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Dissertation

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Recycling of EPDM Rubber Waste Particles by Chemical Activation with Liquid Polymers

von

Ana-Maria Lepadatu
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I dedicate this work to my grandma Maria

“Some people come into our lives and quickly go. Some stay for a while, leave footprints on our hearts, and we are never, ever the same.”

Flavia Weedn (1929-2015)

“Here, where the land ends and the sea begins...”

Luís de Camões (ca. 1525-1580)

Promotionskommission:

Hauptberichterstatter: **Prof. Dr. Uwe Beginn**
University of Osnabrück

Zweitbericherstatter: **Prof. Dr. habil. C. Simona Asaftei**
University of Applied Sciences Osnabrück

Weitere Mitglieder: **Prof. Dr. Norbert Vennemann**
University of Applied Sciences Osnabrück

Dr. Dietrich Steinmeier
University of Osnabrück

This doctoral thesis was carried out at University of Osnabrück, Institute of Chemistry of New Materials, Faculty of Biology/Chemistry, Organic Materials I under the supervision of Prof.Dr. habil. C. Simona Asaftei and Prof. Dr. Uwe Beginn.

The experimental work was performed in the period from April 2011 to March 2015.

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Chapter 1

General Introduction

"The starting point of all achievement is desire."
Napoleon Hill (1883 – 1970)

This chapter introduces the general problem concerning the demand for efficient rubber recycling methods with special emphasis on ethylene-propylene-diene rubber (EPDM). A short description of EPDM rubber, its properties and applications is given. The concept and the objectives of this research are presented and the structure of the thesis is outlined.

1.1 THE DEMAND FOR RUBBER RECYCLING

Due to the extensive utilization of rubber in various applications, the recycled rubber market presents a high development potential in the recycle research area. Although the main attention in the recycling research is focused on rubbers used in the tire industry, due to their extensive utilization in the market, non-tire rubbers, such as EPDM rubber, are also of great importance in the recycling industry. For instance, EPDM rubber is used in the Federal Republic of Germany in large quantities, more than 100 000 tonnes/year, for the manufacture of flexible sheets, hoses, cable insulation and processed seals. [1,2] EPDM represents 7% of total synthetic rubber consumption and is one of the most widely used non-tire rubber and possessing the highest annual growth rates. [1-3]

Since a further increase in rubber demand and production is expected and in order to keep the rubber industry functional, it is essential that waste management infrastructure develops accordingly. This has become a major issue in many countries, especially in developing ones, where one of the most used methods was to discard the post-consumer rubber waste in landfills. As a result of this practice, fields with discarded rubber waste became breeding areas for insects, especially mosquitoes, carriers of various diseases, such as malaria.

Due to these serious environmental problems, the 2006 EU Landfill Directive [4] has restricted this route of disposal. Further European legislation concerning waste management [5] was adopted with the aim to prevent and limit pollution from incineration and co-incineration of waste.

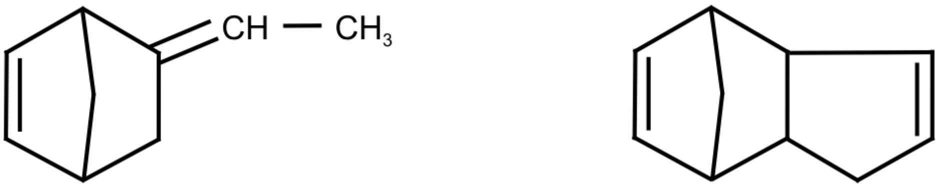
Taking the new EU directives into consideration, the development of new technologies and better recycling methods is required. Although various approaches have already been studied, the main drawback of these methods is the limitation of using high amounts of recycled rubber for obtaining high quality rubber products. [6] Since the recycling processes used for natural rubber (NR) has not been successfully applied to the synthetic rubber, i.e. EPDM, efforts in finding more efficient routes should be investigated.

1.2 ETHYLENE – PROPYLENE – DIENE RUBBER

EPDM is a synthetic rubber terpolymer consisting of ethylene (E), propylene (P) and a third monomer which is a diene (D). The letter M in EPDM rubber denotes a rubber with a saturated chain that is a polymethylene type, i.e. it has repeated ($-CH_2-$) units in the backbone of the polymer. [7]

Almost 40 years ago, when it was first introduced on the market, EPDM was predominantly produced using the coordination polymerization technique in aliphatic hydrocarbon solvents (e.g. pentane, hexane) which is based on the Ziegler Natta catalysis. Vanadium salts (VCl_4, $VOCl_3$) were used as catalyst and aluminium alkyl halide such as Et_2AlCl or $Et_3Al_2Cl_3$ as co-catalyst. Later a new technology was developed for the production of EPDM using a metallocene catalyst in solution or in a gas phase reactor. [8] This technology allows not only for the recovery of propylene and diene, but also for the recovery of the ethylene used in the process. Using this technology, polymers with uniform molecular architecture and better properties than those obtained using Ziegler Natta catalyst are obtained.

A wide variety of dienes has been studied [9] as a third monomer, of which nowadays only two are commercially used, 5-ethylidene-2-norbornene (ENB) and dicyclopentadiene (DCPD) as shown in Figure 1.1, the most common of these is ENB. The non-conjugated dienes monomers contain two olefin units. One is used in the terpolymerisation reaction with ethylene and propylene and the other, from the side chain, serves as crosslink when curing with sulphur or resin. In the peroxide vulcanisation, the diene monomer acts as coagent allowing for a faster attack of radicals on the remaining double bond. The amount of diene added is between 0.5 and 12%. [10] In comparison with other termonomers used, ENB presents a high rate of polymerisation and is very active with respect to sulphur vulcanisation. The chemical structures of the termonomers are shown in Figure 1.1.



ENB

DCPD

Figure 1.1 Commercial dienes used as termonomer in EPDM

Since its introduction in the early 1960’s, EPDM is the most widely used and highly developing synthetic rubber, occupying the third place in the synthetic rubber consumption after styrene butadiene and butadiene rubber. The chemical formula of EPDM with ENB as a third monomer is presented in Figure 1.2.

The weight ratio of ethylene to propylene, from the main chain of the polymer, can vary between 45:55 and 75:25. Usage of high ethylene content (over 60 wt %) produces polymers with a partially crystalline structure, better tensile strength and hardness, lower glass-transition temperature, better extrusion and mixing characteristics.

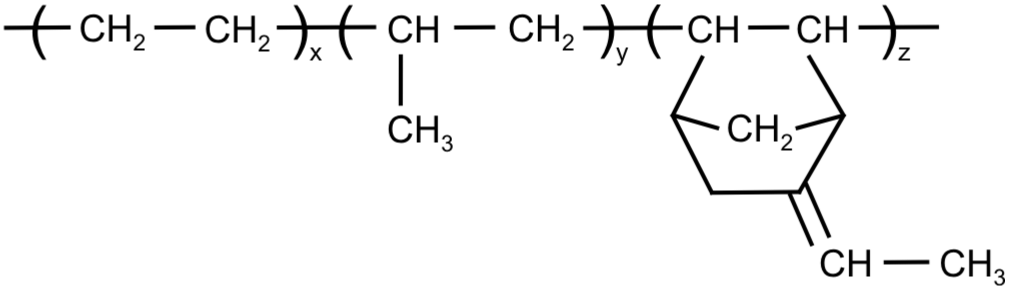


Figure 1.2 Chemical structure of EPDM with ENB

1.2.1 *EPDM – Properties and Applications*

The properties of EPDM rubber are influenced by the molecular weight, molecular weight distribution, ethylene/propylene ratio and the content and type of unsaturation given by the termonomer. These parameters can be manipulated during the operation condition in the production process according to an end-use application of the final material.

General properties of the EPDM rubber include:

- excellent weather resistance;
- excellent resistance to polar fluids like alcohols, acetates, ketones and certain esters;
- resistance to water and aqueous solution;
- very good heat, oxygen and ozone resistance due to the absence of unsaturated bonds in their polymer backbones;
- high filler and plasticizer loading capacity that is still able to give good processability and properties of the final product;
- the ability to be crosslinked by conventional sulphur vulcanisation due to carbon-carbon unsaturation from the side chain given by the third monomer;
- good low temperature flexibility;
- excellent electrical properties;
- classification as non-hazardous;

Besides the main properties of the EPDM-rubber, the quality of the final products is also influenced by the other ingredients used in the formulation recipe, e.g. type and amount of: filler, oil, curing system and other processing aids.

EPDM are synthetic rubbers that are widely used where their heat and weathering resistance is required. Their primary application, in terms of EPDM utilization, is in the non-tire automotive sector such as: radiator and heater hoses, belts, body and chassis parts, cable insulation, seals, weatherstrips and mats. Polymer modification, sealing and fitting systems, building and construction, wire and cable insulation, lubricant additive, moulded goods, etc. are other fields where this type of rubber is required and used.

1.3 CONCEPT AND OBJECTIVES OF THE THESIS

The work in this thesis responds to the demand for an efficient recycle method for EPDM rubber waste. A solvent-free chemical activation method to recycle EPDM rubber waste which provides high-quality recycled products, despite of the high amount of recycled particles used as a substitute of the raw material, was developed. The process needed to be both environmentally sustainable and applicable on an industrial scale without requiring special equipment. The final aim of this project was to use the activated particles in the production of seals and sealing systems on an industrial scale. In order to demonstrate the potential of the activated particles as a substitute for the raw material, aspects were investigated including:

(1) characterization of the EPDM rubber waste particles;
(2) optimization of the ratio between the waste rubber particles and the low molecular weight polymers;
(3) investigation of the influence of various amounts of curing system;
(4) study of the effect of the diene and ethylene percentage contained by the low molecular weight polymer used for activation of the particles;
(5) investigation of the influence of the amount of activated particles used as substitute of the raw material;
(6) study of the type of curing system used and
(7) application of the process on an industrial scale.

In order to achieve this, the recycling of EPDM rubber waste particles by means of chemical activation using low molecular weight polymers (liquid polymers) was investigated. These liquid polymers are highly compatible with the waste rubber particles from the EPDM rubber and also suitable for sulphur vulcanisation. In comparison with other methods used for recycling of rubber and when considering environmental and economic aspects, chemical activation at the surface particle using low molecular weight polymers offers great recycling potential.

A schematic representation of this method is presented in Figure 1.3. The waste particles are activated using liquid polymers and a curing system. These activated particles can be further vulcanised or used together with the raw material as a substitute and subsequently vulcanised.

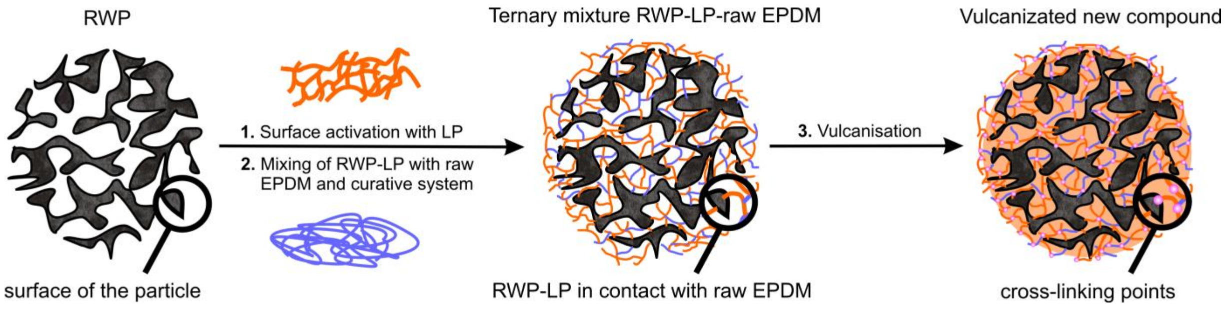


Figure 1.3 Schematic representation of chemical activation of EPDM rubber waste particles (RWP) using liquid polymers (LP)

1.4 STRUCTURE OF THE THESIS

Chapter 2 introduces the various methods of rubber recycling used over the years with a particular focus on EPDM rubbers. The motivation of the thesis is presented as well.

In **Chapter 3,** the activation of the EPDM rubber waste particles by means of low molecular weight polymers is described. First, the EPDM rubber waste particles are characterised. Secondly, the optimisation of the ratio between the waste rubber particles and the low molecular weight polymers is investigated, and thirdly, the amount of curing system is studied.

Chapter 4 investigates the influence of four different types of activated EPDM rubber waste particles used as a substitute for the raw material. The influence of the diene and ethylene amount contained in the liquid polymers used for activation of rubber waste particles was studied in order to determine which polymers are more suitable to be used for further applications, i.e. seals and sealing systems. The activated particles were used to substitute the raw material from 25 vol% up to 75 vol%.

Chapter 5 is focused on the type of curing system used. In this case, two types of accelerators were applied and studied. The goal was to obtain materials with advantageous vulcanisation parameters and desired mechanical properties.

Chapter 6 reports an application study on an industrial scale using recycled particles as substitute of the raw material. The batch experiment was performed using a Co-Kneader and the raw material was substituted by activated particles with 25 vol% and 50 vol%, respectively. Furthermore, the material was vulcanised using the injection moulding technique. The quality of the products was evaluated and compared with a reference product.

Chapter 7 draws together the final conclusions of this thesis. Some suggestions and recommendations for future research are given.

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Chapter 2

A Literature Overview of Rubber Recycling Methods

> *"Look up at the stars and not down at your feet. Try to make sense of what you see, and wonder about what makes the universe exist. Be curious."*
> *Stephen Hawking (1942 –present)*

A comprehensive study of various methods of rubber recycling, in general is outlined in this chapter. A particular emphasis is put on the recycling of the EPDM rubber. Among the various methods presented in the literature the most efficient approach is the application of a solvent - free chemical surface activation by means of low molecular weight polymers. The motivation of the present research project is presented.

2.1 INTRODUCTION

With the discovery of sulphur vulcanisation by Charles Goodyear in 1839 the rubber industry evolved very fast and consequently the problem of rubber recycling emerged. The problem arises from the fact that rubbers are chemically crosslinked materials that can neither be molten, nor be dissolved. In comparison with other types of waste, rubber waste represents a very important issue since the vulcanisation process increases its durability, resulting thus in a very slow degradation once it is discarded. As an alternative to natural rubber, during The First and Second World War Germany and USA started to produce synthetic rubber. As a consequence of the extensive use of rubber for a wide range of applications an exponential growth of the post-consumer and production waste is unavoidable, becoming a major concern. Since the variety of rubber types is very broad and the production of end rubber products is more durable and sophisticated, finding a suitable approach to recycling represents a great challenge.

The worldwide production of EPDM rubber in 2009 was about 1.2 million tonnes [1] with an expected increase of production capacity after 2015 of more than 1.65 million tonnes. [2] The highest consumption of EPDM rubber is in the automotive industry, followed by polymer modification, roofing material, electrical cable and wire, oil additives and others. Table 2.1 presents the most important methods used in rubber recycling. Retreading and reuse of the used tires in other applications, such as civil engineering and agricultural purposes, represent the simplest and uncomplicated approach applied to rubber recycling. Retreading is the method by which the tyre carcasses are passed through a recapping system where the old tread of a used tire is replaced by a new one. The replacement with a new tread can be applied up to three times before the tire can finally be discarded. Nevertheless, this approach produces tires with lower quality than new tires, therefore presenting a low market potential.

Table 2.1 Methods used in rubber recycling

Repeated use	Retreading Re-use in other applications
Energy recycling	Incineration
Feedstock recycling	Pyrolysis Gasification Hydrogenation
Material recycling	Grinding Reclaiming Surface activation of the particles

Re-use as whole tires or tire parts in artificial reefs, crash barriers, fenders, footwear, playground equipment and rubberized pavements are just few examples of how the discarded tires can be used. In countries such as New Zealand, Australia, USA and Japan millions of discarded tires are used to create artificial reefs. [3] However, some of these applications can lead sometimes to higher costs [4] or may cause environmental problems. [5]

Hereafter the methods used for rubber recycling will be presented, with focus on EPDM rubbers. In comparison to repeated use, these methods present greater potential in achieving better properties of the recycled product, which increases their potential to be applied in high quality products.

2.2 ENERGY RECYCLING

Energy recycling is the process by which the energy recovered from waste materials is converted into electrical or thermal energy. The energy content of tire-derived fuel (TDF), which is about 32-36 MJ/kg, exceeds that of coal (30 MJ/kg) or wood (10 MJ/kg), while the production of sulphur oxide is the same or less than coal when burned.[6] The energy recovered from TDF represents only one part of the energy consumed in the production of the tire rubber industry.[7] The caloric value generated in the tire incineration process is widely used as a fuel supplement for coal or gas in cement kilns, pulp and paper mills, power stations or rubber processing. In the USA a high quantity of TDF is used in cement plants to obtain clinker, which represents the primary component for the production of Portland cement. The energy cost per kWh for TDF is the lowest (0.0086 €) in comparison with coal (0.0155 €) or wood (0.0146 €).[6] However, due to the smoke emissions produced during the process, the total amount of tire-derived fuel consumption shows a decreasing trend of about 33% between 2005 and 2011.

2.3 FEEDSTOCK RECYCLING: RECOVERY OF THE RAW MATERIALS

Various recycling technologies have been developed employing processes that convert waste rubber into petroleum feedstock or raw materials. These processes are aimed at material recovery by transforming the waste into basic chemicals. The most common processes used as feedstock recycling are:

- Pyrolysis
- Hydrogenation
- Gasification

Pyrolysis

Pyrolysis can be defined as an irreversible thermo-chemical decomposition of an organic material into low molecular weight products, in the absence of oxygen or air, using elevated temperatures within 400 °C to 800 °C. The typical products recovered by pyrolysis of waste rubber are usually pyrolytic char, oil and gas fraction, while the polymeric structure is lost. Yields, composition and quality of these products depend on process parameters values (temperature, heating rate, pressure, residence time, material granulometry) and on the volatile fraction condensation temperature. [8] The yield of gas, light oil fraction and char increases with increasing pyrolysis temperature, whereas the yield of the tar fraction decreases. [9]

The char obtained from the thermal conversion of waste rubber is a blend of carbon black, ash and other inorganic materials, such as zinc oxide, carbonates and silicates. [10] The pyrolytic carbon black has a lower quality. Therefore it is normally upgraded before being used, e.g. by a treatment using steam [11] and carbon dioxide, [12] or mixed in combination with original carbon black and used as a filler in rubber blends. [13] The gas fraction and oil can be used as fuel in the pyrolysis process and to enable the separation and purification of other fractions. [3,13]

Hydrogenation

In the process of hydrogenation the rubber scrap is converted in oil and gas products in the presence of hydrogen using a temperature between 350 °C and 425 °C. [14,15] Materials such as steel and textiles are removed before applying the process. By increasing temperature and reaction time the total conversion is not affected but the oil yield decreases. [16]

Gasification

Gasification is a thermal process which occurs in a higher temperature range than pyrolysis and hydrogenation, i.e. 480 – 1600 °C with very little air or oxygen. In this process rubber waste is converted mainly in gaseous products such as methane, CO and hydrogen, together with small amounts of tar and charcoal as by–products. Hydrogen is considered to play an important role in future energy systems. By applying catalytic stream gasification at high temperatures a great yield of hydrogen can be obtained from waste tyres. [17,18]

2.4 GRINDING AND SIZE REDUCTION TECHNOLOGY

In rubber recycling technologies reduction of the average size of the rubber waste parts is a useful and widely used preliminary step. The process applied is established according to the requirements of the final product, such as particle size and particle size distribution, morphology and purity of the rubber powder. The processes used for this purpose depend on the equipment (e.g. knives, shredders, granulators, extruders, rotary mills, disc grinders, hammer mills) and the grinding conditions (ambient, wet or cryogenic). [7]

2.4.1 Cutting and Shredding

Cutting is considered a preliminary comminution step by which the vulcanised rubber is reduced to pieces of about few centimetres in size. The devices used for the cutting process are mechanical and hydraulic knives. Because of the high wear of the cutting equipment the processes used on a larger scale are based on a combination of cutting and shredding. [19] The next step used in comminution of the material is shredding. The equipment widely used for tire shredding is a rotary shear shredder with two counter-rotating shafts that work at a low speed of about 20-40 rpm and high torque. [20]

2.4.2 Ambient grinding

The ambient grinding is a mechanical process by which shredded vulcanised rubber pieces are further grounded to a smaller particle size of about 10 to 30 mesh (0.5 to 2.0 mm) using granulators, rotary mills, extruders or cracker mills. By using the ambient grinding process particles with a rough surface, an irregular shape and a higher surface area relative to the cryogenically produced particles are obtained. It is as well possible that due to the temperature and shear effects the surface of the powder is partially devulcanised. [7] The smaller the particle size, the higher the price of the ground rubber.

2.4.3 Wet grinding

Wet or solution process grinding is a modified process of the dry grinding during which water is usually used as a liquid medium. In this process the coarse ground rubber particles are grinded between two grinding wheels which are continuously sprayed with water to ensure the cooling of the powder. After the grinding process the particles are separated from the water and dried. [6] In a study regarding the effect of various ground rubber tire (GRT) materials in ground rubber/LLDPE blends it was shown that wet ambient ground rubber GRT based composites give particles with better impact energy and higher surface oxidation in comparison with cryogenically or ambient ground GRT based composites. [21]

2.4.4 Cryogenic grinding

Cryogenic grinding is the process by which the rubber pieces previously shredded are cooled down at a temperature below -80 ºC using liquid nitrogen. By using this low temperature most rubbers get into a glassy state becoming embrittled and therefore allowing for the material to be efficiently grounded by impact using a mill. In this case an impact mill or a hammer mill is used. Thereafter, the particles are dried, and a fibre and metal separation is being conducted, followed by a sorting according to size. Aspiration and screening is applied to remove the fibre while magnets are used to separate the steel from the material. By using this process the particle size of the ground rubber produced is less than 30 mesh (0.6 mm). [19,22] Production of a finer crumb requires a secondary cryogenic grinding step that can reduce the final particle size up to 80 mesh (0.18 mm). [6,22] The materials obtained through this process present a very smooth surface and a low specific surface area, which makes them less active for re-vulcanisation in comparison with the ambiently ground material. [19] Compared with ambient grinding the operating costs of cryogenic grinding may be higher due to the utilization of liquid nitrogen. Cryogenic grinding costs depend on the degree of particle fineness required and the quantity of nitrogen purchased. Nitrogen costs are typically between 0.044 - 0.132 € per kilogram of rubber. [22]

Depending on the market application of the rubber waste material, either cryogenically or ambient (wet or dry) crumb can be applied. Further, the obtained particles can be used as filler or mixed in various blends with other polymers up to a certain percentage without deteriorating the processability and the mechanical properties of the new materials.[23,24] However, the application of these particles without any further improvement is generally limited to low quality products. The use of these powders as a filler material in high quality rubber products can be done by using low concentration only (up to 10%).[25]

2.5 GROUND VULCANISED WASTE AS FILLER

De and coworkers [23,26,27] investigated the effect of ground EPDM waste on the processing, rheological behaviour and mechanical properties of the EPDM virgin rubber. The vulcanised EPDM was ground at room temperature using a mechanical grinder with a silicon carbide abrasive wheel rotating at 2950 rpm. They observed that ground waste EPDM (W-EPDM) acts as filler in raw EPDM matrix (R-EPDM). The addition of W-EPDM into virgin rubber leads to an increase of Mooney viscosity and a decrease of the scorch time. This phenomenon was attributed to the accelerator migration from W-EPDM to the matrix. By adding a higher percentage of vulcanised powder (more then 25%) the maximum torque decreases, which can be ascribed to the sulphur migration from the R-EPDM to the waste particle rubber, leading to a decrease of the apparent crosslinking density of the matrix. The elongation at break, hysteresis, tear strength and tensile strength are improved, showing the carbon black reinforcing nature contained in the W-EPDM. In the case of hardness and low strain modulus the effect of the filler was counter balanced by the crosslinking effect. The drop in resilience and the marginal increase in heat build-up have been attributed to the filler effect. By substituting the virgin EPDM with W-EPDM in EPDM/PP blends it was also shown that up to 45% of R-EPDM can be replaced by W-EPDM without affecting the processability and the mechanical properties of the blends.[24]

2.6 PHYSICAL AND CHEMICAL RECLAIMING PROCESSES OF RUBBER

Both physical and chemical processes applied in rubber reclaiming are used to cleave the crosslinking network of rubber formed during vulcanisation and to obtain a reprocessable material. The scission of the crosslinks can be done using mechanical or thermal energy and various chemical reclaiming agents. However, in the currently applied reclaiming processes the carbon - carbon bonds within the polymer chain are also broken, having as a consequence the reduced quality of the recycled material.

Devulcanisation is the ideal case where only the cleavage of monosulphidic, disulphidic and polysulphidic crosslinks of the vulcanised rubber takes place, without destroying the polymer chain. Nonetheless, factors as small differences in bond energies, thermal inhomogeneity within the material, uncontrolled temperature or energy, type or concentration of the reclaiming agent makes difficult the control of the process without involving the degradation of the rubber chains.

2.6.1 Mechanical Reclaiming

In the mechanical reclaiming process scrap rubber is attempted to be devulcanised by means of strong shear stresses using a two-roll mill or an internal mixer. It was shown that the use of a nip opening of 0.010 inches and 30 passes through the two-roll mill represents the optimum condition for the devulcanisation of NR and SBR cryogenically ground crumb.[28] Solid shear state extrusion (SSSE) [29] and high stress mixer (HSM)[30] technologies have been used as well in the mechanical reclaiming process.

2.6.2 Thermo-Mechanical Reclaiming

In this process the scrap rubber is subjected to shear or/and elongational stresses using suitable equipment such as open mills or twin-screw extruders at high temperatures, enough to cause thermal degradation. Mouri et al. [31-34] investigated the devulcanisation of sulphur-cured EPDM using a twin-screw reactive extruder for continuous reclaiming within a short time (10 minutes). The effect of the devulcanisation agent (DVA), temperature and screw speed has been studied. It was found that devulcanisation could be achieved under suitable conditions (shear rate, pressure and temperature) in the extruder without adding any desulphuriser.[35] A temperature within the range of 280 ºC to 330 ºC was claimed to be suitable for sulphur vulcanised EPDM with a shear stress between 1 and 15 MPa.[36] An addition of up to 25% of the reclaimed EPDM was possible from the processability point of view.

Insight studies were made by Janssen et al., [37] which developed an engineering kinetic model to study the response of devulcanisation processes of the EPDM rubber. In the kinetic model parameters such as crosslinking density, devulcanising agent concentration, shear rate, time and temperature were included. They observed that the devulcanisation rates between two different EPDM compounds are influenced neither by the temperature nor by the screw speed, but show different tendencies in their response with regard to the feed rate. [38] These results showed that the EPDM devulcanised by a thermo-mechanical process under specific process conditions exhibits good mechanical properties compared to a virgin vulcanised EPDM. [39] Jalivand et al. [40] used a co-rotating twin-screw extruder and a devulcanisation agent to study the devulcanisation process of EPDM. The effect of the extruder conditions, such as shear stress and barrel temperature, as well as the effect of the devulcanisation agent were investigated. The mechanical properties of the revulcanised samples were found to be slightly inferior compared with those of the virgin rubber.

2.6.3 Ultrasound Reclaiming

Ultrasonic energy represents a powerful energy that can be also applied in the process of devulcanisation. The ultrasonic waves, in the presence of pressure and temperature, can quickly break up the three-dimensional rubber network. In 1973, Pelofsky [41] reported for the first time the ultrasound method used in reclamation of rubber such as tires. He treated solid rubber material immersed into a suitable solvent using a source of ultrasonic radiation within the range of 10 to about 40 KHz and at the power intensity of about 100 W/cm^3 of material. Upon contact with the ultrasonic waves the bulk rubber is disintegrated being dissolved and/or suspended in the liquid and subsequently separated. In his patent Pelofsky explained the process of devulcanisation by using ultrasound energy but he did not present the properties of the reclaimed rubber. Later on in 1987 Okuda and Hatano [42] accomplished the devulcanisation of NR in a batch process using an ultrasonic energy of 50 kHz for 20 minutes. They found that the properties of the revulcanised rubber are similar to those of the original one, claiming that only C-S and S-S crosslinks cleaved and the C-C bonds remained unbroken.

Extensive studies of ultrasonic devulcanisation on various types of rubbers were performed by Isayev et al. [43,44] The ultrasonic devulcanisation of unfilled rubbers such as SBR, NR and EPDM rubbers was performed in a continuous process using a coaxial ultrasonic reactor. [45,46] In this case it was found that the devulcanisation of EPDM rubber is much more difficult than the devulcanisation of NR and SBR. The mechanical properties of the revulcanised SBR and EPDM were improved, possibly as a result of the extension of nonaffine deformation of bimodal network, which is likely to appear in the process of revulcanisation of ultrasonically devulcanised rubber. The devulcanisation of carbon black-filled EPDM was also performed using a continuous ultrasonic grooved-barrel reactor. [47-49] In comparison with the coaxial reactor used in earlier studies, by using this reactor it was possible to increase by two times the output of devulcanised rubber. The dynamic viscoelastic properties indicated that the reclaimed EPDM rubber is more elastic than uncured virgin EPDM, while revulcanised EPDM rubber is less elastic than the virgin vulcanised rubber. The revulcanised rubber samples exhibited good mechanical properties, which were found to be closed to those of the virgin vulcanised rubber. An addition of up to 25% of devulcanised EPDM rubber into the virgin filler rubber is possible without a significant decrease of material properties. Studies of ultrasonically devulcanised rubber show that the breakdown of C-S and S-S bonds is accompanied by the partial degradation of the rubber chain. [50]

2.6.4 Microwave Reclaiming

Microwaves are an electromagnetic radiation of high frequency, between 0.3 GHz and 300 GHz, which can interact with polar groups and induce their orientation. During the orientation process the electromagnetic energy is transformed into thermal energy and used as a heating source. Microwave energy has been used for the devulcanisation of sulphur cured EPDM rubber waste. [51] This process is accomplished by application of a certain amount of microwave energy, between 325 and 1404 kJ/kg, sufficient to cleave C-S and S-S bonds without affecting the C-C bonds. For this method the material used has to be polar enough, so that the microwave energy can generate the heat necessary for devulcanisation. EPDM is a non-polar polymer and therefore it cannot absorb the microwave energy, but it is usually highly loaded with carbon black that absorbs the microwave energy producing the heat necessary for the devulcanisation process. The type and the particle size of the fillers have an influence upon the devulcanisation rate. The method can be either continuous or a batch process requiring expensive equipment. An addition of maximum 25% of devulcanised rubber was added to the raw material leading to products with mechanical properties equivalent to the original vulcanised one. Fix [52] used the microwave continuous devulcanisation for EPDM and butyl rubber. After treatment the particles were blended with virgin rubber, obtaining compounds which exhibited mechanical properties comparable with the control samples. Some preliminary investigation of devulcanised and recovered bromobutyl rubber (BIIR) using the microwave process was done by Landini et al. [53] They investigated the effect of microwave energy and irradiation time concluding that the best conditions for the devulcanisation of BIIR were obtained at 2000W and for a time of 13 min. The microwave treatment of ground SBR scraps was studied by Crespo et al. [54] The SBR particles, which were devulcanised at different times of exposure to the microwave energy, were revulcanised and compared to a control sample. The SBR sample exposed to the microwave energy for 3 minutes exhibited the best mechanical properties, with 25% of the tensile strength and 41% of the tear strength of the control sample. They assumed that the microwave treatment of the rubber presumably caused both crosslink scission and main chain degradation, obtaining thus composites with low mechanical properties. The kinetic degradation parameters and the influence of paraffinic oil presence in EPDM residues upon the rate of devulcanisation using microwave radiation was studied by Zattera et al. [55,56] They found that the presence of paraffinic oil in EPDM affects the devulcanisation process. Good results were obtained when the paraffinic oil was extracted and the sample was exposed for a short time to microwaves (up to 4 min).

2.6.5 Chemical reclaiming

In comparison with physical reclaiming the chemical processes present the advantage of a better selectivity towards cleavage of the different bonds. Different types of chemical agents have been used to initiate scission of sulphur crosslinks or to act as radical scavenger with the free radical chains formed as a result of C-S, S-S and C-C bond scission [57,58]. Numerous types of organic chemicals such as thiols, disulfides, phenols and amines are used as reclaiming agents reacting according to a nucleophilic or a radical mechanism.

Van Duin et al.[59] investigated the devulcanisation of EPDM rubber using amines. Neither the basicity, nor the number of protons attached to the nitrogen atom did influence the reactivity of the amines. The presence of an α-C atom with at least one H atom represents an important parameter which has an influence upon reactivity as shown in Figure 2.1.

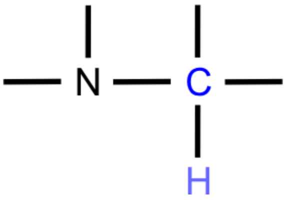

Figure 2.1 Structure of the amine compound used in devulcanisation

They found that by using α-hydrogen containing aliphatic amines i.e hexadecylamine (HDA) the EPDM rubber could be successfully reclaimed.[60] According to their study, primary, secondary and tertiary aliphatic amines as well as benzylic amines are suitable to be used as devulcanisation aids with almost no difference in the reactivity.[61] The use of a high concentration of amines leads to a higher decrease in crosslinking density. Verbruggen et al.[62] studied the thermochemical recycling of vulcanised NR and EPDM using diphenyldisulphide as devulcanising agent. A complete devulcanisation was observed for sulphur-cured NR when heated with diphenyldisulphide at a temperature of 200 °C, albeit for sulphur-vulcanised EPDM almost no devulcanisation occured at the same temperature. A decrease in crosslinking density of 90% was observed when sulphur vulcanised EPDM with diphenyldisulphide where heated to 275 °C in a closed mold for 2h. However, peroxide cured EPDM showed a decrease in crosslinking density of about 40% under the same conditions.

Noordermeer et al. [63] investigated the devulcanisation of EPDM rubber by use of diphenyldisulfide and hexadecylamine in terms of the influence of the third monomer and of the vulcanisation method. It was found that the behaviour of vulcanised EPDM during devulcanisation depends on the diene type built into the polymer. The efficiency, the occurrence of further crosslinking and the mechanism via which devulcanisation occurs are strongly influenced by the type of the diene monomer. The type of curing of the vulcanised EPDM, either sulphur or peroxide vulcanisation, has also an influence upon the mechanism via which devulcanisation occurs.

According to the reaction mechanism proposed by Noordermeer et al. [63] sulphur-cured ENB–EPDM devulcanises via crosslink scission, i.e. C-S and S-S bonds scission, as shown in Figure 2.2.

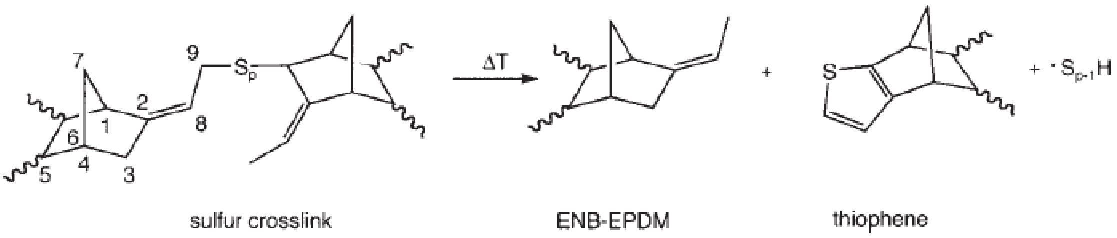

Figure 2.2 Devulcanisation mechanism of sulphur-vulcanised ENB-EPDM [63]

Figure 2.3 presents the simplified mechanism of the peroxide curing of ENB-EPDM. Peroxide-cured ENB–EPDM devulcanises mainly by random main chain scission, i.e. C-C bonds scission, as outlined with blue in Figure 2.3.

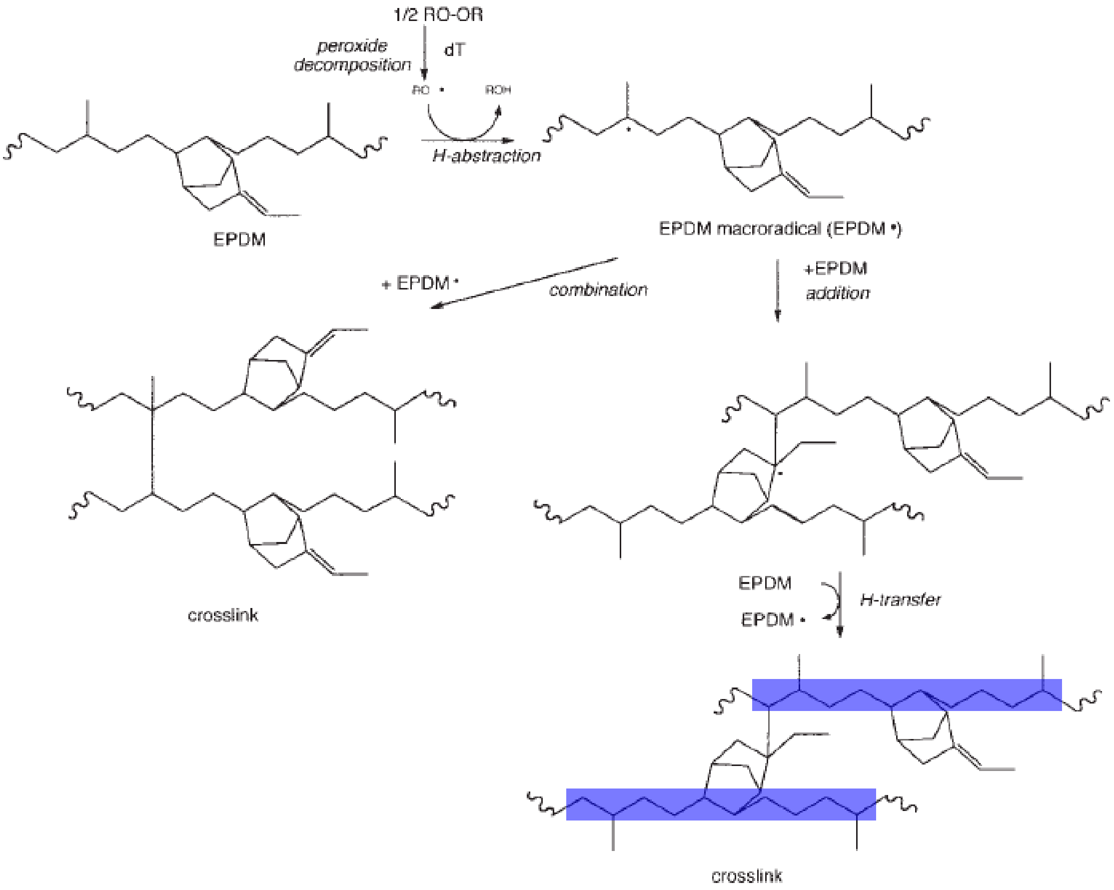

Figure 2.3 Vulcanisation scheme of peroxide-cured ENB-EPDM [64]

A comparative study of two different vulcanised EPDM compounds using HDA as devulcanisation agent was explained by Dijkhuis et al. [65] The reclaim obtained from conventionally vulcanised EPDM, mainly polysulphidic in nature, shows a significant decrease in crosslinking density with increasing hexadecylamine concentration at temperature ranges between 225 °C and 275 °C. Moreover, the reclaiming process of efficiently vulcanised EPDM with primarily monosulphidic crosslinks shows different properties. The addition of HDA has again a positive effect on the reclaim efficiency, with a decrease in crosslinking density at low treatment temperatures of 200 °C and 225 °C. At higher temperatures, the crosslinking density increases with increasing HDA concentration. It was found that conventionally vulcanised compounds devulcanise to a larger extend by crosslink scission in comparison to the efficiently vulcanised compounds, which mainly shows main-chain scission. Both reclaimed compounds were added up to 50% to a virgin EPDM masterbatch showing limited decrease in mechanical properties compared to the values of the original compounds. It was stated that in the case of EPDM rubber the HDA is the most suitable devulcanising agent in comparison with diphenyldisulphide and o'o'-dibenzamidodiphenyldisulphide. [66]

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Another comparative study of efficiently vulcanised (EV) and semi-efficiently vulcanised (SEV) EPDM was conducted by Sutanto et al. [67] In this case the vulcanisation system has an influence upon the mechanical properties of the reclaimed products. The revulcanised blends of devulcanised EPDM with virgin material showed that at least 25% of the devulcanisate can be added without deteriorating the mechanical properties.

The chemical reclaiming by an inorganic catalyst system [68] and chemical probes [69] has been used as well in the recycling of various types of rubber. A phenylhydrazine-iron chloride system [70], alkali metals [71] and several onium salts [72] have been used in the chemical reclaiming by an inorganic catalyst system. The main drawbacks of the above mentioned processes are the toxicity of the chemicals, the poor mechanical properties (because of the polymer main chain scission) and the difficult application on an industrial scale. [58]

2.7 SURFACE ACTIVATION

The purpose of surface activation is to increase the interaction between waste rubber particles and a new matrix when rubber crumbs are mixed with a new material. Various methods have been developed to activate the surface of the rubber waste particles, aiming to increase the bonding strength between the waste particles and a new rubber matrix. In the case of these methods the reaction zone is on the particles surface and not throughout the particles. The activation processes can be classified into 4 groups:

- Biological activation
- Mechanical activation
- Physical activation
- Chemical activation

2.7.1 Biological Activation

Various methods of biological activation of rubber surface using various types of microorganisms have been published. The microbial desulphurisation is possible using chemolithotrophic Thiobacillus bacteria which are able to oxidize the polysulphidic bonds to soluble sulphates. [73] The reaction is limited to a surface layer with a thickness of less than 1 µm and the oxidation process takes place within several weeks. The thermophilic archaeon Pyrococcus furiosus was used with success in the anaerobic treatment of NR and butadiene rubber resulting in a decrease of sulphur on the surface of the rubber particles and an increase of the sulphur reduction to hydrogen sulphide. [74] Sulfolobus acidocaldarius archaea is able to break C-S bonds oxidising the sulphur in a stepwise reaction to sulphate. [75] By testing various types of sulphur oxidizing microorganisms, which are able to oxidize sulphur in cryoground tyre rubber, Christiansson et al. [76] found out that Thiobacillus ferrooxidans microorganisms are the most efficient in terms of released sulphate. Recent studies showed that Thiobacillus ferrooxidans can be used in microbial desulphurisation of NR waste rubber using a modified 9K medium [77] and further used as a filler in an SBR matrix. By using 40 phr of desulphurised ground rubber in SBR compounds good improvements of tensile strength and elongation at break were shown. The drawbacks of these treatments are the low rate of desulphurisation, the application to only certain types of rubber because of their inhibited growth when different agents are used in rubber formulations, the leaching process applied before desulphurisation and the long periods of time needed for the oxidation processes.

2.7.2 Mechanical Activation

Mechanical activation of the rubber crumb surface can be attained by milling the material on a two-roll mill with a narrow gap at a temperature within 0 ºC to 100 ºC or at room temperature for ca. 7 min. In this process the particle size of the waste rubber must be below 10 mm, preferably 1 mm. Softeners together with other aids and fillers are added additionally during or after the activation process. Rubber particles from various sources, including natural rubber (NR), isoprene rubber (IR), isobuthylene isoprene rubber (IIR), styrene butadiene rubber (SBR), butadiene rubber (BR), nitrile rubber (NBR), silicone rubber (Q), EPDM and polyurethane rubber (PUR), were used in this process. [78] Other devices that can be used in this process instead of a mill are internal mixers, extruders and calendars. [58] Cryogenic EPDM and NR/SBR rubber waste particles were activated using peroxide as an oxygen radical donor by means of a heating and cooling mixer combination. A mixer temperature range between 105 ºC and 135 ºC over 60 to 240 seconds is required for mechanical activation of the ground rubber. [79]

2.7.3 Physical Activation

A physical process used for the surface activation treatment of rubber waste particles is the plasma treatment under atmospheric pressure. The process permits continuous treatment activating the surface of the waste rubber and obtaining a hydrophilic surface thereby improving the compatibility with other polymers, e.g. polymethylmethacrylate. [7] Nitrogen, oxygen and air are the most preferred reactive gases used for the introduction of the functional groups into the surface of the waste particles. [7,80] For this purpose the treatment with cold plasma gas was also used. The activated particles exhibit good properties when blended with a matrix or a flowable binder which are cured or set, obtaining new articles. This treatment was used for various vulcanised particles based on polymers such as NR, SBR, NBR, butadiene rubber, butyl rubber, EPDM rubber, polychloroprene rubber or blends of any of these. [81]

2.7.4 Chemical Activation

The most common way of chemical activation is the treatment of the waste rubber powder using a crosslinkable polymer together with a curing system. A process used to activate vulcanised waste rubber particles is the treatment of the vulcanisate with rubber latex and a curing system, followed by drying the particles for a short period of time using not too high temperatures. [82] In this case the latex is based on NR and/or SBR rubber with a molecular weight within 200.000 to 2.000.000 g/mol. Another study using chemical activation by adding a crosslinkable polymer and a curing system has been conducted for powders with specific surface area, based on various polymers such as natural rubber (NR), styrene-butadiene rubber (SBR), nitrile rubber (NBR), and ethylene-propylene-diene rubber (EPDM). [83] An activating process has been reported using solid, low molecular weight polymers like poly-octenamer, which are dissolved in paraffin oil using a temperature of 80 -100 ^{o}C. [84] This liquid is then mixed with the rubber powder in a concentration of up to 35% and other additives like curing agents, fillers, colorants and flame retardants can be added. The activated powder is then cured under high pressure. This process can be applied to a wide range of waste rubbers.

Studies using a low molecular weight polymer to treat various types of scrap rubber (as from the automobile industry) such as butyl, nitrile, polychloprene, EPDM, SBR and natural rubbers were described by Stark et al. [85,86] It was found that by treating the surface of a particule of vulcanised rubber with a sulphur–curable polymeric binder having ethylenic unsaturation and a curing agent the resulting powder could be used at in a high concentration as an additive to virgin rubber, with moderate loss of physical properties. This process requires the use of various solvents such as hexane or benzene that are able to solubilise the polymeric binder.

It was shown that the particle size and the grinding technique have an effect upon the mechanical properties of scrap-extended SBR compounds. Even if the treatment greatly diminishes the effect of the particle size, better mechanical properties were obtained for the ambient mill grinded particles with smaller size. Properties such as tensile strength, elongation and tear strength are reduced by adding the treated particulate. Calendaring, compression moulding and extrusion can be accomplished using blends of the compounds with the treated particles. For this process the polymers generally have molecular weights not greater than about one million, but ideally their molecular weight should be in the range of 1000 to 50.000 g/mol. [87]

A direct process based on grafting rubber granulate with ethyl acrylate rubber was developed by Adam et al. [88] Waste polybutadiene (BR) rubber was surface activated by grafting using a redox catalytic method or by gamma radiation. The grafted granulate was then added to polybutadiene rubber and polyacrylic rubber. An improvement of the properties was found when grafted polybutadiene granulate was used in blends with polyacrylate rubber, due to the interaction of polar groups in the polymeric chain of BR rubber. Giese et al. [89] studied the chemical modification of rubber powder by grafting of maleic anhydride and epoxidation or hydroxylation followed by a coupling reaction with silane. Both treatments improved the properties of a compound containing the rubber powder compared with the same compound containing untreated rubber powder. Maleic anhydride (MA) was also applied in the modification of ground rubber tire (GRT). [90] The modified GRT particles were further used to partially substitute the natural rubber in LLDPE/NR blends. The results showed that the MA is able to improve the bonding between GRT and matrix, giving blends with better mechanical properties in comparison with those where unmodified GTR particles were used.

To increase the polarity of the surface rubber particles Smith et al. [91] used the halogenation process using chlorine. This treatment increases the compatibility of the rubber powders with polar polymers such us polyurethane. Due to the dehydrogenation process, the concentration of the double bonds on the surface of the modified rubber particles increases, improving the curing efficiency. A maximum of up to 15% surface-treated rubber was mixed with polyurethane obtaining samples with good mechanical properties in comparison with the original product.

2.8 MECHANICAL PROPERTIES OF VULCANISATES

2.8.1 Hardness

Hardness is defined as the material resistance to indentation as measured under standard conditions using specified test instruments. According to ISO 7619:2010 standards, the hardness of rubber, vulcanised or thermoplastic, can be measured by using a durometer method (Shore hardness) or the International Rubber Hardness Degree (IRHD). The hardness of the rubber as measured by the above mentioned methods is determined from the response of the rubber to an applied indentation.

Shore hardness testers (ISO 7619-1:2010) are very simple and inexpensive devices which can be used to measure the Shore hardness. The Shore A scale is used to express the hardness of soft rubbers while the Shore D scale is used for the harder ones. The higher the durometer value, the harder the material. The penetrator has the shape of a truncated cone. The resistance against the penetration of the cone indicates the hardness of the material.

IRHD (ISO 7619-2:2010) is used to determine the indentation hardness of vulcanised rubber by means of a pocket hardness meter calibrated in IRHD. The use of such meters is primarily intended for control and not for specification purposes.

