of the activity was the preparation of pyrrole compounds. They were:



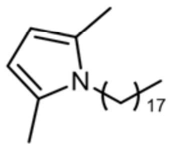
serinol pyrrole
(SP)



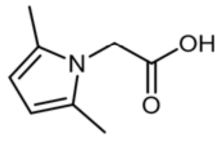
trimethyl pyrrole
(TMP)



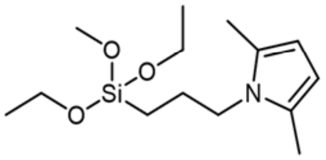
dodecyl pyrrole
(DDcP)



octadecyl pyrrole
(ODcP)



glycil pyrrole
(GlyP)



3 – (triethoxysilyl) – 1H pyrrole
(APTESP)

Then, functionalization of carbon black with these PyC was performed. The functionalization yield was determined.

Experimental activity was performed in order to estimate the solubility parameter. Dispersions of carbon black adducts with pyrrole compounds were prepared in different solvents. Calculation of Hansen solubility parameters was made by applying a method developed in the Group. Characterization of the adduct was performed.

Functionalization was then performed on Powder rubbers coming from different sources. Two of them were form commercial sources: Austin’s Rubber, Lehighs Rubber. Moreover, fluorinated rubber wastes were from a private company. Due to confidentiality reasons, we were not allowed to have information on the original commercial source of the fluorinated rubber.

Rubber composites were prepared, by replacing with the fluorinated rubber waste either a rubber (NR) or a filler (silica). The waste was either pristine or functionalized with either SP or DDcP. Objective was the investigate if the RP could be suitable to replace either a rubber or a filler and if the functionalization could promote the compatibility with the rubber matrix.

In this thesis different techniques and analysis were used, such as: ^{1}H NMR analysis, ^{1}C NMR analysis, Thermogravimetric analysis (TGA), Fourier Transformed Infrared Spectroscopy (FTIR), UV – Vis spectroscopy, Brunner – Emmett – Teller analysis (BET), Solubility tests, Contact angle.

List of tables

List of figures

Figure 10.9 – Loss modulus G” [MPa] versus strain amplitude [%] for rubber compounds containing: 20 phr of pristine RP (blue curve); 25 phr of pristine CB (purple curve); 22 phr of RP-SP (10 mass%) (red curve); 22 phr RP-ODcP (10 mass%) (grey curve).

Figure 10.10 – Tan delta versus strain amplitude [%] for crosslinked composites of **Table 10.4.**

Figure 10.11 – Rheometric curves obtained at 170°C for rubber compounds containing: 25 phr of pristine silica Zeosil 1165 MP (blue curve); 10 phr of pristine silica + 15 phr of pristine RP (red curve); 10 phr of pristine silica + 15 phr of RP-SP (grey curve).

Figure 10.12 – Dynamic compression tests. In the left: E’ [MPa] vs temperature [°C]; In the right: tan delta vs temperature [°C] for rubber composites of **Table 10.7**.

Figure 10.13 – Stress [MPa] vs strain amplitude [%] for composites of **Table 10.7**.

List of abbreviations

^{1}HNMR: Nuclear Magnetic Resonance Spectroscopy
APTESP: triethoxysilyl pyrrole
ATR: Attenuated Total Reflectance Infrared spectroscopy
BC: Rubber Improved Bitumen
BET: Brunner-Emmett-Teller analysis
BMAVC: Rubber Modified Bitumen with High Viscosity
BMC: Rubber Modified Bitumen
BR: *Butadiene Rubber*
CB: Carbon Black
DDcP: Dodecyl pyrrole
ELTs: End – of –life tires
EPR: Extended Producer Responsibility
FKM: Fluorinated Rubber Waste
FTIR: Fourier Transformed Infrared Spectroscopy
GlyP: Glycil pyrrole
IR: Isoprene rubber
NR: Natural Rubber
ODcP: Octadecyl pyrrole
OTR: Off-The-Road
PBR: Polybutadiene rubber
PyC: Pyrrole Compound
RP: Rubber Powder
RP1: Austin's Rubber
RP2: Lehigh's Rubber
RP3: FKM Rubber waste
RRP: Reclaimed Rubber Powder
SBR: Styrene-butadiene rubber
SCF: Supercritical Fluids
SP: Serinol pyrrole
TGA: Thermogravimetric analysis
TDF: Tyre derived fuel
TMP: Trimethyl pyrrole

ACKNOWLEDGEMENTS

This work was carried out during my stay as a Master of Science student for Environmental and Land Planning Engineering at the Polytechnic University of Milan.
At facing the finishing time of my internship, I have to express my appreciation to all people who helped, supported and accompanied me to complete this work.

First of all, I have to express my sincere appreciation and gratitude to Professor Maurizio Stefano Galimberti who gave me a chance to be under his supervision in my research work. Always, he had an open door and was passionate, creative, generous, and helpful. I have to appreciate him for his excellent support and patience during the past years.

I place on record, my special thanks to Dr. Andrea Bernardi, for his supports and kind attentions to me to carry out my work on laboratory. This work was not possible without his support. He has given me a lot of favors and helped me with all he could whenever I needed.

Life without surrounding friends is nothing. Therefore, I take the opportunity to thank the help and enjoyment received from my colleagues and friends during this course of study. Fruitful discussions, encouragement and entertaining times are considered as all supporting forms which contribute to this work.

I am extremely grateful to all beloved members in my family. Unconditional love and support throughout my life can always be received from my solid backing, my parents who I could not be where I am without them. I can hardly find meaningful words to appreciate my parents. They gave me everything they ever could and supported me in every phase of my life. I will never forget their great encouragement and strong back at all levels. Words cannot express the magnitude of my gratitude to my beloved siblings for their constructive help and guide.

This work was not possible without the support and accompanying of my lovely husband. His sacrifices and encouragement have been the most important and powerful motivator to my work. I would like to express my honest and eternal gratitude towards him for his understanding, help and patience during the past years. I never forget his encouragement and strong back at all levels.