2.8.2 Tensile stress-strain properties

Besides hardness, stress-strain properties are very important indicators in the characterization of an elastomer. The tensile test using a tensile testing machine is the most frequently used type of test.

Tensile strength is defined as the maximum tensile stress recorded on stretching the test specimen to the breaking point. By convention the force required is expressed as force per unit area of the original cross section of the unstrained specimen and is calculated as:

$$\text{Tensile strength (MPa)} = \frac{\mathrm{F}}{\mathrm{A}} \qquad 2.1$$

where F is the force magnitude of rupture (N) and A is he cross-sectional area of the unstrained test specimen (mm^2).

Elongation at break is usually termed the ultimate elongation at the break point and is defined as the elongation at which breaking of the specimen occurs upon application of a continued tensile stress. Elongation at break is calculated as:

$$\text{Elongation at break (\%)} = 100\left[\frac{(\mathrm{L}-\mathrm{L}_0)}{\mathrm{L}_0}\right] \qquad 2.2$$

where L is the distance between bench marks at which the specimen breaks (mm) and L_0 represent the original distance between bench marks (mm).

2.9 THE FLORY REHNER THEORY OF THE GEL SWELLING

According to the Flory–Rehner theory [92] the maximum degree of swelling of the network in contact with a pure solvent is related to the degree of crosslinking. The crosslinking density of elastomers is determined by swelling measurements using various solvents which are selected according to the elastomer type. A chemically crosslinked polymer is able to increase its volume severalfold by absorbing large amounts of solvent. [93] The amount of solvent uptake, namely the degree of swelling, is known to be dependent upon the crosslinking density of the polymer networks, which means the higher the degree of crosslinking the lower the degree of swelling.

An uncrosslinked elastomer will dissolve completely in an appropriate solvent while in a crosslinked elastomer the solvent will diffuse into the elastomer until the osmotic pressure of the solvent is equal to the elastic retractive forces of the stretched polymer chains. The Flory-Rehner theory assumes linear superposition of the free energy changes associated with the swelling of the network. [93] The swelling of a network can be described in terms of two free energies, the free energy of mixing ΔF_m and the elastic free energy, ΔF_{el}.

$$\Delta F_{system} = \Delta F_m + \Delta F_{el} \qquad 2.3$$

ΔF_{el} describes the reorganisation of the network structure by absorbing the solvent. Consequently a decrease in the chain configurational entropy is produced by swelling. Opposing, ΔF_m describes the incorporation of the solvent into the network, thus an increase in entropy upon mixing. In other words ΔF_m drives swelling and ΔF_{el} opposes swelling. [92] When $\Delta F_m + \Delta F_{el}$ is negative this indicates that swelling is favoured and solvent diffuses into the network. As more and more solvent is absorbed by the polymer ΔF_m gets less negative and ΔF_{el} gets more positive until equilibrium will be attained, that is $\Delta F_m + \Delta F_{el} = 0$. At equilibrium these opposing entropies, the entropy of the chain configuration and the mixing entropy, become equal in magnitude and opposite in sign, thus $-\Delta F_m = \Delta F_{el}$. The crosslinking density is calculated by applying the Flory-Rehner equation.

$$\upsilon_e = -\frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_S\left(V_r^{\frac{1}{3}} - \frac{V_r}{2}\right)} \qquad 2.4$$

where V_r is the polymer volume fraction, V_S is the molar volume of the solvent and χ represent the polymer-solvent interaction parameter.

2.10 TEMPERATURE SCANNING STRESS RELAXATION

The temperature scanning stress relaxation (TSSR) is a relatively newly developed method [94] used for many applications where the mechanical and thermal behaviour of thermoplastic elastomers, plastics and elastomers needs to be characterised. [95] Crosslinking density of thermoplastic vulcanisates [96] and conventional elastomers, e.g. EPDM [97], has been examined and determined by means of TSSR measurements.

During conventional stress relaxation tests a constant deformation is applied to the sample and the reacting force is monitored as a function of time. In conventional tests the temperature is usually kept constant. The force decays exponentially with time. The relaxation modulus E is a function of time and temperature E=E (t, T). At constant temperature the time dependent stress, $\sigma(t)$ is given by Equation 2.5.

$$\sigma(t) = E_{iso}(t) \cdot \varepsilon_0 \qquad 2.5$$

where ε_0 is the applied strain and $E_{iso}(t)$ represent the time dependent modulus under isothermal conditions.

The time dependent modulus is given by Equation 2.6. [98]

$$E_{iso}(t) = \int_{-\infty}^{+\infty} H(t) \cdot e^{-t/\tau} d \ln\tau + E_{\infty} \qquad 2.6$$

According to Alfrey's law [99], by differentiating E_{iso} (t) with respect to In t the relaxation spectrum $H'(\tau)$ at t = 0, where t is the relaxation time constant, is obtainable in first approximation by Equation 2.7.

$$H'(t) = -\left(\frac{dE_{iso}(t)}{d\ln t}\right)_{t=\tau} = -t \cdot \left(\frac{dE_{iso}(t)}{dt}\right)_{t=\tau} \qquad 2.7$$

In the case of the TSSR method the temperature is not kept constant during testing, but increases at a constant heating rate β. The resulting non-isothermal relaxation modulus $E_{non\text{-}iso}$ (T) is a function of temperature at a constant heating rate. By differentiating $E_{non\text{-}iso}$ (T) with respect to temperature T, the relaxation spectrum $H = H(T)$ is obtained according to Equation 2.8.

$$H(T) = -T \cdot \left(\frac{dE(T)_{non-iso}}{dT}\right)_{\beta=const} \qquad 2.8$$

A test result obtained from TSSR measurements for a conventionally vulcanised EPDM rubber and a dynamically cured EPDM/PP blend is presented in Figure 2.4. The stress-temperature dependency of the vulcanised EPDM rubber is mainly influenced by two phenomena. Starting at room temperature the stress slightly increases with temperature due to the entropy effect.

According to the theory, the slope of the increased force corresponds to the crosslinking density of the rubber network. The crosslinking can be calculated from the experimentally obtained value of the temperature coefficient by using Equation 2.9.

$$\upsilon_e = \frac{\kappa}{R \cdot (\lambda - \lambda^{-2})} \qquad 2.9$$

where υ_e is the crosslinking density (mol/m^3), and κ represents the temperature coefficient of stress, i.e. the derivative of mechanical stress with respect to temperature.

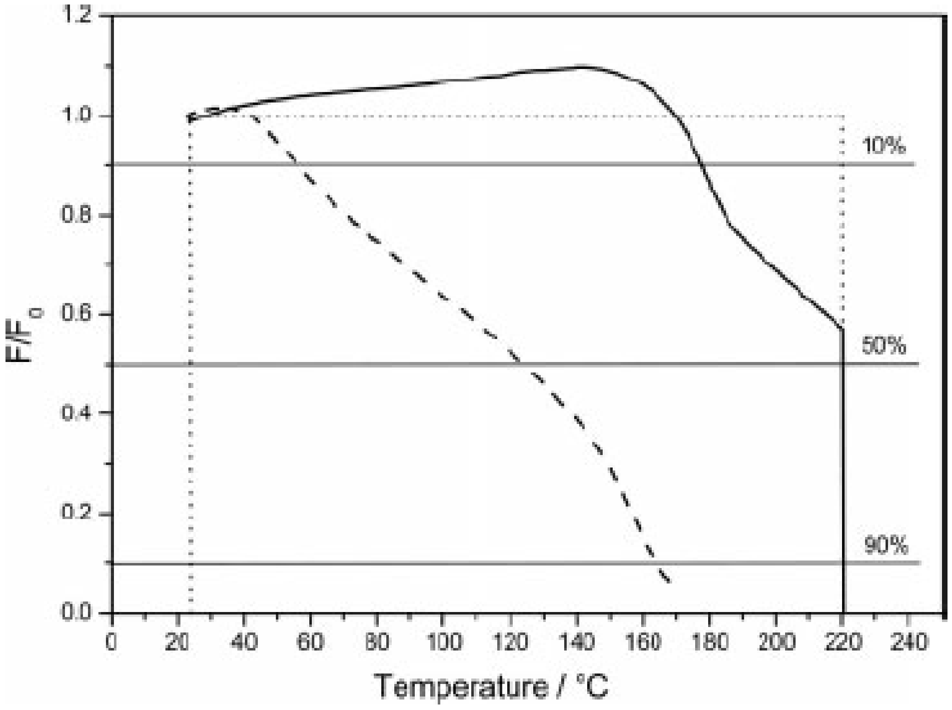

Figure 2.4 Normalised force-temperature curves for vulcanised EPDM rubber (solid line) and a dynamically cured EPDM/PP blend(dashed line) from TSSR measurements [94]

It is noted that Equation 2.9 is based on the well known theory of rubber elasticity but it applies only for ideal rubber networks. Therefore, application of Equation 2.9 leads to apparent crosslinking density values in this case, because of the complex composition and structure of the investigated compounds.

After a certain temperature the effect of stress relaxation overcompensates the entropy effect resulting in a stress decrease to zero within a small temperature range. In this range stress relaxation occurs due to the chemical changes, especially thermo-oxidative chain scission. [94]

In the case of a thermoplastic elastomer (TPE) sample (i.e. a dynamically cured EPDM/PP blend) it can be clearly seen that the thermo-mechanical behaviour is significantly different compared with the EPDM rubber. In the case of TPE an increase of stress is observed over a narrow range at low temperatures while an abrupt increase with a wider temperature range was observed for the EPDM sample. With respect to TPE's properties the effect of stress relaxation is more important than the entropy effect. This behaviour is due to the thermally reversible physical crosslinks which can be untied at higher temperatures. [94]

2.11 RHEOLOGY

Rheology is the science of the deformation and flow properties of matter under the effect of an applied force. Deformation is the reversible or irreversible shape change of a body due to the applied forces. For example, if an ideal liquid, e.g. water is deformed the stresses return to zero nearly immediately after the deformation is completed. This means that water is not reverted to the original state when the force is removed and the energy cannot be recovered. On the other side, cured rubber represents an ideal elastic solid at sufficiently small deformations.

In this case, when a cured rubber is deformed the stresses persist and only return to zero when the original shape of the material has been regained. This means that when the applied force is removed the body reverts to its original state and the energy is recovered. The viscoelastic materials, e.g. uncured rubber, are a combination of a Newtonian fluid (ideal viscous) and a Hookean body (ideal elastic).

Viscosity is defined as a measure of resistance against flow. In the case of Newtonian liquids the proportionality coefficient (η) named viscosity is constant, which assumes that shear stress (τ) is direct proportional to shear rate ($\dot{\gamma}$) as shown in Figure 2.5. The Newton law is given by Equation 2.10.

$$\tau = \eta \cdot \dot{\gamma} \tag{2.10}$$

Uncrosslinked high molecular materials such as elastomers behave as a non-Newtonian liquid of high viscosity, which assumes that their apparent viscosity change as the shear rate is varied. In other words, in the case of non-Newtonian behaviour the relation between shear stress and shear rate is not linear and the apparent viscosity decreases as the shear rate is increased as shown in Figure 2.6

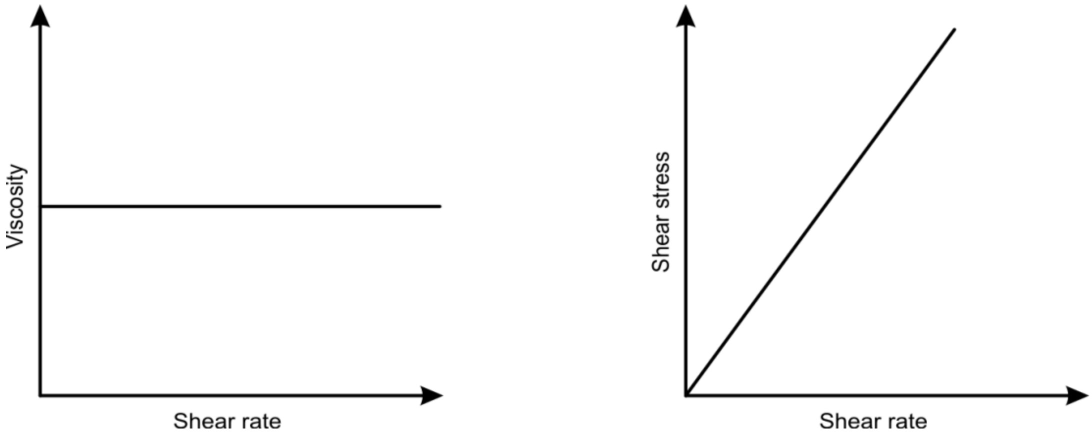

Figure 2.5 Relation between shear rate/shear stress and shear rate /viscosity for a Newtonian flow

In the case of viscoelastic materials, e.g. uncured elastomers which present an ambivalent behaviour (viscous and elastic behaviour), the characterization of the material is very important for processing. For this purpose the determination of complex viscosity is essential for the characterization of the uncured material.

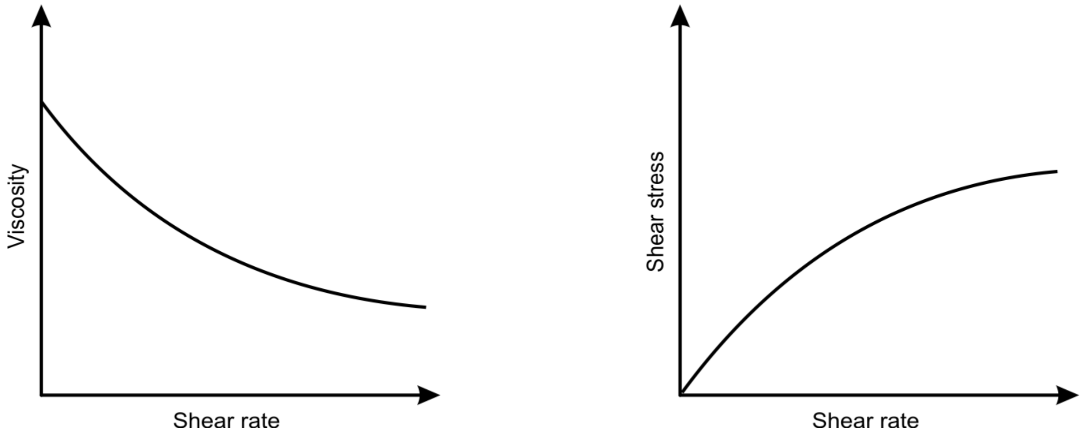

Figure 2.6 Relation between shear rate/shear stress and shear/viscosity for a pseudoplastic or shear-thinning flow

The complex viscosity (η^*) is composed of an in-phase component η’ and an out-of-phase component η'', and can be calculated according to the Equation 2.13. [100]

$$\eta^* = \eta' - i\eta'' \tag{2.11}$$

$$\eta' = \frac{G''}{\omega} \quad \text{and} \quad \eta'' = \frac{G'}{\omega} \tag{2.12}$$

$$\eta^* = \sqrt{(\eta')^2 + (\eta'')^2} \tag{2.13}$$

where:

η^*	–	complex viscosity
η'	–	real component of the complex viscosity (dynamic viscosity)
η''	–	imaginary component of the complex viscosity
ω	–	angular frequency
G'	–	shear storage (elastic) modulus
G''	–	shear viscous (loss) modulus

2.12 MOTIVATION OF THE THESIS

The steady growth of the rubber industry requires attention regarding the waste management and the methods applied in recycling and in the reclaiming processes.

Reusability of the EPDM production waste material in new products is a desideratum considering the poor availability of methods applied for this type of rubber. Developing an efficient method which allows the utilization of high amounts of recycled rubber and which facilitates the up-scaling of the process from the laboratory to the industrial scale represents the motivation of the present thesis.

The most promising and suitable approach for accomplishing this is the use of a solvent-free activation process for the rubber waste material particles surface employing low molecular weight polymers and a curative system. The applied research of this thesis consists in the use of the recycled particles as a substitute for the raw material in the production of high quality seals and sealing systems.

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Chapter 3

Recycling of EPDM Rubber Waste Powder by Chemical Activation with Liquid Polymers

"Imagination is more important than knowledge. For knowledge is limited to all we now know and understand, while imagination embraces the entire world, and all there ever will be to know and understand."

Albert Einstein (1879 – 1955)

Sulphur-cured EPDM rubber waste powder was chemically activated using low molecular weight polymers with different degree of unsaturation. The cure characteristics, mechanical properties, crosslink density, and morphology of the EPDM rubber waste particles activated using liquid polymers had been analysed. These properties presented different values which were correlated to the ratio between liquid polymer and rubber waste powder, the amount of the curing system used and the 5-ethylidene-2-norbornene percentage that were used. By increasing the amount of rubber waste particles in the composition, an improvement of mechanical properties was observed. The influence of the amount of the curing system used was clearly reflected in the properties and morphology of the final compounds indicating that the addition of a curing system in the composition of the sample was needed. Additionally, the use of high levels of sulphur content resulted in a blooming effect. Moreover, the presence of a higher amount of 5-ethylidene-2-norbornene in the liquid polymer used for the activation suggested the possibility of obtaining samples with better properties. Also, the empirical results obtained by using the above-mentioned method revealed its potential use for further applications, e.g. the use of activated particles as substitute of raw material.

Parts of the research described in this chapter have been presented at the 10th Fall Rubber Colloquium, KHK, 7th-9th November 2012, Hannover, Germany and has been published in the January/February 1-2/2014 edition of Kautschuk Gummi Kunststoffe.

3.1 INTRODUCTION

Non-biodegradable waste, i.e. discarded rubber, constitute a major problem for the rubber industry nowadays, especially after taking into consideration the implementation of new legislations which concern waste disposal. [1,2] Additionally, by using high amount of rubber granulate, between 25 and 50%, only low quality goods can be obtained, such as automobile floor mates, shoe soles and/or materials for road construction.

EPDM is currently the most common non-tire elastomer on the market with wide range of applications. [3,4] This type of rubber is widely used in different fields for variety of purposes, such as electrical insulation, automotive applications, roofing systems, thermoplastics vulcanizates, wires, cables and lubricant additives. Besides, due to its excellent chemical resistance, e.g. to mild acids, detergents, alkalis, silicone oils and greases, ketones, alcohols, and its superior ozone resistance, EPDM has gained wide acceptance in the O-ring and rubber seal industry. EPDM O-rings are frequently used to seal in brake systems and in many hot water and steam applications. The market studies estimate a steady growing demand for EPDM rubber in the next years. [5]

As a consequence of the continuous production of rubber, the recycling of waste has become a very important research topic nowadays for many industries major implications on environmental protection, progressive industrial growth and economy. In order to solve this problem, there have been different attempts with regard to recycling EPDM rubber. The recycling or reclaiming processes are very difficult and not completely understood until now due to the irreversible three-dimensional cross linking of rubbers. [6] Due to the different chemical nature of EPDM, the recycling conditions are different and more strenuous in comparison with other types of diene rubbers, i.e. NR [7] or SBR. [8]

A first step in the recycling process of rubber waste is to transform it to granulate or fine powder. This process can be made either using ambient cryogenic or wet grinding method as presented in Chapter 2, followed by upgrading the waste particles, or by surface treatment or reclaiming process. [9]

The most frequently used recycling methods for EPDM rubber waste powder are based on devulcanisation techniques, which assume that only cross-links are broken by mechanical, [10-12] thermo-mechanical, [13,14] ultrasonic, [8,15] microwave [16-18] and chemical [19-21] processes. Although devulcanisation is estimated to give a high quality recycled rubber, in terms of processing and properties, there are still several important shortcomings that should be taken into consideration. A common disadvantage results from the fact that not only cross-links are cleaved, but also scission of the main chain of the polymer partially occurs. This leads to branched macromolecules with broader molecular weight distributions than the original elastomer and thus having a considerable influence on worsening the mechanical properties of the reclaim process. Another major shortcoming of the devulcanisation process stems from the fact that general safety is compromised as high quantities of odorous chemicals are required. [22] In order to be able to recycle at industrial scale, a safe and an easily applicable process is preferred.

Taking into consideration the above mentioned issues, this project reports a novel solvent-free recycling method of EPDM ground waste rubber particles. Here, the EPDM waste rubber particles (RWP) were activated by low molecular weight polymers (LP) which are highly compatible with RWP and also suitable for sulphur crosslinking.

In the early 1980s Stark et al. [23,24] proposed a novel technology whereby the surface modification of the cured rubber scrap was prepared using a liquid unsaturated polymer soluble in a certain solvent and a curing agent. The yielded dry crumb particles were further used at high concentrations as an additive to virgin rubber to give products with acceptable loss of physical properties. The elastomer types of rubber scrap were essentially hydrocarbons, i.e. NR, CR, NBR, SBR, IIR and EPDM, mostly coming from automobile tires industry. In his work, Stark presented the method in an elemental way, with little information on the processability and mechanical properties of the recycled samples.

Therefore, in order to get a better insight of this process a comprehensive and systematic work was necessary to be carried out. For this purpose, within the frame of the present study, two different types of liquid polymers with the trade name

Trilene® are used for the activation of the EPDM rubber waste particles. Trilene® liquid polymers belong to a category of viscous, low molecular weight ethylene-propylene non-conjugated diene terpolymers. These types of polymers are randomly polymerized to produce liquid elastomers with stable, saturated hydrocarbon backbone. The terpolymer, which gives their reactivity from pedant unsaturation, can be used in further applications that require curing, i.e. in sulphur vulcanisation process.

Having the advantage of being in a liquid state, possessing a low viscosity, low molecular weight, and additionally, having the potential to exploit their unsaturation functionality, given by the third monomer, these types of polymers can be further used in crosslinking reactions for surface chemical activation of waste rubber particles. Due to the fact that the ground rubber exhibits a very low reactivity on the particle surface, the chemical activation using liquid polymers together with a curing system gives the possibility of obtaining new materials with improved mechanical properties. This work focuses on upgrading EPDM vulcanized rubber powder by chemical surface activation with an objective aiming to further utilization of the activated particles, used in substitution of the raw material, in obtaining high quality rubber products, i.e. sealing systems.

To get a better insight of the process this chapter focuses on the chemical activation of sulphur cured EPDM rubber waste particles using LP in two components system: only RWP and LP, respectively. The investigations were initially started with the characterisation of the rubber waste powder. Thereafter the attention was given to:

1) finding the optimal ratio between the rubber waste particles and the liquid polymers
2) studying the effect of different amounts of activators, accelerators and sulphur
3) investigating the effect of the percentage of double bonds in the liquid polymers on the properties of the final product.

Finally, the mechanical properties of the optimised product were compared with a commercial EPDM recipe used in production of sealing systems.

3.2 EXPERIMENTAL

3.2.1 Materials

The EPDM rubber waste particles (RWP) were supplied by M.D.S. Meyer GmbH, Germany and were obtained by ambient grinding from a typical sulphur-cured EPDM vulcanizate. The liquid polymers (LP) with the trade name Trilene®, used for activation of the rubber waste particles, were supplied by Lion Copolymer, USA and the main properties are given in Table 3.1. The zinc oxide (ZnO) and sulphur (S) were obtained from Melos GmbH, Germany. The stearic acid was obtained from Carl Roth GmbH + Co. KG, Germany, and N-Cyclohexyl-2-benzothiazolesulfenamide (CBS) was obtained from Sun & Bright Industrial Ltd., China.

S was used as vulcanizing agent, ZnO and stearic acid were used as activators and CBS was used as accelerator for vulcanisation process. Toluene (99.7%), which was used for equilibrium swelling measurements, was purchased from Sigma – Aldrich Chemie GmbH, Germany. All chemicals were used as received with no further purification.

Table 3.1 The main properties of the ethylene-propylene-ethylidene norbornene low molecular weight polymers

Properties	**Trilene® 67**	**Trilene® 66**
Colour	pale yellow	pale yellow
Specific gravity	0.86	0.84
Molecular weight, Da	7.700	8.000
Degree of unsaturation, % Diene	9.5	4.5
Diene type	ENB[a]	ENB[a]
Ethylene/propylene	45/55	45/55

[a] ENB – 5-ethylidene-2-norbornene

3.2.2 Characterisation of EPDM Rubber Waste Particles

a) Physical Characterisation

The particle size distribution was measured by laser diffraction technique using a HELOS (Helium-Neon Laser Optical System) laser diffraction sensor, compliant with ISO 13320-1:2009 (Sympatec GmbH, Germany). A sample of a known weight (8.33g) is measured using R7 HELOS with a measuring range of 0.5/18.0-3500 µm and 76.03 s. To verify the reproducibility of the HELIOS system and the quality of dispersion, three samples were precisely measured.

The void volume of the RWP was measured at room temperature as determined by ASTM D7854-method (Brabender, Germany). Samples of a known weight and density were introduced in a graduated cylinder and compressed by applying a pressure of 250 MPa for 60 sec. At the end, the pressure was reduced and the void volume was calculated from the difference between sample volume compression and decompression. Three measurements were performed using samples with different weights (1g, 1.5g and 2g) and the void volume was calculated by the median of the obtained values.

The density of the sample was determined by means of an ELATEST device from Brabender GmbH, Germany. Samples with a defined weight between 50 and 70 g were tested using an inlet pressure of 6 bars. The density was calculated by the mean value of 5 measurements.

b) Thermal Characterisation

The thermal characterisation was performed by means of thermal gravimetric analyses (TGA). The TGA analysis was used to determine the composition of the RWP using a Mettler TGA / sDTA 851e thermogravimetric analyzer (Mettler-Toledo GmbH, Germany). The sample (ca. 5-10 mg) was heated from ambient temperature to 600 ^{0}C in N_2 atmosphere, then switched to O_2 atmosphere and heated up to 900 ^{0}C, with a heating rate of 10 ^{0}C min $^{-1}$ under 50ml min^{-1} N_2 and O_2 atmospheres, respectively.

3.2.3 Compounds Recipes

The formulations of the samples composition are presented in Table 3.2 and Table 3.3. Samples listed in Table 3.2 were obtained using two different types of LP, type A with 9.5% ENB and type B with 4.5% ENB, using a constant ratio of curing system. The content of waste rubber particles (RWP) was varied from 0.5 to 0.9

volume fractions. Table 3.3 presents the formulations for the samples where the content of curing system was varied and the amount of LP and RWP content was kept constant (volume fraction 0.8 RWP).

Table 3.2 Composition of RWP/LP samples with different RWP content and constant vulcanisation system

Ingredients	**Sample name**									
	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5
	Amount (phr)[a]									
LP[b]			100					100		
	(42.4)	(33.8)	(24.5)	(16.1)	(7.6)	(42.5)	(32.8)	(24.0)	(15.8)	(7.6)
RWP	140	210	330	560	1300	145	220	340	570	1300
	(56.6)	(66.2)	(75.5)	(83.9)	(92.4)	(57.5)	(67.2)	(76.0)	(84.2)	(92.4)
ZnO			2					2		
Stearic acid			1					1		
CBS[c]			3					3		
Sulphur			1.2					1.2		

[a] phr- parts per hundred liquid polymer; [b] LP-A: Trilene67; LP-B: Trilene66; [c] CBS – N-Cyclohexyl-2-benzothiazolesulfenamide. The values in parentheses are the equivalent of LP+curing system and RWP, respectively calculated in weight percent (wt %).

Table 3.3 Composition of RWP/LP samples with constant RWP content and variable vulcanisation system

Ingredients	**Sample name**											
	A4						B4					
	a	b	c	d	e	f	a	b	c	d	e	f
	Amount (phr)											
LP	100						100					
RWP	560						570					
ZnO	0	2	4	6	8	10	0	2	4	6	8	10
Stearic acid	0	1	2	3	4	5	0	1	2	3	4	5
CBS	0	3	6	9	12	15	0	3	6	9	12	15
S	0	1.2	2.4	3.6	4.8	6	0	1.2	2.4	3.6	4.8	6

3.2.4 *Mixing and Vulcanisation*

The preparation of RWP/LP compounds was performed in a laboratory internal mixer, Haake Polylab QC from Thermo Scientific, Germany, using conventional mixing procedures that involved two stages: in the first stage the mixing of RWP and the LP was carried out with a fill factor of 0.7, at a chamber temperature of 100 ºC and a rotor speed of 40 rpm for 15 min. In the second stage the blends were mixed followed by addition of the activators (ZnO and stearic acid) and crosslinking agents (CBS and sulphur), in the same mixing chamber at a temperature of 90 ºC, with 40 rpm for 7 min.

The curing characteristics of the rubber compounds were determined according to ISO 6502:2009 using a Dynamic Moving Die Rheometer type D-MDR-3000 from MonTech Werkstoffpruefmaschinen GmbH, Germany. The tests were performed at 180 ºC for 30 min. D-MDR-3000 is a rotorless, dynamical shear vulcameter with a biconal closed test chamber. In the test, the rubber sample with a fixed volume of approximately 4.5 cm^3 is enclosed within the heated chamber. The samples were cut using a Rheometer volume cutter model R-VS 3000 from MonTech Werkstoffpruefmaschinen GmbH, Germany. Vulcanisation was measured by the increase in the torque at a given temperature.

Furthermore, the compounds were compression – moulded at 180 ºC with a pressure of 10 MPa using an electrically – heated hydraulic press type Polystat 200T (Schwabenthan, Germany), according to their respective cure time, t_{90}. The cured sheets had a thickness of 2 mm.

3.2.5 *Characterisation of RWP, LP and RWP/LP samples using ^{1}H-NMR Spectroscopy*

Magic angle spinning (MAS) ^{1}H-NMR spectra were recorded on a Brucker AMX-500 spectrometer at a resonance frequency of 500 MHz. A 4 mm probe head was used with a MAS rate of 8 kHz. The spectra were acquired by means of a single-pulse excitation with 90° pulse of 5 µs and a recycling delay time of 5 s. The (MAS)

^{1}H-NMR were recorded for RWP and the vulcanised samples. The experiments were performed at 20 ºC. Deuterated water was used as a solvent.

^{1}H-NMR (500 MHz) spectra were recorded on a Brucker AMX-500 spectrometer using tetramethylsilane (TMS) as an internal standard and deuterated benzene at 20 ºC as a solvent. The ^{1}H-NMR was used for the characterisation of the accelerator.

3.2.6 Characterisation of the vulcanised samples

3.2.6.1 Mechanical Properties

Hardness – The hardness of the vulcanisates were measured using a Shore A Durometer (Karl Frank GmbH, Germany) according to ISO 7619-1:2010. Samples of 6 mm thickness were used for the measurements and the hardness values were calculated as an average of three measurements for each vulcanisate.

Tensile tests – Tensile tests were performed in accordance with ISO 37:2011 on dumbbell shaped specimens using a universal testing machine Zwick 1120 from Zwick GmbH & Co. KG, Germany. The nominal force of the load cell was 2000 N. For the tensile tests a preload of 1N was applied. The tests were performed at constant crosshead speed of 200mm/min. Shape and dimensions of the dumbbell test specimen ISO 37 (Type 2) are shown in Figure 3.1 and Table 3.4, respectively. Hardness and tensile tests were carried out at room temperature (23±2 ^{0}C).

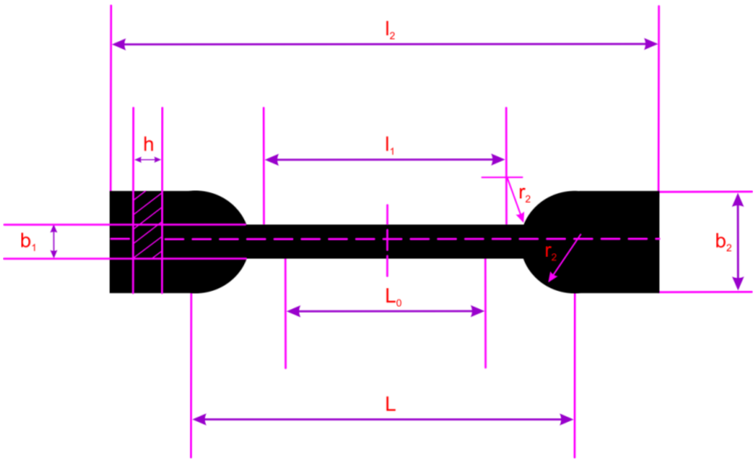


Figure 3.1 Shape of dumbbell test specimen ISO 37 Type 2

Table 3.4 Dimensions of dumbbell test specimen according to ISO 37 Type 2

ISO 37 Type 2 specimen			**Dimensions [mm]**
l_1	-	Length of narrow parallel–sided portions or inner diameter	25 ± 1
l_2	-	Overall length or outer diameter	≥ 75
b1	-	With of narrow portions	4 ± 0.1
b2	-	With of ends	12.5 ± 1
r1	-	Small radius	8 ± 0.5
r2	-	Large radius	12.5 ± 1
L	-	Initial distance between grips	50 ± 2
L_0	-	Gauge length	20 ± 0.5
H	-	Thickness	≥ 2

3.2.6.2 Crosslinking density

a) Equilibrium swelling tests

The crosslinking density of the vulcanised compounds was determined by means of equilibrium swelling in toluene. Rectangular test pieces with dimension of 30 X 10 X 2 mm^3 were immersed in ca. 30 mL toluene at 24 ^{0}C for 4 h until the samples reached the maximum swelling. The solvent was replaced after 24 h with fresh toluene to remove the extracted components.

After 48 h the test pieces were removed from toluene and the surfaces were quickly wiped with tissue paper and weighted to find the swollen weight of the samples. The samples were further dried at 50 ^{0}C for 48 h, cooled in a desiccator and then weighted again. The polymer volume fraction was calculated using the Equation 3.1 [25] below. The density of the solvent in calculations was 0.87 g/cm^3.

$$V_r = \frac{V_P}{V} = \frac{1}{\left(1 + \frac{m - m_d}{m_d}\right) \cdot \frac{\rho_P}{\rho_S}} \qquad 3.1$$

where:

V_r - polymer volume fraction;
V_P - volume of the dry sample;
V - total volume of the swollen sample;
m - mass of the swollen sample;
m_d - mass of the sample after drying;
ρ_P - density of the sample;
ρ_S - density of the solvent.

The density of the sample, ρP, was the mean value calculated from the density of RWP and the density of the LP. The crosslinking density, which represented the effective number of chains segments per unit volume, was calculated according to the Flory-Rehner Equation: [26]

$$\upsilon_e = -\frac{\ln(1-V_r)+V_r+\chi V_r^2}{V_S\left(V_r^{\frac{1}{3}}-\frac{V_r}{2}\right)} \tag{3.2}$$

where

ν_e - crosslinking density., i.e. number of crosslinks per unit volume (mol/m^3);
V_S - solvent molar volume; 106.5 cm^3/mol for toluene;
χ - polymer–solvent interaction parameter; 0.49 for EPDM/toluene system. [27]

The Flory-Rehner equation was used to calculate the crosslinking density for a non-filled system. In the case of filled compounds, especially for compounds with different filler compositions where it was necessary to compare the crosslinking densities of the samples, the Kraus correction was applied. [28] In such case no filler is added to the composition. The compounds contained only the filler embodied in RWP composition, which was the same for all samples, therefore the apparent crosslinking densities of the compounds could be precisely compared without the Kraus correction. The values obtained from swelling measurements are presented in Table 3.5

Table 3.5 Values obtained from swelling measurements for LP-A, A1-A4, B1-B4, A4a-f, B4 a-f and RWP

Samples	m_0 [g]	m [g]	m_d [g]	V_r
A1	0.3629	1.1211	0.2725	0.20631
A2	0.3944	1.0769	0.2969	0.23401
A3	0.3739	0.8946	0.2840	0.26945
A4	0.3889	0.8504	0.2931	0.29254
A5	0.3836	0.7585	0.2904	0.32496
B1	0.3850	1.1593	0.2719	0.20103
B2	0.3849	1.0170	0.2728	0.22992
B3	0.3764	0.8929	0.2687	0.25794
B4	0.3879	0.8236	0.2852	0.29681
B5	0.4000	0.7770	0.2967	0.32730
A4a	0.3552	0.7783	0.2530	0.27591
A4c	0.3849	0.8085	0.2973	0.31211
A4d	0.3592	0.7306	0.2791	0.32425
A4e	0.3757	0.7468	0.2933	0.33335
A4f	0.3848	0.7518	0.3013	0.34017
B4a	0.3783	0.7309	0.2494	0.29248
B4c	0.3888	0.8250	0.2921	0.30348
B4d	0.3864	0.8018	0.2940	0.31429
B4e	0.3786	0.7705	0.2902	0.32283
B4f	0.3925	0.7851	0.3027	0.33048
LP-A	0.3720	2.1463	0.2861	0.13485
RWP	2.0908	8.9418	1.8112	0.14809

b) Temperature scanning stress relaxation tests

Besides swelling measurements, the crosslinking density of the samples were determined as well from the anisothermal stress relaxation test (AISR) using a TSSR instrument. A commercial TSSR instrument (Figure 3.2) manufactured by Brabender GmbH (Duisburg, Germany) was used to perform the tests. The instrument consists of an electrical heating chamber where the sample is placed between two clamps. The clamps are connected to a linear drive unit to apply a certain uniaxial extension to the sample. A high signal amplifier is used in combination with a high resolution AD-converter to enable the detection and digitisation of analogue signals of the high resolution force transducer and the thermocouple. All signals were transferred to a computer with a custom-made software which is used to process and evaluate the data as well as to control the machine system.

During the test, a constant tensile strain of at least 50% was applied to a dumbbell test specimen (ISO 37, Type 2), which was placed in an electrically heated test chamber (Figure 3.2). After applying the initial strain of 50%, the test procedure started with the pre-condition of the samples for 2 h at 23 °C. During the isothermal test most of the short time relaxation processes occurred and the sample reached a nearly stable state. After the isothermal relaxation test period was completed, the sample was heated linearly at a constant rate of 2K/min, until the stress relaxation had been fully completed or rupture of the sample has occurred.

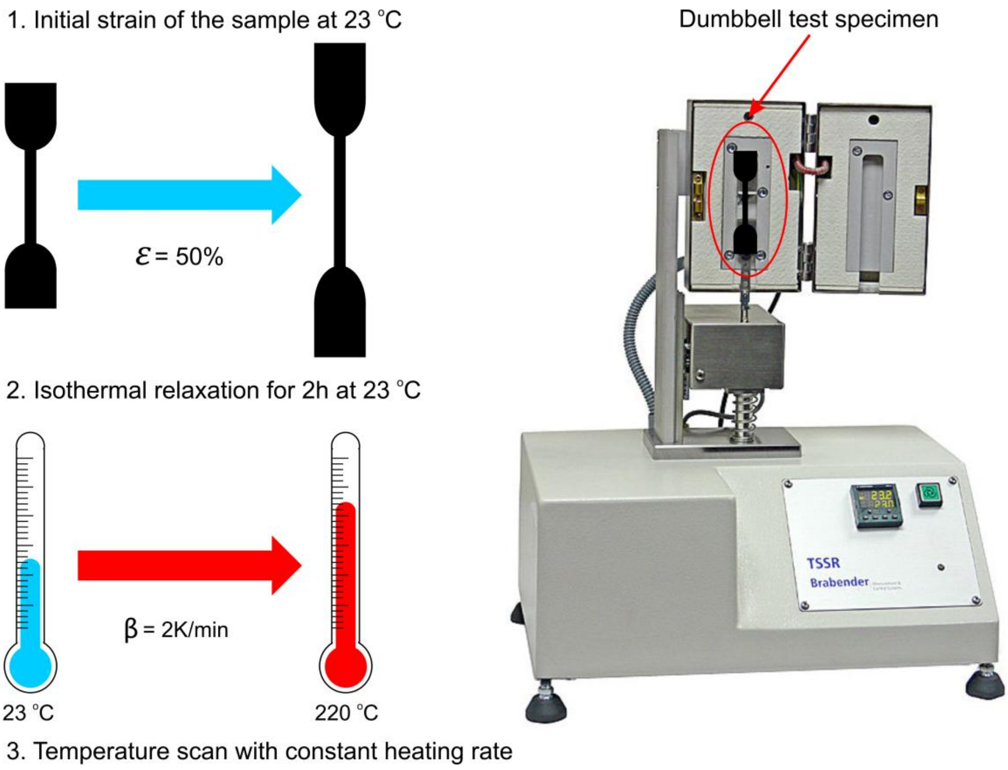


Figure 3.2 TSSR-Meter instrument and test procedure [29]

According to the well-known theory of rubber elasticity the mechanical stress σ is proportional to the absolute temperature T [30,31] and can be expressed by Equation 3.3.

$$\sigma = \frac{\rho \cdot R \cdot T}{M_c}(\lambda - \lambda^{-2}) \qquad 3.3$$

where ρ is the mass density, R is the universal gas constant, λ is the strain ratio and M_c is defined as the average molar mass of the elastically active network chains.

At constant strain the slope of the stress versus temperature plot reveals the crosslinking density. The crosslinking can be then calculated from the empirical values of the temperature coefficient, by using Equation 3.4.

$$\upsilon_e = \frac{\kappa}{R \cdot (\lambda - \lambda^{-2})} \qquad 3.4$$

where υ_e is the crosslinking density (mol/m^3), and κ represents the temperature coefficient of stress, i.e. the derivative of mechanical stress with respect to temperature.

It is noteworthy that Equation 3.4 is based on the well-known theory of rubber elasticity but it applies only for ideal rubber networks. Therefore, application of Equation 3.4 leads to an apparent crosslink density values in this case, because of the complex composition and structure of the investigated compounds.

3.2.7 Scanning Electron Microscopy (SEM) Studies

SEM studies were carried out on tensile fracture surfaces of EPDM-P and EPDM-P/LP samples using a JEOL JSM 6510 scanning electron microscope (JEOL GmbH Germany). Cryogenically fractured surfaces were coated with a thin layer of gold prior to examination, using a Fine Coater JEOL JFC 1200.

3.3 RESULTS AND DISCUSSION

In order to test the effectiveness of the liquid polymers (LP) to be used in the chemical activation process of the rubber waste particles (RWP), different approaches were applied. First studies were carried out to investigate the influence of the rubber waste particles amount and to determine the optimal ratio between the LP and the RWP. Afterwards, the effect of different amounts of curing system was studied on a defined ratio between LP and RWP. Concomitant with the above mentioned investigations, the influence of the double bonds concentration were studied as well. The cure characteristics, mechanical properties and the morphology of the studied compounds were analysed. Prior to these tests, the rubber waste particles used in this work were characterised.

3.3.1 Characterisation of EPDM rubber waste particles

a) Physical Characterisation of RWP

It has been already reported that the grinding processes of the vulcanisate profile scraps could produce different types of powder with different shapes and surface roughness. Moreover, according to the specifically intended application, a standard formulation for pipe joint seals could be prepared with different loadings of ingredients like carbon black, plasticiser, vulcanisation agents, accelerators, activators… etc.

While the formulation of the rubber waste particles was unknown, as in this reported case, a prior characterisation of the waste grounded particles was necessary to be done in order to find a suitable utilisation in further regenerations processes. In this study, the physical characterisation of the RWP was achieved by particle size distribution, void volume and density. In this thesis the terms RWP and EPDM rubber waste particles are interchangeable.

The particle size distribution of the RWP was measured by means of a laser diffraction method. This technique allows analysing particle sizes from 0.1 µm to 3.5 mm. [32] Figure 3.3 illustrates the volume concentration versus the particle size of the particles.

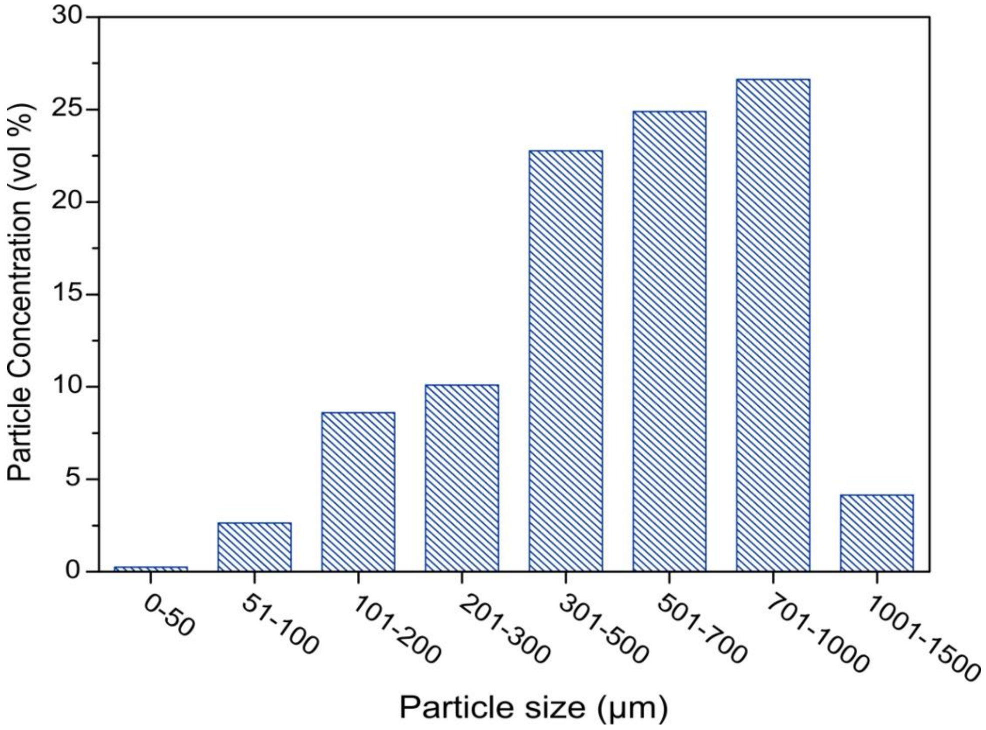


Figure 3.3 Particle size distribution of RWP obtained by laser diffraction method

It was found that most of the particles, a percentage of 74 %, had an average size between 300 and 1000 µm (50 and 18 mesh). The ambient grinding technique produced a powder with an irregular shape, rough surface and relatively large surface area. [33,34]

In a study regarding the rubber powder characterisation by using solid shear extrusion process, Bilgili et al. [11] mentioned that the particles with rough surface and irregular shape enhanced particle - matrix adhesion, which represented a positive aspect in the case of surface activation process where the interfacial adhesion between the activated RWP and the polymer matrix is of high importance.

In order to determine the void volume of the RWP, also known as free space, the samples were introduced in a cylinder and compressed by applying a certain pressure and time. Afterwards, the pressure was reduced and the void volumes were calculated from the difference between sample under compression and after decompression. A typical void volume of 30% was found for RWP.

With regard to the density of the particles, a sample of a known weight was compressed in a measuring cylinder. During compression any gas present in the sample was released from the system. From the sample weight and volume, the density was automatically calculated. The density of the pressed particles was found to be 1.19 g/cm^3.

b) Thermal Characterisation of RWP

The content of volatile and thermally decomposable compounds as well as the thermal stability of RWP were determined with the help of thermogravimetric analysis (TGA). The measurements were effectuated until 600 ºC under N_2 flow and switched to O_2 flow until 900 ºC. The gas switch was used to determine the carbon black and ash content. The TG-DTG curve of RWP analysis is shown in Figure 3.4.

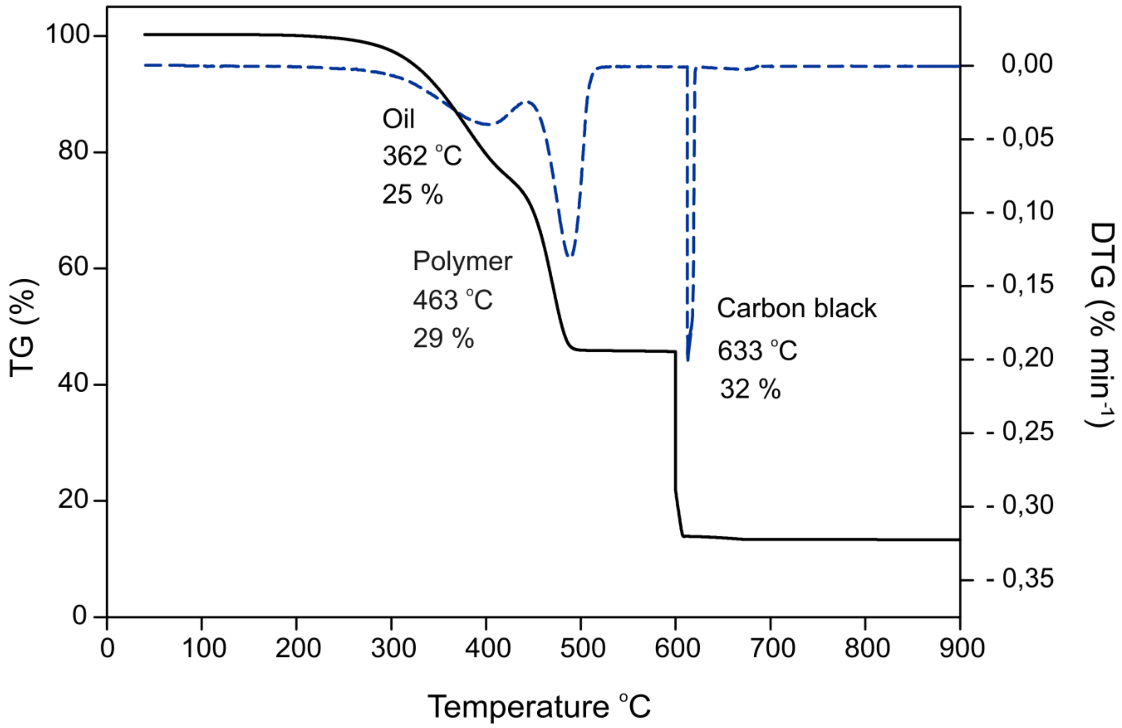


Figure 3.4 Thermogravimetric analysis of RWP under N_2 (up to 600 ºC) and O_2 (up to 900 ºC) flow with a heating rate of 10 ºC

The first mass loss at 362 ^{0}C is due to the volatilisation of the oil present in the particles. The second mass loss at 463 ^{0}C appears to be due to polymer degradation and the third mass loss at 633 ^{0}C attributed to the carbon black content present in the sample. From the TGA results it can be concluded that the RWP contain a paraffinic oil [35] type that represents 25 wt% of the sample composition. The polymer content in the sample is 29.4 wt% and carbon black content is about 32%. A residual mass of 13.6 wt% represents the non-volatile residues (ash) corresponding mainly to inorganic fillers such as metallic oxides.

3.3.2 Characterisation of RWP, LP and RWP/LP samples using 1H-NMR Spectroscopy

The formulation and the preparation of the investigated samples were performed following the protocol described in the Section 3.2. First, the RWP amount was varied between 0.5 to 0.9 volume fraction and two different types of LP were used for activation, LP-A (A1-A5 samples) and LP-B (B1-B5 samples), respectively (see Table 3.2). Second, the ratio between RWP and LP was kept constant at 4:1, respectively, and the curing system was varied from 0 to 6.0 phr sulphur. Under these conditions, twelve different formulations were prepared as shown in Table 3.3, six with the LP-A (A4a-f) and the other six with the LP-B (B4a-f). The mixing procedure was done by using an internal mixture and the vulcanisation of the samples was performed at 180 ^{o}C for 30 min by using a rheometer. Prior to testing, the investigated samples were obtained via vulcanisation according to their cure times (t_{90}) that was recorded from rheometer tests.

Whereas the NMR technique can give some specific information about the compounds only some relevant samples were chosen to be studied: the non-activated RWP, vulcanised LP-A, unvulcanised A4 and vulcanised A4 samples. The samples were cured according with the optimum cure time (t_{90}) using the curing system presented in Table 3.2. Sample A4 contained a volume fraction of 0.8 RWP and 0.2 LP-A (Section 3.2, Table 3.2).

Any remaining double bonds in the recycled rubber powder as previously mentioned by Giese and co–workers, [6] can be used as reactive centre for chemical modification of waste particles surface towards achieving a better grafting onto a virgin rubber matrix. According to Giese, the double bond concentration is higher for the fine-grained powder compared to coarse–grained ones. However, this technique cannot be applied for sulphur-cured EPDM rubbers because of the fact that during vulcanisation the sulphur substitution occurs only at the allylic positions while the double bonds remain intact.[36] Yet, NMR technique represents a valuable tool to identify protons from EPDM rubber and protons from the accelerator.[37] And in this case, it was possible to identify one type of the accelerator that has been used in RWP formulation.

Figure 3.5b-e shows the MAS ^{1}H-NMR spectra of RWP, vulcanised LP-A, unvulcanised A4 and vulcanised A4 compounds. As a reference, the ^{1}H-NMR spectra of the N–Cyclohexyl–2–benzothiazolesulfenamide (CBS) accelerator that was used in this investigation is shown in Figure 3.5a. The chemical structure of the compound is also presented in Figure 3.6.

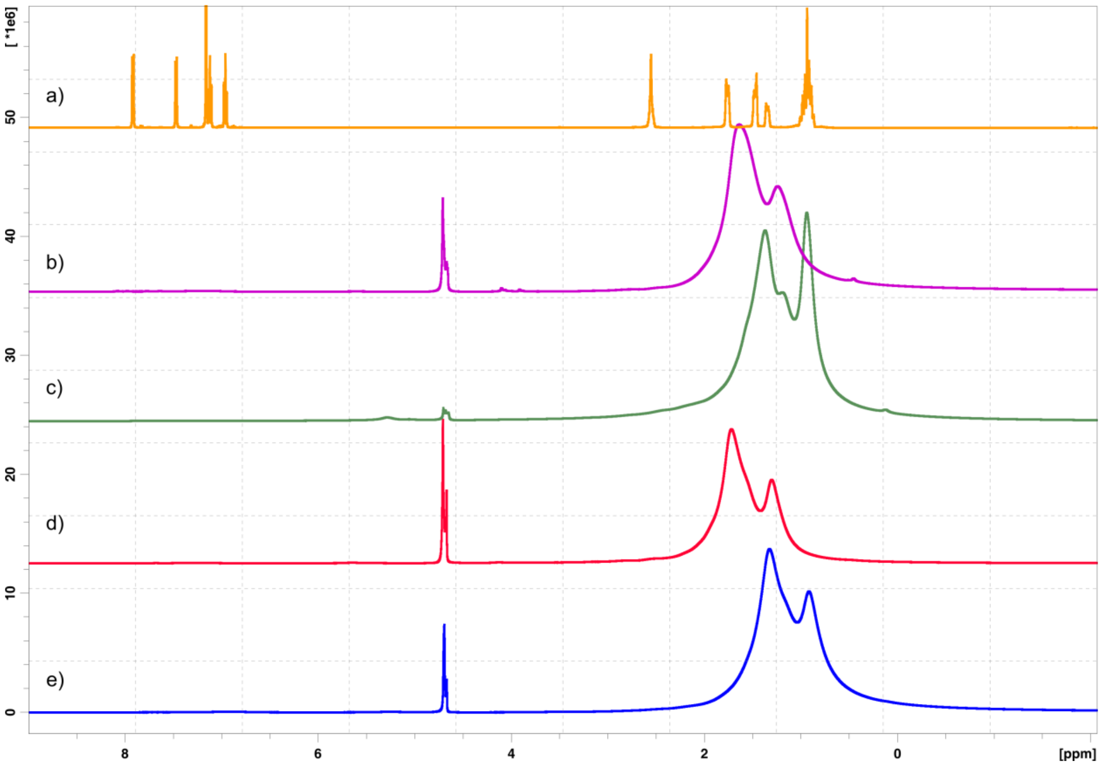


Figure 3.5 ^{1}H-NMR spectra of: a) CBS; b) RWP; c) vulcanised LP-A; d) unvulcanised A4 and e) vulcanised A4

In all four spectra presented in Figure 3.5b-e, it is possible to identify the characteristic signals of the aliphatic protons of the ethylene-propylene units (EPM) at chemical shift ranging from 0.7 to 2.0 ppm, [37] while the double–bond protons cause a more narrow signal around 4.7 ppm. [38]

In the case of CBS spectra shown in Figure 3.5a the region 6.9 – 8.0 ppm represents the aromatic protons from benzene ring. The solvent residual peak, deuterated benzene, can be detected at ca. 7.2 ppm (Figure 3.5a). The signals from N-Cyclohexyl ring can be observed at chemical shift ranging from 0.8 to 2.6 ppm.

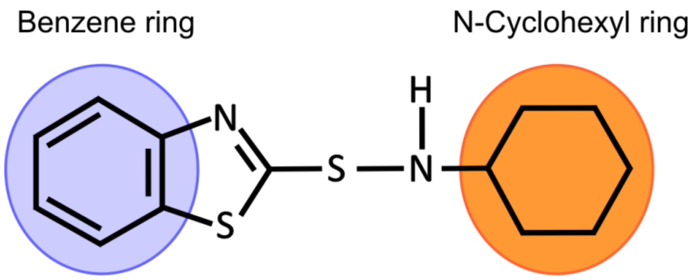


Figure 3.6 Chemical structure of N-Cyclohexyl-2-benzothiazolesulfenamide (CBS)

Applying higher resolution as in Figure 3.7, the signals of the vinyl protons of ENB unit can be seen in the spectral range from 4.5 to 5.8 ppm, [38] while the signals of unreacted accelerators are also present in the spectral range from 7.6 to 8.2 ppm (Figure 3.7b and Figure 3.7d). In the spectra of the RWP it is still possible to observe remainings of the curing system (Figure 3.7b). These affirmations can be made based on the spectra presented in Figure 3.7d-e.

Figure 3.7d shows the spectra of sample A4 before vulcanisation and Figure 3.7e presents the spectra of the same sample after vulcanisation. It is obvious that the signal in the range of 7.6 – 8.2 disappears after vulcanisation proving that the curing system participates in the crosslinking process. The chemical shifts of the ENB residues, protons of RWP (Figure 3.7b) and of the unvulcanised A4 sample (Figure 3.7d) are present as a broad signal from 5.3 to 5.8 ppm, while in the vulcanised LP-A (Figure 3.7c) and vulcanised sample A4 (Figure 3.7e) these signals are shifted to lower field, from 5.0 to 5.4 ppm respectively. The subsequent difference in the chemical environment is sufficient to induce a shift of EBN protons, which suggests that the crosslinking agents have been largely converted as a result of crosslinking reactions between LP and RWP. The signals detected in Figure 3.7b and Figure 3.7d in the range from 3.9 to 4.2 could be attributed to another type of accelerator that may have been used in the formulation of RWP and could not be identified. This affirmation is made on the basis that the samples of LP-A shown in Figure 3.7c does not exhibit those signals. Additionally, those signals disappear after vulcanisation proving that the remaining accelerators participated further in crosslinking reactions (Figure 3.7e).

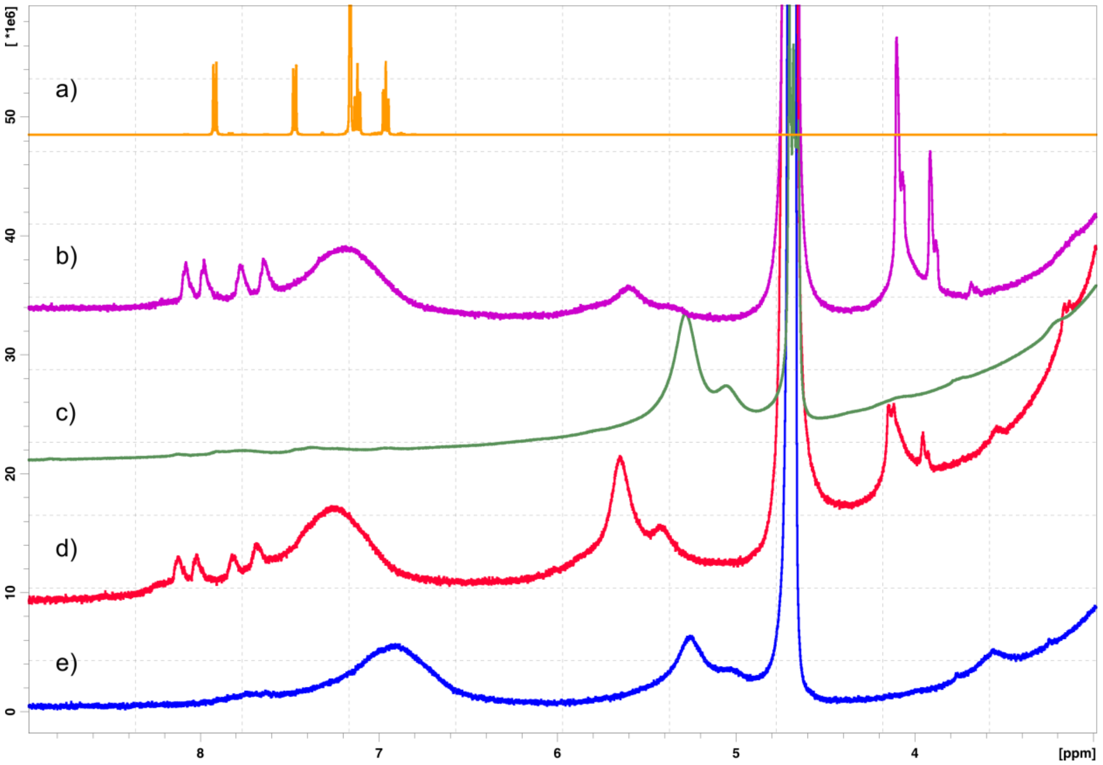
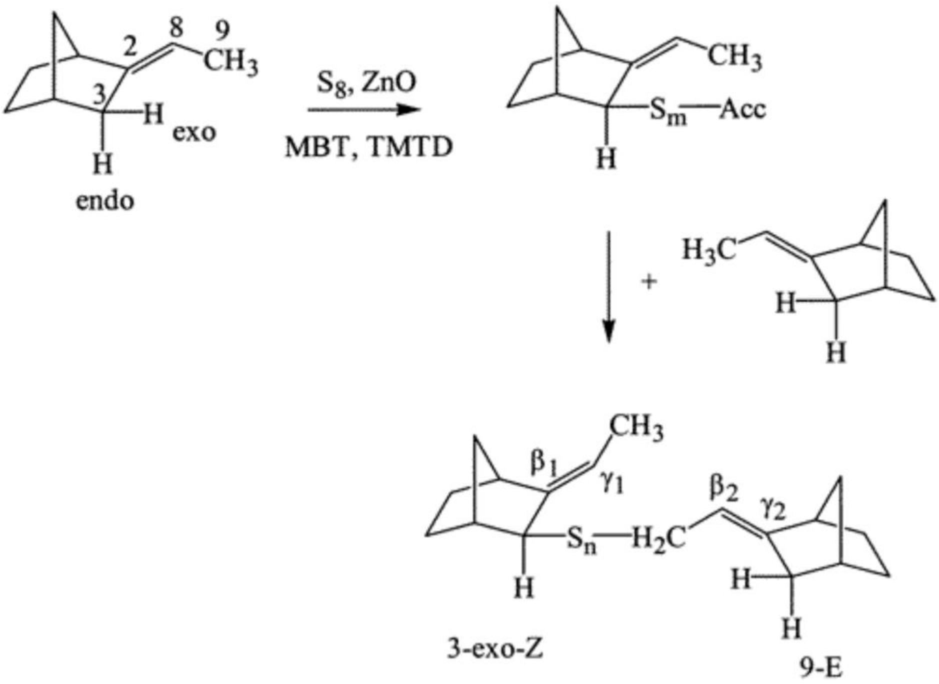


Figure 3.7 ^{1}H-NMR spectra of: a) CBS; b) RWP; c) vulcanised LP-A; d) unvulcanised A4 and e) vulcanised A4



Scheme 3.1 Accelerated sulphur vulcanisation of ENBH (Acc = accelerator residue)[39]

This results indicate that a chemical reaction takes place in RWP, LP and presumably between RWP and LP to a certain extent during the vulcanisation process, most probably due to the formation of a sulphur crosslinking network via substitution at the α-position next to the residual double bond of ENB as shown in the reaction scheme (Scheme 3.1) of the sulphur vulcanisation of 2-ethylidene-norbornane (ENBH). [39]

3.3.3 Cure Characteristics – Influence of RWP content

In order to characterise and verify the processing conditions of a rubber compound the curing process was monitored by using a rheometer. The extent and rate of crosslinking as measured by the rheometer is given by a typical curve, as presented in Figure 3.8, where the measured torque is plotted as a function of the curing time.

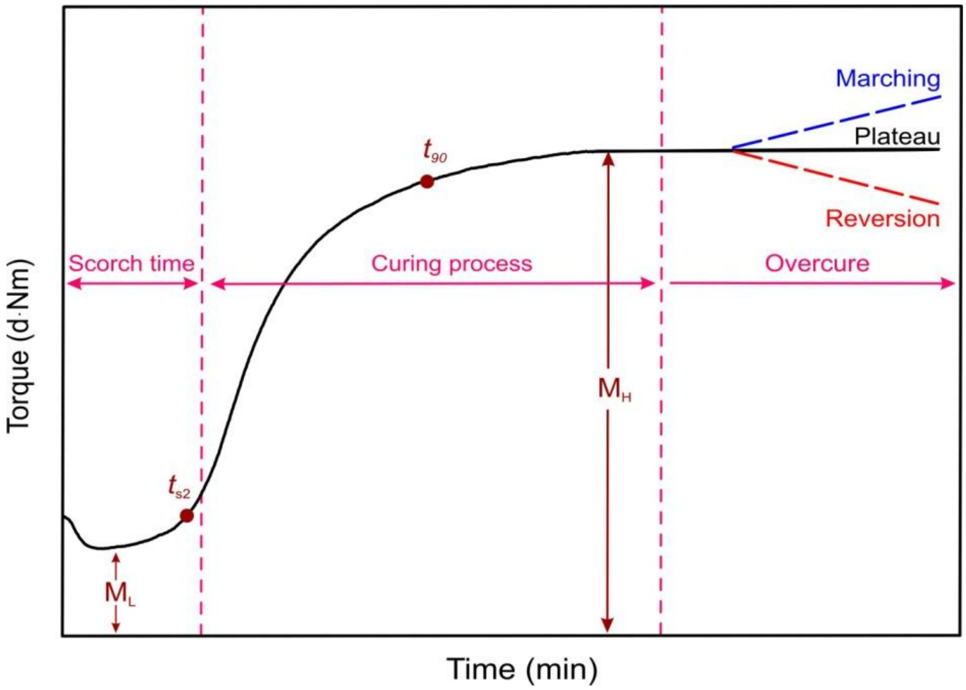


Figure 3.8 Typical rheometer curve showing the curing characteristics

The overall process involves three stages: scorch time or induction period, curing or crosslinking stage and the overcure region, where the modulus can decrease, remain constant or increase depending on the temperature and vulcanisation system.

The curve exhibits a number of features which are used to compare cure. The minimum torque (M_L) represents the lowest torque on the vulcanisation curve, being correlated to the viscosity of the uncured compound. The maximum torque (M_L) represents the highest torque on the vulcanisation curve, being correlated to the vulcanisate stiffness at the end of the vulcanisation process. The difference between the maximum M_H and the minimum M_L torque (ΔM) is correlated to the crosslinking density of the vulcanisate compound.

Another important characteristic is the scorch time (t_{s2}), which is the time required for an increase of 2 units in torque above M_L. The scorch time indicates the time required for the beginning of the crosslinking process providing at the same time a measure for the process safety of the rubber compound. The cure time (t_{90}) represents the time required for reaching 90% of the maximum achievable torque, being also considered the optimum time for vulcanisation.

In order to investigate the potential of the RWP to be chemically activated by use of liquid polymers (LP) and to find an optimal formulation which can be further used as a substitute of raw material, various formulations were prepared following the protocol described in Section 3.2, Table 3.2. Accordingly, ten mixtures were prepared, for which the RWP content was varied from 0.5 to 0.9 volume fractions. Five of the samples, denoted here as A1-A5, were compounds with RWP activated by using a LP with a high amount of double bonds (LP-A = Trilene 67) and the other five samples, denoted by B1-B5, represented compounds where the RWP were activated by using the LP with a lower content of double bonds (LP-B = Trilene 66).

Figure 3.9 shows the rheometric curves of the compounds containing various contents of RWP and Table 3.6 summarises the vulcanisation parameters of the compounds. The obtained data show that the increase of the RWP content in the sample composition resulted in an increase of minimum (M_L) and maximum torque (M_H) with both types of samples. The rise in minimum torque was expected considering that the viscosity of the RWP is much higher than that of the LP. Therefore, the initial viscosity of the uncured compounds increases when increasing the RWP amount. The higher values obtained for the maximum torque in the case of the samples with LP-A in the composition were assigned to the higher ENB percentage of the liquid polymer, which plays an important role in controling the crosslinking density. The increase of the maximum torque may be attributed to the good interaction between LP and RWP. This increase can also be related to the carbon black content of the RWP.[40] The thermal analysis showed (Figure 3.4) that the content of active filler (carbon black) in the RWP was 32%. Therefore, by increasing the RWP content, the content of carbon black was also increased.

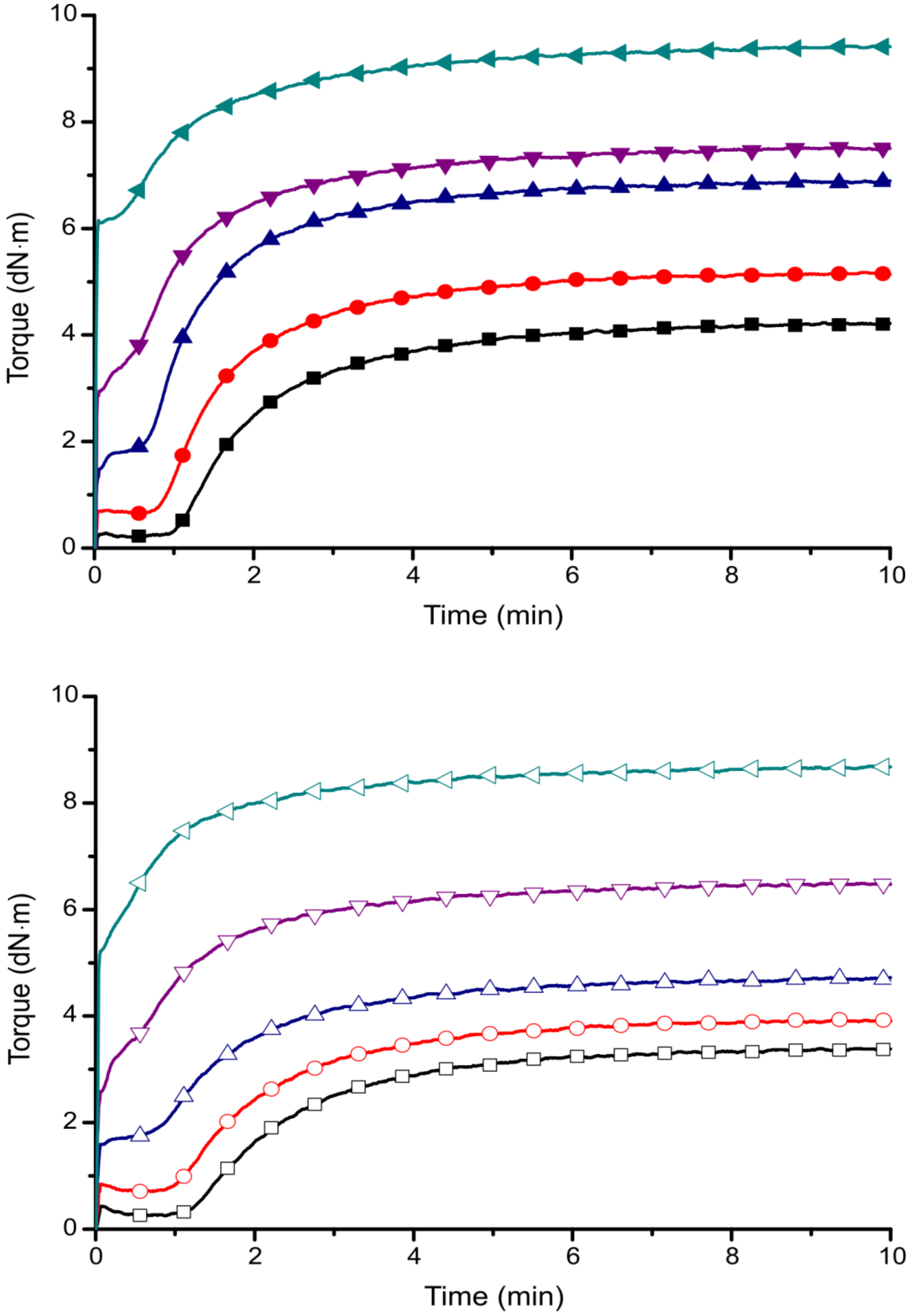


Figure 3.9 Rheometer curves at 180 ^{o}C of:
RWP/LP-A (–■– A1 –●– A2 –▲– A3 –▼– A4 –◄– A5) and
RWP/LP-B (–□– B1 –○– B2 –△– B3 –▽– B4 –◁– B5) composites with constant curing system and variable RWP content

Table 3.6 Cure characteristics of the compounds with variable RWP content and constant curing system tested at 180 °C for 30 min

Samples	M_L (dNm)	M_H (dNm)	ΔM (dNm)	t_{s2} (min)	t_{90} (min)
A1	0.20	4.23	4.03	1.81	4.61
A2	0.65	5.18	4.53	1.39	4.07
A3	1.81	6.94	5.13	1.07	3.66
A4	3.53	7.55	4.02	1.13	4.04
A5	6.39	9.46	3.07	1.76	4.82
B1	0.25	3.41	3.16	2.63	4.98
B2	0.71	3.97	3.26	2.30	4.68
B3	1.73	4.75	3.02	2.17	4.61
B4	3.48	6.54	3.06	1.76	4.45
B5	6.07	8.71	2.64	2.32	4.54

Plots of the reaction times t_{90} and t_{s2} versus the volume fraction of RWP are shown in Figure 3.10.

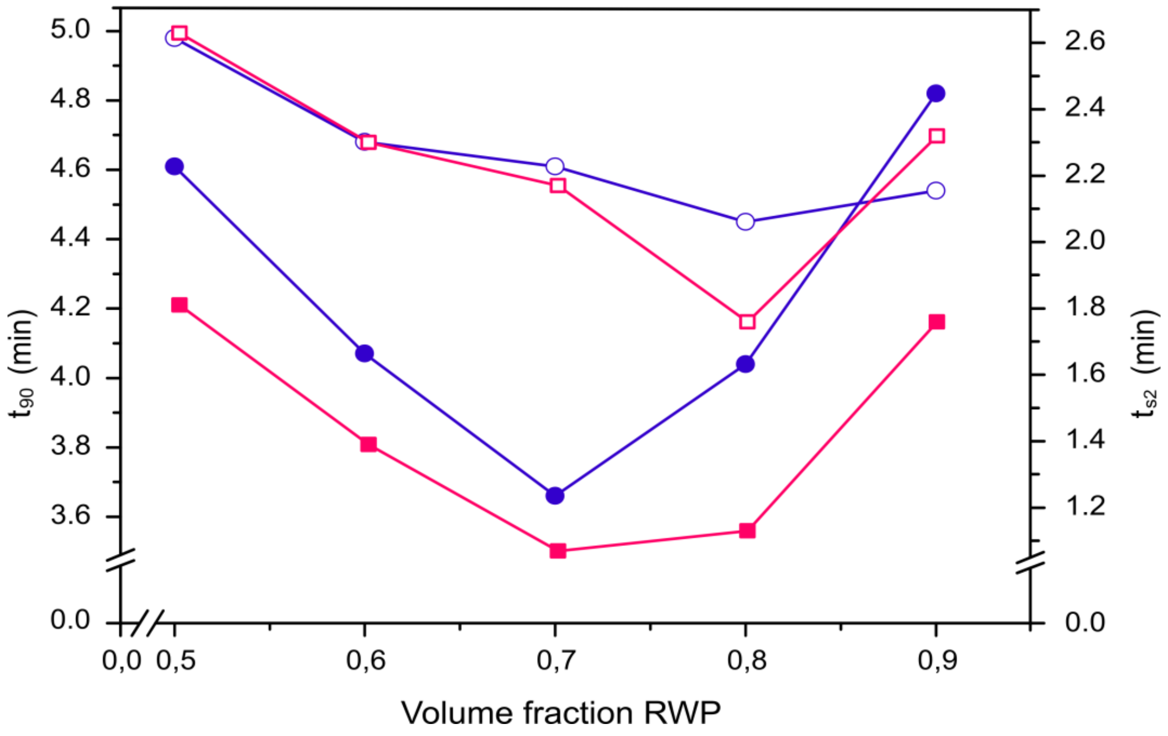


Figure 3.10 Influence of RWP content on t_{s2} (square) and t_{90} (circle) of vulcanised samples: RWP/LP-A (full symbols) and RWP/LP-B (empty symbols)

The optimum cure time (t_{90}) decreased upon increasing the RWP content in the composition up to 80 vol%, suggesting that there are still active curatives contained in the non-activated RWP (see Figure 3.7b), which may participate in the vulcanisation process. When using 90 vol% of RWP, an increase in t_{90} was observed.

On the other hand, the scorch time (t_{s2}) of the RWP/LP compounds, a measure of premature vulcanisation, decreased with increase of the RWP content. This behaviour may be explained by the migration of unreacted accelerators from the RWP to the liquid polymer phase [41,42].

3.3.4 Mechanical properties – Influence of RWP particles

The vulcanised samples A1-A5 and B1-B5, cured according to their optimum cure time derived from rheological measurements were investigated with respect to hardness, tensile strength and elongation at break. For comparison reasons, vulcanised LP-A and RWP are also presented. The LP-A was vulcanised according to the t_{90} using the same curing system as the one used for the investigated samples (Table 3.2). The pure LP-B could not be tested because of the stickiness of the vulcanised sample. The RWP were pressed for 4 minutes at 180 °C.

The mechanical properties of the RWP/LP compounds strongly depended on the amount of RWP and the type of LP used. The variations in hardness, tensile strength and elongation at break with increasing volume fraction of RWP in the RWP/LP compounds are shown in Figures 3.11 – 3.13.

The indentation hardness of the samples was determined as the resistance to penetration measured based on the penetration depth of a truncated cone shaped indentor. As expected, the hardness of the LP-A was very low in comparison with the investigated samples and with the RWP. By increasing the content of RWP in RWP/LP compounds for both types of samples an overall increase in hardness was observed. Figure 3.11 shows a clear linear increase of the hardness of the samples with increase of the volume fraction of RWP. The hardness of the RWP is close to the one of the samples, where 80 vol% of RWP and 20 vol% of the LP were used, namely ca. 37 Shore A units. The samples which contained the LP-A exhibited hardness values from 2 up to 5 Shore A units higher compared to the samples where LP-B was used.

Hardness is influenced by the amount [40] and type [43,44] of carbon black used in the sample formulation. Based on the empiric results, we can conclude that in this case the hardness was influenced by the amount of carbon black contained by the particles as well as by the type of LP used for the activation of the RWP. The use of small quantities of LP and high amounts of RWP strongly enhanced the hardness of the samples.

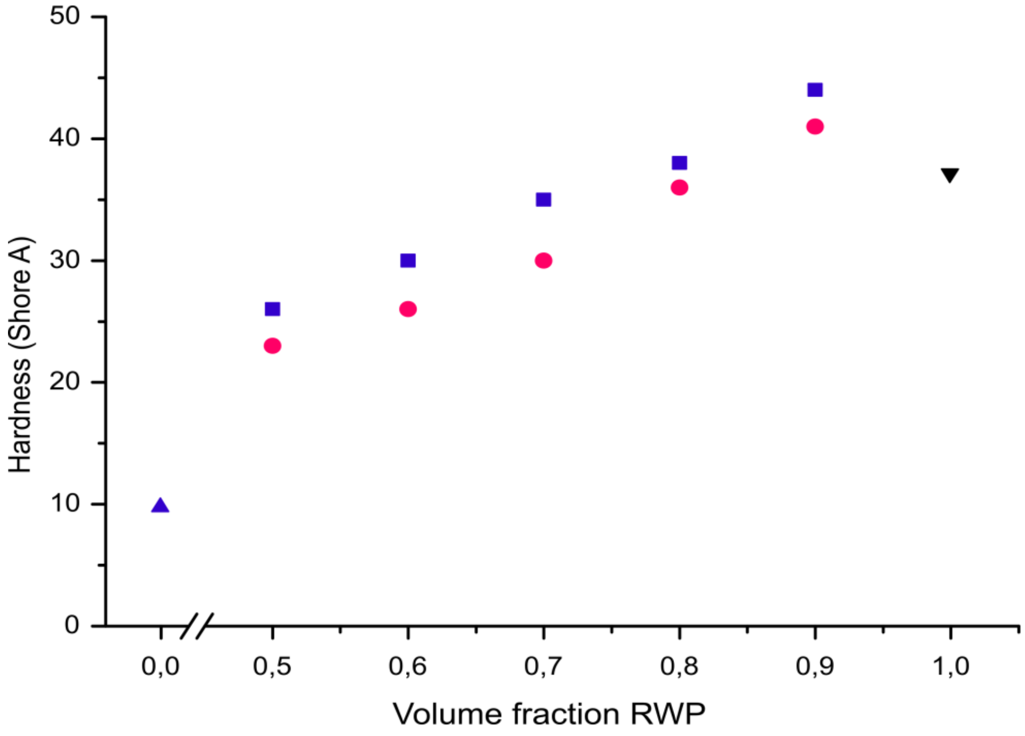


Figure 3.11 Influence of RWP content on hardness of vulcanised samples: LP-A (▲); RWP/LP-A (■); RWP/LP-B (●); RWP (▼)

The tensile tests measure the force required to break a specimen and the extent to which the specimen elongates to that breaking point. The tensile strength followed the same tendency as the hardness, as shown in Figure 3.12. The tensile strength value of the LP-A was very low in comparison with the RWP and the investigated compounds. The gain in tensile strength was much lower with LP-B than with LP-A upon increasing the volume fraction of RWP. In other words, the tensile strength was significantly influenced by the ENB content, showing a considerable improvement in the case of the LP-A samples which had a higher amount of ENB. [45] Thus, the use of small amounts of LP for activating the RWP seems to be a very good option in terms of the enhancement of tensile strength values.

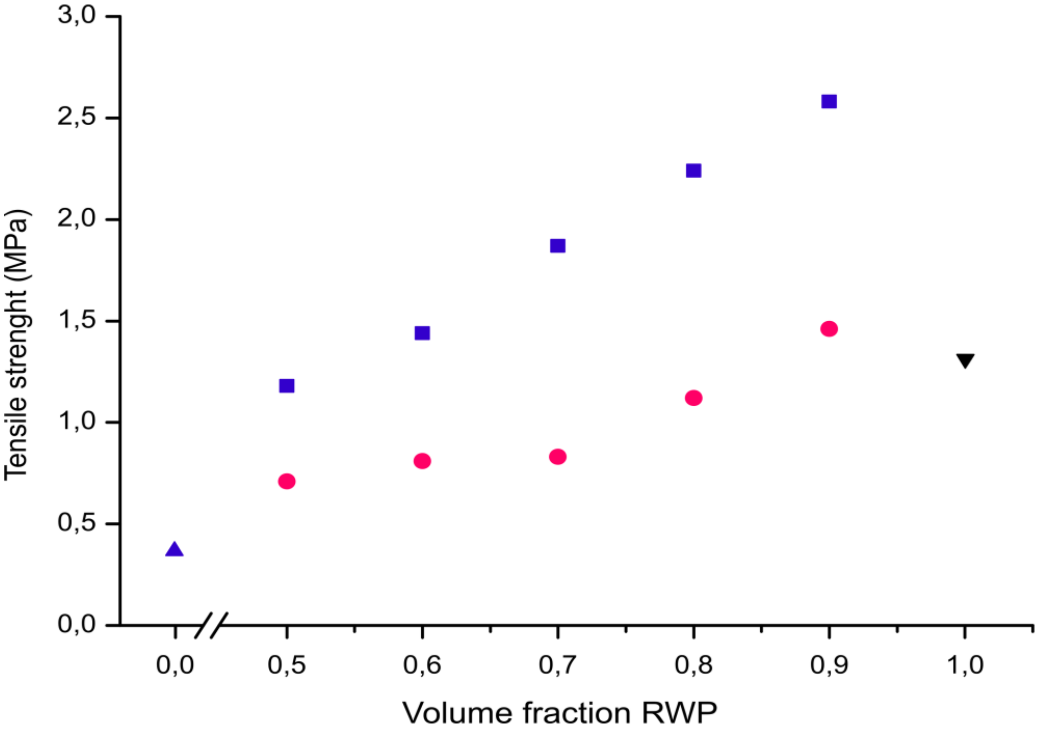


Figure 3.12 Influence of RWP content on tensile strength of vulcanised samples: LP-A (▲); RWP/LP-A (■); RWP/LP-B (●); RWP (▼)

An increase of the tensile strength values can also be correlated to the type and the amount of chemical crosslinks formed during the curing process. The higher the amount of polysulphidic bonds the higher the tensile strength values. [46]

According to a hypothesis proposed by Mullins [47], the polysulphidic crosslinks give a higher tensile strength due to their capability to dissipate localised stress concentration. Herz [48] stated that due to the bond substantial rotation and bond linear motion the polysulphidic crosslinks have the ability to realign under stress (crosslink mobility), thereby enhancing the tensile strength [48].

For the elongation at break (ε_R) some major differences were observed between the samples activated with the LP-A and the samples activated with the LP-B. The dependence of elongation at break on the volume fraction of RWP (Figure 3.13) reveals higher values for the RWP/LP-A samples. The maximum values for elongation at break were obtained for the samples A3 and A4 with 70 vol% and 80 vol% of RWP ($\varepsilon_R \approx 260\%$). On increasing the amount of RWP to 90 vol%, the elongation at break dropped down to a value close to the sample, which contains 60 vol% of RWP ($\varepsilon_R = 230\%$).

The samples with LP-B did not show a clear correlation between RWP content and elongation at break. Figure 3.13 shows a slight increase in elongation at break with increase of RWP content.

However, the sample with 70 vol% RWP exhibited a much lower elongation at break compared with all other samples where the LP-B was used. The RWP revealed a very low value of elongation at break in comparison with the investigated compounds and the LP-A. It is evident from these results that the values of elongation at break show an enormous increase upon the addition of LP-A.

As a short summary of the results obtained in this part of the investigation it can be concluded that the LP can be used with success in the activation of the RWP. The use of the liquid polymer showed positive effects, generating compounds with improved properties in comparison with inactivated particles. Moreover, LP-A, which had a higher double bonds content, showed a superior performance compared to LP-B, which had a lower double bonds content. 80 vol % RWP and only 20 vol % LP proved to be the best ratio for further use as a substitute of raw material. The improvement of the mechanical properties can be attributed to the filler contained by the RWP and to the good interfacial adhesion between particles and liquid polymer.

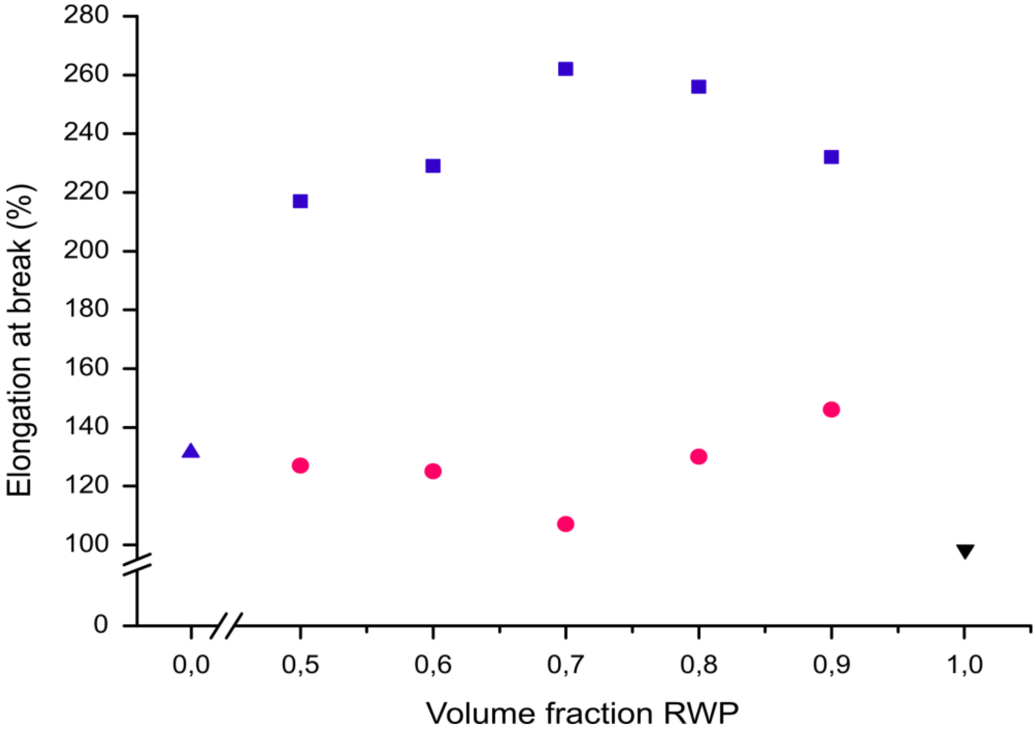


Figure 3.13 Influence of RWP content on elongation at break of vulcanised samples: LP-A (▲); RWP/LP-A (■); RWP/LP-B (●); RWP (▼)

3.3.5 Cure characteristics – Influence of the Curing System Content

In order to study the effect of the curing system content, twelve different formulations were prepared following the protocol described in the Section 3.2, Table 3.3. The samples were prepared by using a constant volume fraction of RWP (80 vol %) and LP (20 vol %) and a variable curing system content.

These mixtures were based on sample A4, which exhibited the best properties with respect to RWP content. The sample A4 exhibited a hardness of 38 Shore A, a tensile strength of 2.24 MPa and an elongation at break of 256 %. For comparative purposes and for a better insight into the effect of LP-B, the analogues basis mixture B4 was included in this series of experiments. The samples A4 a-f were the samples activated with the LP containing 9.5% ENB, and the samples B4 a-f represented the samples where the LP with 4.5% ENB was used. The samples A4 a-f and B4 a-f were prepared in the same way as the samples A1-A5 and B1-B5. In all mixtures, N-Cyclohexyl-2-benzothiazolesulfenamide (CBS) was used as an accelerator with a constant sulphur/accelerator ratio of 0.4 and a vulcanisation temperature of 180 °C.

The applied curing system consisted of zinc oxide, stearic acid, CBS and sulphur (S) with a relative weight ratio of 1/0.5/1.5/0.6. Throughout this thesis the weight of curing agents is given in units of phr, which means parts of any non-rubbery materials per hundred parts of raw gum elastomer (rubbery material).

Parts can mean any unit of weight, as long as the same weight unit is used throughout the formulation. Note that the A4b and B4b samples make the connection to the previous series of samples (A1-A5 and B1-B5, respectively). In this section samples A4 and B4 are identical to samples A4b and B4b, which have been prepared with the curing system 2/1/3/1.2.

Figure 3.14 shows the rheometric curves obtained during the curing process of A4/RWP and B4/RWP. The vulcanisation parameters are summarized in Table 3.7.

The samples without curing system, A4a and B4a, illustrated in Figure 3.14 by black curves, were vulcanised only to a small extent, an effect which may be attributed to the residual curing system which migrated from the RWP into the liquid polymer phase or possibly to the further crosslinking which can take place in the RWP phase. However, by increasing the curing system amount an evident increase of the maximum torque, M_H, was observed in the case of both of LP–types. At a higher content of curing system (A4f and B4f) the curves remained almost constant, indicating that nearly no crosslinking reactions took place anymore (Figure 3.14).

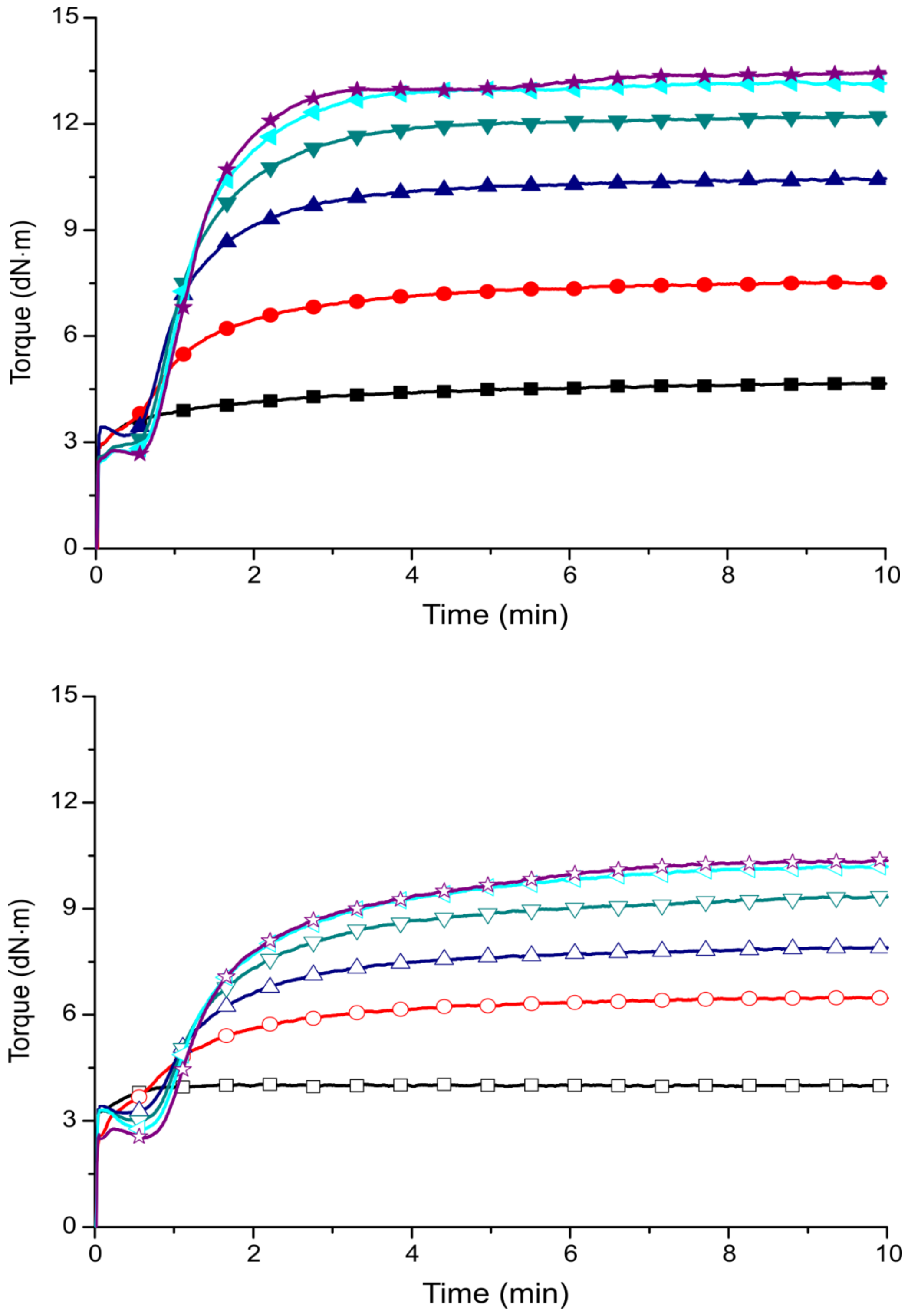


Figure 3.14 Rheometer curves at 180 ^{o}C of:
A4/RWP-LP-A (—■— a —●— b —▲— c —▼— d —◄— e —★— f) and
B4/RWP-LP-B (—□— a —○— b —△— c —▽— d —◁— e —☆— f) composites with constant
RWP amount and different curing system content

ΔM, calculated as the difference between the minimum and the maximum torque, is a parameter which demonstrates the degree of crosslinking.[44] With a systematical increase of the curing system content, the ΔM increased as well. In other words, the crosslinking density increased with increase of the amount of curing system, exhibiting better values for the LP-A type. The ΔM values were lower for the compounds containing the LP-B type, suggesting that the degree of crosslinking was lower in this case. These results indicated that the presence of higher amount of double bonds had a high influence on the crosslinking density of the sample.

Table 3.7 Cure characteristics of the compounds with variable curing system and constant RWP content

Samples		M_L (dNm)	M_H (dNm)	ΔM (dNm)	t_{s2} (min)	t_{90} (min)
A4	**a**	2.86	4.73	1.87	0.00	6.08
	b	3.53	7.55	4.02	1.13	4.04
	c	3.19	10.51	7.32	0.80	2.87
	d	2.58	12.32	9.74	0.79	2.79
	e	2.41	13.49	11.08	0.83	2.83
	f	2.45	14.12	11.67	0.87	3.26
B4	**a**	3.05	4.04	0.99	0.00	0.87
	b	3.48	6.54	3.06	1.76	4.45
	c	3.23	8.01	4.78	1.15	4.23
	d	3.00	9.52	6.52	1.10	4.97
	e	2.76	10.28	7.52	1.09	4.70
	f	2.49	10.71	8.22	1.11	5.70

The minimum torque, M_L, is a cure property measured in the uncured state and it is correlated to the viscosity of the uncured samples. Regarding the M_L of the studied compounds, shown in Figure 3.15, it can be observed that the samples A4a and B4a, with no curing system, showed lower torques in comparison with samples A4b and B4b, where 1.2 phr S was used. Anyhow, upon increasing the curing system content, the values of the M_L continuously decreased. Nevertheless, the changes in M_L were of maximum 1.5 d·Nm units, which indicates that there were no significant differences between the sample viscosities. These results were not surprising taking into consideration that the amount of RWP was maintained constant for all samples. Therefore, it could be concluded that M_L is only slightly influenced by the amount of added curing system.

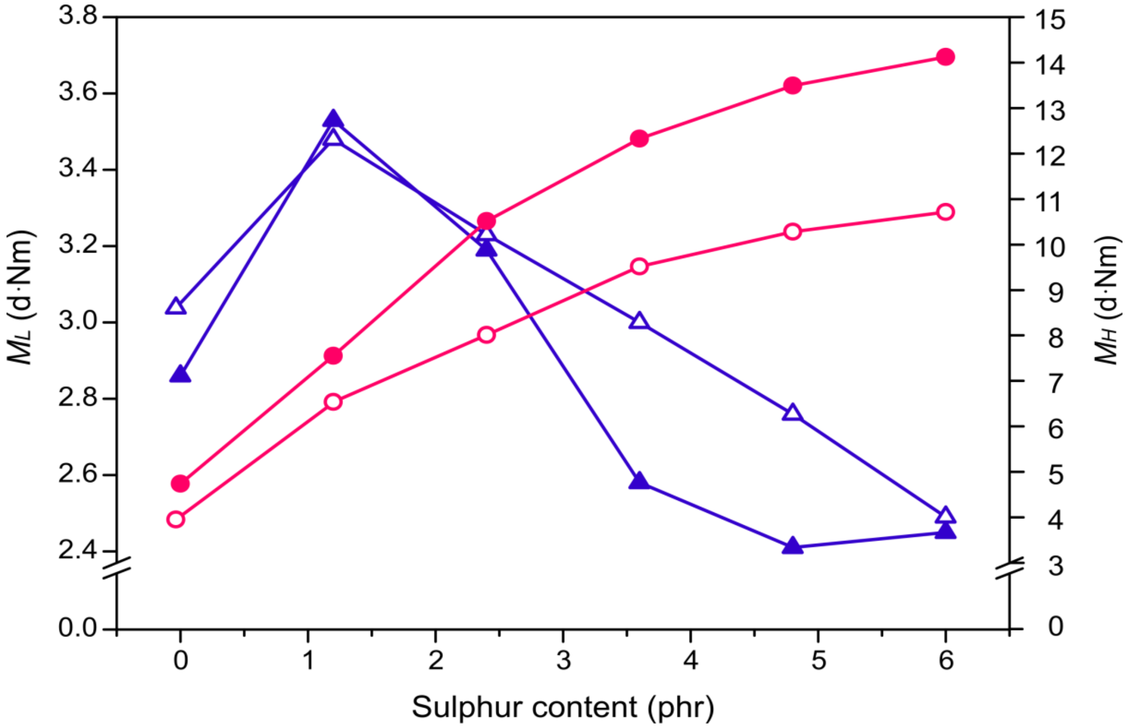


Figure 3.15 Influence of curing system content on M_L (triangle) and M_H (circle) of vulcanised samples: A4 a-f (full symbols) and B4 a-f (empty symbols)

Concerning the scorch time, t_{s2}, both types of compounds followed similar trends when a curing system was added, showing among all compounds the highest scorch resistance for the B4 samples (Table 3.7). For the samples without a curing system a value of zero was registered for both types of compounds.

When using only 1.2 phr S, the compounds presented the highest scorch safety, in comparison with the rest of the samples where the curing system amount was increased and lower scorch time values were obtained. When using more than 1.2 phr S, the t_{s2} values showed very slight differences, exhibiting values of about 1.1 min for the B4 c-f samples and circa 0.8 min for the A4 c-f samples.

The data presented in Table 3.7 and plotted in Figure 3.16 indicates that the vulcanisation time t_{90} shows different trends for the A4 and B4 compounds. For the samples where no curing system was used, outlier values were obtained showing a very high value of 6.08 min for the A4a sample, while for the B4a sample a minimum value of 0.87 min was registered. For the samples where a curing system was used, A4b-f and B4-b-f, lower t_{90} values were obtained for those samples where LP-A was used, resulting in shorter vulcanisation times.

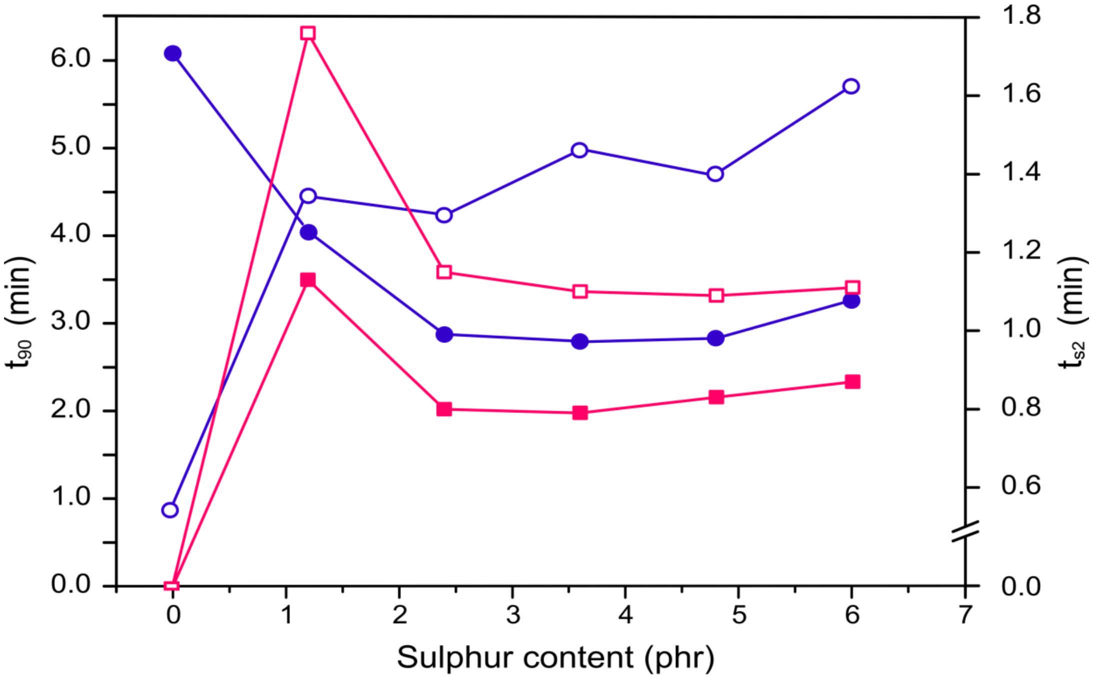


Figure 3.16 Influence of curing system content on t_{s2} (square)and t_{90} (circle) of vulcanised samples: A4 a-f (full symbols) and B4 a-f (empty symbols)

However, for the A4 b-f compounds the t_{90} values decreased when increasing the curing system content up to 4.8 phr S, followed by a slight increase for the A4f sample, where 6.0 phr S was used. The B4 b-f compounds showed an oscillating behaviour upon increasing the curing system content.

It is worthwhile noting that the amount of curing system and the type of LP used for activation had a noticeable influence on all vulcanisation parameters, exhibiting overall better values for the LP-A samples.

Based on the results obtained from this investigation, it can be concluded that the curing system amount induced significant differences in the vulcanisation curves and consequently in the vulcanisation parameters (Table 3.7).

3.3.6 Mechanical properties – Influence of the curing system content

The samples obtained after curing were characterised with respect to hardness, tensile strength and elongation at break.

The test results for the mechanical properties of the investigated compounds containing various amounts of curing system are shown in Figure 3.17 –3.19, where they were plotted as a function of sulphur loading. Because the ratio between the curing system formulations is constant, the rest of the curing formulation will increase systematically by increasing the sulphur content.

For all samples, hardness, tensile strength and elongation at break increased on increasing the curing system content, presenting better values for samples where LP-A, with a higher amount of ENB, was used. The samples containing LP-A and LP-B, respectively, revealed different mechanical properties as a consequence of the double bonds concentration present in the liquid polymers.

The hardness, presented in Figure 3.17, showed a steady increase with increase of the curing system content. For samples A4a and B4a, where no curing system was added, the hardness of the A4a sample was double that of the B4a sample. Nonetheless, upon addition of a curing system, the differences between A4 b-f and B4 b-f were not as strong anymore, showing only a difference between 2 and 5 Shore A.

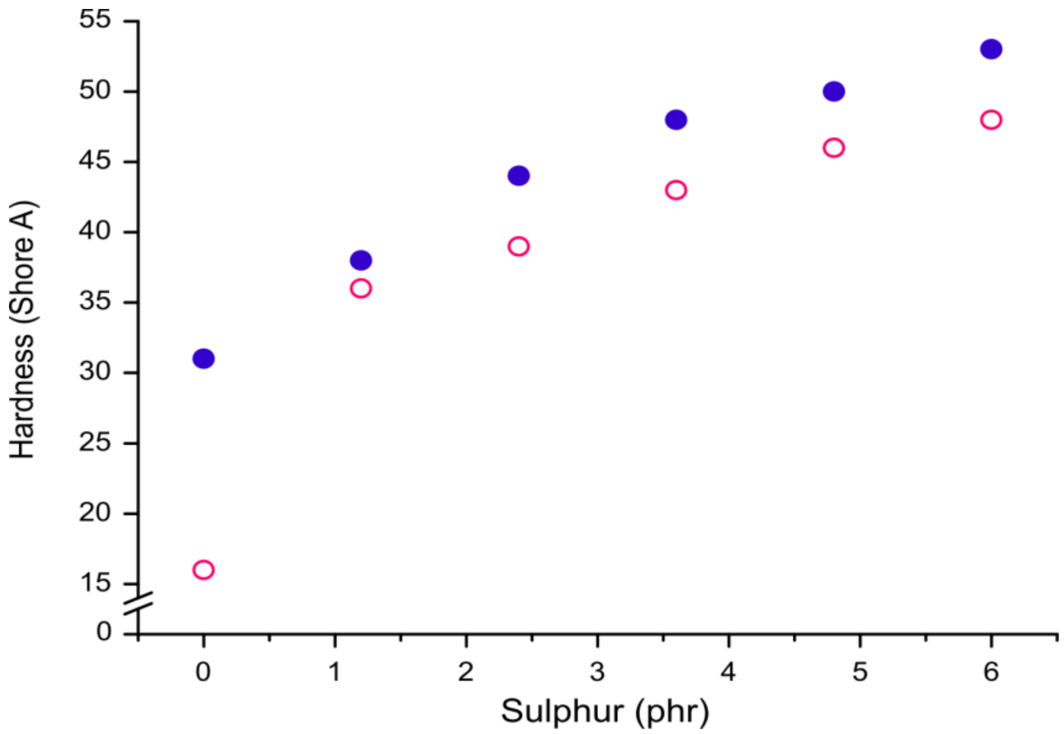


Figure 3.17 Influence of curing system content on hardness of vulcanised samples with: LP-A (●) and LP-B (○)

The tensile strength presented in Figure 3.18 showed a rise upon increasing the curing system amount. In the case of the samples with LP-B, the increase was linear, while the samples with LP-B showed a different trend. When using up to 1.2 phr S, the increase was linear, resulting into a tensile strength value of up to 2.2 MPA, while when using 2.4 phr S, a sharp rise of the value to 5.1 MPa was observed. When using more than 3.6 phr S, the values showed insignificant changes, with the value of tensile strength reaching about 6 MPa.

Concerning the elongation at break, the same trend as in the case of tensile strength could be observed, as illustrated in Figure 3.19. As the amount of curing system increased, the elongation at break raised, albeit for samples with LP-A a slight decrease was observed when more than 3.6 phr S is used.

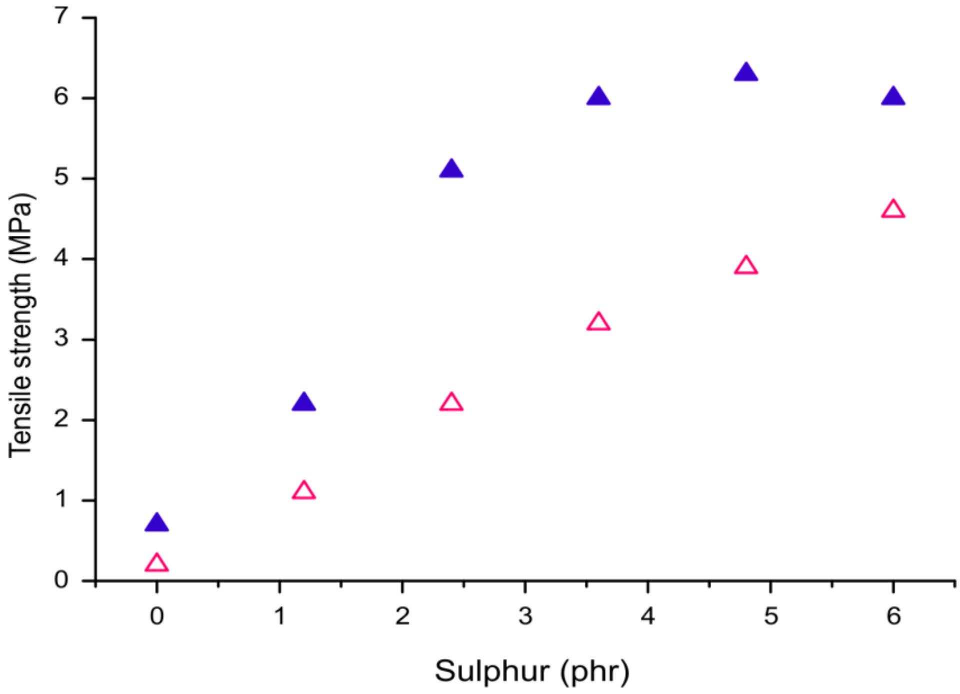


Figure 3.18 Influence of curing system content on tensile strength of vulcanised samples with: LP-A (▲) and LP-B (△)

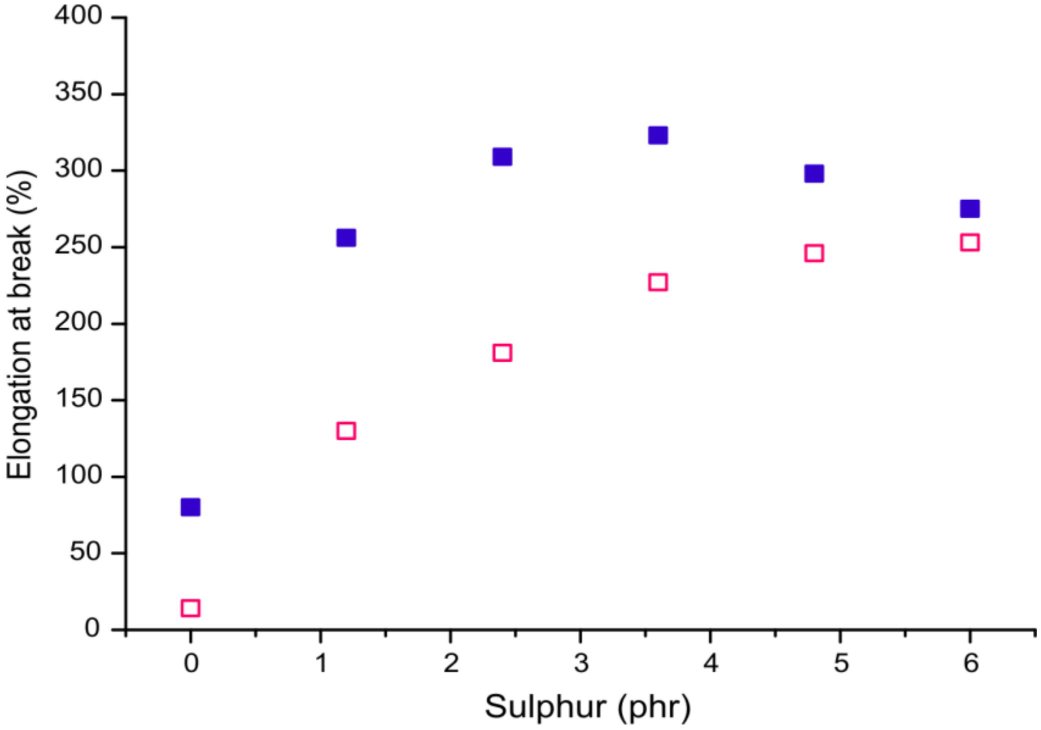


Figure 3.19 Influence of curing system content on elongation at break of vulcanised samples with: LP-A (■) and LP-B (□)

Due to the dosage level above the solubility limit, the migration of the curing system may cause the so called ’’blooming effect’’ by forming a bloomed layer on the rubber surface. [49] Blooming is the process of diffusion of one or more compounding ingredients to the rubber surface, followed by crystallisation.[50] In this case, a blooming effect was visible for the samples where a high amount of curing system (more than 3.6 phr S) was used. Figure 3.20 presents a picture of the compounds A4b (1.2 phr S) and A4e (4.8 phr S) where the blooming layer can be clearly seen on the sample with a higher amount of curing system.

Figure 3.20 Picture with different the surface of cured samples in storage at ambient temperature for: a) A4b and b) A4e

It can be thus concluded that a suitable amount of curatives (up to 3.6 phr sulphur), together with the LP containing a high percentage of ENB, led to samples with a significant improvement of mechanical properties.

3.3.7 Determination of Crosslinking Density

a) Equilibrium Swelling Tests

The apparent crosslinking density was determined by swelling measurements in toluene for the A1-A5 (with LP-A) and B1-B5 (with LP-B) samples containing a different volume fraction of RWP and a constant amount of curing system (Table 3.2). Figure 3.21 shows that the apparent crosslinking density significantly increased with increase of the volume fraction of RWP.

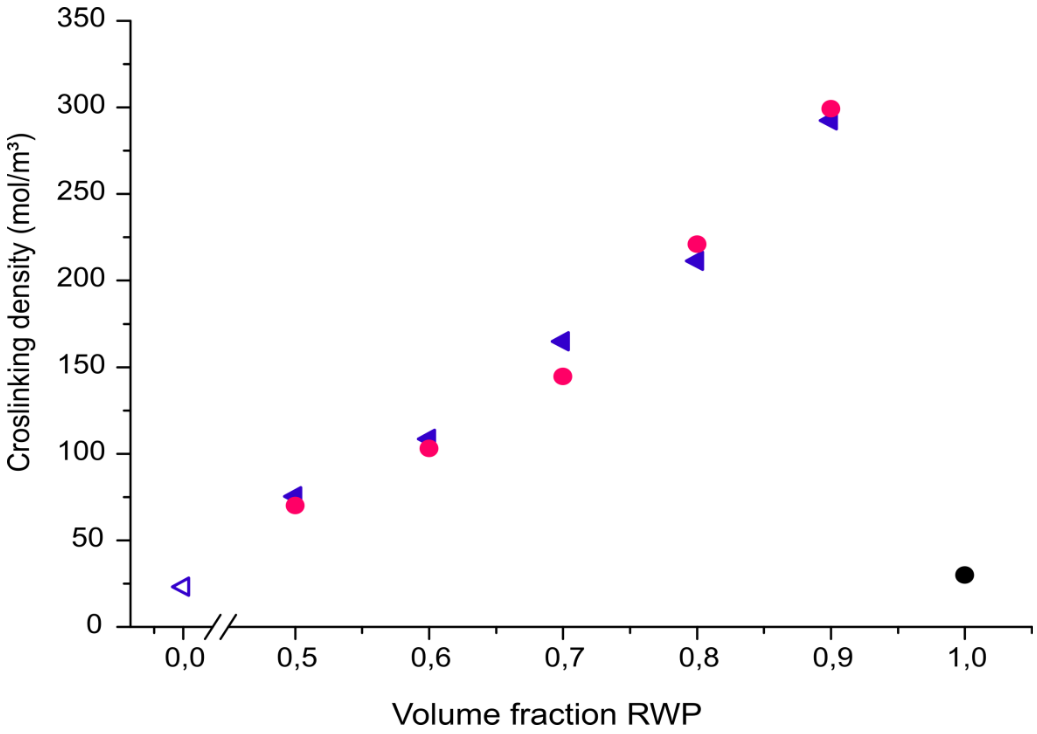


Figure 3.21 Influence of RWP content on crosslinking density of vulcanised samples: LP-A (◁); RWP/LP-A (◀) and RWP/LP-B (●) and RWP (●) determined by swelling

The crosslinking density of vulcanised LP-A and RWP was very low in comparison with the activated samples. By increasing the RWP content and using the LP the crosslinking density increased gradually for both type of samples.

Figure 3.22 shows the data obtained from swelling experiments for a set of samples with a constant volume fraction of RWP, i.e. 0.8, and a different amount of curing system (Table 3.3). As expected, the increase of the curing system content led to an increase of the crosslinking density. Interestingly, the samples A4a-b, where LP-A was used, showed a lower crosslinking density in comparison with the samples B4a-b, where LP-B was employed. Nevertheless, when using a higher amount of curing system the samples with a higher content of double bonds (A4c-f) exhibited higher values of crosslinking density in comparison with those samples where the content of double bonds was lower, B4c-f. It can be observed that the curing system amount has a significant effect on the consolidation of the network structure.

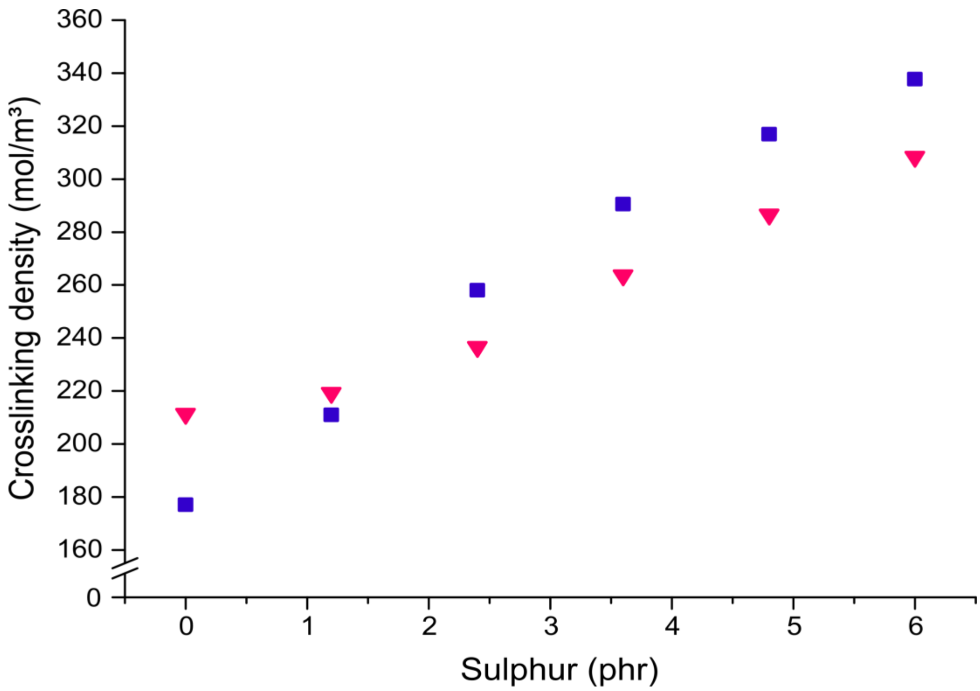


Figure 3.22 Influence of curing system content on crosslinking density of vulcanised samples: RWP/LP-A (■) and RWP/LP-B (▼) determined by swelling

b) *Temperature scanning stress relaxation tests*

TSSR tests represent another method used to determine the crosslinking density of the compounds. The apparent crosslinking density was calculated by using

Equation 3.4. Figure 3.23 shows the data obtained for the vulcanised LP-A, A1-A5 and B1-B5 samples. The test could not be performed for the RWP because of the brittleness of the sample. Here, the same tendency was observed as in the case of swelling tests (Figure 3.21), i.e. the apparent crosslinking density increased when increasing the volume fraction of RWP.

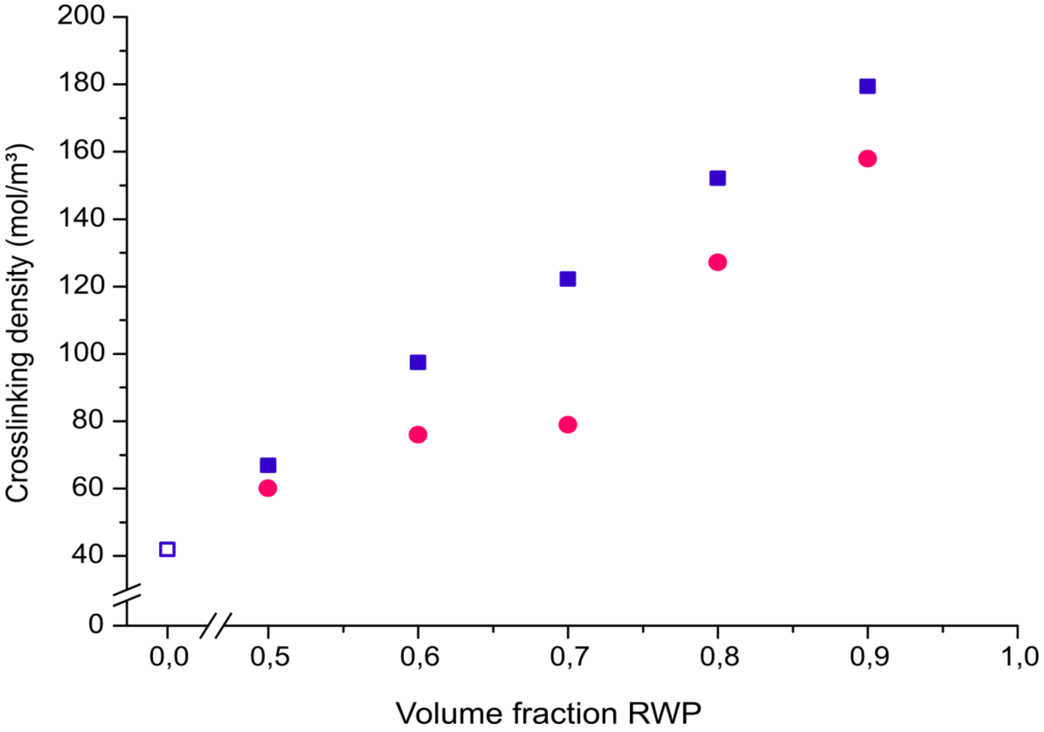


Figure 3.23 Influence of RWP content on crosslinking density of vulcanised samples: LP-A (□); RWP/LP-A (■) and RWP/LP-B (●) determined by TSSR

Figure 3.24 shows the data obtained from TSSR tests for the samples with a constant volume fraction of RWP, i.e. 0.8, and a different amount of curing system (Table 3.3). As already observed in equilibrium swelling tests, the apparent crosslinking density obtained from TSSR measurements showed the same tendency, an increase of crosslinking density with increase of the curing system content. Due to the higher ENB content, the samples A4a-f, where LP-A was used, exhibited a higher apparent crosslinking density in comparison with the samples B4a-b, where LP-B was employed. Due to the brittleness of the sample, compound B4a could not be measured.

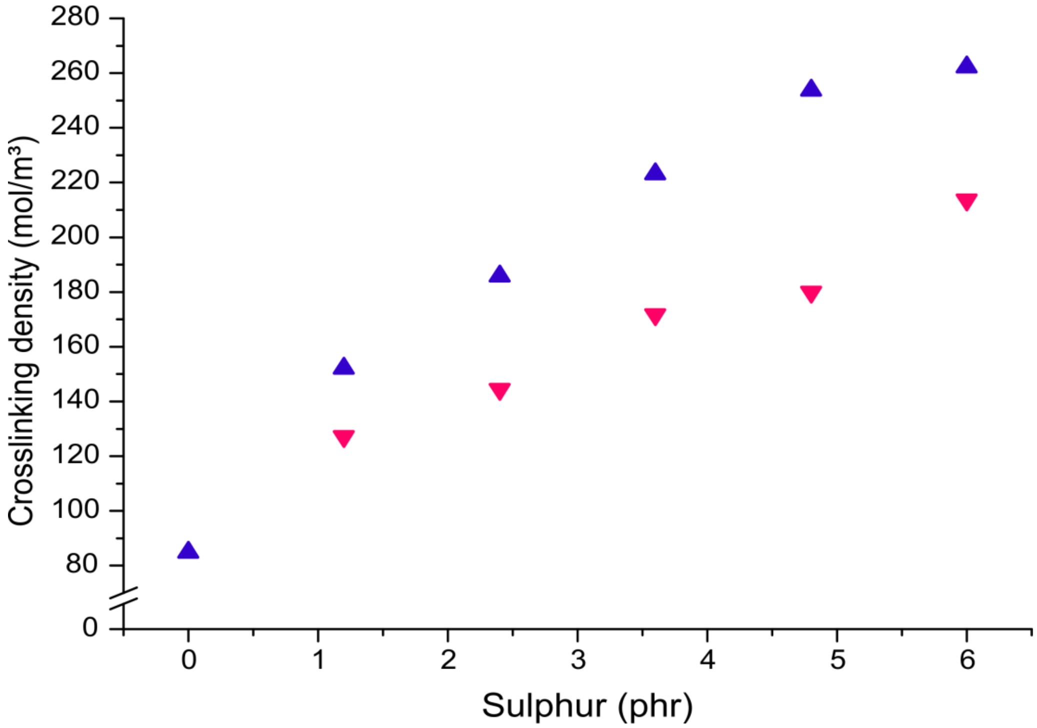


Figure 3.24 Influence of curing system content on crosslinking density of vulcanised samples: RWP/LP-A (▲) and RWP/LP-B (▼) determined by TSSR

Due to the complex composition and structure of the investigated compounds, the values obtained via these two methods were not identical. Nevertheless, the results obtained from the solvent swelling studies were in very good agreement with the data obtained from TSSR tests, exhibiting the same tendency.

Moreover, the results obtained using these two different methods supported the changes in torque illustrated by the cure curves generated from the rheometer measurements.

3.3.8 Scanning Electron Microscopy

The morphologies at the fracture surface of tensile specimens of the RWP pressed at 180 ºC for 4 min. with a pressure of 10 MPa, of the liquid polymer (LP-A), of the compounds RWP/LP-A without (A4a) and with (A4b) curing system and of the commercial EPDM vulcanised material, as well as the morphology of the non-pressed RWP were studied by scanning electron microscopy (SEM). The SEM micrographs are shown in Figure 3.25.

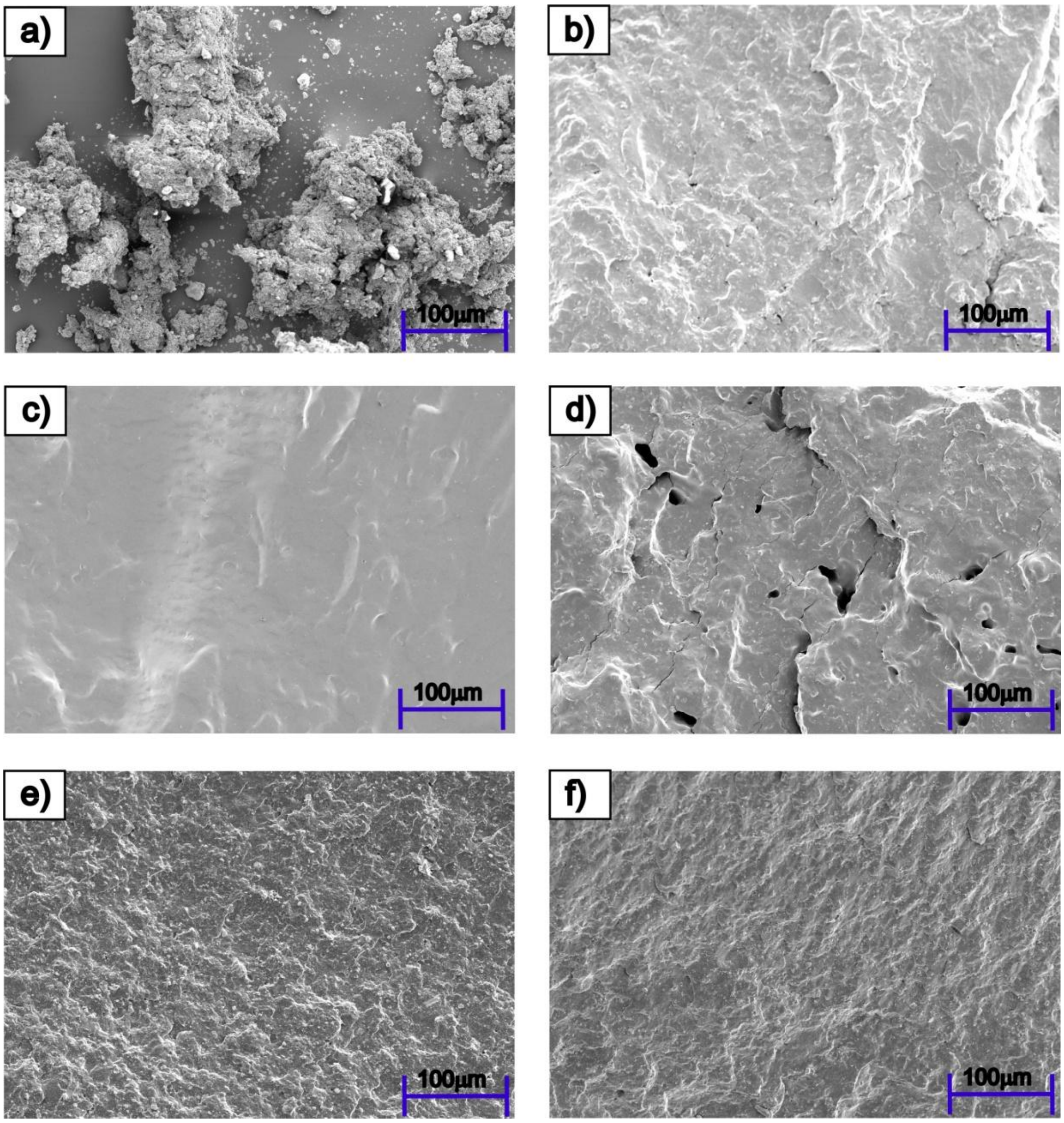


Figure 3.25 SEM images of: a) RWP; b) RWP pressed at 180 ºC; c) vulcanised LP-A; d) A4a; e) A4b; f) commercial EPDM vulcanised material

The images offer an insight into the blend morphology with regard to the homogeneity and compactness of the RWP/LP compounds. The non-pressed RWP (Figure 3.25a) revealed the presence of spongy agglomerates with high surface roughness. After pressed at 180 °C, the morphology of the RWP changed showing a smoother surface with brittle fissures (Figure 3.25b). The vulcanised LP-A (Figure 3.25c) presented a uniform and smooth surface.

The interaction between LP-A and RWP without a curing system led to a brittle surface containing voids, indicating the absence of inter-rubber crosslinking (Figure 3.25d).

The surface of the RWP/LP compound (0.8 vol% RWP) with curative system after vulcanisation showed a higher degree of compactness similar to the vulcanized EPDM material (Figure 3.25f). The commercial EPDM material used for the production of sealing systems showed a good uniformity and homogeneity (Figure 3.25e).

The architectural homogeneity indicated much better phase adherence due to efficient interfacial crosslinking. The compact structure of the RWP/LP composite was accompanied by a significant enhancement of mechanical properties.

In order to demonstrate the potential of the activated particles for further utilization, i.e. as a possible substitute of raw material for the production of seals and sealing systems, a comparison between a commercial EPDM used for the production of sealing systems on the one hand and activated and non-activated RWP on the other hand was made. Table 3.8 presents the mechanical properties of the commercial EPDM, of the RWP and of the vulcanised A4d sample. The values of the mechanical properties of the RWP are rather low in comparison with the commercial EPDM and the vulcanised sample.

Table 3.8 Mechanical properties of commercial EPDM, LP-A and RWP/LP-A (sample A4d)

Mechanical properties	**Sample**			**EN 681-1/A3**
	commercial EPDM	RWP	A4d	min. values
Hardness, Shore A	59	37	48	50 ± 5 Shore A
Tensile strength, MPa	9.1	1.3	6.0	≥ 9 MPa
Elongation at break, %	558	100	323	≥ 375 %

Therefore, by using a high amount of RWP (80 vol%) activated with a small quantity of liquid polymer (20 vol%) containing a high percentage of ENB, the mechanical properties were considerably improved, making it possible to obtain compounds with more than half of the mechanical properties values of the commercial EPDM material. The A4d sample exhibited 96% hardness, 66% tensile strength and 86% elongation at break of the minimum values required for the production of sealing systems.

3.4 CONCLUSIONS

In conclusion, the results presented in this chapter confirm the high potential of the liquid polymers to be used for chemical activation of EPDM rubber waste particles. The rubber waste particles' loading, the variation of ENB content in the liquid polymers and different ratios of the curing system lead to vulcanised compounds with various crosslinking densities, mechanical properties and morphology. The influence of the amount of RWP and of curing system amount on the mechanical properties of vulcanised compounds is significant. The maximum torque increases when increasing the RWP content as a consequence of the good interaction between RWP and LP, leading to compounds with improved mechanical properties. Due to the migration of the curing system residues from the RWP to the LP phase, a decrease of the scorch time is observed.

In addition, by keeping a constant ratio between RWP and LP, and by increasing the curing system amount, the mechanical properties and the crosslinking density are improved. When no curing system is added, the mechanical properties and the morphology of the compounds are deteriorated. Due to the limited solubility of the curing system, a blooming effect is observed when more than 3.6 phr sulphur was used. The compounds for which the liquid polymer with higher amount of ENB was applied presents better properties, containing more unsaturated sites which can participate in forming more crosslinks.

The composition containing 80 vol% RWP, 20 vol% LP-A and 3.6 phr sulphur exhibited 80% hardness, 66% tensile strength and 58% elongation at break of the values of commercial EPDM and 96% hardness, 66% tensile strength and 86% elongation at break from the minimum values required for the production of sealing systems. These results shows a positive potential for the activated particles to be used in a subsequent stage as a substitute of raw material in obtaining products of high quality, i.e. seals and sealing systems.

It is proposed as a model (Figure 3.26) that the LP form a thin liquid film around the RWP, in particular filling all gaps and voids in-between the highly irregular shaped particles. Upon crosslinking the thin LP-layer is hardened.

Because of the combination of physical absorption, mechanical entanglement and, to any yet unknown extend of chemical bonds between LP and RWP-phase, the LP acts as a highly effective glue that holds together the rubber particles. It cannot be excluded that reactive compounds mutually diffuse from the LP in the RWP-phase and vice versa, hence allowing the RWP to enhance their degree of crosslinking.

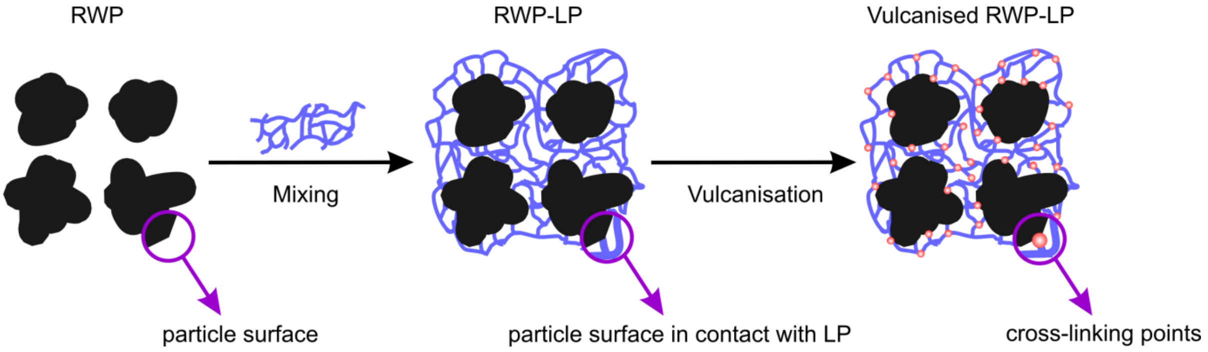


Figure 3.26 Proposed model of LP action

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Chapter 4

Investigation of new Composites Based on Activated EPDM Rubber Waste Particles by Use of Liquid Polymers

> *"Sometimes attaining the deepest familiarity with a question is our best substitute for actually having the answer."*
>
> *Brian Greene (1963 – present)*

The previous chapter showed the potential of rubber waste particles (RWP) to be chemically activated by use of liquid polymers. The present chapter investigates the influence of the content of four different types of activated rubber waste particles (RWP-LP) in new substitute composites. By varying the amount of RWP-LP in a range from 25 vol% up to 75 vol% information about optimized compositions for the new substitute compounds was obtained. It was found that the ratio and type of RWP-LP induce significant differences in terms of processability, cure characteristics, mechanical properties, crosslinking density and morphology. Promising results with a high potential for application in the production of seals and sealing systems on an industrial scale were obtained by using up to 50 vol% of RWP-LP with a low ethylene amount. By using RWP-LP with a high amount of ethylene the substitution of the raw material was possible only up to 25 vol%.

Parts of the research described in this chapter have been presented at the 29th International Conference of the Polymer Processing Society, 15th-19th July 2013, Nuremberg, Germany, and at the North European PhD Seminars on Rubbers, 11th – 13th June 2014, Tampere, Finland and have been published in the Journal of Applied Polymer Science (2015, 132, 42097).

4.1 INTRODUCTION

In comparison to thermoplastic materials, which can be reshaped when heat is applied, a thermoset material is more difficult to be recycled due to the irreversible three-dimensional networks formed during vulcanisation. [1]

Despite the different methods used for rubber recycling, [2] the chemical activation of EPDM has been less studied in comparison with diene rubbers originating from the tyre industry. As mentioned in the previous chapter, first studies were performed by Stark, [3,4] who modified rubber scrap by using a liquid unsaturated polymer soluble in a solvent and a curing agent. The yielded dry crumb particles were further used at high concentrations (25 to 75 %) as an additive to virgin rubber to obtain products with an acceptable loss of physical properties.

Later, the Vredestein rubber recycling company developed a product named Surcrum® based on crumb rubber, activated with a high molecular weight polymer dispersion and a curing system. The process was applied for various industrial and post-consumer waste, such as NR and SBR. The NBR- and EPDM-based Surcrum® is still under development. [5]

In the previous chapter the solvent free activation method of EPDM rubber waste particles (RWP) by means of a low molecular weight polymer, also referred to as liquid polymer (LP), was studied. The LP was used to activate particle surfaces and acts as a compatibilizer with the raw polymer matrix. The chemical activation of the rubber waste particles with liquid polymers enhances the ability of the activated particles to form covalent bonds with a fresh raw polymer matrix during vulcanisation. The obtained results exhibited a high potential of the RWP-LP to be further used as substitute of the raw material in new composites.

Therefore, the objective of this chapter is to investigate raw material substitute compounds that contain between 25 and 75 vol% of RWP-LP and to compare their properties with a reference compound. The application area of the new composites is in the production of seals and sealing systems.

Moreover, two new types of activated particles were applied in this study. The particles were activated with two LPs containing a high amount of ethylene and a different amount of 5-ethylidene-2-norbornene. The advantage of using a higher amount of ethylene offers the possibility to obtain composites with better flow at a high extrusion temperature, higher tensile strength values and a higher loading potential. The RWP-LP were used in the rubber compounds as a substitute of the raw material and not as filler. The influence of the amount and type of RWP-LP was investigated in terms of cure characteristics, mechanical properties, crosslinking density and morphology of the recycled compounds in comparison with a reference sample.

4.1 EXPERIMENTAL

Materials

The EPDM waste rubber particles used in this investigation are the same as described in Chapter 3. Keltan 9650Q, composed of 53 wt% ethylene and 6.5 wt% 5-ethylidene-2-norbornene (ENB), was used as EPDM raw material in the reference recipe (from Lanxess, Germany). The Mooney viscosity ML (1+8) measured at 150 ^{0}C was 60 MU. Carbon black of type N550 was supplied by Avokal GmbH, Germany. As plasticizer the paraffinic oil type Mabanol Base Oil 500 MSN from Mebanol GmbH & Co. KG, Germany was used. The liquid polymers with the trade name Trilene®, used for activation of the RWP, were supplied by Lion Copolymer (USA); their main properties are given in Table 4.1 and Table 3.1 (Chapter 3). Toluene with a purity of 99.7% from Sigma – Aldrich Chemie GmbH, Germany was used for the swelling measurements. The zinc oxide (ZnO) and sulphur (S) were obtained from Melos GmbH, Germany. The stearic acid was obtained from Carl Roth GmbH + Co. KG, Germany, and N-Cyclohexyl-2-benzothiazolesulfenamide (CBS) was obtained from Sun & Bright Industrial Ltd., China.

Table 4.1 Main properties of the ethylene-propylene-ethylidene norbornene low molecular weight polymers

Properties	**Trilene® 77**	**Trilene® 76**
Colour	pale yellow	pale yellow
Specific gravity	0.86	0.86
Molecular weight, Da	7.500	7.500
Degree of unsaturation, % Diene	10.5	4.0
Diene type	ENB[a]	ENB[a]
Ethylene/propylene	75/25	75/25

[a]ENB – 5-ethylidene-2-norbornene

Methods

Thermal characterisation of reference and raw material substitute compounds

The thermal characterisation was performed by means of thermal gravimetric analyses (TGA) using a Mettler TGA / sDTA 851e thermogravimetric analyzer (Mettler-Toledo GmbH, Germany). The TGA analysis was used to determine the thermal and oxidative stability and the composition of the reference compound and of the raw material substitute compounds. The samples (ca. 5-10 mg) were heated from ambient temperature to 600 ^{0}C in N_2 atmosphere, then switched to O_2 atmosphere and heated up to 900 ^{0}C, with a heating rate of 10 K min^{-1} under 50ml min^{-1} N_2 and O_2 atmospheres, respectively.

Compounding and curing

1) Mixing of the compounds

The preparation of ternary mixtures consisting of EPDM, RWP and -LP was performed in two mixing steps using a laboratory internal mixer of type Haake PolyLab QC from Thermo Scientific, Germany. In the first stage, the LP and the RWP were mixed for 15 minutes at 100 ^{0}C and a rotor speed of 40 rpm. The resulting particles are denoted in the following as activated particles. In the second stage, the EPDM raw polymer was mixed for 10 minutes at 90 ^{0}C and 40 rpm together with the activated particles, followed by addition of carbon black, oil, activators (ZnO and stearic acid), and crosslinking agents (CBS and sulphur).

The formulations of the reference sample and of the activated particles are compiled in Table 4.2. The composition of the RWP-LP contains 560 phr RWP and 100 phr LP, which corresponds to 0.8 and 0.2 volume fractions, respectively. Furthermore, rubber compounds with a varying content of activated rubber particles were produced and investigated. Those compounds are based on the reference compound, which was substituted with 25, 50 and respectively 75 vol% by the RWP-LP. The R abbreviation is standing for the reference sample, the letters A (Trilene®67), B (Trilene®66), C (Trilene®77) and D (Trilene®76) are standing for the type of the liquid polymer used for activation, and the numbers 25, 50 and 75 are standing for the percentage (vol%) of the RWP-LP used to substitute the raw materials from the reference sample. In this case the raw material refers not only to the raw polymer but to the whole compound, including also oil, carbon black and curatives, as described in the reference sample recipe.

Table 4.2 EPDM compounds formulations

Ingredient	**Reference Sample**	**RWP-LP**[a]
	Amount (phr)[b]	
Keltan 9650Q	100	
LP[c]		100
RWP[d]		560
Carbon black N550	120	
Paraffinic oil	100	
ZnO[e]	4	2
Stearic acid	2	1
CBS[f]	3	3
Sulphur	1.5	1.2

[a]RWP-LP- activated EPDM rubber waste particles; [b]phr- parts per hundred rubber (including liquid polymer); [c]LP- liquid polymer; [d]RWP- rubber waste particles; [e]ZnO- zinc oxide; [f]CBS- N-Cyclohexyl-2-benzothiazolesulfenamide

To simplify the name of the new compounds abbreviations were used. For example RA25, RA50, RA75 are standing for the samples where the reference compound was substituted with 25, 50 and respectively 75 vol% by the RWP-LP used to activate the particles. The letter A stands for the type of polymer used for the activation (Trilene® 67).

2) *Vulcanisation of the compounds*

The curing characteristics of the rubber compounds were determined according to ISO 6502:2009 using a Dynamic Moving Die Rheometer of type D-MDR 3000 from MonTech Werkstoffpruefmaschinen GmbH, Germany. The cure curves of the samples were measured at 180 ^{0}C. Sheets of 2 mm thickness were prepared from the compounds by compression moulding at 180 ^{0}C and 10 MPa pressure in an electrically heated hydraulic press of type Polystat 200T (Schwabenthan, Germany), according to the optimum cure times obtained from the rheometer tests.

The cure rate index (CRI) was calculated using the following relation:

$$\mathrm{CRI} = \frac{100}{\text{cure time} - \text{scorch time}} \tag{4.1}$$

3) *Dynamic viscoelastic measurements*

The complex shear viscosity (η^*) was determined by dynamic viscoelastic measurements using a rotorless rheometer, D-MDR 3000 (MonTech Werkstoffpruefmaschinen GmbH, Germany). Frequency-sweep measurements of the uncured samples were determined at 100 ^{0}C in a frequency range from 0.2 to 20 Hz with a strain amplitude of 6%.

4) *Mechanical Properties*

The hardness of the vulcanisates was measured using a Shore A Durometer (Karl Frank GmbH, Germany) according to ISO 7619-1:2010. Tensile tests were performed in accordance with ISO 37:2011 on dumbbell shaped specimens using a universal testing machine Zwick 1120 from Zwick GmbH & Co. KG, Germany. The nominal force of the load cell was 2000 N. For the tensile tests a preload of 1N was applied. The tests were performed at constant crosshead speed of 200mm/min. Hardness and tensile tests were carried out at room temperature (23±2 ºC).

Compression set tests were performed using standard test specimens with a diameter of 13 mm and a thickness of 6 mm, at various temperature and time conditions, in accordance with ISO 815-1/-2:2014: at 23 ºC for 72h, 70 ºC for 24h and -10 ºC for 70h. In all tests, the compression strain used was 25%. The allowed recovery time was 30 minutes.

5) Determination of the crosslinking density

The crosslinking density of the samples was determined by swelling and TSSR measurements as described in Chapter 3. The values obtained from swelling measurements are presented in Table 4.3.

Table 4.3 Values obtained from swelling measurements for R, RA, RB and RC samples

Samples	**m_0 [g]**	**m [g]**	**m_d [g]**	**V_r**
R	0.3175	0.5371	0.2244	0.33347
RA25	0.4254	0.7796	0.3106	0.31467
RA50	0.4028	0.7978	0.2990	0.29364
RA75	0.3719	0.7807	0.2776	0.27635
RB25	0.3766	0.6959	0.2693	0.30595
RB50	0.3868	0.7480	0.2823	0.29626
RB75	0.3433	0.7087	0.2525	0.27770
RC25	0.4134	0.7496	0.2947	0.31051
RC50	0.4101	0.7912	0.3011	0.29817
RC75	0.3908	0.8089	0.2905	0.27911
RD25	0.4009	0.7315	0.2856	0.30837
RD50	0.3209	0.6169	0.2334	0.29643
RD75	0.3129	0.6315	0.2310	0.28429

6) Determination of the Morphology of the samples

The morphology of the samples was investigated by using scanning electron microscopy (SEM). The SEM images of the tensile fractured surfaces of the specimens were obtained using a JEOL JSM 6510 scanning electron microscope (JEOL GmbH Germany). The cryogenically fractured surfaces were coated with a thin layer of gold prior to examination using a Fine Coater JEOL JFC 1200.

4.2 RESULTS AND DISCUSSION

4.2.1. Thermal characterisation of the compounds

Thermogravimetric analyses (TGA) were performed to verify the composition and thermal stability of the activated particles, of the reference sample and of the raw material substituted compounds. TGA is a thermal method which is used to measure the changes in mass in a material as a function of temperature. This study investigated the activated particles (RWP-LP), the reference sample (R) and the substituted compounds (RA25, RA50 and RA75). The samples were mixed and vulcanised as described in Section 4.2 by using the formulations as shown in Table 4.2. The investigated compounds contained the waste particles activated with the LP type A (Trilene® 67) and the raw material was substituted with 25, 50 and respectively 75 vol% by the RWP-LP. Figure 4.1 shows the corresponding TGA curves of the RWP-LP, R and the substituted compounds RA25, RA50 and RA75.

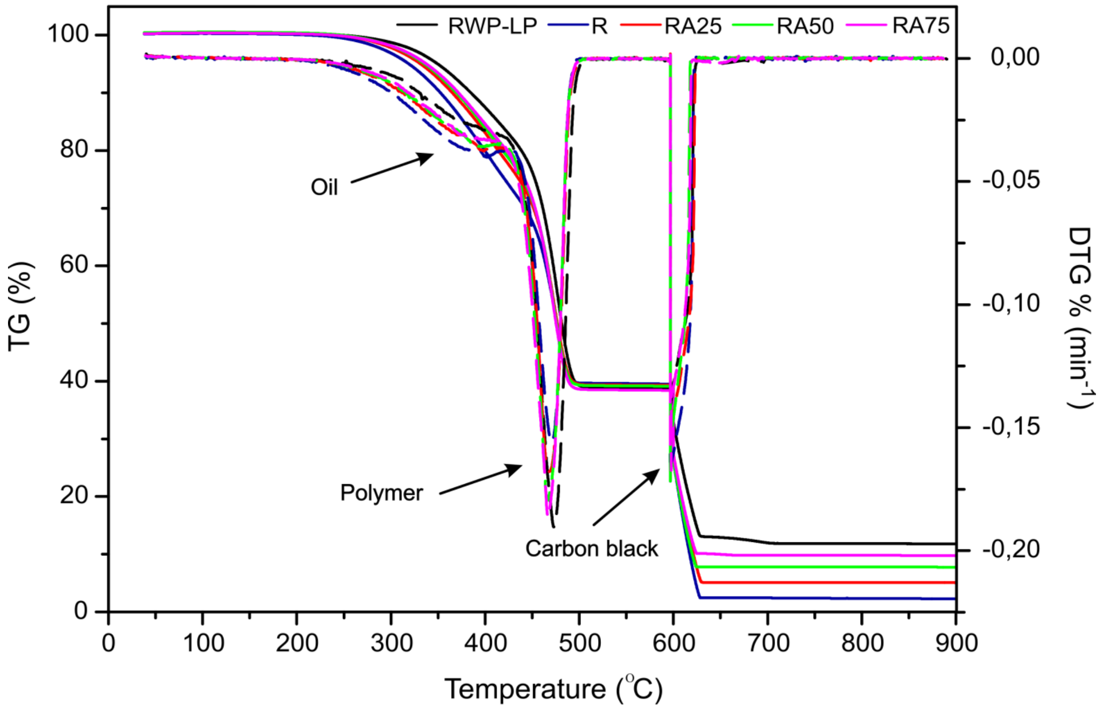

Figure 4.1 Thermogravimetric analyses of the compounds under N_2 (up to 600 °C) and O_2 (up to 900 °C) flow with a heating rate of 10K/min (solid lines –TG curves; dashed lines – DTG curves)

The thermograms were measured under N_2 flow up to 600 ^{o}C, and then the purge gas was changed to O_2 up to 900 ^{o}C. The oxidative step was introduced to surely remove all traces of organic compounds. By analyzing the TGA curves (Figure 4.1) a similar behaviour of the different compounds upon heating was observed. The volatilization of the oil took place in a temperature range of 364 to 366 ^{0}C, the degradation of the polymer in a range of between 462 and 478 ^{0}C, and the weight loss of carbon black due to the oxidation occurred in a range of 595-608 ^{0}C. The mass-loss values of the tested compounds and the peak temperatures are summarized in Table 4.4 and plotted in Figure 4.2.

Table 4.4 Samples composition calculated from TG-DTG curves

Description	Oil	Polymer	Carbon black	Residue
Tp[a]	364-366 ^{0}C	462-478 ^{0}C	595-608 ^{0}C	>600 ^{0}C
mass loss	Wt %[b]			
RWP-LP	17.9	43.4	25.7	13.0
R	27.3	33.0	37.0	2.5
RA25	22.3	38.7	34.1	5.1
RA50	21.5	39.6	31.1	7.8
RA75	20.1	41.6	28.3	10.0

[a] Tp is the peak of the first derivative; [b] Wt – weight percent

In Figure 4.2 it can be observed that RWP-LP contains the highest content of polymer and residue and the lowest carbon black and oil content when compared to R and to substituted compounds (RA25, RA50, and RA75). The data from Table 4.4 shows that with increasing RWP-LP content in the substituted rubber compounds the oil fraction of the obtained rubber materials decreased from 27.3 wt% (R) to 20.1 wt% (RA75) and the carbon black content decreased from 37.0 wt% (R) to 27.3 wt% (RA75). Concerning the polymer and the residue amount, the obtained data shows a polymer content increase from 33.0 wt% (R) to 41.6 wt% (RA75), while for the residue an increase from 2.5 wt% to 10.0 wt% was found.

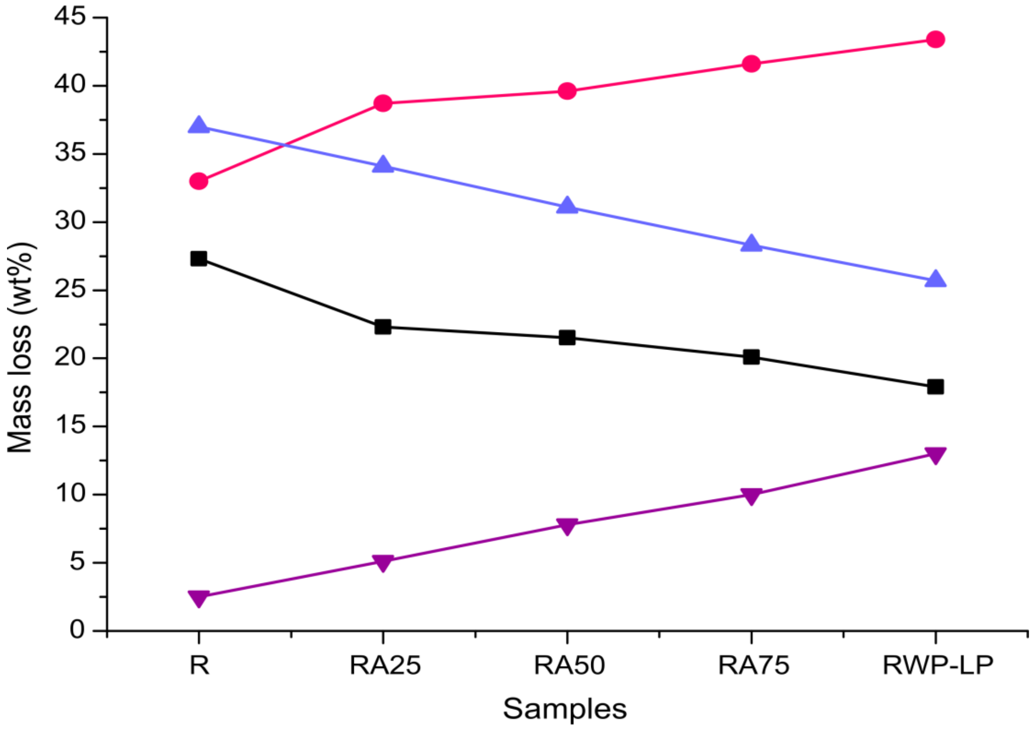

Figure 4.2 Determination of the mass loss of the samples from thermogravimetric analysis: Oil (—■—), Polymer (—●—), Carbon black (—▲—), Residue (—▼—)

4.2.2. Compound Properties – Complex Dynamic Viscosity

The rheological properties of the recycled compounds are important from a processability point of view. A good processability of the uncured rubber is very important to allow for its conversion into end products such as sealing systems, hoses, tyres etc. Unlike Newtonian liquids, which have a constant viscosity independent of the applied shear rate and shear frequency, the viscosity of rubber compounds, which are basically non-Newtonian materials, is dependent on the applied shear rate. With respect to ”shear thinning” behaviour, the complex viscosity decreases with increasing shear rate or frequency. A viscoelastic material, such as an uncured rubber compound, is a material that can exhibit both viscous and elastic behaviour. The complex viscosity, η*, represents an important parameter characterising material viscoelasticity giving information regarding the processability of the uncured composites.

It is a well known fact that the deformation mode from the oscillatory flow in a tensional rheometer is quite different from the steady flow in a capillary rheometer.[6] However, the results of the oscillatory frequency-sweep measurements, when plotted as complex viscosity (η^*) versus angular frequency (ω), can be equated to the apparent viscosity (η_a) plotted against shear rate ($\dot{\gamma}$). This convenient equivalence is known as the Cox-Merz relation (Equation 4.2). [6,7]

$$\eta_a(\dot{\gamma}) = |\eta^*(\omega)|_{\omega=\dot{\gamma}} \qquad 4.2$$

η_a = viscosity at a constant shear rate $\dot{\gamma}$ (s^{-1}) in a capillary rheometer and η^* = dynamic complex viscosity at an oscillatory frequency ω (rad/s).

In order to investigate how the amounts of added activated particles influence the viscosity of the material composites the viscoelastic properties of the uncured samples were determined. For verifying the influence of the liquid polymer used for particle activation control samples containing non-activated rubber particles were used. The frequency-sweep tests of the uncured samples were conducted at 100 ^{0}C in a frequency range from 0.2 to 20 Hz with a strain amplitude of 6%. Figure 4.3 shows the Cox-Merz plot, i.e. the complex viscosity of the uncured samples containing different amounts of activated (RWP-LP-A) and non-activated (RWP) rubber waste particles versus the angular frequency.

Both types of rubber compounds are compared with the reference sample (R). Figure 4.3 shows that R exhibits the lowest complex viscosity compared to other samples. Irrespective to particle type, activated or non-activated, it can be observed that the complex viscosity increases with increase of the particle amount in the sample composition. As it can be seen in Figure 4.3, all compositions exhibit a decrease of viscosity values with increasing frequency, i.e. all samples exhibit a shear thinning behaviour. Nevertheless, the samples containing the activated particles reveal lower viscosity values in comparison with those of the control samples. By calculating the slopes of the straight lines fitted to the data points, it can be observed that there occurs a systematic variation of the slope with increase of the amount of particles for both types of samples.

The slopes become larger with increase of the activated RWP content. On the other hand, the slope values of the samples containing non-activated particles exhibit higher negative values than those of the samples with activated RWP.

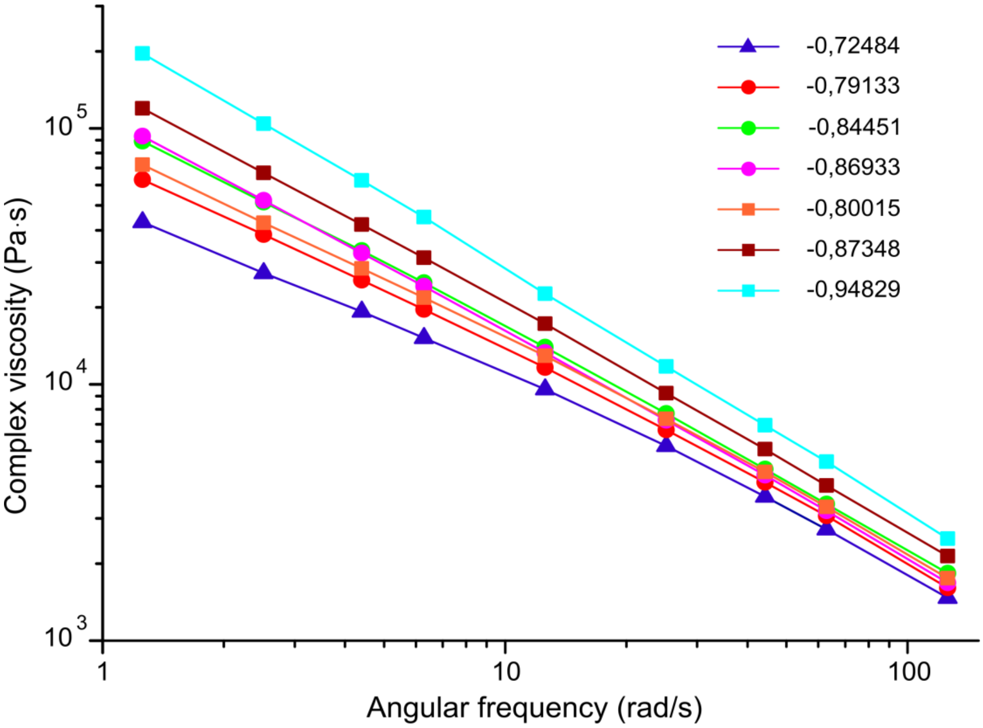

Figure 4.3 Complex viscosity as a function of angular frequency measured at 100 °C of: R (—▲—), RA25 (—●—), RA50 (—●—), RA75 (—●—), R25-RWP (—■—), R50-RWP (—■—), R75-RWP (—■—)

Figure 4.4 displays the values of the complex viscosity at constant angular frequency (2.5 s^{-1}) plotted versus the volume fraction of the rubber waste particles. By use of non-activated RWP it can be clearly seen that the complex viscosity of the sample increases significantly with increase of the amount of particles in the newly substituted compounds, while the viscosity increase levels off in the case of the samples containing the RWP-LP. Therefore, the compounds containing activated particles exhibit lower values of complex viscosity in comparison with the control samples, where the non-activated particles were used. Based on the results reported in the literature, the increase in viscosity can be related to factors such as the amount of waste particles added in the composition, [8,9] the morphology and the rubber surface chemistry [5] or the particle type. [10] In the present case it can be assumed that the LP acts as a kind of lubricant reducing the friction between the RWP and the rubber-matrix.

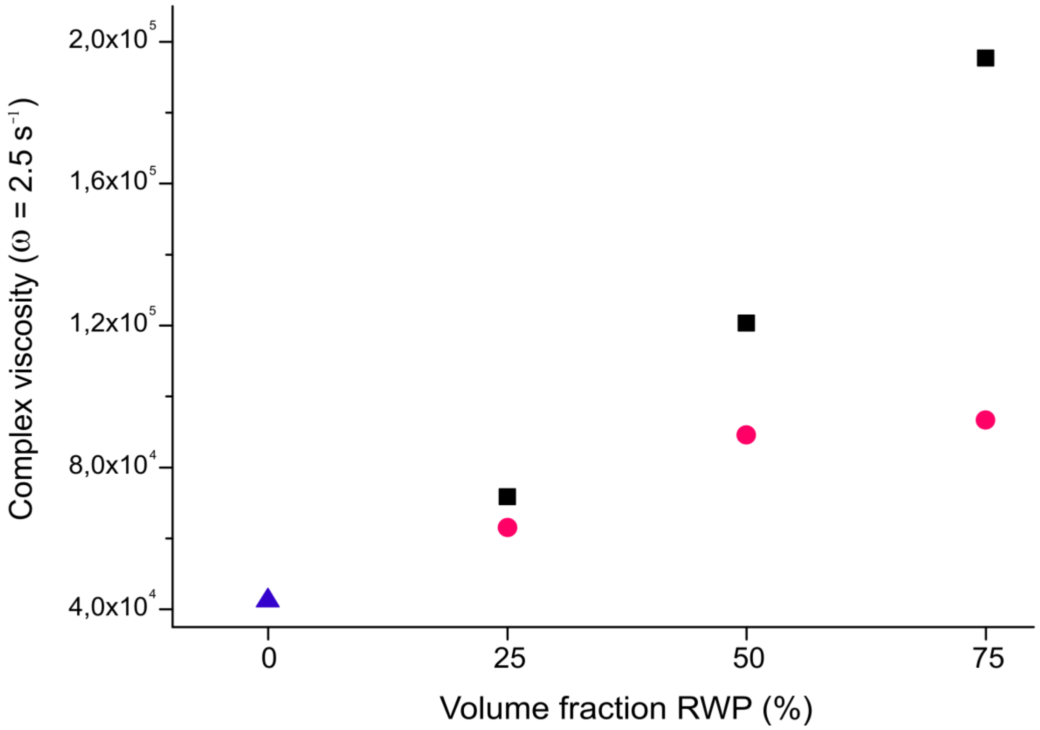

Figure 4.4 Complex viscosity of the samples versus the volume fraction of added RWP: R (▲), R with RWP (■) and R with RWP-LP-A (●)

Here, the increase in viscosity occurs due to the amount of particles used in the composition and the particle type, i.e. activated or non-activated. On the one hand, the higher values of complex viscosity obtained for the compounds where non-activated particles were used may be attributed to the particle agglomeration. On the other hand, this could be due to the roughness of the particles, [11] which might be reduced by using LP and thereby lowering the viscosity values. Hence, the processability of the rubber compounds containing particles activated with liquid polymers is improved.

4.2.3. Influence of content and type of the activated particles on curing characteristics

In order to study the effect of the amount of various types of activated particles used as a substitute of the raw polymer matrix in new composites twelve different formulations were prepared following the protocol described in Section 4.2, Table 4.2. Based on the results obtained in Chapter 3 the RWP were activated with 20 vol% of the LP. For comparison reasons a reference samples (R) was chosen. Moreover, in order to investigate the influence of the RWP-LP the reference sample was substituted with 25 vol%, 50 vol% and 75 vol% by the RWP-LP. In the present investigation four different types of liquid polymers were used to activate the RWP surface. Two of the liquid polymers contained a lower amount of ethylene and different diene percentages, being noted here with the letters A (Trilene® 67) and B (Trilene® 66), as presented in Chaper 3, Table 3.1. The other two liquid polymers used in the present study contain a higher amount of ethylene and a different diene percentage, being noted here with the letters C (Trilene® 77) and D (Trilene® 76), as presented in Table 4.1. These abbreviations were used to simplify the names of the compounds. The letter R stands for the reference sample. The letters next to R define the type of LP used for the activation of the particles, and the numbers represent the amount of RWP-LP used to substitute the raw polymer matrix. For example, RA25, RA50, RA75 denote the samples where the reference compound was substituted with 25 vol%, 50 vol% and 75 vol% by the RWP-LP-A (Trilene® 67).

The first step in characterizing the samples was to determine their cure characteristics by monitoring the increase of the torque over time at a specific temperature in a vulcameter. From the cure curves important parameters can be determinate as shown in Table 4.5. The vulcanisation temperature was in all cases 180 ^{0}C. Figure 4.5 a-b and Figure 4.5 c-d show the vulcanisation curves of the compounds containing different types and amounts of RWP-LP. Each type of compound is compared with the reference sample (R).

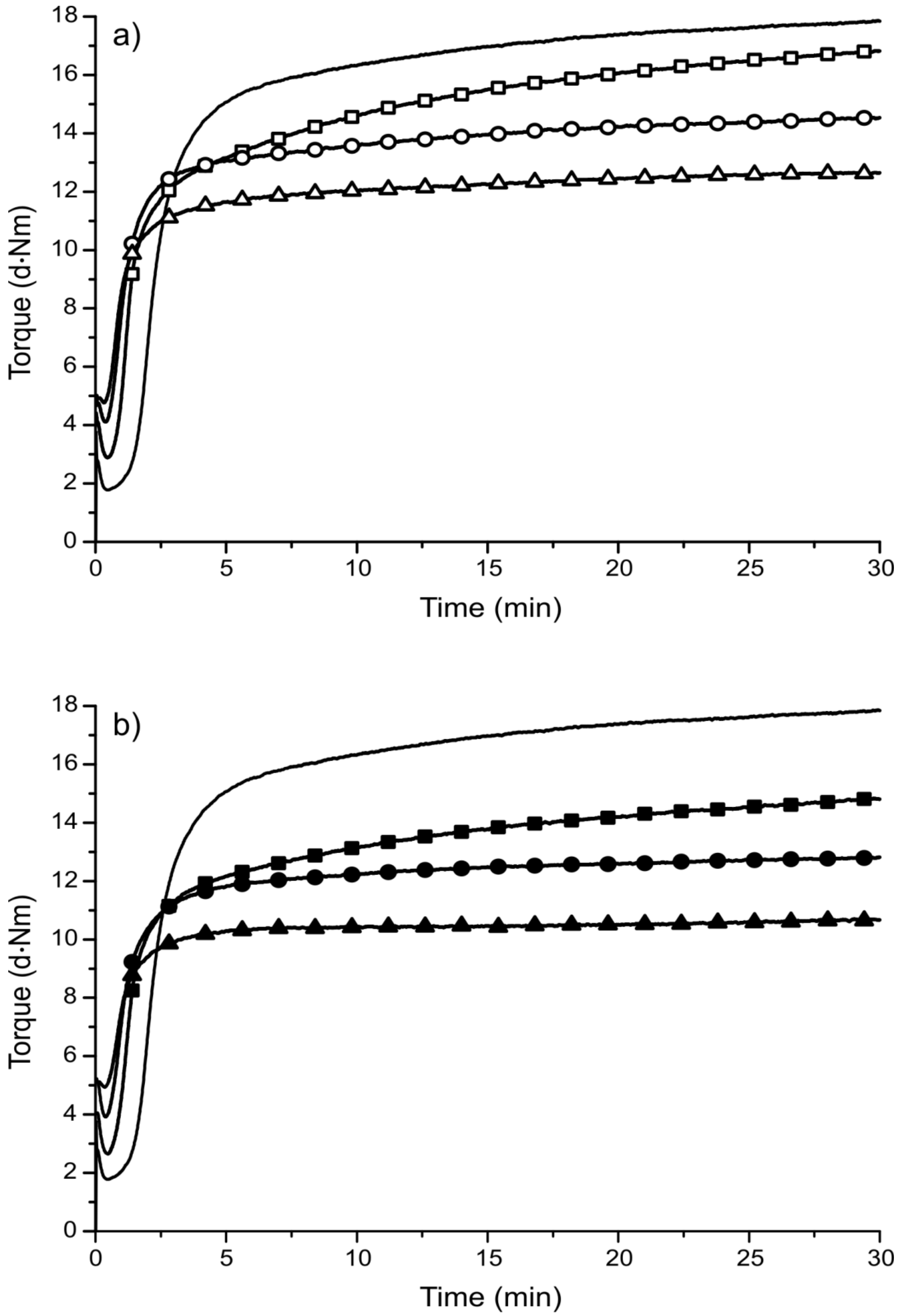

Figure 4.5a-b Vulcanisation curves of: a) RA25(—□—); RA50(—○—); RA75(—△—); b) RB25(—■—); RB50 (—●—); RB75(—▲—) compounds in comparison with R(——)

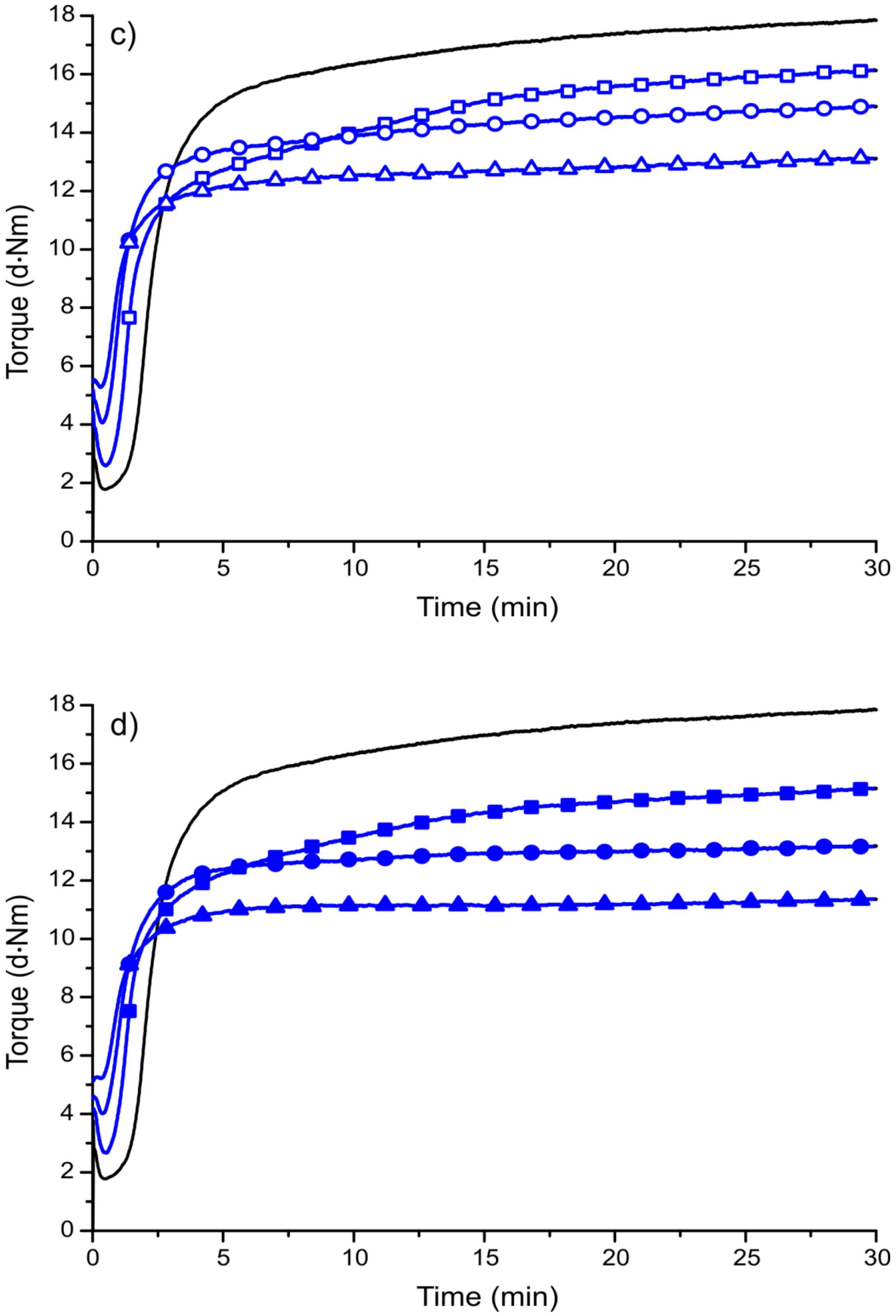

Figure 4.5c-d Vulcanisation curves of: c) RC25(—□—); RC50(—○—); RC75(—△—); d) RD25(—■—); RD50 (—●—); RD75(—▲—) compounds in comparison with R(——)

Figure 4.5a shows the rheometric curves of the samples containing waste particles activated with LP-A, i.e. the ones with a low ethylene content and a high amount of diene. In this case, it was observed that by adding 25 vol% of RWP-LP a maximum value of the M_H is obtained. By increasing the amount of the RWP-LP a decrease of the M_H has been observed.

Table 4.5 Cure characteristics of EPDM compounds

Samples	M_L[a] (dNm)	M_H[b] (dNm)	ΔM[c] (dNm)	t_{90}[d](min)	t_{s2}[e] (min)	CRI[f] (min^{-1})
R	1.78	17.86	16.08	9.50	1.69	12.7
RA 25	2.89	16.82	13.93	14.55	0.98	7.4
RA 50	4.12	14.54	10.42	8.77	0.79	12.5
RA 75	4.77	12.65	7.88	6.87	0.74	16.3
RB 25	2.65	14.83	12.18	13.33	0.99	8.1
RB 50	3.92	12.83	8.91	5.78	0.83	20.2
RB 75	4.94	10.70	5.76	3.85	0.87	33.6
RC 25	2.59	16.15	13.56	13.47	1.09	8.1
RC 50	4.07	14.90	10.83	9.08	0.82	12.1
RC 75	5.28	13.14	7.86	6.88	0.76	16.3
RD 25	2.68	15.16	12.48	12.21	1.08	9.0
RD 50	4.02	13.18	9.16	4.30	0.89	29.3
RD 75	5.14	11.36	6.22	3.84	0.85	33.4

[a]M_L – minimum torque; [b]M_H – maximum torque; [c]ΔM (= M_H – M_L) – the difference between the maximum and the minimum torque during curing ; [d]t_{90} – cure time; [e]t_{s2} – scorch time; [f]CRI – cure rate index

Regarding the samples containing LP-B (Figure 4.5b), LP-C (Figure 4.5c) and LP-D (Figure 4.5d) the same tendency has been observed. In all cases the maximum torque (M_H) decreases upon increasing the RWP-LP content. Nevertheless, the samples which contain the LPs with a higher amount of ENB (RA and RC) exhibited higher values of the maximum torque in comparison with the samples with a lower amount of ENB (RB and RD). Notably, all substituted compounds exhibit lower values than the reference sample (R).

In Table 4.5, the values of the most important parameters, such as minimum torque (M_L), maximum torque (M_H), ΔM (M_H – M_L), cure time (t_{90}), scorch time (t_{s2})

and cure rate index (CRI), are presented. The obtained values show that the increase of the RWP-LP content in the rubber compounds leads to an increase of the minimum torque M_L and a decrease of the maximum torque $M_{H,}$ and of the torque difference ΔM (= M_H - M_L) in comparison with the reference sample (R).

The increase of M_L is related to the viscosity of the samples. Since the void volume of the RWP is 30 %, it could be possible that the raw EPDM is trapped in these voids, increasing the effective volume fraction of RWP and consequently increasing the samples' viscosity. Consequently, it can be stated that the processability of the material is significantly improved by use of RWP-LP. It is possible that the liquid polymer is able to occupy the free space between the rubber waste particles and to reduce the space where the raw material can be trapped, therefore reducing the viscosity. This statement is supported by the results obtained from the frequency-sweep measurements, where it was shown that the activated particles exhibit a very low viscosity compared with that of the non-activated particles (Figure 4.4). A comparable behaviour was observed in a study conducted by Gibala et al., [12] where compositions containing ambiently ground rubber showed a higher viscosity in comparison with those containing cryogenically ground rubber.

The reduction of the maximum torque can possibly be attributed to the migration of sulphur from the raw EPDM into the RWP phase. [13,14] Both the scorch time t_{s2} and the cure time t_{90} decrease, while the cure rate index increases with RWP-LP loading. The values of the cure rate index, which is a measure of the rate of the cure reaction, [15] become lower on addition of the RWP-LP for all compounds where the LPs with a higher content of ENB were used (RA and RC) in comparison with the compounds where the LPs with a lower content of ENB were applied (RB and RD).

The decrease in scorch time may be possible due to the migration of the accelerators from RWP to the matrix. [16] Similar observations were made in other studies, where different compounds, such as SBR, [14] EPDM [17] or NR, [18] containing ground vulcanised rubber were used. The cure time t_{90} is decreasing by increasing the volume fraction of RWP-LP, exhibiting lower values in comparison with the reference sample (R) when 50 vol% and 75 vol% of the RWP-LP are added. The decrease in cure time is extremely favourable because it increases the production rate. [15]

4.2.4. Influence of content and type of the activated particle on the mechanical properties of the cured samples

The mechanical properties of the vulcanised reference sample (R) and the vulcanised new substituted composites (RA, RB, RC and RD) containing various amounts of activated particles are shown in Figure 4.6 – 4.9. These compounds were vulcanised at 180 °C according with their optimum cure time obtained from rheological measurements. The mechanical properties of the new substitute composites exhibit different values upon increasing the amount and varying the type of RWP-LP. The horizontal dashed lines are used to guide the eye, indicating in the case of hardness, tensile strength and elongation at break the minimum values required for elastomeric seals according to ISO7619-1:2010.

The values of the indentation hardness (Shore A) shown in Figure 4.6 decreases by increasing the content of the activated particles in the compound. Figure 4.6 shows that for the samples RA, RB and RC only up to 50 vol% of RWP-LP can be added without falling short of the technically required minimum hardness of 45 Shore A, while for the sample RD more than 75 vol% can be used without violating the 45 Shore A hardness. Nevertheless, although the type and the amount of RWP-LP slightly decrease the hardness values, by substituting up to 50 vol% of the raw material the hardness of all four types of samples remains in the required range for elastomeric seals, according to the requirements of the standard ISO 7619-1:2010, namely 50±5 Shore A.

Stress-strain tests were performed to study the effect of the content and type of RWP-LP on the physical properties of the raw material substitute compounds. The obtained stress-strain curves offer a direct indication of the material properties, such as stress at different strain ratio, elongation at break and tensile strength (ultimate strength). The stress-strain curves for all four vulcanised compounds are shown in Figure 4.7 a-d. The stress-strain curves for each type of compound are compared in each figure with the curve of the reference sample (R).

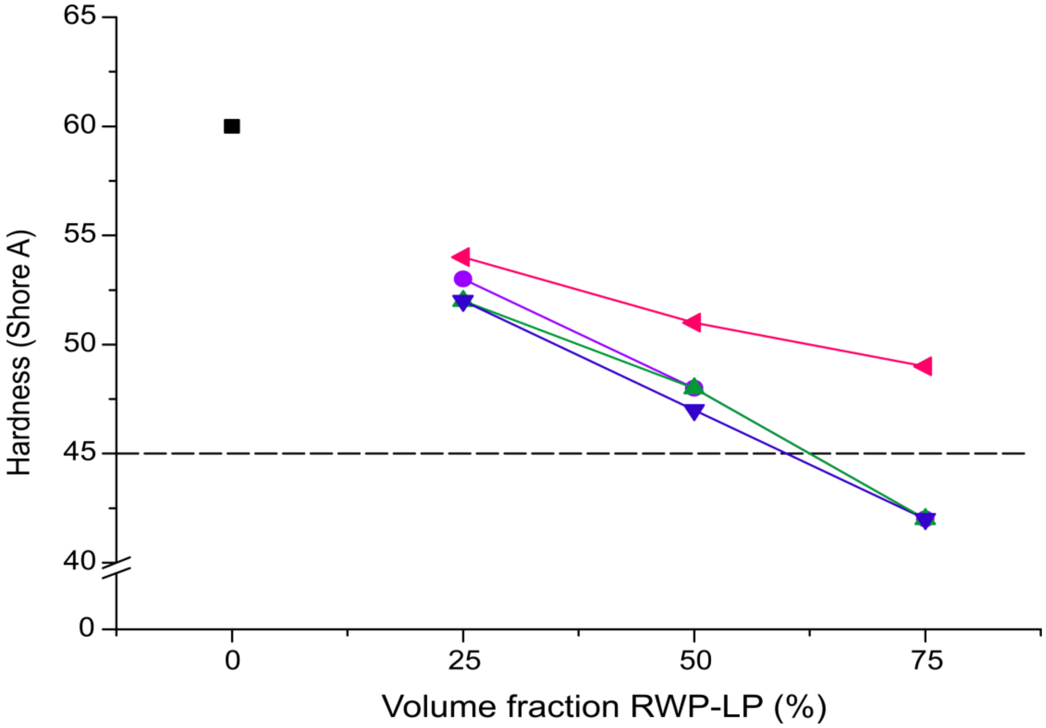

Figure 4.6 Influence of content and type of RWP-LP on the hardness of the vulcanisates: R(■); RA(—●—); RB(—▲—); RC(—▼—); RD(—◄—) minimum required value (−−)

In Figure 4.7 a-b are shown the stress-strain curves of the samples RA and RB in comparison to R. It can be observed that the samples where the raw material was substituted up to 50 vol% exhibit higher values than those of R.

When increasing the amount of RWP-LP to 75 vol% a significant decrease of the stress-strain curves is observed in both cases. For the samples RC and RD shown in Figure 4.6 c-d the same behaviour as in the case of the RA and RB samples (Figure 4.6 a-b) can be observed, namely higher values in comparison with R for the samples where the raw material was substituted up to 50 vol% and a considerable decrease when 75 vol% of the RWP-LP was used. The values obtained for tensile strength (Figure 4.8) and elongation at break (Figure 4.9) from stress-strain curves for all four types of compounds are illustrated and compared with the values of the reference sample.

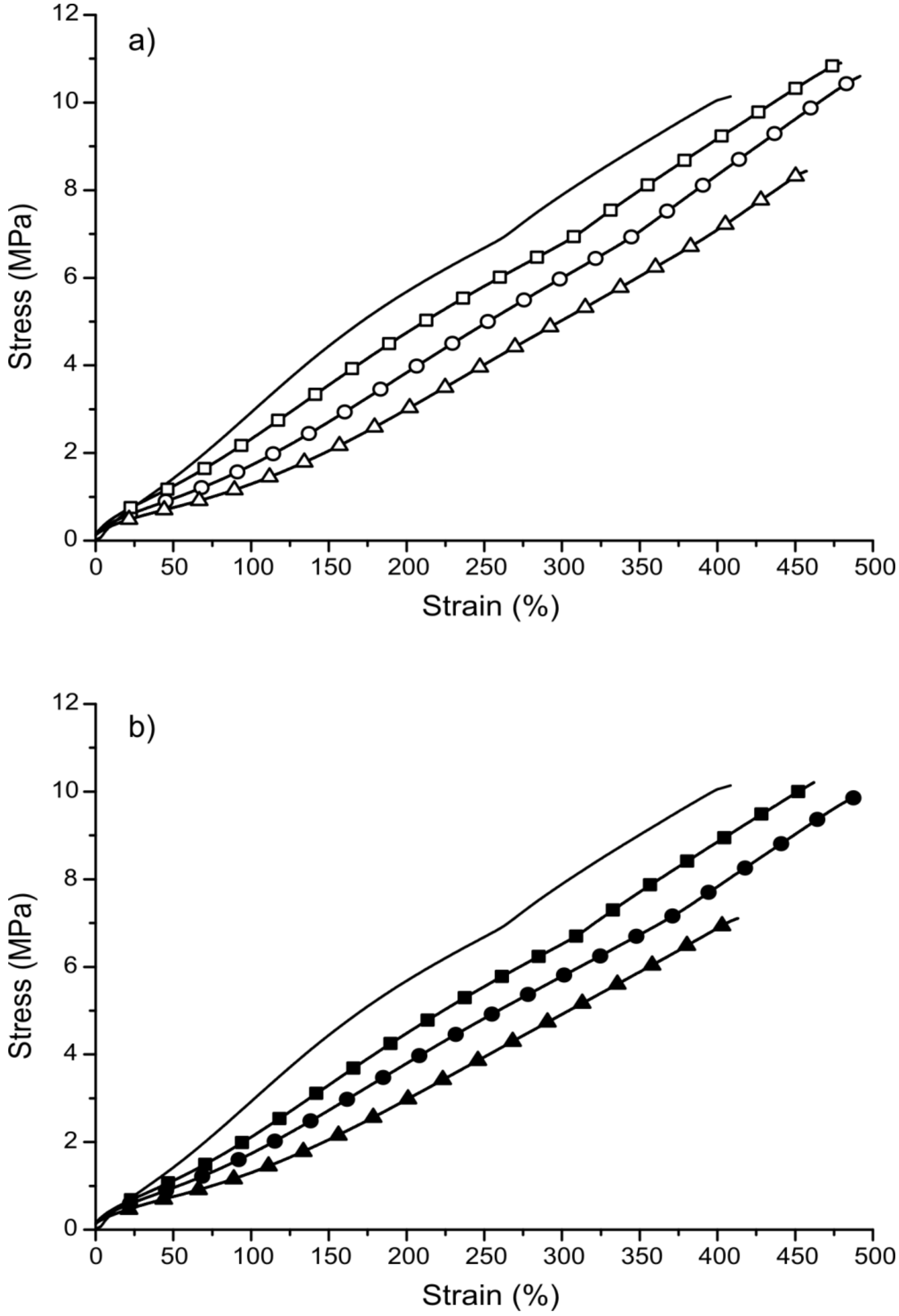

Figure 4.7a-b Stress-strain curves of: a) RA25(—□—); RA50(—○—); RA75(—△—); b) RB25(—■—); RB50 (—●—); RB75(—▲—) compounds in comparison with R(——)

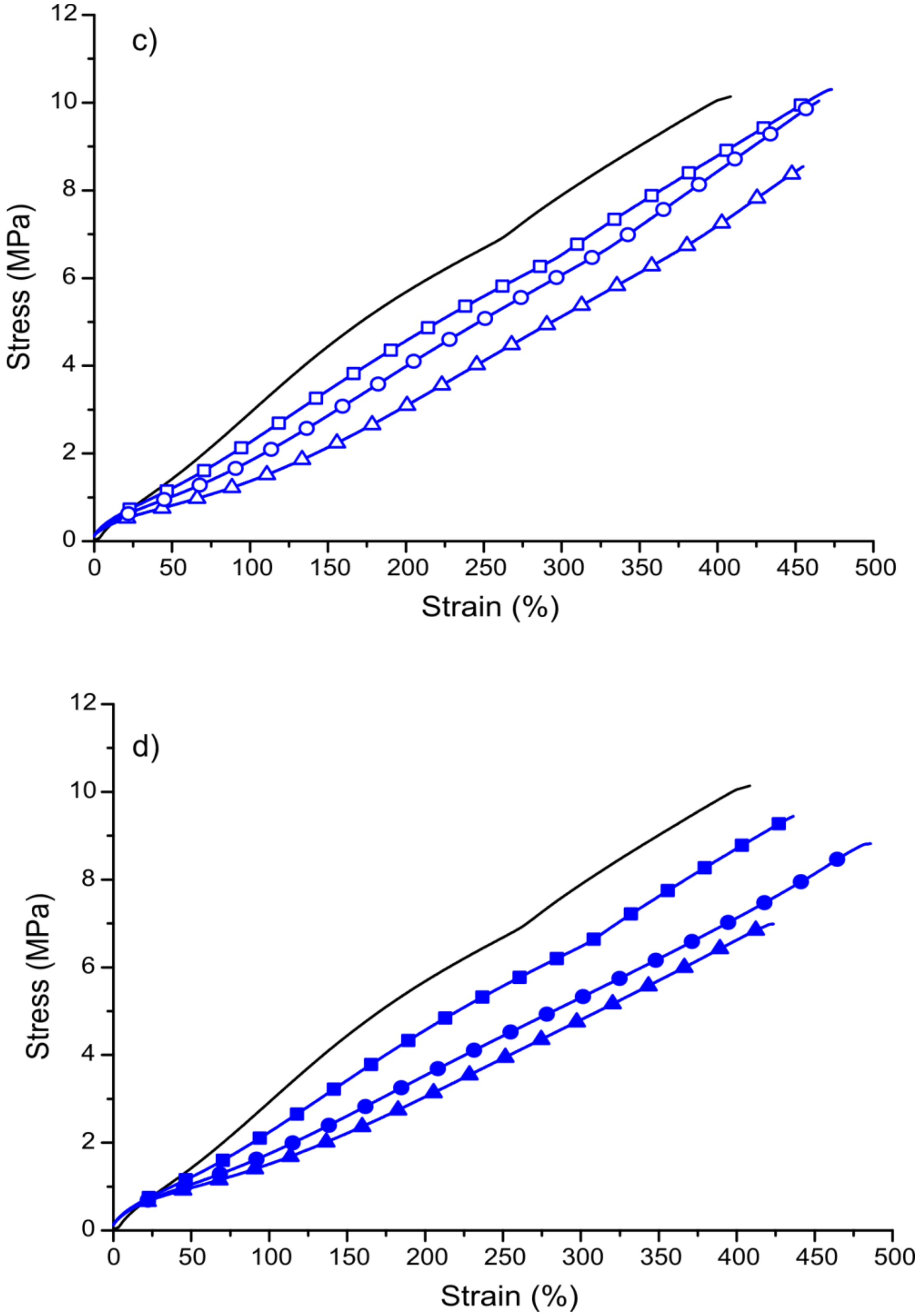

Figure 4.7c-d Stress-strain curves of: a) RC25(—□—); RC50(—○—); RC75(—△—); b) RD25(—■—); RD50 (—●—); RD75(—▲—) compounds in comparison with R(——)

The tensile strength decreases with increasing RWP-LP content showing higher values for the samples RA and RC where the content of ENB is higher, as presented in Figure 4.8. It was observed that the tensile strength exhibits approximately the same values up to 50 vol% RWP-LP for the samples RA, RB and RC, while RD exhibits continuously decreasing values. Notably, where 75 vol% of RWP-LP was used the tensile strength collapses below 9 MPa for all samples.

Nevertheless, by substituting up to 50 vol% of the raw material with the activated particles (excepting the RD sample) the obtained tensile strength values are above the requirements of 9 MPa, according to the standards for elastomeric seals (ISO 37:2011), being even higher for the RA samples in comparison with the reference sample (Figure 4.8).

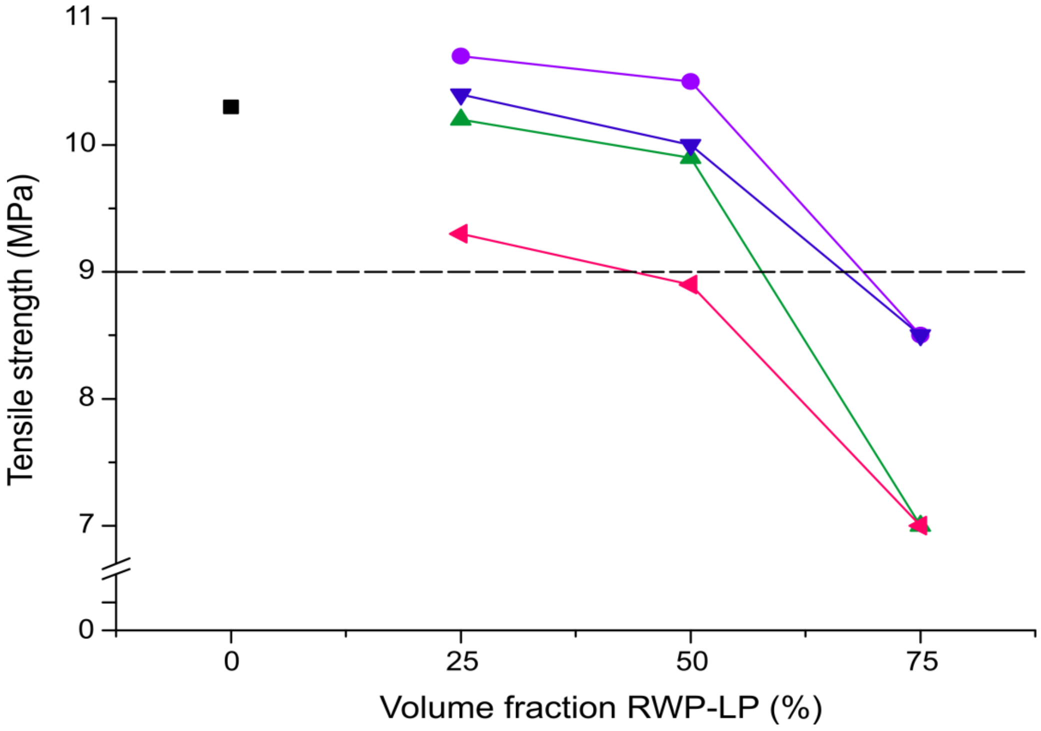

Figure 4.8 Influence of content and type of RWP-LP on the tensile strength of the vulcanisates: R(■); RA(—●—); RB(—▲—); RC(—▼—); RD(—◄—)
minimum required value (−−)

Concerning the values of elongation at break the obtained results show that by increasing the RWP-LP content all samples exhibit higher values in comparison with the reference compound (R) as presented in Figure 4.9. In the case of the RA, RB and RD samples a similar behaviour was observed, namely a fluctuation upon increasing the RWP-LP amount, while the RC sample exhibits a continuous decrease.

In comparison with other studies, this represents a significant result, taking into consideration that it is possible to substitute up to 75 vol% of the raw EPDM and to obtain an elongation at break higher than 400%. These results fully fulfil the standard requirements for elastomeric seals, which require a minimum value of the elongation at break of 375%.

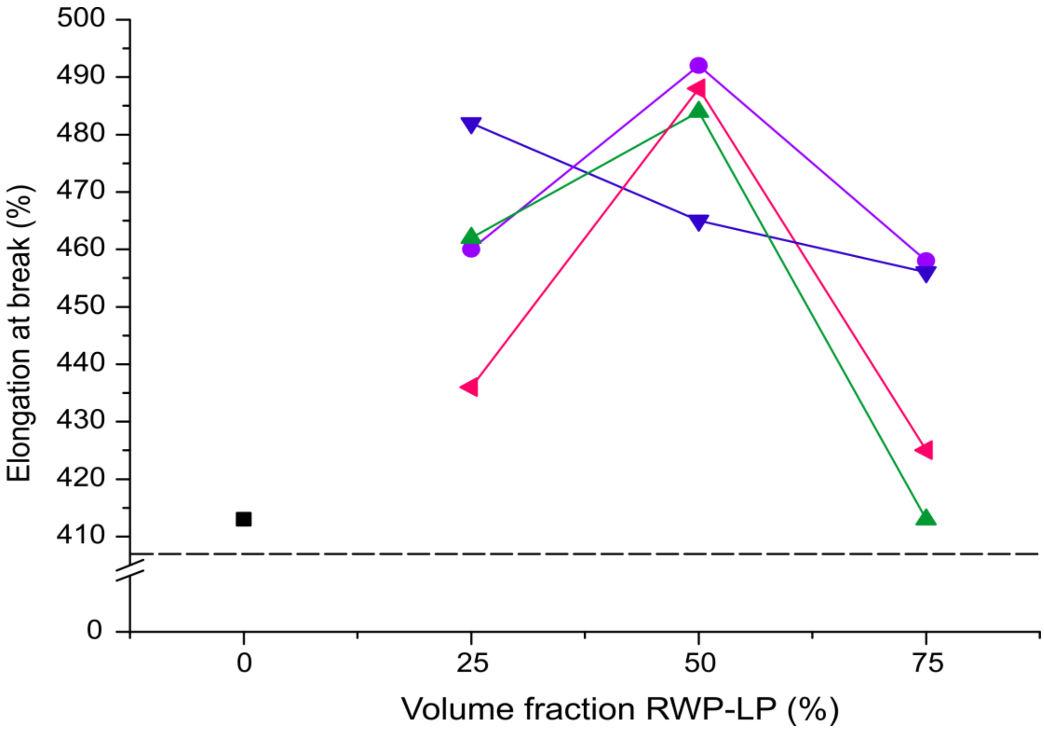

Figure 4.9 Influence of content and type of the RWP-LP on elongation at break of the vulcanisates: R(■); RA(–●–); RB(–▲–); RC(–▼–); RD(–◄–) minimum required value (−−)

The results obtained for the elongation at break are in contrast to the results obtained in other studies, [18,19] but are in agreement with the results reported by De and co-workers. [17] While studying the effect of crumb rubber on the properties of rubber compounds based on SBR, Kruželák et al. [19] reported that the addition of the modified crumb rubber causes a significant decrease of elongation at break. Phadke et al. [18] reported as well a decrease of elongation at break while studying the effect of cryoground rubber (CGR) in powder form on properties of NR. It has been noted that stress concentration around the ground particles and the poor adhesion between the two phases caused the reduction of tensile strength and elongation at break. Contrariwise, in a study performed by De et al. [17] on EPDM compounds it was reported that the addition of ground vulcanisate leads to an increase of elongation at break. In this case, the increase of elongation at break was attributed to the effect of the filler contained by the ground vulcanisate.

Based on the results obtained in our study, it can be stated that the improvement of the elongation at break values is due to the liquid polymers used for the activation of the RWP. Using the activated particles leads to a better adhesion and compatibility between the raw rubber matrix and the RWP-LP.

Besides hardness, elongation at break and tensile strength, an essential property of the sealing systems is the remaining deformation, characterized by the determination of the compression set. Compression set testing measures the ability of an elastomeric material to return to its original thickness after prolonged compressive stresses at a defined temperature and deflection. When a rubber material is compressed over time, it loses its ability to return to its original thickness. This loss of resiliency may reduce the capability of an elastomeric seal to perform over a long period of time. Compression set results are expressed as the percentage of the original deformation not recovered after a recovery period (generally 30 minutes).

Therefore, for performing under high stress over a long period of time a low compression set value is necessary. To assess the flexibility of the material at high and low temperature, compression set tests at three different temperatures were performed as described in Section 4.2. The horizontal dashed lines are used to guide the eye, indicating in the case of compression set tests the maximum values accepted for elastomeric seals according to ISO 815-1/-2:2014.

The results show that the ethylene content influences the behaviour of the samples in terms of compression set values (Figure 4.10-4.12). The compression set tests performed at -10 ^{0}C are shown in Figure 4.10. The high ethylene content seems to induce an unwanted increase of the remaining deformation (RC and RD samples) while a low ethylene content exhibits in all cases only minimal changes (RA and RB samples), keeping the compression set values close to the value of the reference compound.

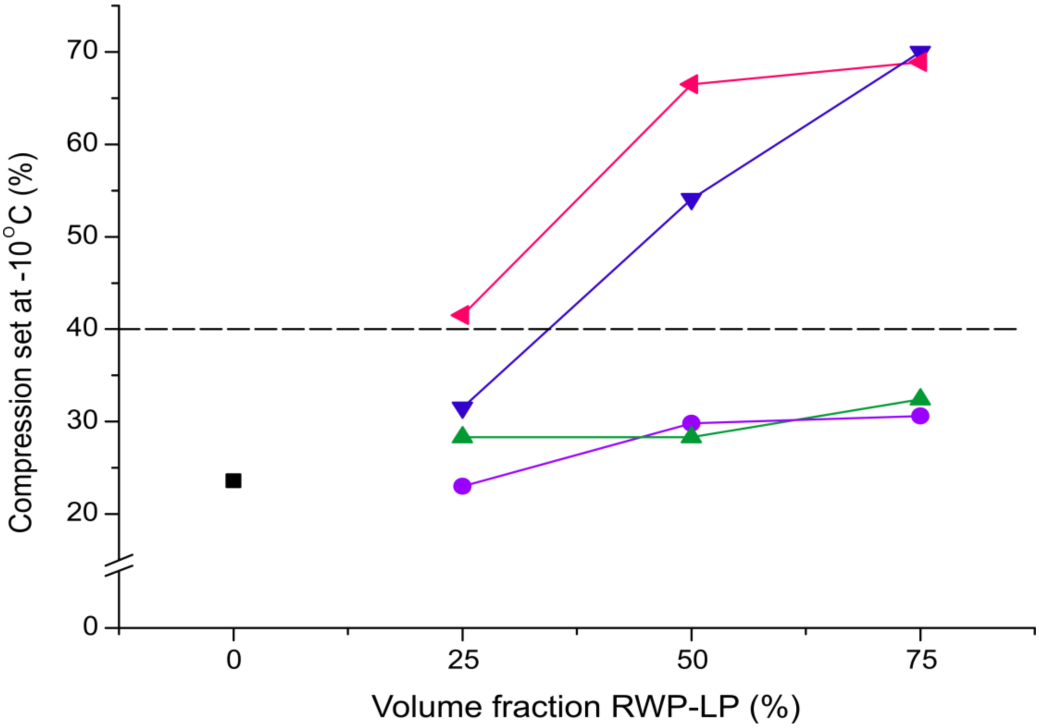

Figure 4.10 Influence of content and type of the RWP-LP on the compression set of the vulcanisates at -10 ^{o}C: R(■); RA(–●–); RB(–▲–); RC(–▼–); RD(–◀–) maximum accepted value (−−)

A similar behaviour was observed for the sample tested at 23 ^{o}C, which is presented in Figure 4.11.The samples with a low ethylene content (RA and RB) exhibit very good compression set values at 23 ^{o}C, these being even lower in comparison with the reference compound (R). Interestingly, for these samples the amount of RWP-LP has no (RA) or only small (RB) influence on compression set values. Contrariwise, the compounds with a higher content of ethylene (RC and RD) show a strong increase of the compression set values with increase of the content of RWP-LP.

By increasing the test temperature to 70 ^{o}C all samples exhibit an increase of the compression set values when increasing the activated particles content (Figure 4.12). Although at this temperature the influence of the ethylene content on the remaining deformation is minor, the ENB percentage seems to be of major importance. Samples with low ENB content (RB and RD) show a significant increase of compression set values with increase of the RWP-LP content. Interestingly, in the samples with a high ENB percentage (RA and RC) the RWP-LP can substitute up to 75 vol% of the raw material and the remaining deformation is still below the required limit for this type of products, i.e. sealing systems.

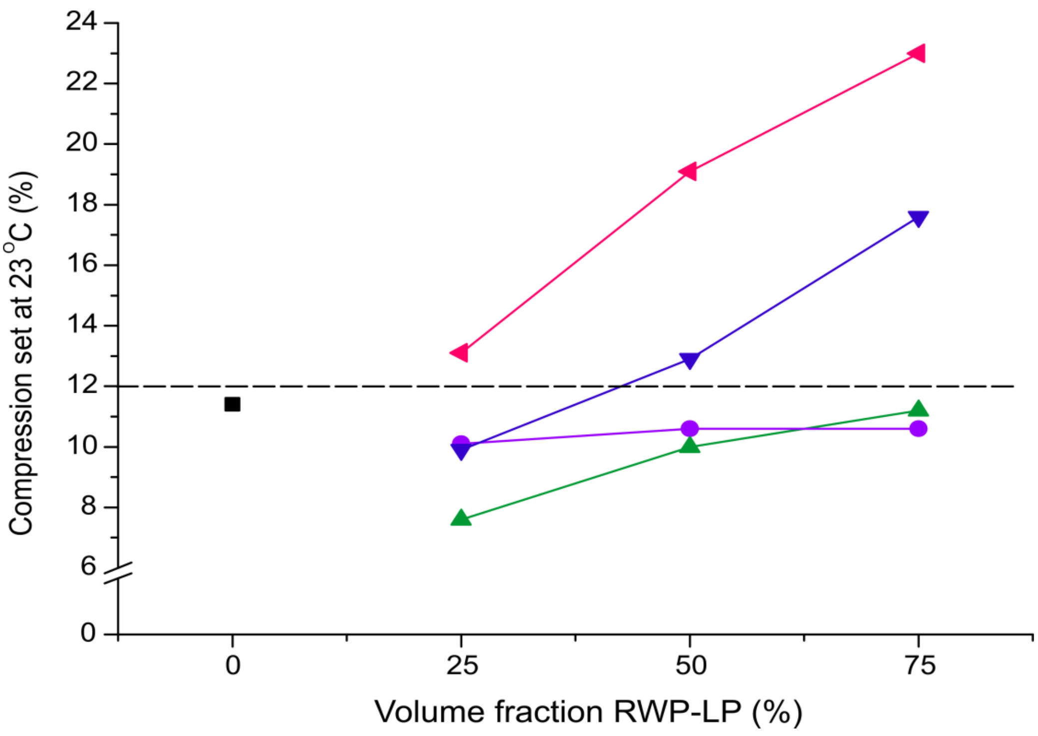

Figure 4.11 Influence of content and type of RWP-LP on the compression set of the vulcanisates at 23 ^{o}C: R(■); RA(—●—); RB(—▲—); RC(—▼—); RD(—◄—) maximum accepted value (−−)

It was previously shown that the ethylene content in EPDM rubber has a considerable impact on its low temperature behaviour. [20] When the ethylene content is higher than 65% the possibility to form semi-crystalline segments increases and therefore the polymer behaves more thermoplastic. Accordingly, the compression set values are highly dependent on the test temperature. At high temperatures, such as 70 ºC, the ethylene crystalline segments melt and the polymer becomes fully amorphous, resulting in relatively low compression set values. [20]

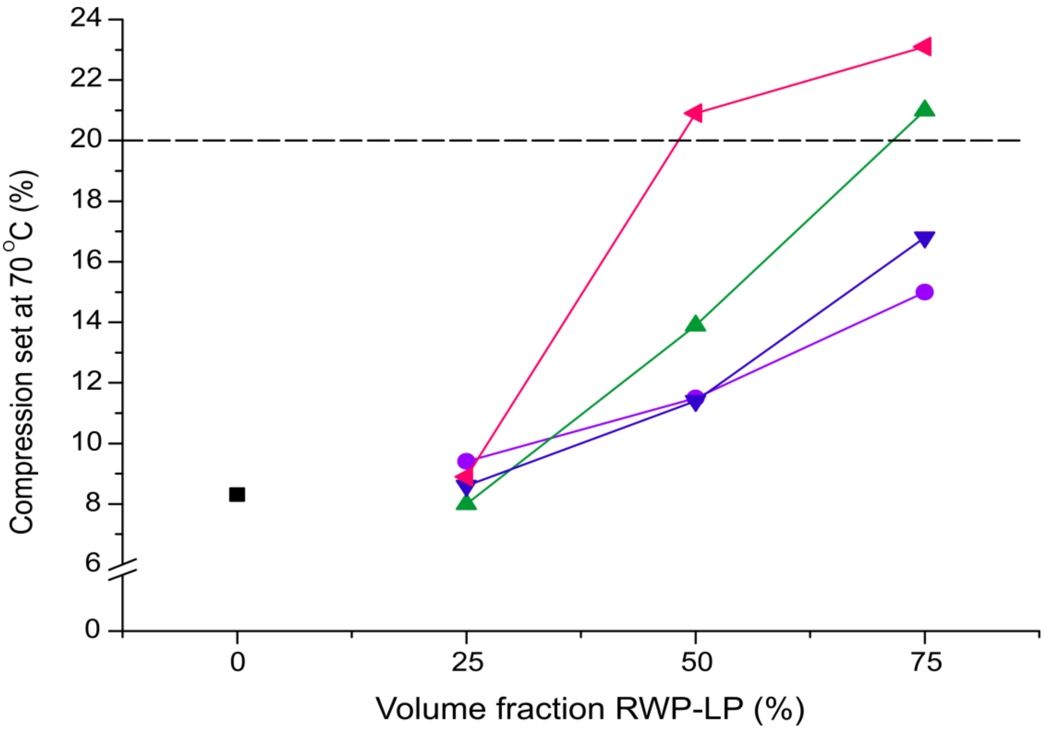

Figure 4.12 Influence of content and type of RWP-LP on the compression set of vulcanisates at 70 ºC: R(■); RA(─●─); RB(─▲─); RC(─▼─); RD(─◄─) maximum accepted value (−−)

By lowering the temperature, the ethylene content already leads to higher compression set values at 23 ºC, while at -10 ºC this effect is extreme, inducing very poor compression deformation behaviour. However, this drawback can be overcome by increasing the ENB content in the compound. As the results show, a higher ENB content improves the compression set at 70 ºC. The samples with the same ethylene content but a higher ENB percentage gave at all three set temperatures better compression set values than the samples with lower ENB percentage. This behaviour is attributed to the ability of ENB to disrupt the crystalline segments developed by the ethylene content, [20,21] thus decreasing crystallisation and consequently improving the compression set values at low temperatures. The ethylene content and ENB percentage of the LP used for the activation of the RWP have a strong influence on the compression set values even at a low concentration, namely 0.2 volume fractions.

4.2.5. Influence of the activated particle type and content on the crosslinking density of the samples

The apparent crosslinking density of the cured samples determined by swelling measurements in toluene was calculated according the Flory-Rehner equation, as described in Chapter 3. The crosslinking density values obtained by swelling measurements are depicted in Figure 4.13.

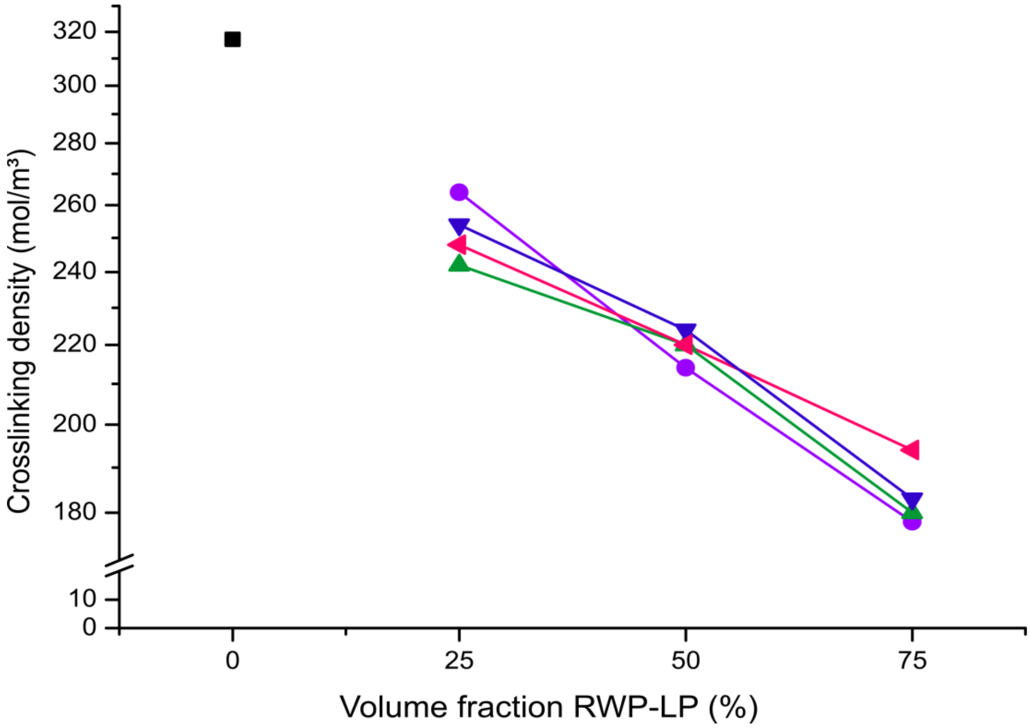

Figure 4.13 Crosslinking density determined by equilibrium swelling tests: R(■); RA(—●—); RB(—▲—); RC(—▼—); RD(—◀—)

The results show that the apparent crosslinking density of the samples shows a linear decrease on increasing the RWP-LP loading in the compounds in comparison with the reference recipe.

As described before, the temperature coefficient values determined from the initial part of the stress-temperature curves was used to calculate the crosslinking density of the samples according to Equation 3.4, as described in Chapter 3. The crosslinking density determined by TSSR is plotted against the volume fraction of RWP-LP as shown in Figure 4.14.

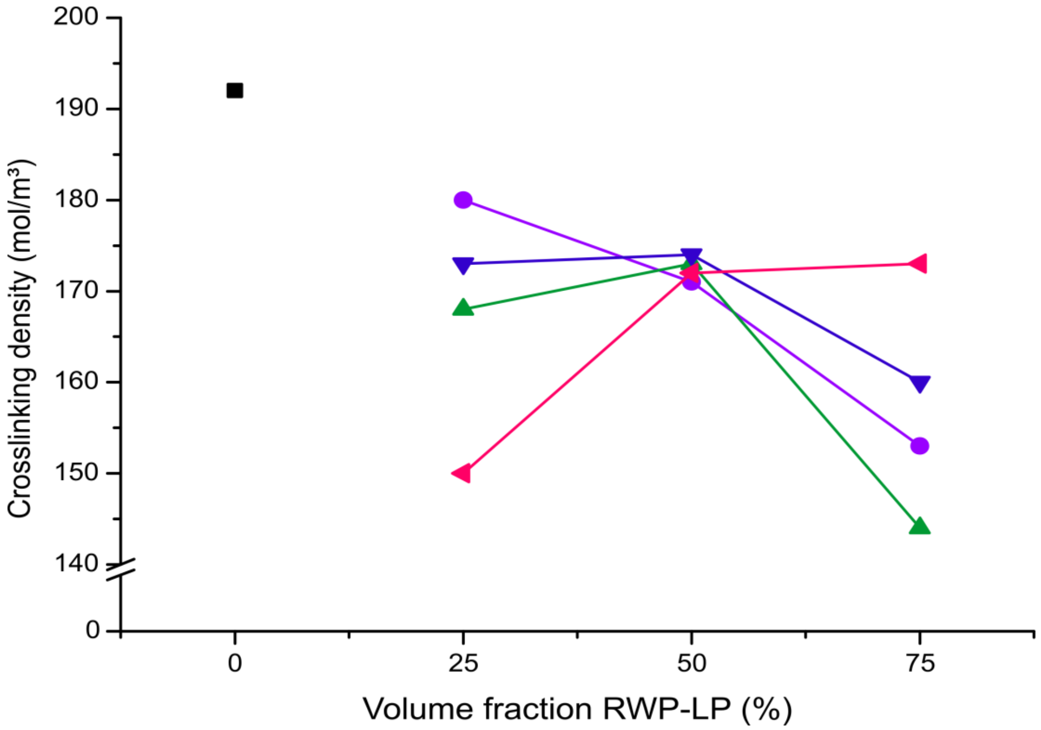

Figure 4.14 Crosslinking density determined by TSSR tests:
R(■); RA(—●—); RB(—▲—); RC(—▼—); RD(—◀—)

The results obtained via this method show the same tendency as the results obtained from swelling tests, namely a decrease of crosslinking density when increasing the amount of activated particles. However, upon increasing the activated RWP amount a decrease of the crosslinking density values was observed with the exception of samples RB25, RC25, and RC25, where 25 vol% of RWP-LP was used. These samples present a lower crosslinking density value in comparison with the samples where 50 vol% of RWP-LP was added.

As already mentioned, due to the complexity of the system the absolute values obtained via these two methods are not identical but it is obvious that the results obtained from TSSR measurements are qualitatively consistent with the results obtained from swelling: the apparent crosslinking density decreases with increase of the activated particles content in the compounds. The results obtained via the above mentioned methods are thus in good agreement with the results obtained from the rheometer curves.

The substitution of the raw material with various amounts and types of RWP-LP has a significant influence on the processability, cure characteristics, mechanical properties, crosslinking density and the morphology of the new raw material substitute compounds. With increase of the RWP-LP amount an increase of M_L and CRI and a slight decrease of cure time, M_H, ΔM and scorch time occurs (Table 4.5). As mentioned, CRI is a measure of the vulcanisation rate. Therefore, the shortest t_{90} of compounds results in the highest value of CRI. In this case, the samples with a high ENB content (RA and RC) present smaller CRI values, indicating a slower cure. This behaviour is attributed to the high ENB content, which requires a higher cure time due to the more active crosslink sites in the rubber compound.

In Figure 4.15, a schematic sketch of the variation of several vulcanisate properties as a function of the RWP-LP volume fraction is presented. As the volume fraction of the RWP-LP increases, hardness (– · –), crosslinking density (——) and tensile strength (- - -) decreases. The compression set (------) increases, while the elongation at break (- - -) typically exhibits a maximum behaviour, followed a decrease.

The decrease of hardness with increase of the fraction of RWP-LP in the raw material substitute compounds can be ascribed to a higher amount of LP and a lower content of carbon black in the final rubber composite.

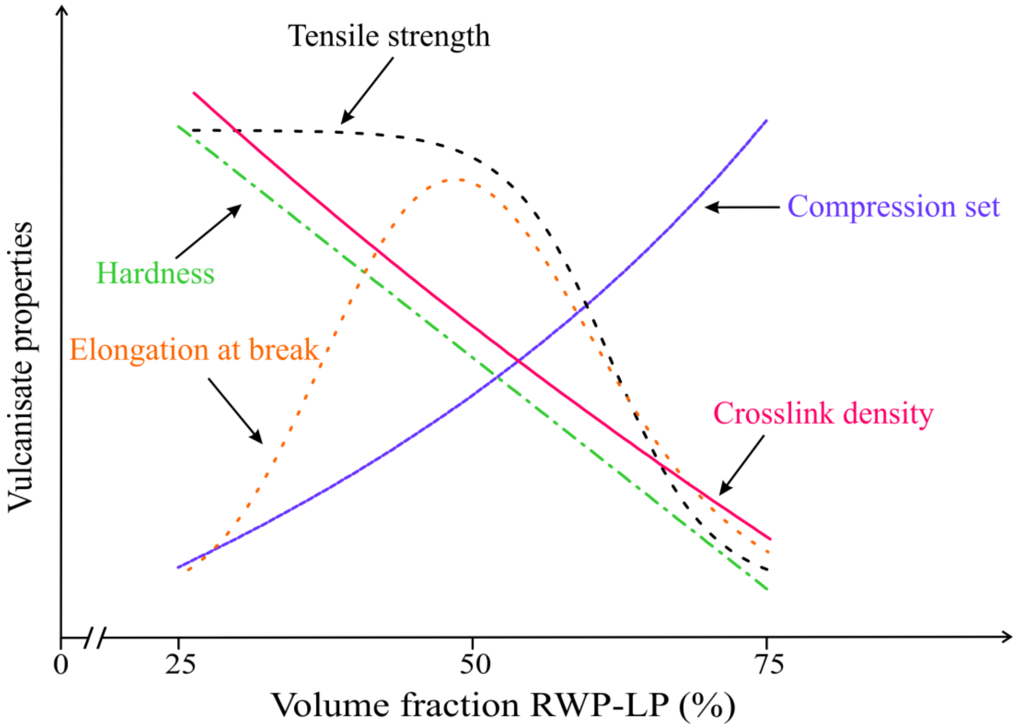

Figure 4.15 Vulcanisate properties versus volume fraction of RWP-LP (%)

As can be seen from the TGA results (Table 4.4), a higher amount of RWP-LP leads to a decrease of carbon black content, and thus to a decrease of hardness. Due to its low molecular weight a high amount of LP in the compounds can be another reason of the decrease in hardness. The excellent values obtained for elongation at break can be assigned to the LP used for activation of the RWP, which can act as a coupling agent between the particles and the raw polymer matrix, making the material more flexible.

Based on the obtained results it seems likely that values of the tensile strength are more influenced by the ENB content than by the ethylene amount, as expected. This behaviour can be ascribed to the ENB content which has a strong impact on crosslinking density. The higher the ENB content, the higher the number of reactive centres for sulphur cured networks.

The compression set values are influenced by both ethylene and ENB content. At -10 °C and 23 °C the samples with a lower amount of ethylene exhibit lower or slightly increased values, while the samples with high ethylene content show a continuous increasing trend in comparison with the reference compound (R). This behaviour is due to the crystalline regions formed by the ethylene sequences at high ethylene content. Due to crystallinity, the mobility of the polymer chains is reduced and thus the ability of the material to return back into the undeformed state is hindered. At a test temperature of 70 °C all samples show an increase of compression set values with increase of the amount of RWP-LP. A possible explanation for this might be that at high temperatures the polymer networks tend to rearrange and at the same time the possible polysulphidic crosslinks may convert into shorter bonds, which consequently can inhibit the full recovery of the material. However, the samples with a higher ENB content present better values and this is attributed to the possibility of forming more crosslinks and therefore improving the compression set. These results correspond to the trends which are expected for these properties, as already described in the literature.[22]

The compounds obtained by using up to 50 vol% of activated particles with a low ethylene amount for the substitution of the raw material present a high potential of application on an industrial scale. For the activated particles which have a high content of ethylene the substitution of the raw material was possible only up to 25 vol%.

4.2.6. Morphology using SEM

Scanning electron microscopic images have been recorded in order to gain an insight into the dispersion behaviour of the samples and to analyse the microstructure of the compounds. The liquid polymer used in all cases was Trilene® 67 (Type A). The morphologies at the fracture surface of the tensile specimens for the reference sample, activated particles and the compounds containing 25 vol% and 75 vol% of activated respectively non-activated particles are shown in Figure 4.16 a-f.

The reference sample (R) presents a smooth surface with a good uniformity and homogeneity (Figure 4.16a). The RWP-LP-A (Figure 4.16b) and the RA samples with 25 vol% (Figure 4.16c) and 75 vol% (Figure 4.16d) of activated particles show a very good dispersion and uniformity. Despite the high content of particles (Figure 4.16b, d), which are visible in the SEM images, the samples reveal a good homogeneity and uniformity in comparison with the reference sample (R).

For a lower RWP-LP content (Figure 4.16c) the particles are not that visible anymore, showing a structure close to R. On the contrary, the compounds which contain 25 vol% (Figure 4.16e) and 75 vol% (Figure 4.16f) of non-activated particles reveal an inhomogeneous structure with rough surface and fissures. It can be clearly seen that even when the content of non-activated particles is low (Figure 4.16e) the particles show a poor dispersion in the rubber matrix, forming agglomerates.

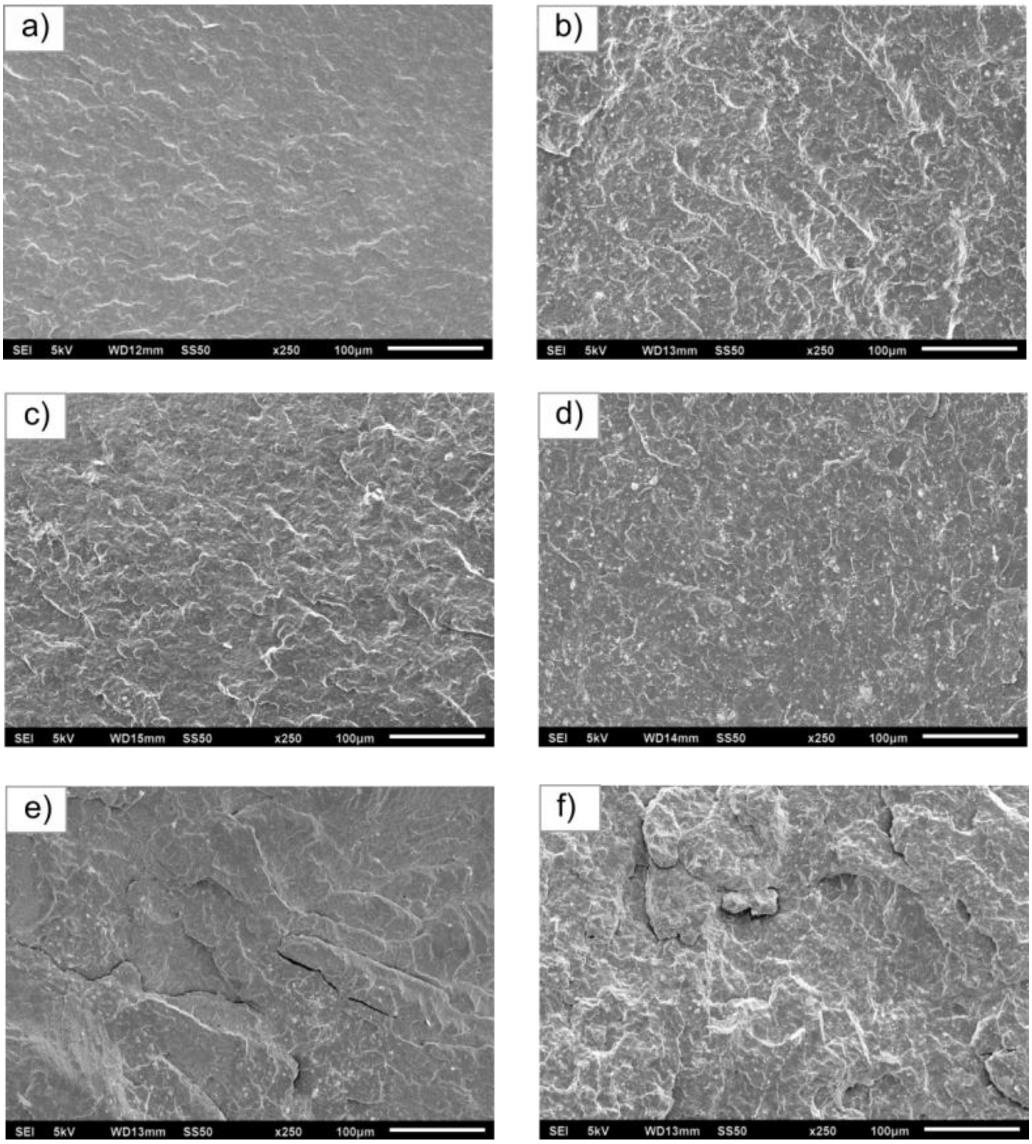

Figure 4.16 SEM images of: a) R; b) RWP-LP-A (80 vol% RWP); c) RA25; d) RA75; e) R with 25 vol% RWP; f) R with 75 vol% RWP

4.3 CONCLUSIONS

The vulcanisation of new substitute composites containing various types of activated particles results in cured materials with various cure characteristics and mechanical properties. Moreover, it was shown that the advantages of using RWP-LP instead of non-activated RWP are a reduced viscosity, an excellent homogeneity and a good morphology of the samples. The diene and ethylene content of the LP used for activation proved to play an important role with respect to the compression set values of the samples. The compression set was strongly influenced by the ethylene content at -10 ºC and 23 ºC and by the ENB percentage at -10 ºC, 23 ºC and 70 ºC.

The crosslinking density determined by equilibrium swelling measurements and TSSR tests shows the same tendency for all samples, namely a slow decrease with increase of the RWP-LP content. The SEM images reveal a good compatibility and homogeneity of all samples in comparison with the reference compound (R), even when a high amount of RWP-LP was used. It can be concluded that the obtained new compounds are suitable for the production of high quality products, such as elastomeric seals according to ISO 7619-1:2010 standards. In order to fulfil the above mentioned standard, the particles activated with the liquid polymers containing a lower ethylene content (LP-A and LP-B) are the most adequate to be used for the production of sealing systems. By using these types of polymers it was possible to substitute the raw material with RWP-LP up to 50 vol% with very promising results. On the contrary, for the samples where the LPs have a higher content of ethylene, the substitution of the raw material was possible only up to 25 vol%. This was due to the poor compression set values obtained.

The present study provides an important framework for rational recycling methods designed to produce raw material substitutes from recycled elastomers, aiming to contribute to an economic and environmental sustainability by minimizing the disposal costs and conserving the resources.

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Chapter 5

The effect of the curing system type on the processability and properties of EPDM rubber recycled compounds

> *”Whilst it has been long been appreciated, albeit intuitively, that sulphur vulcanisation is a very complex chemical process, the actual complexity (......) is probably far in excess of what has been envisaged.”*
>
> Leslie Clifford Bateman [1] (1915-2005)

This chapter evaluates the influence of the curing system type on various rubber compounds with varying amounts of activated particles. Considering that the mercapto and benzothiazole sulfenamides class is the most widely used accelerator in the sulphur vulcanisation of EPDM, its influence on the cure characteristics, mechanical properties and crosslinking density was investigated. The sulfenamide type accelerator was found to be more convenient in terms of the processability of the material. The mechanical properties and the crosslinking density of the compounds have proven to be less influenced by the accelerator type. However, the mercapto accelerator revealed lower values of compression set in comparison with the sulfenamide type. The ratio of activated particles shows the same tendency for both types of materials. Both types of activated particles can substitute up to 50 vol% of the raw material with moderate losses of properties.

Parts of the research described in this chapter have been presented as a poster presentation at the 11th Fall Rubber Colloquium, KHK, 26th-28th November 2014, Hannover, Germany.

5.1 INTRODUCTION

In this chapter the emphasis is put on the accelerated sulphur vulcanisation in the presence of two different organic accelerators. Sulphur vulcanisation can only be applied to rubbers containing unsaturation, either in the backbone, e.g. NR, BR, SBR and IIR, or in the side chain, e.g. EPDM. The vulcanisation using sulphur alone, also known as un-accelerated vulcanisation, is very slow and gives products with poor properties. Nowadays, the vulcanisation with high amounts of sulphur is used to obtain ebonite. For an efficient vulcanisation, chemical activators and accelerators are needed. The commonly accepted mechanism for accelerated sulphur vulcanisation of EPDM is presented in Figure 5.1. Initially, the active sulphurating species, formed by the reaction of accelerator(s) and activators (ZnO and stearic acid) with sulphur, react with the polymer chains via a sulphur bridge, yielding alkenyl sulphides.[2] Subsequently, the initial sulphur crosslinks are formed.

The residual double bond of the ENB in the side chain is used to activate the allylic positions, but it is not consumed during sulphur vulcanisation. It was shown that accelerated sulphur vulcanisation of ENB takes place at allylic C atoms respectively at C-3exo, C-3endo and C9.[2-4] At increased temperatures desulphuration occurs, yielding shorter sulphur bridges.[5,6] It was found that when heated for extended periods of time at elevated temperatures the formation of carbonyls occurs due to the oxidation, and thiophene-like compounds are formed due to the reversion of the material.[3]

The accelerator system is decisive for the needed scorch safety and cure time, as well as for the other properties. The efficiency of the first delayed action accelerators was discovered in the early 1900s with the introduction and the development of mercapto accelerators.[7-9] Later on, in 1934, Zaucker and Bögemann[10] introduced the first commercial benzothiazolesulfenamide accelerators presenting a better delayed action and fast curing in comparison with the mercapto class. Discovered by Harman in 1937[11], CBS is one of the most widely used accelerators of the sulfenamide type, representing a derivative of 2-mercaptobenzothiazoles obtained by bounding an amine to the mercapto sulphur.

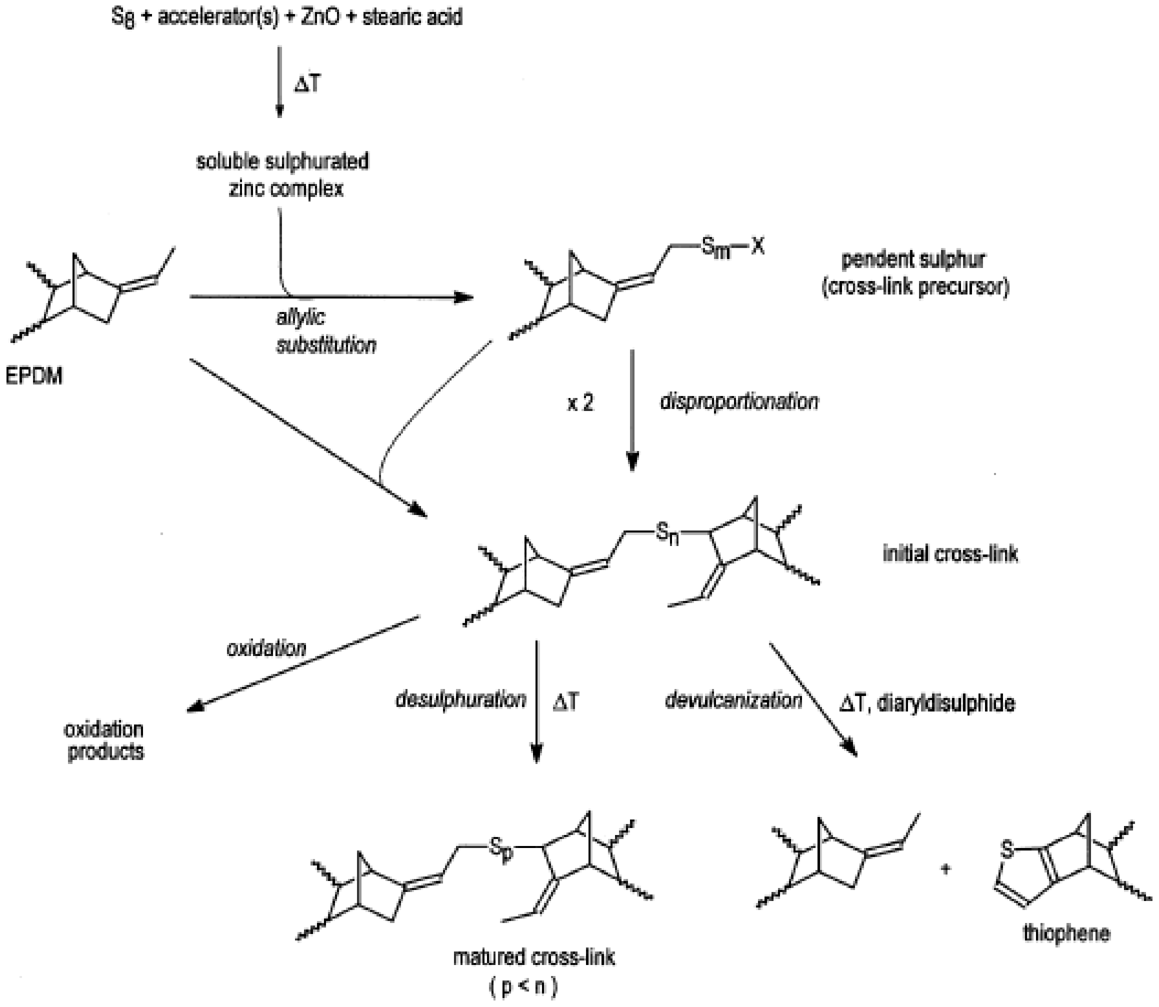


Figure 5.1 Reaction mechanism and products of accelerated sulphur vulcanisation of EPDM (X-accelerator residue)[2]

Both accelerators belong to the thiazoles class and are classified as primary accelerators, being the most used accelerators in terms of economic profitability and vulcanisate properties. A comparison of the most important accelerator types is shown in Figure 5.2, where the cure rate after scorch is plotted against scorch resistance.

The accelerators were also chosen because of ecological aspects, none of them shows the possibility to form carcinogenic N-nitrosamines by-products. Although the chemical structures of the two accelerators are different, it can be emphasized that both of them include a common functionality, respectively N=C–S. Due to the fact that the rest of the curing system contained by the RWP is not completely known, in the new formulation systems only one type of accelerator was used. Therefore, a comparative study between two different types of accelerators is investigated in this chapter: 2-mercaptobenzothiazole (MBT) and N-cyclohexyl-2-bezothiazole sulfenamide (CBS).

In order to obtain final composites with competitive costs and an optimum performance the selection of a proper formulation and an adequate mixing are requested.

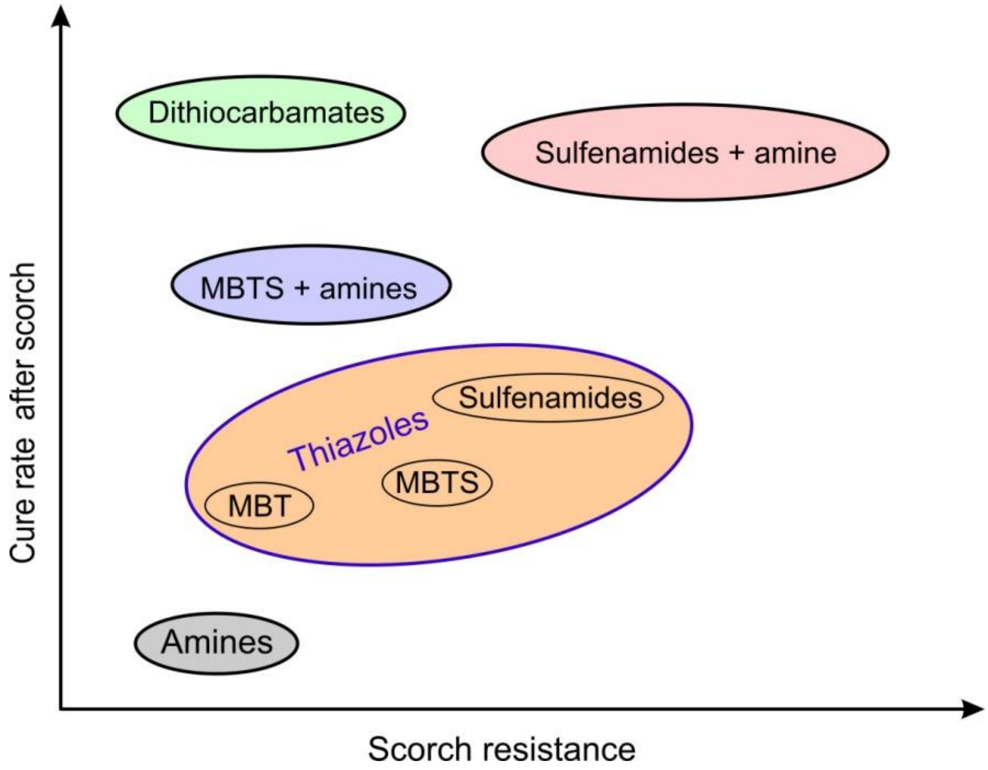


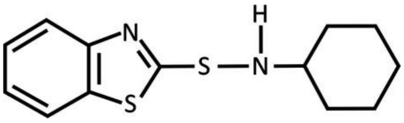
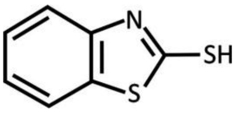
Figure 5.2 Comparison of various accelerators systems with regard to vulcanisation characteristics [12]

5.2 EXPERIMENTAL

5.2.1. Materials and compound recipes

The two types of accelerators used for the compounds vulcanisation were supplied from Avokal GmbH, Germany. Compound names and the chemical structures of the accelerators are given in Table 5.1.

Table 5.1 Compound names and chemical structures of the accelerators used in sulphur vulcanisation

Compound name	**Abbreviation**	**Chemical structure**
N-cyclohexyl-2-bezothiazole sulfenamide	CBS	
2-mercaptobenzothiazoles	MBT	

The composition of the reference compounds and activated particles are presented in Table 5.2. The composition of the samples where CBS was used as accelerator and the materials used in the present investigation are described in detail in Chapter 4. The type of liquid polymer used is Trilene® 67 (LP-A).

Table 5.2 Composition of the reference compounds and activated particles

Ingredients	**R1**[a]	**R2**[b]	**RWP-LPA1**[a]	**RWP-LPA2**[b]
		Amount (phr)		
Keltan 9650Q	100	100		
Carbon black N550	120	120		
LP-A			100	100
RWP			560	560
Paraffinic oil	100	100		
ZnO	4	4	2	2
Stearic acid	2	2	1	1
MBT		3		3
CBS	3		3	
Sulphur	1.5	1.5	1.2	1.2

[a]R1, RWP-LPA1 - samples with CBS; [b]R2, RWP-LPA2 - samples with MBT

5.2.2. Mixing and Vulcanisation

Mixing and vulcanisation of the samples were performed as described in Chapter 4.

5.2.3. Characterisation of the vulcanised samples

The hardness, tensile strength and elongation at break tests were performed in accordance with ISO Standards as described in Chapter 4.

5.2.4. Compression set tests

The compression set tests were performed at various temperature and time conditions, in accordance with ISO 815-/-2:2014, as described in Chapter 4.

5.2.5. Crosslinking density

The apparent crosslinking density of the vulcanised samples was determined by swelling and TSSR measurements as described in Chapter 3. Table 5.3 summarises the values obtained from swelling measurements for the investigated samples.

Table 5.3 Values obtained from swelling measurements for the investigated samples

Samples	**m_0 [g]**	**m [g]**	**m_d [g]**	**V_r**
R1	0.3175	0.5371	0.2244	0.33347
R1-25	0.4254	0.7796	0.3106	0.31467
R1-50	0.4028	0.7978	0.2990	0.29364
R1-75	0.3719	0.7807	0.2776	0.27635
R2	0.4290	0.7183	0.2978	0.33091
R2-25	0.4522	0.8187	0.3224	0.31103
R2-50	0.5271	1.0215	0.3888	0.29821
R2-75	0.4990	1.0400	0.3700	0.27658

5.3 RESULTS AND DISCUSSION

In order to study the effect of the accelerator type, eight different formulations were prepared according to the protocol described in Section 5.2. In the present study two different reference samples were used as presented in Table 5.2. One reference recipe was vulcanised using as accelerator CBS (R1), and for the other one MBT (R2) was used. Raw material from the reference samples was substituted with 25, 50 and 75 vol% RWP-LP. The accelerator type used in the RWP-LP formulation (Table 5.2) is identical to the one used in the reference sample. The reference samples R1 (CBS) and R2 (MBT), and the substituted compounds vulcanised with CBS (RA1-25, RA1-50, and RA1-75) and MBT (RA2-25, RA2-50, and RA2-75) were compared in terms of cure characteristics, mechanical properties and crosslinking density. The liquid polymer used was Trilene® 67 (LP-A). The compounds containing CBS are the same as in Chapter 4 and they are used just for comparison.

First, the influence of the accelerator type on the curing behaviour of the reference rubber compounds as well as of the compounds where the raw material was substituted by the RWP-LP was evaluated on the basis of their curing characteristics, e.g. the minimum torque M_L, the maximum torque M_H, scorch time t_{s2} and cure time t_{90}. Based on the obtained values, the cure rate index (CRI) was calculated. [13] The values were determined from the corresponding vulcanisations curves measured at 180 °C, as presented in Figure 5.3. As already indicated in Chapter 4, Figure 5.3 clearly shows that the maximum torque of the samples decreases as the amount of activated particles increases. However, the samples with MBT present inferior values in comparison with the samples where CBS was used. In addition, samples where MBT was used as accelerator show a marching behaviour.

Nevertheless, as the amount of activated particles increases this marching behaviour is almost totally diminished, as shown in Figure 5.3 (RA2-50 and RA2-75). A marching modulus occurs when the stiffness of the rubber compound continues to increase during cure. [14] Conversely to reversion, where the break-down of rubber networks occurs, the marching modulus may be a result of additional cross-links induced by a reaction of the vulcanisation agent. [15]

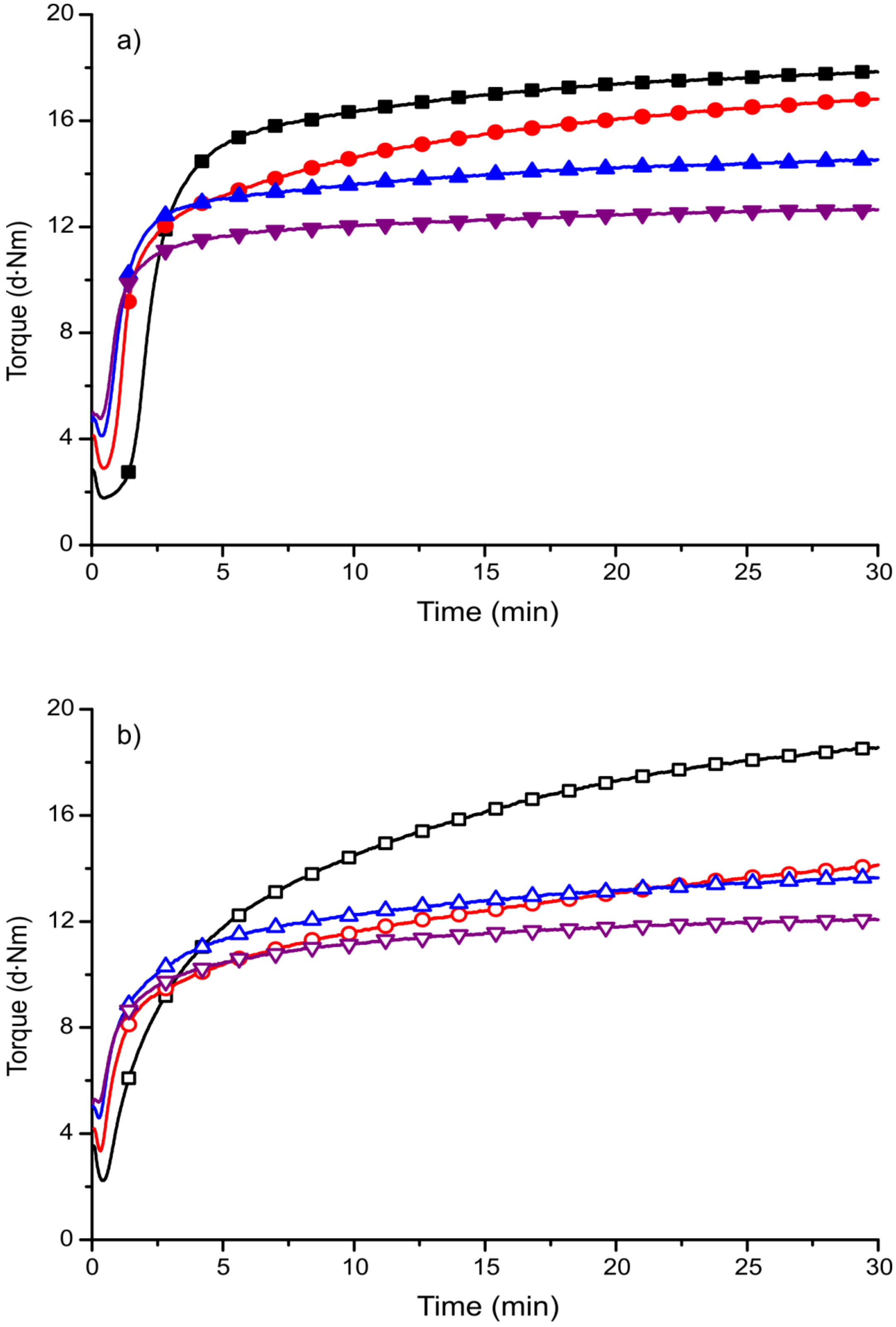


Figure 5.3 Vulcanisation curves of the EPDM compounds vulcanised with: a) CBS: R1(—■—); RA1-25(—●—); RA1-50(—▲—); RA1-75(—▼—) and b) MBT: R2(—□—); RA2-25(—○—); RA2-50(—△—); RA2-75(—▽—)

Figure 5.4 shows clearly that the M_L increases gradually as the loading of RWP-LP in rubber compounds increases and that it presents lower values for the compounds where the CBS accelerator was used. Since the minimum torque is related to the viscosity of the vulcanisate [16] and has an influence upon the processability of the composite, e.g. extrudability, the obtained results indicate that the use of CBS as accelerator in rubber compounds offers the possibility of obtaining composites with lower viscosity in comparison with those where MBT was used, thus improving the processability.

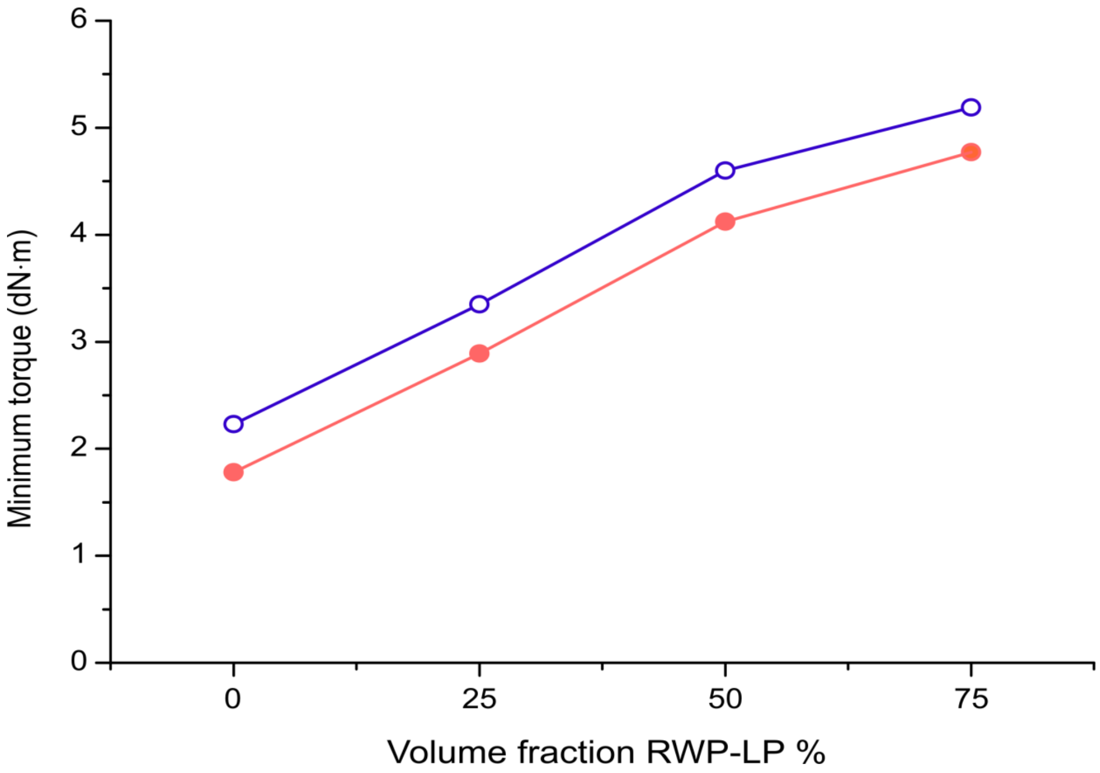


Figure 5.4 The influence of the curing system type on minimum torque values of rubber compounds with CBS (—●—) and MBT (—○—)

The values of maximum torque of all compounds are presented in Figure 5.5. For the reference compounds slightly higher values were obtained when MBT was used compared to the sample for which CBS was used. Nevertheless, the more raw material is substituted with RWP-LP, the higher are the values obtained for the compounds where CBS was used.

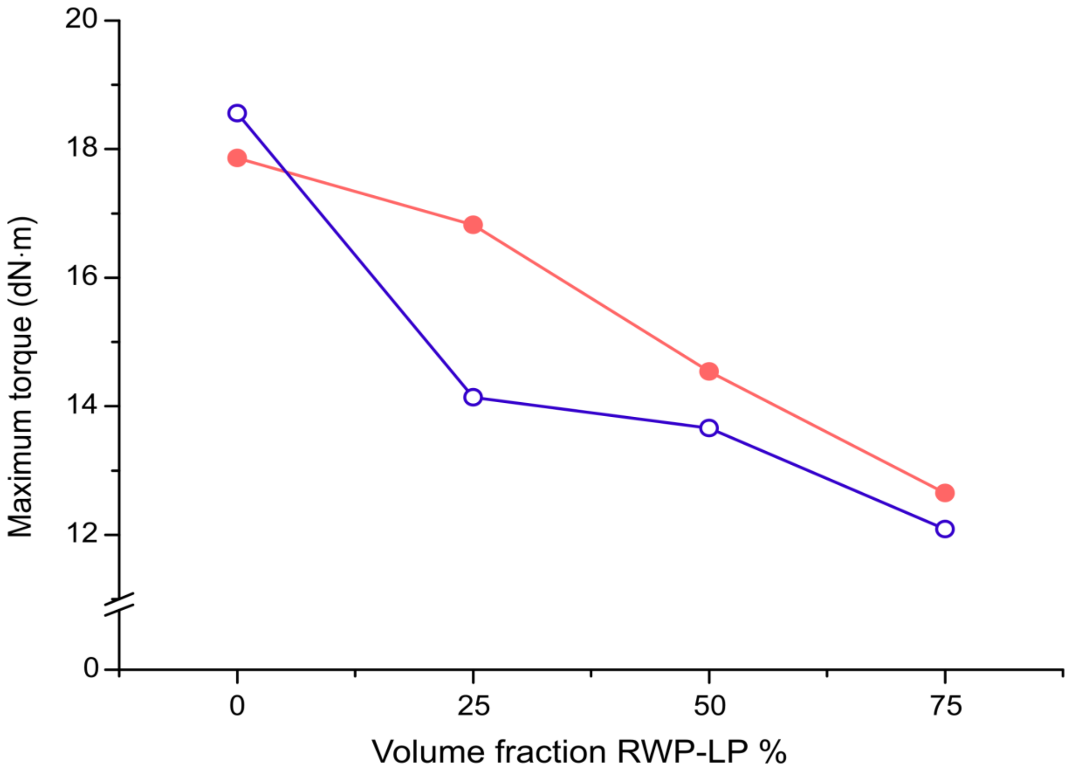


Figure 5.5 Influence of the curing system type on maximum torque values of rubber compounds with CBS (—●—) and MBT (—○—)

The decrease of maximum torque, which is generally correlated with the stiffness and the crosslinking density of the compounds, [16] is attributed to the filler content present in the composites. The data obtained from TGA measurements (see Chapter 4) shows that the carbon black content decreases with increase of the RWP-LP content, ergo having an influence on these values.

The scorch time helps to determine the process safety of the compounds. For controlling this parameter the accelerator type is much more important than the level. The results have clearly shown that the compounds where CBS was used as accelerator present better scorch time values in comparison with those where MBT was employed as shown in Figure 5.6. In comparison with the reference compounds the scorch time is reduced with the addition of RWP-LP.

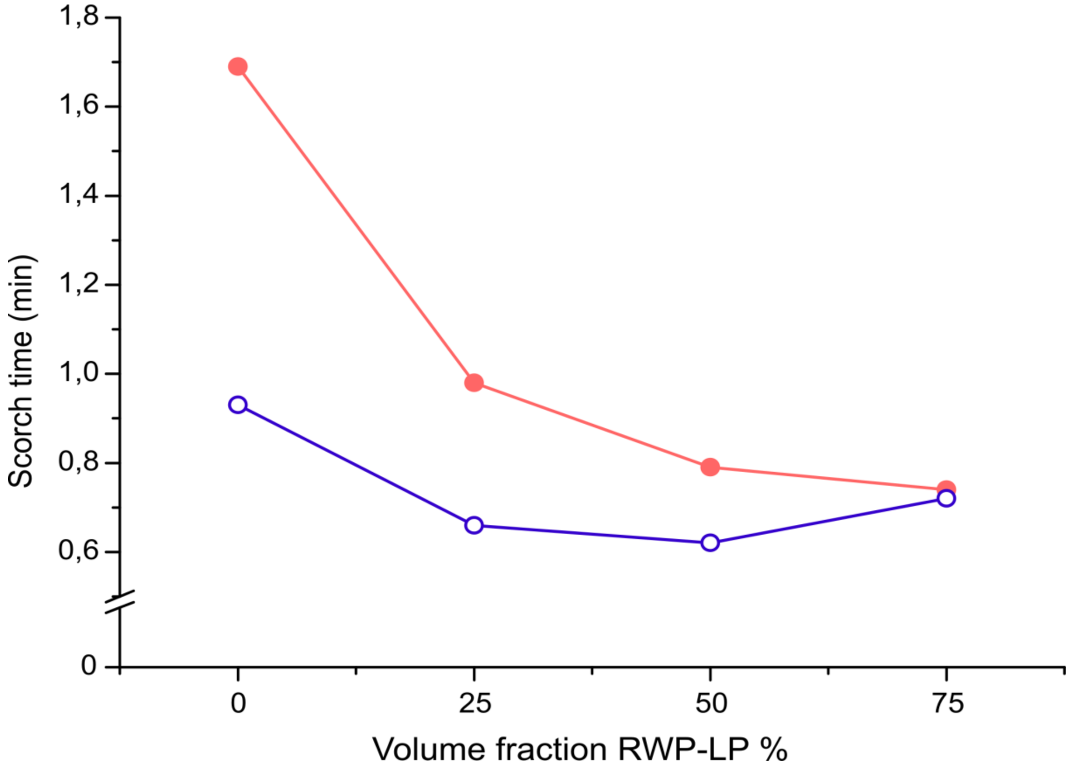


Figure 5.6 Influence of the curing system type on scorch time values of rubber compounds with CBS (—●—) and MBT (—○—)

The cure time values are presented in Figure 5.7. The cure time is considered in most cases the optimum cure time and represents the time required for the torque to reach 90% of the maximum achievable torque, M_H. The optimum cure time is very important and is defined as the time necessary for the cured rubber to attain optimal properties.[15] When using 25 vol% of the RWP-LP to substitute the raw material an increase of the cure time is observed for both samples compared to the reference compounds. However, when increasing the content of the RWP-LP with more than 25 vol% the cure time of the compounds decreases. In other words, by increasing the amount of activated particles in the compounds the cure times are improved. By calculating the CRI,[17] which is a measure of cure reaction,[18] it was determined that the CBS samples show higher CRI values in comparison with samples where MBT was used (Figure 5.8), therefore shorter cure times. These results indicate that both the type of accelerator and the incorporation of RWP-LP in the studied compounds lead to a shortening of the scorch time and to an acceleration of the curing process. This behaviour has been observed in other studies as well, and the results are in good agreement with the literature. [13,19,20]

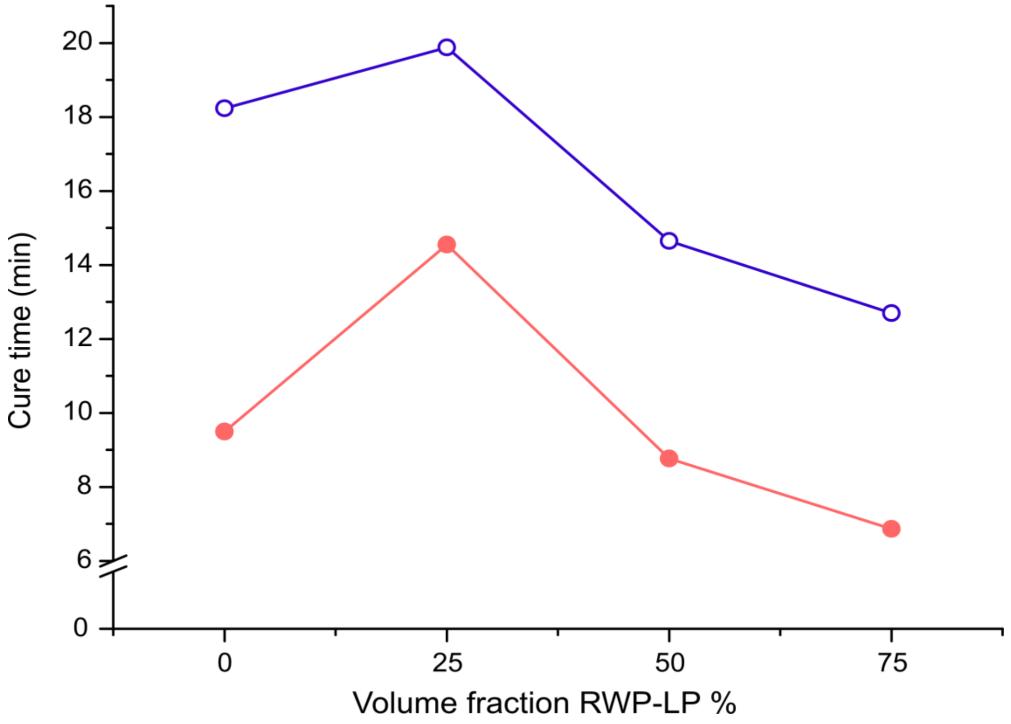


Figure 5.7 Influence of the curing system type on cure time values of rubber compounds with CBS (—●—) and MBT (—○—)

The stress-strain properties of the reference samples and of the raw material substitute compounds are shown in Figure 5.9 and the influence of the curing system type on the mechanical properties of the reference and the substitute material compounds are depicted in Table 5.4.

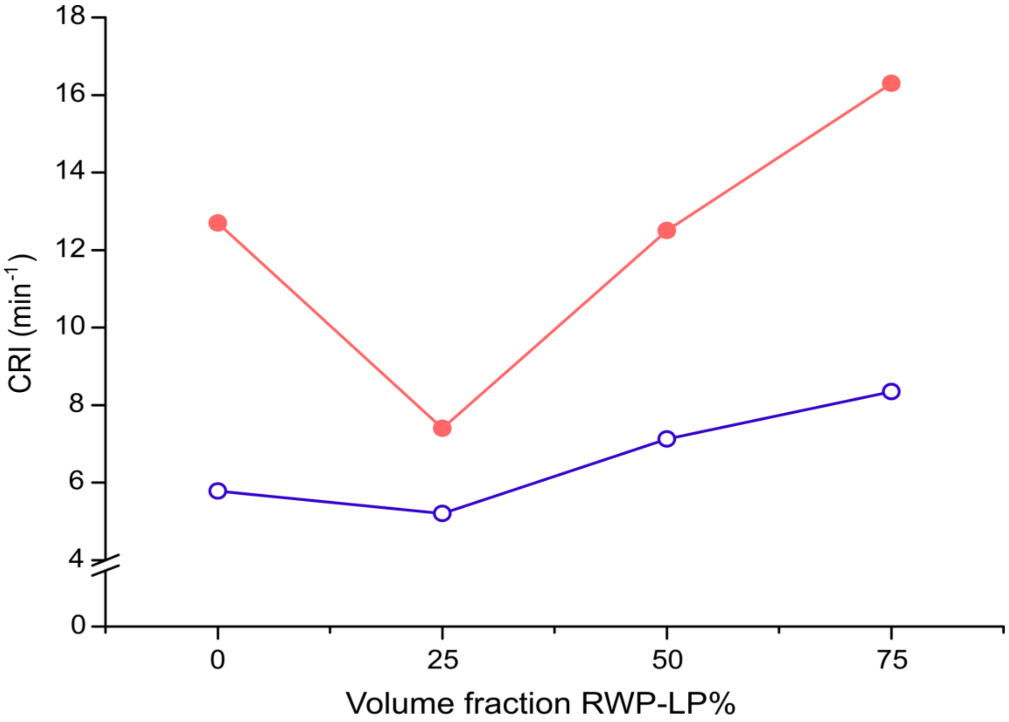


Figure 5.8 Influence of the curing system type on CRI values of rubber compounds with CBS (–●–) and MBT (–○–)

Hardness decreases with increasing the RWP-LP content in rubber compounds and shows very minor differences between the CBS and MBT samples. This decrease was expected considering that the carbon black content decreases as the RWP-LP content increases.

The tensile strength of the composites follows the same trend. Without activated particles in the composition the MBT sample presents higher values. When substituting the raw material up to 50 vol% it can be observed that the tensile strength for the MBT samples decreased with about 1 MPa, while the CBS samples present tensile strength values greater than those of the reference sample. By using 75 vol % of activated particles in the recycled composites, a reduction of tensile strength with about 2-2.5 MPa was observed for both types of samples.

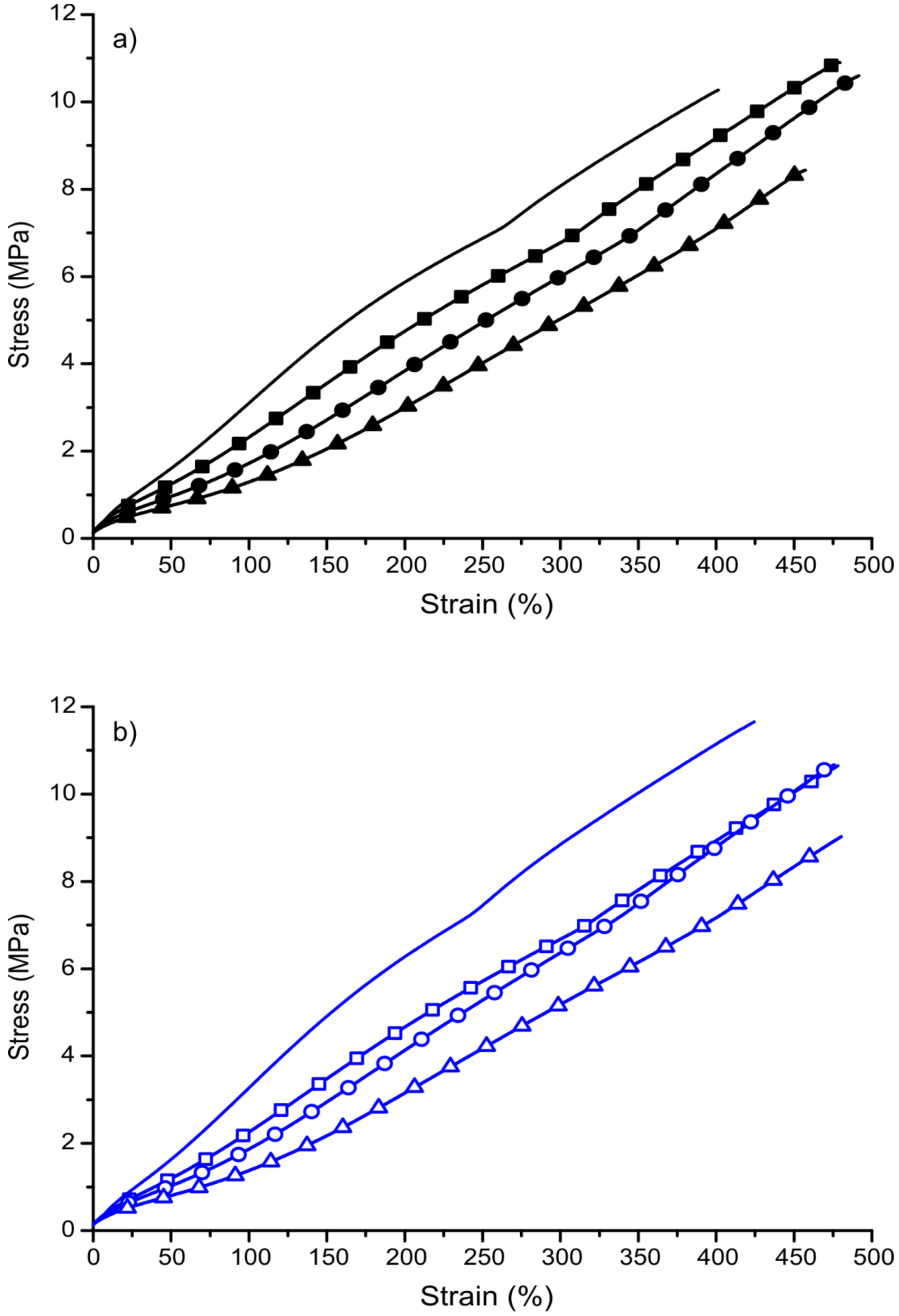


Figure 5.9 Stress-strain curves of the EPDM compounds vulcanised with:
a) CBS: R1(——); RA1-25(–■–); RA1-50(–●–); RA1-75(–▲–) and
b) MBT: R2(——); RA2-25(–□–); RA2-50(–○–); RA2-75(–△–)

Table 5.4 Mechanical properties of the samples

Samples	Hardness (Shore A)	Tensile strength (MPa)	Elongation at break (%)	Compression set at 23 ºC (%)	Compression set at -10 ºC (%)	Compression set at 70 ºC (%)
R1	60	10.3	413	11.4	23.6	8.3
RA1-25	53	10.7	460	10.1	23.0	9.4
RA1-50	48	10.5	492	10.6	29.8	11.5
RA1-75	42	8.5	458	10.6	30.6	15.0
R2	59	11.4	429	7.0	12.9	10.9
RA2-25	53	10.6	478	6.3	15.9	12.9
RA2-50	49	10.5	476	6.1	20.9	10.7
RA2-75	43	9.0	479	6.6	24.0	13.2

On the other hand, the elongation at break exhibits a significant increase for both types of samples when increasing the activated particles amount in the composites. The same behaviour was previously also observed by Choi [21] in a study regarding the influence of liquid polybutadiene on properties of SBR rubber compounds.

Compression set values of the reference and of the raw substitute compounds present differences between the two types of samples for all three test temperatures as listed in Table 5.4. At 23 ºC both the CBS and the MBT samples present an improvement of the compression set when increasing the amount of activated particles in the composition. Here, the MBT samples present lower values in comparison with the CBS samples. At -10 ºC and 70 ºC an increase of the compression set values is observed in both types of samples, with higher values for the CBS samples.

The accelerated sulphur vulcanisation chemistry of rubber is a very complex process since several chemical reactions start simultaneously unfolding at their own speed at the selected cure temperature. Throughout the years, several studies have been carried out in order to understand the reaction mechanisms and to describe the kinetics in rubber vulcanisation with sulphur in the presence of various accelerators and activators. [22-24]

In the present study, CBS and MBT have been selected for the vulcanisation of EPDM rubber compounds. It is well known that these types of accelerators provide the considerable scorch safety required for material processing and medium fast cure. [25] Taking into consideration that the residues of curing system embedded in the waste rubber particles are unknown, with the exception of CBS, that was detected by NMR studies (see Chapter 3), the formulation of the new recipes is kept simple by using only one type of accelerator.

When analysing the obtained data it can be emphasized that the CBS accelerator presents better cure characteristics in comparison with MBT. These results are not surprising taking into consideration that the CBS accelerator is a fast-delay action accelerator in comparison with MBT, which is a semi-ultrafast accelerator. It is a well known fact that a sulfenamide accelerator such as CBS presents a better scorch safety and thus a better processing safety in comparison with the thiazole class, represented by MBT here. These results become clear if we compare the reaction mechanisms of CBS (Figure 5.10) and MBT (Figure 5.11) during the vulcanisation process. As shown in Figure 5.10, during vulcanisation the CBS thermally decomposes in the presence of sulphur into MBT and cyclohexylamine. The formed MBT reacts with another molecule of CBS to form MBTS (2,2'-dithiobenzothiazole) and the amine.

These two reactions provide the scorch delay for the sulphenamide accelerator type. The produced amine acts as a strong secondary accelerator for the MBT and thereby the curing proceeds very fast after the delayed start. [26] First, a soluble sulphurated Zn complex is formed (ZnMBTS), which reacts in the next step with sulphur. Further on, the active sulphurating agent reacts with rubber molecules to form crosslink precursors and subsequently the initial sulphur crosslinks are formed, e.g. EPDM vulcanisation as shown in Figure 5.1. [2]

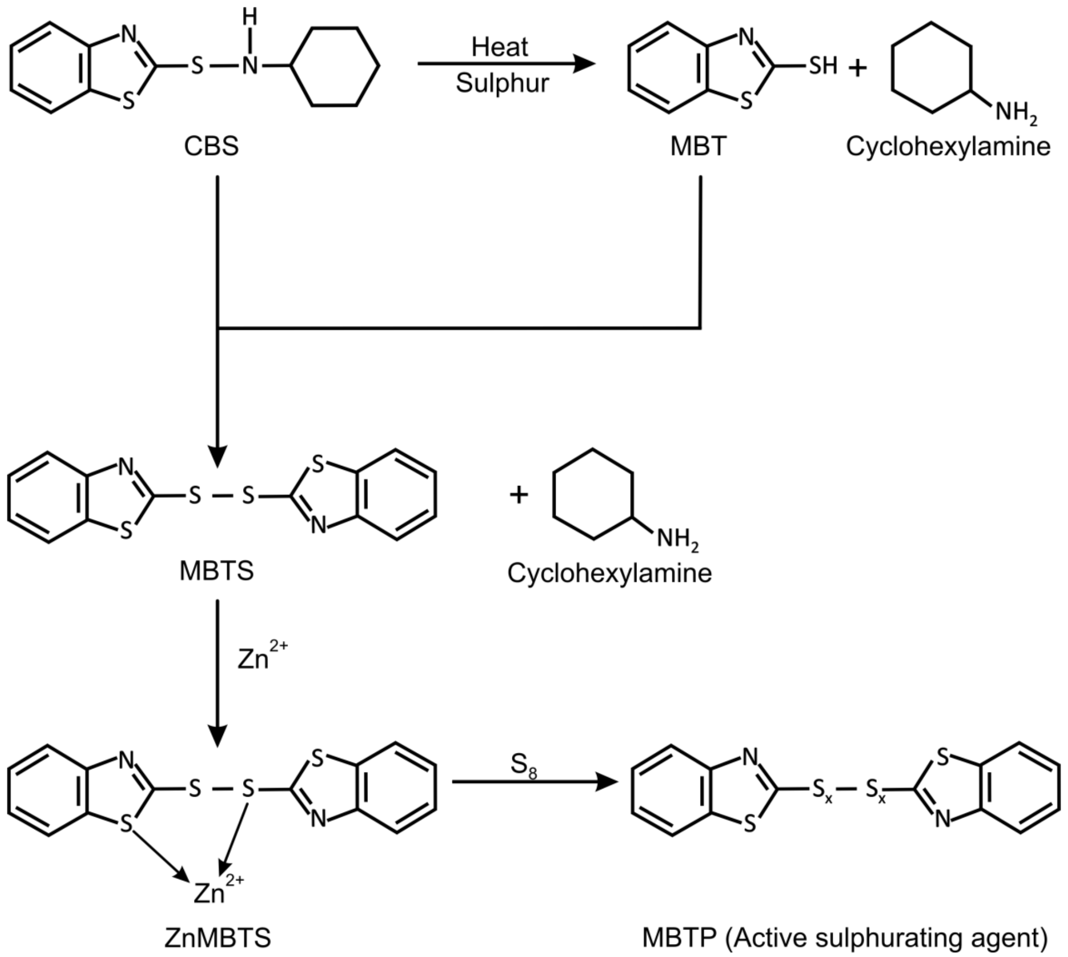


Figure 5.10 The reaction mechanism of CBS during the scorch delay region with formation of active sulphurating agents

In the case of MBT, various studies have revealed that upon heating ZnO readily forms zinc-complexes with MBT, as shown in Figure 5.11. [22,27] It was found that although the reaction of MBT with zinc oxide readily occurs it does not proceed to completion. [28]

As previously mentioned, the results obtained in the present study are in good agreement with the studies regarding the reaction mechanisms of CBS and MBT. The sulfenamide accelerator gives a longer scorch resistance and thus a greater processing safety and higher vulcanisation speeds, which reduces the consumption of energy and the costs in comparison with the mercapto type.

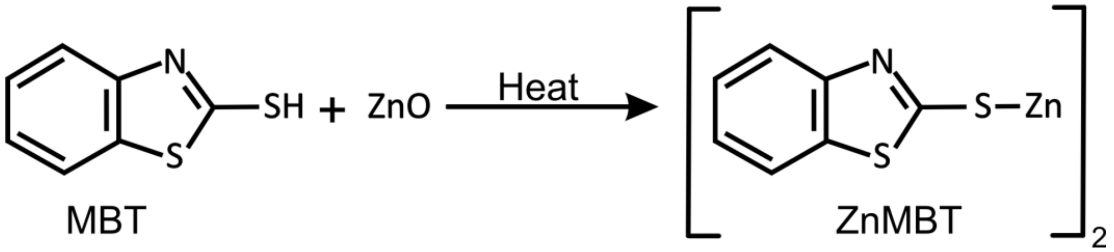


Figure 5.11 Reaction of MBT with ZnO during the scorch delay region

The scorch delay of sulfenamide type accelerators varies according to the thermal stability which is given based on the nature of the nitrogen substituents as shown in Figure 5.12. The highest process safety is given by CBS, followed by TBBS, MBS and DCBS.

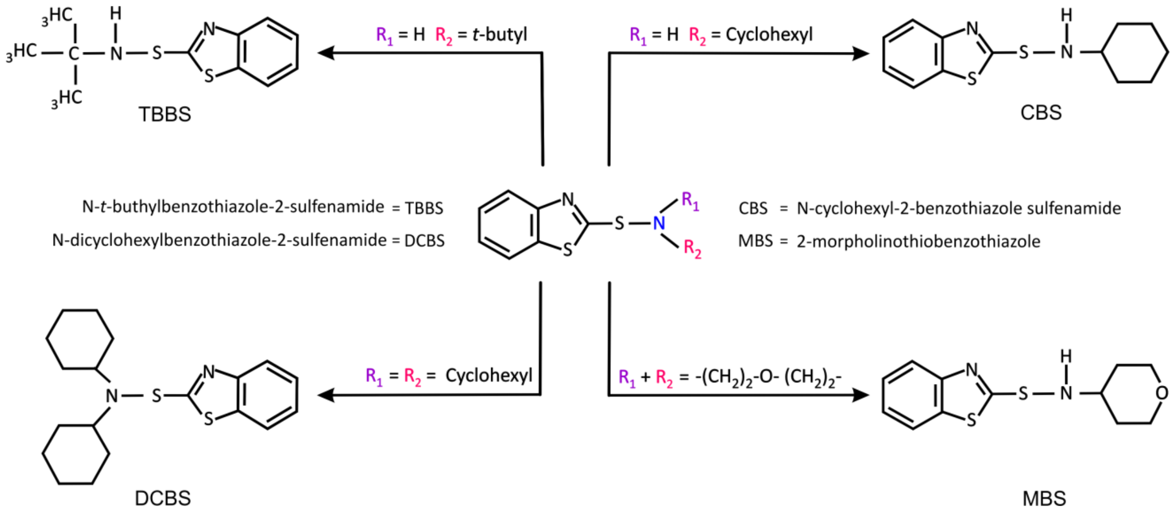


Figure 5.12 Chemical structure of sulfenamide accelerators with various possible substituents

A preliminary conclusion of this chapter would be that the accelerator chemistry which takes place in the induction region (see Chapter 3, Figure 3.6) is very intricate and very difficult to monitor. In order to get a better insight into the interactions between curatives various studies have been carried out. [28-34] In order to investigate these interactions various techniques such as differential scanning calorimetry (DSC), high-performance liquid chromatography (HPLC) and NMR have been applied.

DSC was used to study the curative interactions in systems without rubber where no,[29] respectively only one type of accelerator[32-35] has been used in combination with activators and sulphur. A combination of DCS, HPLC and NMR has been used for very simple systems, e.g. polyisoprene/accelerator/S/ZnO. In these systems stearic acid has not been used.[27,30,31,36]

However, these investigations could be carried out for very simple systems, where each step could be verified. In our study the system is very complex considering that while the raw rubber and the RWP-LP formulations are known, the residues contained by the waste particles are unknown. In this situation a detailed examination is not achievable due to the intricate nature of the system.

A comparison of the two different types of accelerators is very important for the last part of the present study and also for the application of the process on an industrial scale. For the technique applied on an industrial scale, e.g. an injection molding process, the induction period should be long enough to allow for the material to be molded and to provide the fast curing rate in the main vulcanisation stage.

The apparent crosslinking density determined by swelling measurements and TSSR tests is presented in Figure 5.13. As already illustrated in Chapter 4, for the compounds containing CBS, which have been used in the present study only in order to be compared with MBT compounds, a decrease in crosslinking density is observed when increasing the content of activated particles. The values obtained for both types of samples are very close and follow the same trend. A steeper decrease in crosslinking density is observed both for the CBS and for the MBT samples when the values are determined using the swelling measurements method.

When the TSSR method was used to calculate the crosslinking density of the samples, the slope of the curve is smaller, showing not such a high difference between samples upon increasing the RWP-LP content. The values obtained via these two methods are not identical, but the results are in good agreement by showing a similar trend.

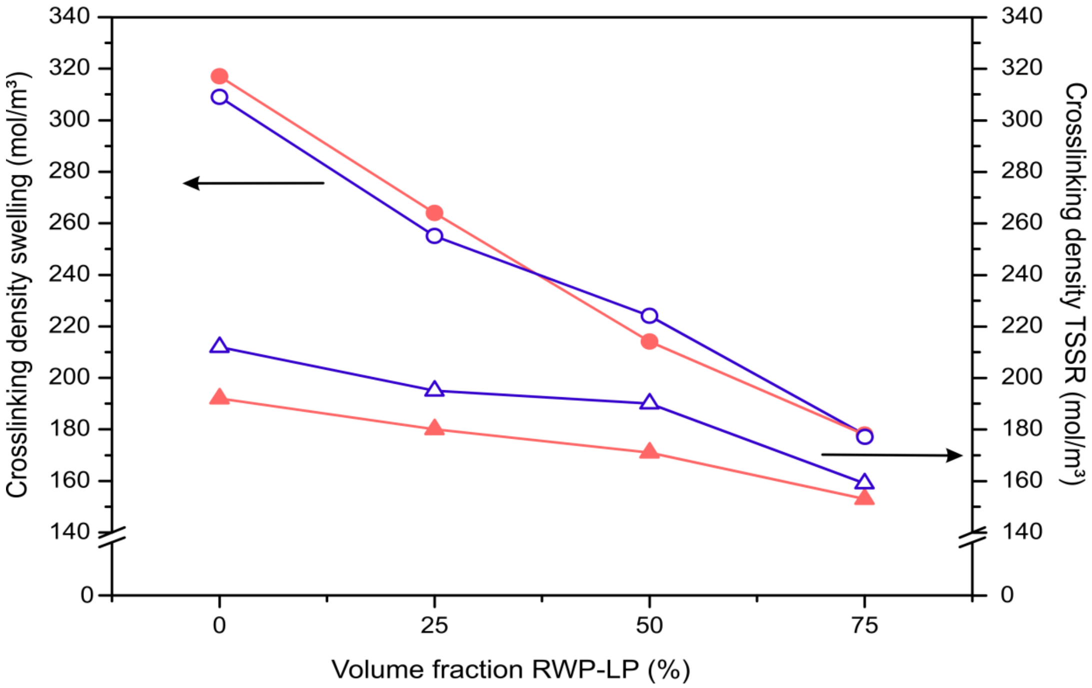


Figure 5.13 Influence of the curing system on the crosslinking density of the EPDM compounds vulcanised with CBS (full symbols) and MBR (empty symbols) determined by swelling (circle) and TSSR (triangle)

5.4 CONCLUSIONS

In the present chapter two types of accelerators have been examined and evaluated for the vulcanisation of new substitute composites with various amounts of activated particles.

The results show that the type of accelerator used in recycled EPDM compounds has an influence upon processability, mechanical properties and crosslinking density of the final composites. The use of CBS as accelerator in the formulation of the new composites revealed that the safe processing of the new compounds can be improved by obtaining a longer scorch safety and faster cure times. In other words, the process reliability is improved and a reduction of energy consumption is achieved. While the minimum torque increases and the maximum torque of both types of compounds slightly decreases when substituting the raw material with activated particles, the CBS samples present better values than the MBT samples.

Hardness, tensile strength and elongation at break show a slight difference between the two systems, while the compression set presents higher values for the CBS samples. From the obtained results it can be concluded that both CBS and MBT can be used as an accelerator system for the recycling of EPDM, since in both cases the substitution of the raw material is possible up to 50 vol%. However, the utilization of CBS is more desirable considering the safety processing of the recycled compounds.

To sum up this chapter, it can be concluded that rubber materials substituted with activated particles and crosslinked with various types of curing systems can give compounds with good properties comparable to or sometimes even superior to those of the reference samples. This suggests that raw material substitute compounds may be of importance in certain applications such as seals and sealing systems.

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Chapter 6

Application of activated EPDM particles on an industrial scale for the production of seals and sealing systems

“A fact is a simple statement that everyone believes. It is innocent, unless found guilty. A hypothesis is a novel suggestion that no one wants to believe. It is guilty, until found effective.”

Edward Teller (1908 – 2003)

The final aim of the present thesis was the application of the developed recycling process from the laboratory scale to an industrial production scale. Therefore, the application study of the activated EPDM particles was performed on an industrial scale for the production of seals and sealing systems.

A semi-continuous process was used for the mixing and the production of the recycled material. First, the rubber waste particles were activated with the liquid polymer in a high speed mixer. Secondly, the activated particles were mixed with the raw materials in a Co-Kneader. The activated EPDM rubber waste particles were blended with raw EPDM at a ratio of 25/75 and 50/50. Thirdly, the extruded profiles were vulcanised into sealing profiles using the injection moulding technique.

The cure behaviour, mechanical properties, crosslinking density and ageing properties were compared with the original properties of a sealing product. The morphology pictures showed a good distribution of the particles in the rubber matrix. As expected, a slight decrease in mechanical properties occured with the substitution of the raw material by the RWP-LP, compared with an original product, a decrease which is though in the standard limits and which can be corrected by adjusting the compound recipe.

6.1 INTRODUCTION

Various methods of rubber recycling were studied over the past decades as presented in Chapter 2. [1] However, the recycling of EPDM rubber waste particles by chemical activation was investigated in less depth. Because of their low crosslinking density on the surface, rubber waste particles can replace the raw material in small amounts only (max. 10 up to 15%) without affecting the quality of the product or can be used in low quality rubber products. However, in the previous chapters it was shown that by using activated particles the potential of substituting the raw material is substantially increased. The activated particles can substitute the raw material from 25 vol% to 75 vol%, preferably up to 50 vol% in order to maintain a high quality of the recycled products.

In this chapter, the application of the recycled particles activated by a liquid polymer is investigated on an industrial scale. The experiments were performed at the company M.D.S. Meyer GmbH (Bakum, Germany) that produces sealing and fitting systems and from where the waste particles applied in the present project were supplied. The activation of the EPDM rubber waste particles was performed by mixing the particles with the liquid polymer in a high speed mixer for a short time. The compounding of the material was made by using a Co-Kneader. The type of Co-Kneader used for compounding was a low-shear rotating and reciprocating single-screw extruder designed for shear and temperature sensitive compounds and a high kneading efficiency. The flights on the screw are interrupted and interact with three rows of stationary kneading pins fixed on the barrel wall. The interaction between the moving flights and the stationary pins from the barrel wall provide dispersive and distributive mixing simultaneously. The material is finally extruded, water-cooled, automatically cut into stripes and packed. Afterwards, the co-extruded stripe profiles are vulcanised into sealing systems using injection moulding machines for various seal profiles. Two batch experiments were performed. In the first experiment, the raw material was substituted with 25 vol% by the activated particles and in the second experiment, 50 vol% of activated particles were used to substitute de raw material. The quality of the recycled products is evaluated and compared with reference products.

6.2 EXPERIMENTAL

6.2.1. Materials

The ground EPDM rubber waste used in this investigation was obtained from M.D.S. Meyer GmbH, Germany. The particles are based on EPDM rubber with a particle size between 300 and 750 µm. The raw EPDM type for the sealing systems used in the present investigation was Keltan 9650Q obtained from Lanxess, Germany. The polymer contains 53 wt% ethylene and 6.5 wt% ENB, and its Mooney viscosity ML (1+8) measured at 150 ºC is 60 MU. To achieve a good mixing the raw rubber is used in crumb form. The liquid polymer used is Trilene 67 with 45/55 ethylene/propylene content and 9.5% ENB.

PEG 4000 is a high molecular polyethylene glycol used in rubber compounds as a process aid. Polyethylene glycols can serve in the rubber industry as heat transfer agents, lubricants, mold release agents and rubber compounders, and they also have an influence on the vulcanisation rate, modulus of plasticity and scorch time. In this investigation, PEG 4000 is used as a plasticizer improving the lubrication of the extruded material, the friction and vulcanisation rate.

Zinc dibenzyldithiocarbamate (ZBEC) and tetramethylthiuram disulfide (TMTD) are used in the formulation recipe as secondary accelerators and were obtained from Avokal GmbH, Germany. ZBEC has the best scorch resistance among zinc dithiocarbamate accelerators and TMTD improves scorch resistance when used in combination with sulfenamide type accelerators. The other materials used in the formulation are described in Chapter 4.

6.2.2. Mixing and vulcanisation

The ground EPDM rubber waste particles were activated with the liquid polymer in a high speed mixer (model SHR-300 from Jiangsu Xinda Science & Technology Co., Ltd., China) for 6 minutes and at a temperature up to 65 ºC. Previously, the liquid polymer was heated up to 120 ºC in order to obtain a lower viscosity and to get a homogeneous activation of the particle surface.

Subsequently, the activated particles were used in a percentage of 25 vol% and 50 vol% as a substitute of the raw material in an EPDM recipe employed in the production of seals and sealing systems.

The compounding of the recycled material was performed on an industrial scale using a Co-Kneader of type SJW 200 (C) from Jiangsu Xinda Science & Technology Co., Ltd., China, with screw diameters of 200 mm. The configuration of the Co-Kneader is shown in Figure 6.1. Afterwards, the extruded profiles were vulcanised into sealing profiles using an injection molding machine. The samples were vulcanised using a temperature of vulcanisation between 190-200 ºC for about 120-150 sec. The obtained products were investigated and compared with reference products.

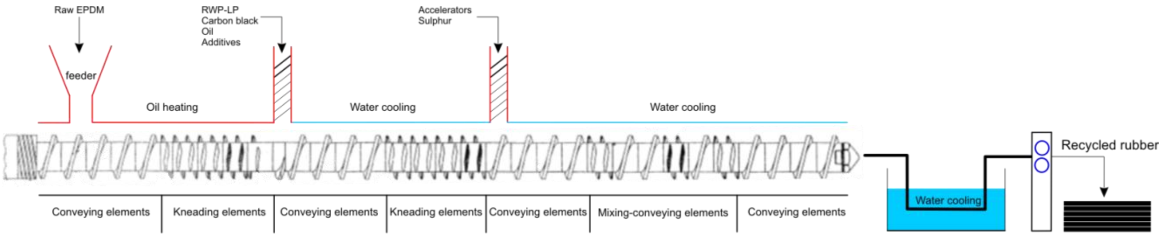

Figure 6.1 Co-Kneader screw configuration used for recycling of EPDM

The formulation of the recycled materials was adjusted according to the reference recipe used in production. The formulations of the original recipe and of the activated particles are presented in Table 6.1

Table 6.1 Formulation recipes of the samples

Ingredient	**Reference recipe**	**RWP-LP**
	Amount(phr)	
Keltan 9650Q	100	
LP		100
RWP		560
Carbon black N550	103	
Paraffinic oil	118	
ZnO	4	2
Stearic acid	2	1
CBS	2	3
S	1.2	1.2
PEG 4000	4	
ZBEC	0.4	
TMTD	0.3	

6.2.3. Mechanical properties

The hardness of the samples was measured using a Shore A Durometer according to ISO 7619-1. Tensile tests were performed according to ISO 37. Compression set tests were performed in accordance with ISO 815-1/-2. The description of these methods is given in Chapter 4.

6.2.4. Swelling studies

The degree of swelling was calculated in order to determine the crosslinking density of the samples. The swelling tests and the calculation of the crosslinking density were performed as described in Chapter 3. Table 6.2 presents the values of the samples before and after ageing, obtained from swelling measurements.

Table 6.2 Values obtained from swelling measurements for reference and recycled compounds before and after ageing

Samples	m_0 [g]	m [g]	m_d [g]	V_r
Reference compound	0,7414	1,3260	0,5253	0,30789
Compound with 25%RWP-LP	0,7650	1,3702	0,5213	0,29569
Compound with 50%RWP-LP	0,9080	1,7365	0,6356	0,28447
After ageing at 70 °C for 7 days				
Reference compound	0,7317	1,2242	0,5063	0,32143
Compound with 25%RWP-LP	0,5565	0,9812	0,3797	0,30076
Compound with 50%RWP-LP	0,6360	1,1774	0,4440	0,29308

6.2.5. Accelerated ageing and heat resistance tests

Accelerated ageing and heat resistance tests were performed in accordance with ISO 188:2011 method B. The samples were aged at 70 °C for 7 days. Ageing was examined by testing elongation at break, tensile strength and changes of hardness after ageing. The degree of ageing for tensile strength and elongation at break is given by the formula:

$$\frac{x_a - x_0}{x_0} \times 100 \qquad 6.1$$

where x_0 represents the value of the property before ageing and x_a is the value of the property after ageing. The difference $x_a – x_0$ expresses the change in hardness.

6.2.6. Morphology of the samples with SEM

SEM was used to get an insight into the dispersion of the activated particles in the matrix of raw EPDM rubber. Details about the sample preparation are given in Chapter 3.

6.3 RESULTS AND DISSCUSION

In this chapter the new solvent-free activation process was applied on an industrial scale. The use of activated particles as a material substitute for the production of a new high performance recycled material, in this case for the production of sealing systems, was investigated. For this purpose two batch experiments, of about 200 kg each, were performed by using a Co-Kneader. On the basis of the production recipe two new compound recipes were developed where the raw material was substituted with 25 vol% and 50 vol% by the activated particles (see Section 6.2, Table 6.1). Previous to the material compounding in the Co-Kneader the particles were activated by using the liquid polymer Trilene® 67. Afterwards, the co-extruded stripe profiles were vulcanised using an injection molding machine and the obtained products were investigated. Figure 6.2 presents the cure curves of the reference and of the new recycled compounds tested at 180 ºC.

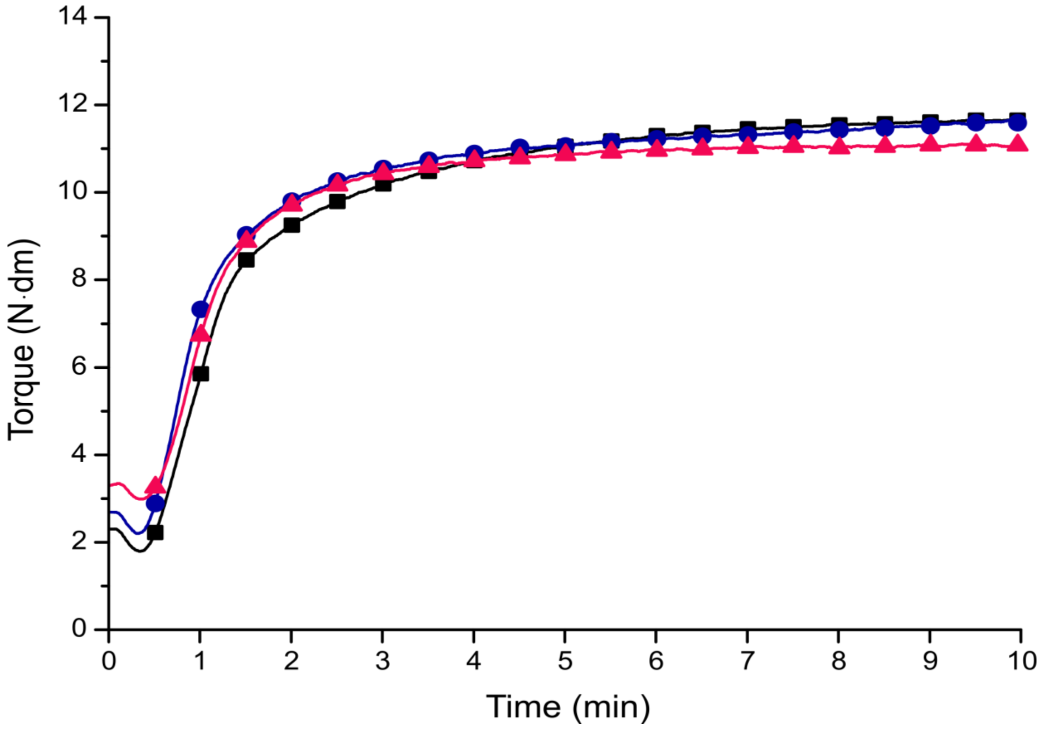

Figure 6.2 Vulcanisation curves of the reference (—■—) and of the recycled samples with 25 vol% (—●—) and 50 vol% (—▲—) RWP-LP measured at 180 ºC

The minimum torque of the samples slightly increases and the maximum torque slightly decreases with increase of the RWP-LP content. The content of the RWP-LP does not have a significant influence on the optimum cure time and the scorch time of the recycled materials.

The mechanical properties of the recycled compounds were evaluated according to the EN 681-1/A3 (2005-08) standard for elastomeric seals used in water and drainage applications as shown in Table 6.3.

Table 6.3 Material requirements for EPDM pipe joint seals used in water and drainage applications with a hardness of 50 Shore A

Property	**EN 681-1/A3(2005-08)**
Hardness	50 ±5 Shore A
Elongation at break	≥375%
Tensile strength	≥9 MPa
Compression set at 23 °C	≤12%
Compression set at 70 °C	≤20%
After ageing at 70 °C alteration of initial value, max	
Hardness	-5/+8 Shore A
Elongation at break	-20%
Tensile strength	+10/-30%

Figure 6.3 shows the influence of the recycled particles on the hardness of the vulcanised products in comparison with the reference product. For both samples, with 25 vol% and 50 vol% RWP-LP, respectively, the values of hardness show a very slight decrease compared with the values of the reference sample. In the case of the product where 25 vol% of the raw material was substituted a decrease of 3.7% was found in comparison with the value of the reference sample. For the samples where 50 vol% of the activated particles were used to substitute the raw material in the reference sample a decrease of 5.6% was calculated in comparison with the reference sample. Nevertheless, both recycled samples fulfill the requirements of the EN 681-1/A3 (2005-08) standard presented in Table 6.3.

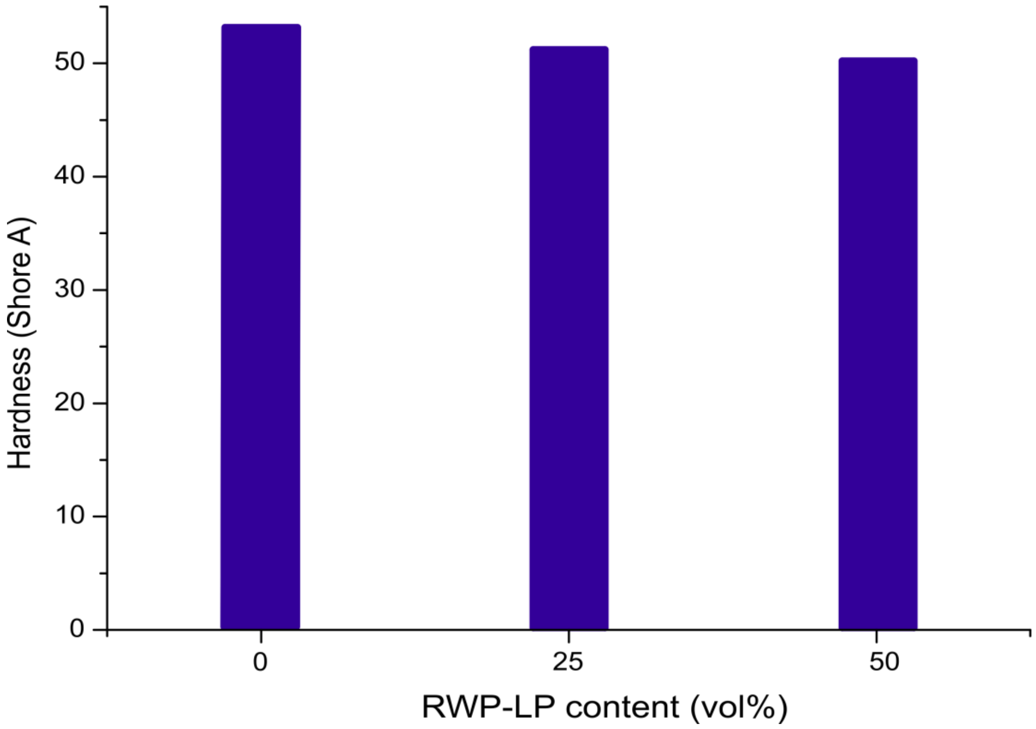

Figure 6.3 Hardness of reference and recycled compounds

The tensile strength and elongation at break (Figure 6.4) show the same tendency as the hardness. Regarding the tensile strength, both recycled materials present a slight decrease in comparison with the reference sample. For the sample containing 25 vol% of activated particles a decrease of 17% was found, while for the sample containing 50 vol% of activated particles only a decrease of 10% was obtained in comparison with the reference sample. The sample with 25 vol% activated particles needs an improvement of the tensile strength value with about 8% in order to fulfill the material requirements presented in Table 6.3.

On the other side, the sample containing 25 vol% of activated particles shows the best results for elongation at break. The value of the sample shows an increase of 2.3% in comparison with the reference sample. For the sample where 50 vol% of RWP-LP was used a decrease of about 6% in comparison with the reference sample was found. Nevertheless, the elongation at break presents very good values for both recycled compounds in comparison with the reference sample. The values obtained for the recycled materials are above those required for pipe joint seals, i.e. ≥ 375%.

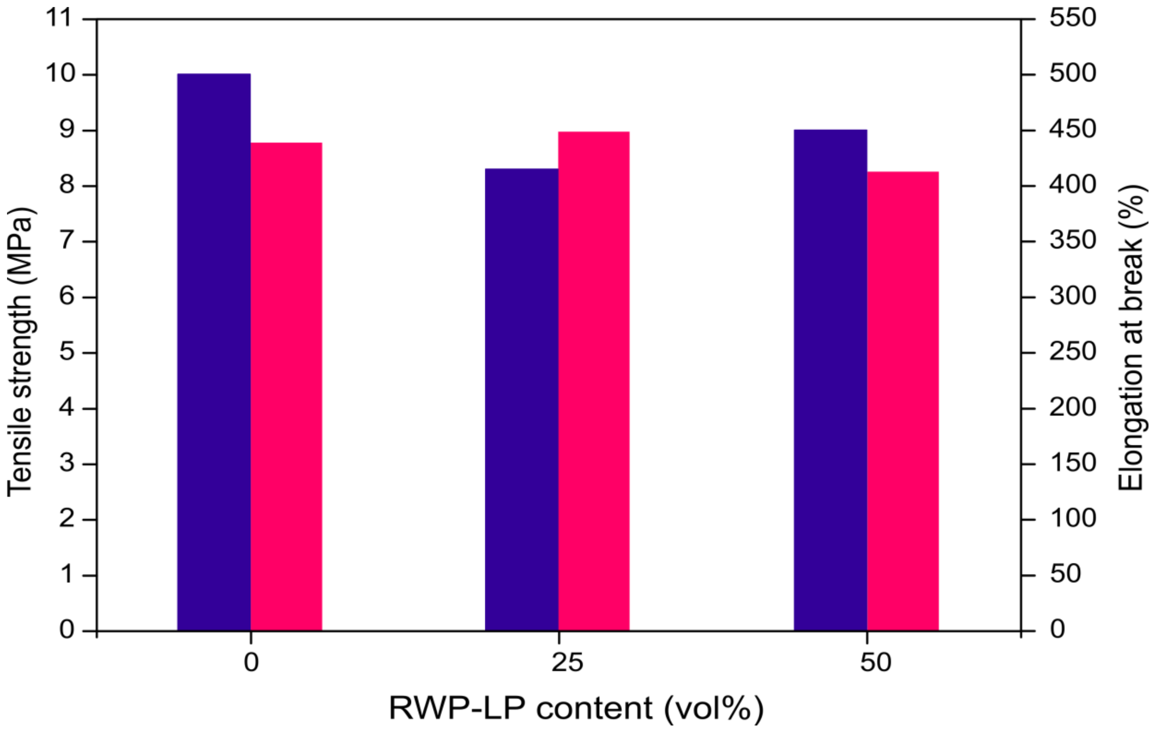

Figure 6.4 Tensile strength (blue) and elongation at break (red) of reference and recycled compounds

The values of the compression set at 23 ºC and 70 ºC are presented in Figure 6.5. The compression set tests at 23 ºC and 70 ºC show a slight increase for the sample with 25 vol% RWP-LP. For this sample an increase of 4.8% was found when tested at 23 ºC, while when testing at 70 ºC an increase of 40% in comparison with the reference sample was calculated. In the case of the samples containing 50 vol% RWP-LP the obtained compression set values are identical to the reference sample, that is 8.2% for the tests at 23 ºC and approximately 10.5% when tested at 70 ºC. According to the material requirements, for the compression set a maximum value of 12% when tested at 23 ºC and of 20% when tested at 70 ºC is required. Hence, both recycled compounds fully fulfill the EN 681-1/A3 (2005-08) standard for EPDM pipe joint seals used in water and drainage applications (see Table 6.3).

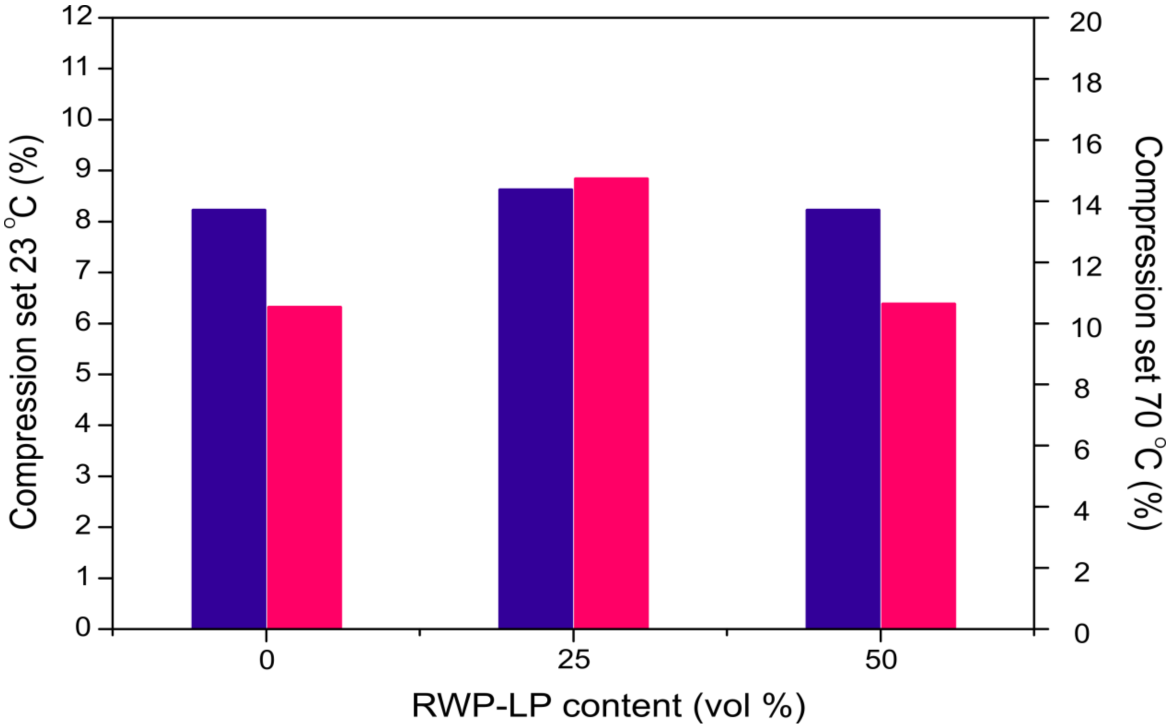

Figure 6.5 Compression set at 23 °C (blue) and 70 °C (red) of reference and recycled compounds

The apparent crosslinking density (Figure 6.6) measured by swelling measurements decreased with increase of the amount of RWP-LP in the new recycled materials. The results are in good agreement with the results obtained from rheometry and mechanical properties.

Table 6.4 presents the results of accelerated heat-ageing experiments according to the EN 681-1/A3 (2005-08) standard. Hardness, elongation at break and tensile strength of the compounds containing 25 vol% and 50 vol% of RWP-LP have been monitored for 7 days at 70 °C. The influence of ageing on hardness and tensile strength is minor, while the elongation at break is stronger affected (9-19% loss).

For the elongation at break and tensile strength the values of the mechanical properties after ageing tend to decrease upon increasing the RWP-LP content compared to the values before ageing.

An increase of hardness is shown for the sample with 50 vol% RWP-LP, while for the sample with 25 vol% RWP-LP a minor decrease is observed. Crosslinking density presents an increase after ageing in all samples, as shown in Figure 6.6. However, the results obtained after ageing tests still fulfill the standards presented in Table 6.3.

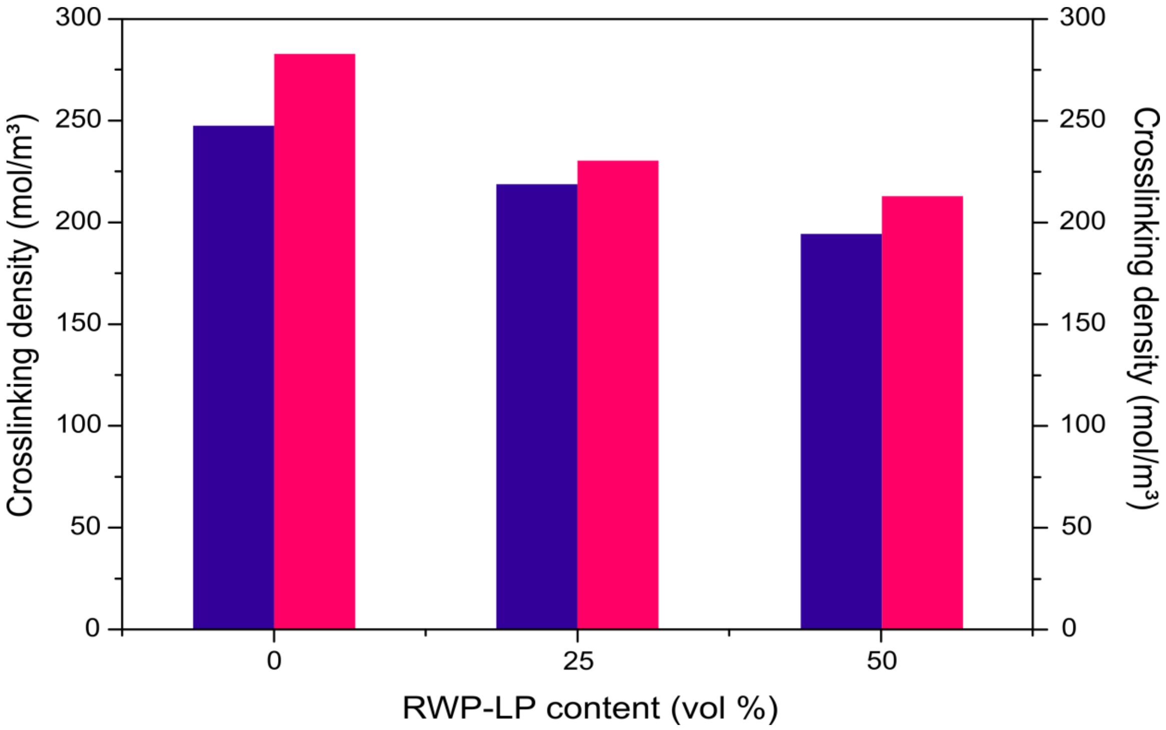

Figure 6.6 Crosslinking density of reference and recycled compounds before (blue) and after (red) ageing

The decrease in tensile strength of the recycled compounds after ageing may be caused by a breakdown of the polymer chain and the destruction of sulphur crosslinks [2] or by the evaporation of the plasticizer, which makes the compound more brittle and which is also the reason for the hardness increase after ageing. [3]

A brief final conclusion would be that the overall properties obtained for the recycled materials show no significant variation in comparison with the reference sample, and both compounds fulfill (before and after ageing) the required standards for EPDM pipe joint seals presented in Table 6.3. Moreover, the results from the laboratory scale presented in Chapter 4 for the RA25 and RA50 samples are comparable with the results obtained on the industrial scale for the samples where 25 vol% and 50 vol% of RWP-LP was used as a substitute of the raw material. The slight differences may appear due to the small changes in the recipe formulations, mixing procedure and vulcanisation technique. Slightly better values of hardness, tensile strength and elongation at break were obtained on the laboratory scale, while the compression set values are better for the samples obtained on the industrial scale. The results obtained for these two batch experiments performed on an industrial scale demonstrate that the use of activated particles as a substitute of the raw material can result in rubber compounds with very good properties.

Table 6.4 Change of the initial values after ageing of the recycled samples

Property	**Change of initial value**	
	Sample with 25% RWP-LP	Sample with 50% RWP-LP
Hardness, Shore A	-0.1	3
Elongation at break, %	-9.12	-19.6
Tensile strength, %	-0.78	-3.77

To check the interaction between the activated particles and the new rubber matrix, as well as the dispersion of the RWP-LP in the matrix, a morphology study was conducted using SEM. Figure 6.7 shows the SEM images of the surface of broken specimens. In comparison with the reference sample (Figure 6.7a), both the samples with 25 vol% (Figure 6.7b) and with 50% of activated particles (Figure 6.7c) show a good interaction of the RWP-LP with the raw rubber matrix. The dispersion of the RWP-LP is very good and the surface of the recycled samples is very close to that of the reference compound.

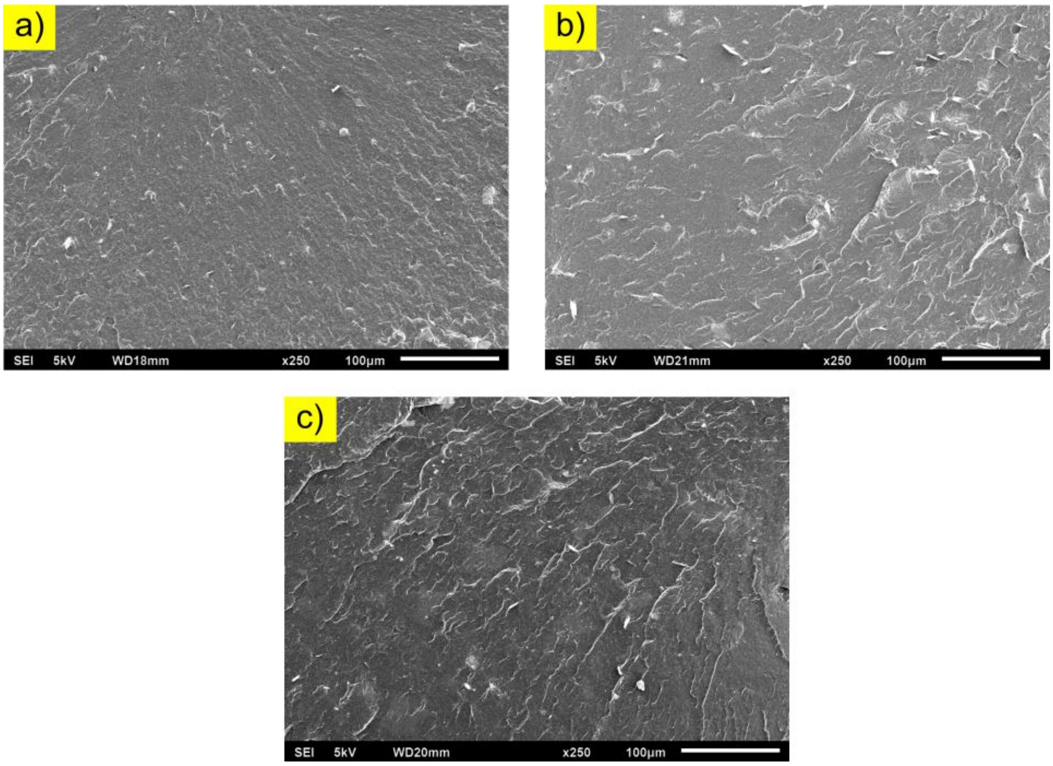

Figure 6.7 SEM images of the surfaces of broken specimens:
a) reference compound; b) recycled compound with 25% RWP-LP and
c) recycled compound with 50% RWP-LP

6.4 CONCLUSIONS

It was demonstrated that EPDM rubber waste particles can be recycled by using small amounts of liquid polymer which enables the activation of the surface particles leading to the formation of new cross-links with the new polymer matrix. An up-scaling from laboratory experiments (100 g) to the application of the process on an industrial scale (200 kg) results in high quality recycled materials.

It was shown that the recycled particles can be used as a substitute up to 50 vol% in a virgin EPDM matrix for a formulation employed in the production of seals and sealing systems.

All mechanical properties present minor differences in comparison with the reference sample, and both recycled compounds comply with the requirements of the EN 681-1/A3 (2005-08) standard for EPDM pipe joint seals.

When the activated particles are vulcanised with a curing system without being mixed with raw material, the properties of the obtained blends are not viable for obtaining high quality products (see Chapter 3). Nevertheless, when the treated particles are used as a substituent in the virgin matrix up to 50%, it is possible to obtain high quality new recycled materials.

An optimization of the material formulation and the mixing process on the industrial scale will help to further improve the new recycling method. The aim of a further optimization should be the energy, material and equipment costs per unit volume of the final product.

6.5 REFERENCES

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Chapter 7

Summary and Outlook

"It always seems impossible until it's done."

Nelson Mandela (1918 – 2013)

This chapter provides a summary of the research described in the thesis. A general evaluation of the main results is given together with some remarks. Finally, some ideas and suggestions for further investigation are presented.

7.1 SUMMARY

The objective of this study was the development of a solvent-free activation process for the chemical recycling of EPDM rubber waste particles by use of liquid polymers. In order to show the feasibility potential on a production scale various types of optimization parameters were studied as explained further below.

Chapter 1 gives a brief introduction regarding the demand of rubber waste recycling. A short review about the introduction of EPDM rubber on the market, routes of syntheses, some main properties and applications of this type of rubber are as well given. The concept and the objectives are presented and the structure of the present thesis is outlined.

Chapter 2 provides a detailed literature overview of various recovery and recycling processes with main attention on EPDM rubber. The most efficient way to achieve a good recycled material is by means of a solvent-free chemical activation process. Applying this method offers the possibility of using high amounts of recycled particles as a substitute of raw material, obtaining products of high quality.

In addition, the presented method has some major advantages over the other methods used for rubber recycling, such as a high process safety, no need to use solvents or any other odorous chemicals, no scission of the polymer main chain and a high potential of application on an industrial scale without requiring special equipment.

Chapter 3 investigated the potential of the rubber waste particles to be chemically activated by using two different types of low molecular weight polymers. Based on the results obtained from the characterization of the rubber waste particle it was found that this type of particles presents a high potential to be chemically activated. Exhibiting a rough structure, an irregular shape and a relatively large surface area, these particles are able to enhance the adhesion with the new rubber matrix.

By studying: a) the influence of the ratio between rubber waste particles and the liquid polymer; b) the effect of the amount of curing system and c) the influence of the content of double bonds contained by the liquid polymers, it was found that all three variable factors examined have a high influence on the quality of the recycled particles. The cure behaviour, mechanical properties, crosslinking density and morphology of the activated particles showed various values.

The best ratio between rubber waste particles and the liquid polymer was obtained by using 0.8 volume fractions RWP and 0.2 volume fractions LP. It was shown that although the RWP contain residues of the curing system they will vulcanize to a very small extent obtaining blends with unsatisfactory properties and morphology. For this system usage of a higher amount of curing system is necessary in order to obtain good results. With respect to the double bond concentration, the particles activated with the liquid polymer containing a high amount of 5-ethylidene-2-norbornene present overall better properties. Due to the higher percentage of unsaturated sites this type of liquid polymer is able to form more crosslinks with the surface of the particles, therefore giving better properties.

It was shown that the properties of the rubber waste particles activated with a small amount of liquid polymer containing a high amount of diene exhibit 80% hardness, 66% tensile strength and 58% elongation at break compared with the values of a commercial EPDM compound.

In **Chapter 4**, the influence of four different types of activated particles used as a substitute of raw material was studied. Besides the particles studied in the previous chapter, two other types of activated particles were used to substitute the raw polymer matrix. The new particles were activated with two liquid polymers with a higher amount of ethylene and a different amount of ENB.

It was found that each type of activated particles behaves differently when it is mixed with the raw polymer matrix and compared to the reference sample. The raw material was substituted by the activated particles with 25 vol%, 50 vol% and 75 vol%, respectively.

By increasing the content of activated particles in the composition, a decrease of cure time, maximum torque and Δtorque is obtained, whereas minimum torque and cure rate index increases. However, the compounds which contain a higher amount of ENB require a longer cure times due to the presence of more active sites used in the process of vulcanization.

In terms of mechanical properties, hardness and tensile strength decrease with higher RWP-LP amount, while elongation at break shows excellent values, irrespective of the RWP-LP content. The compression set tested at three different temperatures is influenced by both ENB and ethylene content. Nevertheless, better values were obtained for the sample with a higher amount of ENB. Moreover, when using activated particles instead of non -activated particles the processability of the material significantly improves and the morphology of the recycled compounds is very good even if high amounts of activated particles are used.

It can be concluded that the particles activated with low ethylene liquid polymers are the most suitable to be used as a substitute of the raw material with application in sealing systems. By using these types of particles it is possible to substitute up to 50 vol% of the raw material and obtain compounds with very good processability, mechanical properties and morphology. On the other side, the particles activated with high ethylene liquid polymers can substitute the raw material only up to 25 vol% due to the unfavourable impact on the compound performance in low temperature applications.

In **Chapter 5**, the influence of the curing system type was studied. For this investigation two types of accelerators were tested in terms of cure behaviour and mechanical properties of the recycled compounds. Based on the results obtained in the previous chapter, the type of activated particles used in this investigation contains the liquid polymer with a high percentage of ENB and low ethylene content, namely Trilene® 67.

It was shown that by using CBS as accelerator a better scorch resistance and faster cure times can be obtain in comparison with the MBT accelerator. Moreover, by using CBS lower values of minimum torque and higher values of maximum torque are achieved. In terms of hardness, elongation at break and tensile strength small differences between the two types of accelerators is observed. With regard to the compression set, at all three temperatures the samples with CBS present higher values. It can be concluded that both types of accelerators can be used to substitute the raw material up to 50%. Nevertheless, a better process safety can be achieved by using CBS as accelerator.

Chapter 6 reported the upscaling of the process on an industrial scale. By applying this innovative activation process it was shown that the developed technique can be easily applied on an industrial scale and the raw material can be substituted up to 50 vol% with only a minor decline of properties. The application development was focused on the use of activated particles as a raw material substitute in the production of seals and sealing systems. Trilene® 67 was used to activate the EPDM rubber waste particles.

Both recycled materials with 25 vol% and 50 vol% of RWM-LP fulfil the standards for elastomeric seals (except the tensile strength for the sample with 25 vol% RWP-LP). An increase of the tensile strength can be achieved by a further optimization of the recipe composition.

It was shown that the industrial application of the solvent-free chemical activation process for the recycling of rubber can be easily applied without the aid of special equipments. The cost and time are more convenient when compared with other recycling processes, e.g. devulcanisation techniques. The obtained results are significant taking into consideration that the rubber waste particles can be added to a sealing system compound only up to 10% without affecting the properties of the final compound.

7.2 OUTLOOK

An important aspect that needs to be studied in more detail and is not covered in the present thesis is the accelerated heat – ageing tests performed at various temperatures and over various periods of time in order to estimate the life-time expectation of the recycled products.

Further research should be carried out by applying this method on various types of scrap rubber using the activated particles as a substitute of raw material in other formulations aiming to products of high quality, e.g. for the automotive industry or the building and construction sector.

Kapitel 7

Zusammenfassung und Ausblick

“Es erscheint immer unmöglich, bis man es gemacht hat.”

Nelson Mandela (1918 – 2013)

Dieses Kapitel stellt eine Zusammenfassung der in der vorliegenden Arbeit beschriebenen Forschungsarbeit dar. Eine allgemeine Beurteilung der wichtigsten Ergebnisse wird ebenso gegeben wie einige Bemerkungen dazu. Schließlich werden einige Ideen und Vorschläge für weitere Untersuchungen präsentiert.

7.1 ZUSAMMENFASSUNG

Die Zielsetzung dieser Studie war die Entwicklung eines lösungsmittelfreien Aktivierungsprozesses für das chemische Recycling von EPDM Kautschukabfallpartikeln mittels Verwendung von Flüssigpolymeren. Um das Machbarkeitspotenzial auf industrieller Ebene darzustellen, wurden verschiedene Optimierungsparameter erforscht, die weiter unten beschrieben sind.

Kapitel 1 gibt eine kurze Einführung bezüglich des Bedarfs an Recycling von Kautschukabfall. Weiterhin wird ein kurzer Rückblick auf die Markteinführung von EPDM Kautschuk, auf Synthesewege sowie auf einige Haupteigenschaften und Anwendungsmöglichkeiten dieser Art von Kautschuk gegeben. Das Konzept und die Zielsetzungen werden präsentiert und die Struktur der vorliegenden Arbeit umrissen.

Kapitel 2 liefert eine ausführliche Literaturübersicht über unterschiedliche Rückgewinnungs- und Recyclingprozesse mit dem Hauptaugenmerk auf EPDM Kautschuk. Die effizienteste Möglichkeit, gutes Recyclingmaterial zu erhalten ist durch Anwendung eines lösungsmittelfreien chemischen Aktivierungsprozesses.

Durch die Anwendung dieser Methode erzeugt man große Mengen von Recyclingpartikeln, die als Rohmaterial für hochwertige Produkte eingesetzt werden können.

Darüber hinaus hat die vorgestellte Methode bedeutende Vorteile im Vergleich zu den anderen Methoden, die zum Kautschukrecycling angewandt werden, wie etwa die Verfahrenssicherheit, die Tatsache, dass keine Lösungsmittel oder andere riechende Chemikalien verwendet werden müssen, keine Kettenspaltung in der Hauptkette des Polymers sowie ein hohes Anwendungspotenzial in industriellem Maßstab ohne Bedarf an Sondergeräten.

Kapitel 3 untersucht die Möglichkeiten der chemischen Aktivierung der Kautschukabfallpartikel durch die Verwendung zweier unterschiedlicher Typen von niedermolekularen Polymeren. Die Auswertung der Charakterisierung der Kautschukabfallpartikel zeigte, dass diese Art von Partikeln ein hohes Potenzial für chemische Aktivierung hat. Durch ihre raue Struktur, ihre unregelmäßige Form und eine relativ große Oberfläche verbessern diese Partikel die Adhäsion mit der neuen Kautschukmatrix.

Die Untersuchung a) der Auswirkung des Verhältnisses zwischen Kautschukabfallpartikeln und Flüssigpolymer; b) der Auswirkung der Menge an Vulkanisationsmittel und c) der Auswirkung der Anzahl der Doppelbindungen im Flüssigpolymer ergab, dass alle drei genannten variablen Faktoren die Qualität der recycelten Partikel erheblich beeinflussen. Das Vulkanisationsverhalten, die mechanischen Eigenschaften, die Vernetzungsdichte und die Morphologie der aktivierten Partikel ergaben verschiedenartige Werte.

Das beste Verhältnis zwischen Kautschukabfallpartikeln und Flüssigpolymer erhielt man durch Verwendung eines Volumenanteils von 0,8 RWP und 0,2 LP. Obwohl die Partikel Rückstände des Vulkanisationsmittels enthielten, härteten sie in nur sehr geringem Maße aus und bildeten Gemische mit unbefriedigenden Eigenschaften und einer unzulänglichen Morphologie. Um gute Ergebnisse zu erzielen erfordert dieses System eine höhere Menge Vulkanisationsmittel. Bezüglich der Konzentration an Doppelbindungen zeigten die Partikel, die mit Flüssigpolymer aktiviert wurden, das eine hohe Menge an 5-Ethyliden-2-Norbornen enthielt, insgesamt bessere Eigenschaften. Durch den höheren Anteil an ungesättigten Kohlenstoffatomen ist diese Type Flüssigpolymer in der Lage, mehr Vernetzungen mit der Oberfläche der Partikel einzugehen, wodurch bessere Eigenschaften entstehen.

Die Untersuchung ergab, dass die Kautschukabfallpartikel, die mit einer kleinen Menge Flüssigpolymer aktiviert wurden, das einen hohen Anteil an Dien enthielt, 80% Härte, 66% Zugfestigkeit und 58% der Reißdehnung aufweisen, die ein handelsübliches EPDM-System erreicht.

Kapitel 4 erforscht die Auswirkungen von vier unterschiedlichen Arten von aktivierten Partikeln, die als Ersatz für Rohmaterial verwendet wurden. Neben den im vorherigen Kapitel unersuchten Partikeln wurden hier zwei weitere Arten aktivierter Partikel als Ersatz für die Polymermatrix verwendet. Die beiden neuen Partikelarten wurden mit zwei Flüssigpolymeren aktiviert, die einen höheren Gehalt an Ethylen und einen anderen Gehalt an ENB aufwiesen.

Die Untersuchung ergab, dass sich jede Art von aktivierten Partikeln im Vergleich zur Referenzprobe unterschiedlich verhält wenn sie mit der Polymermatrix gemischt wird. Das Rohmaterial wurde im Volumenverhältnis 25 vol%, 50 vol% und 75 vol% durch die aktivierten ersetzt.

Durch Erhöhung des Gehalts an aktivierten Partikeln im Gemisch erhielt man eine Verringerung der Aushärtungszeit, des Maximaldrehmoments sowie des Δ Drehmoments, wobei das Mindestdrehmoment und die Vulkanisationsgeschwindigkeit anstiegen. Allerdings benötigen die Gemische, die einen höheren Gehalt an ENB aufweisen, längere Aushärtungszeiten, bedingt durch die größere Aktivität im Verlauf der Vulkanisation.

Betrachtet man die mechanischen Eigenschaften, so nehmen Härte und Zugfestigkeit mit Erhöhen des Gemisches Kautschukabfallpartikel-Flüssigpolymer ab, während die Reißdehnung unabhängig von der Menge exzellente Werte zeigt. Der Druckverformungsrest, der bei drei unterschiedlichen Temperaturen getestet wurde, wird sowohl vom Gehalt an ENB als auch an Ethylen beeinflusst. Dennoch wurden im Falle der Probe mit höherem ENB-Gehalt bessere Werte erzielt. Darüber hinaus verbessert die Verwendung von aktivierten Partikeln statt nicht aktivierter Partikel die Verarbeit-barkeit des Materials erheblich und die Morphologie des Recyclinggemisches ist auch bei Verwendung von großen Mengen aktivierter Partikel sehr gut.

Zusammenfassend kann festgestellt werden, dass die Partikel, die mit Flüssigpolymer mit geringem Ethylengehalt aktiviert werden, am besten geeignet sind, um in der Produktion von Abdichtungssystemen das Rohmaterial zu ersetzen. Diese Partikel können bis zu 50% Volumen des Rohmaterials ersetzen und dabei Gemische mit sehr guter Verarbeitbarkeit, guten mechanischen Eigenschaften und guter Morphologie ergeben. Andererseits können die Partikel, die mit Flüssigpolymer mit hohem Ethylengehalt aktiviert werden, das Rohmaterial nur bis zu 25% Volumen ersetzen, bedingt durch die ungünstigen Auswirkungen auf die Leistung des Gemisches bei Anwendungen im Niedrigtemperaturbereich.

In **Kapitel 5** wird die Auswirkung des Vulkanisationsmittels erforscht. Für diese Untersuchung wurden zwei Arten von Beschleunigern in Bezug auf Härtungsverhalten und mechanische Eigenschaften des Recyclinggemisches geprüft. Aufbauend auf den Ergebnissen im vorherigen Kapitel, enthielten die aktivierten Partikel in dieser Untersuchung das Flüssigpolymer mit einem hohen Anteil an ENB und einem niedrigen Ethylengehalt, nämlich Trilen® 67.

Es wurde gezeigt, dass durch die Verwendung von CBS im Gegensatz zu MBT als Beschleuniger eine bessere Anvulkanisationsbeständigkeit sowie kürzere Aushärtungszeiten erhalten werden. Überdies werden durch die Verwendung von CBS niedrigere Werte für das Mindestdrehmoment und höhere für das Maximaldrehmoment erzielt. In Bezug auf Härte, Reißdehnung und Zugfestigkeit sind nur geringe Unterschiede zwischen den beiden Beschleunigerarten zu beobachten. Bezüglich des Druckverformungsrests weisen die Proben mit CBS in allen drei getesteten Temperaturbereichen höhere Werte auf. Man kann schlussfolgern, dass beide Beschleunigertypen mit den Partikeln verwendet werden können, um bis zu 50% des Rohmaterials zu ersetzen. Jedoch wird eine bessere Verarbeitungssicherheit bei der Verwendung von CBS als Beschleuniger festgestellt.

Kapitel 6 berichtet über die Hochskalierung des Verfahrens auf industriellen Maßstab. Dieser innovative Aktivierungsprozess ist leicht im industriellen Maßstab anwendbar und das Rohmaterial kann zu bis zu 50% durch die Recyclingpartikel ersetzt werden, was zu einer nur sehr geringen Verschlechterung der Eigenschaften führt. Die Entwicklung der Anwendung konzentrierte sich auf die Verwendung von aktivierten Partikeln als Rohmaterialersatz in der Herstellung von Dichtungen und Abdichtsystemen. Trilen®67 wurde zur Aktivierung der EPDM Kautschukabfallpartikel eingesetzt.

Beide recycelten Materialien mit 25 und 50 Vol.-% von Kautschukabfallpartikeln-Flüssigpolymer erfüllen die Anforderungen für Elastomer-Dichtungen (ausgenommen die Zugfestigkeit der Probe mit 25 Vol.-%). Eine Erhöhung der Zugfestigkeit kann durch eine weitere Optimierung der Rezeptur erzielt werden.

Es wurde bewiesen, dass der lösungsmittelfreie chemische Aktivierungsprozess für das Recycling von Kautschuk problemlos und ohne Zuhilfenahme spezieller Geräte im industriellen Maßstab durchgeführt werden kann. Die benötigten Kosten und die Zeit sind niedriger im Vergleich zu anderen Recyclingprozessen, z.B. zu Devulkanisationsverfahren. Die erzielten Ergebnisse sind signifikant wenn man berücksichtigt, dass der Anteil an Kautschukabfallpartikeln in Dichtungssystemen bei anderen Verfahren nur bis zu 10% beträgt, um die Eigenschaften des Endpräparates nicht zu beeinträchtigen.

7.2 AUSBLICK

Ein wichtiger Aspekt, der detaillierter erforscht werden sollte und in der vorliegenden Arbeit nicht abgedeckt wurde, ist der bei unterschiedlichen Temperaturen und über unterschiedliche Zeitspannen durchgeführte beschleunigte Hitzealterungstest, der zur Schätzung der Lebensdauer des wiederverwerteten Produkts dient.

Weitere Forschungsarbeit sollte in die Anwendung dieser Methode an verschiedenen Arten von Altkautschuk investiert werden, indem die aktivierten Partikel als Ersatz für Rohmaterial in anderen Rezepturen verwendet werden. Das Ziel sollte die Herstellung von hochwertigen Produkten z.B. für die Automobilbranche oder das Bauwesen sein.

Symbols and Abbreviations

ºC	Degrees Celsius
AISR	Anisothermal stress relaxation test
ASTM	American Society for Testing and Materials
BIIR	Bromobutyl rubber
BR	Butadienerubber
CBS	N-Cyclohexyl-2-benzothiazolesulfenamide
CR	Polycloroprene
DCPD	Dicyclopentadiene
EN	European Standards
ENB	5-ethylidene-2-norbornene
EPDM	Ethylene propylene diene rubber
EU	European Union
EV	Efficiently vulcanisation
g	Gram
G'	Elastic modulus
G"	Loss modulus
GHz	Gigahertz
IIR	Isobuthylene isoprene rubber
IR	Isoprene rubber
ISO	International Organization for Standardization
kg	Kilogram
kWh	Kilowatt hour
LLDPE	Linear low-density polyethylene
LP	Liquid polymer (Low molecular weight polymer)
LP-A	Liquid polymer Trilene® 67
LP-B	Liquid polymer Trilene® 66

LP-C	Liquid polymer Trilene® 77
LP-D	Liquid polymer Trilene® 76
MBT	2-Mercaptobenzothiazole
min	Minutes
MJ	Megajoule
mm	Millimeter
MPa	Megapascal
NBR	Nitrile rubber
NR	Natural rubber
PEG	High molecular polyethylene glycol
phr	Parts per hundred rubber
PUR	Polyurethane rubber
Q	Silicone rubber
rmp	Revolutions Per Minute
RWP	EPDM rubber waste particles
RWP-LP	Activated EPDM rubber waste particles
S	Sulphur
s	Second
SBR	Styrene-butadiene rubber
SEV	Semi-efficiently vulcanisation
TDF	Tire-derived fuel
TMTD	Tetramethylthiuram disulfide
TSSR	Temperature scanning stress relaxation
VCl_4	Vanadium tetrachloride
$VOCl_3$	Vanadium oxytrichloride
ZBEC	Zinc dibenzyl dithiocarbamate
ZnO	Zinc oxide
η^*	Complex viscosity
µm	Micrometer
υ_e	Crosslinking density

Curriculum Vitae

PERSONAL INFORMATION

Name:	Ana-Maria Lepadatu
Adsress:	Sedanstr. 6, 49076 Osnabrueck, Germany
Telefon:	+ 49 176 6715 7920
E-mail:	alepadatu@uos.com
Date of birth:	26 Nov 1985
Nationality:	Romanian

WORK EXPERIENCE

08/2015 – Present	**Research Assistant** Department of Organic Material Chemistry, Institute of Chemistry of new Materials, University of Osnabrueck, research group OMC I, Prof. U. Beginn
10/2014 – 12/2014	**Project Assistant** Science to Business GmbH - University of Applied Sciences Osnabrueck, Prof. Dr. habil. S. Asaftei Research topic: ”The use of different additives to improve tack in EPDM compounds”
01/2010 – 09/2014	**Research Assistant** Department of Organic Material Chemistry, Institute of Chemistry of new Materials, University of Osnabrueck, research group OMC I, Prof. U. Beginn/Prof. Dr. habil. S. Asaftei
02/2009 – 10/2009	**Graduate Assistant** Department of Organic Material Chemistry, Institute of Chemistry of new Materials, University of Osnabrueck, research group OMC I, Prof. Dr. habil. S. Asaftei

EDUCATION

04/2011 – Present	**PhD in Organic Chemistry** Department of Organic Material Chemistry, Institute of Chemistry of new Materials, University of Osnabrueck, research group OMC I, Prof. U. Beginn/Prof. Dr. habil. S. Asaftei
10/2004 – 07/2009	**Chemical Engineer Diploma** Chemical Engineering , Faculty of Engineering, University of Bacau (Romania)
02/2009 – 10/2009	**Research Internship** Department of Organic Material Chemistry, Institute of Chemistry of new Materials, University of Osnabrueck, research group OMC I, Prof. Dr. habil. S. Asaftei Research topic: ”Synthesis and characterization of hybrid molecules consisting of pyridine and nucleobase units”
04/2008 – 08/2008	**Semester abroad: Erasmus Programme** Institute of Chemistry, Department of Organic Chemistry, University of Osnabrueck
09/2000 – 08/2004	**High School Diploma (Abitur)** National College "Grigore Antipa", Bacau (Romania)

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Erklärung über die Eigenständigkeit der erbrachten wissenschaftlichen Leistung

Ich erkläre hiermit, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe. Die aus anderen Quellen direct oder indirekt übernommen Daten und Konzepte sind unter Angabe der Quelle gekennzeichnet. Niemand hat von mir unmittelbar oder mittelbar geldwerte Leistungen für Arbeit erhalten, die im Zusssammenhang mit dem Inhalt der vorgelegten Dissertation stehen.

Die Arbeit wurde bisher weder im In- noch im Ausland in gleicher oder ändlicher Form einer anderen Prüfungsbehörde vorgelegt.

Osnabrück, 08. October 2015

Ana-Maria Lepadatu