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UTILIZATION OF SIDESTREAMS IN RUBBERS
Master of Science Thesis

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ABSTRACT

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The environmental aspect is highlighted more and more every day in all fields of industry. The environmental aspects need to be noted in used techniques as well as in used raw materials. The utilization of different sidestream materials and wastes is the future also in rubber industries. The focus of the present work is on unconventional filler materials in rubber compounds.

The theoretical part is comprised basic rubber theory, to help understand the rest of the work better, and a review of researches about unconventional filler materials in different rubbers. The rubber theory includes the presentation of the most commonly used elastomers, fillers, and other additional materials in rubber compounds as well as the basis of rubber compounding. In the review chapter, many different kinds of materials studied as a filler for rubber are discussed. Majority of the studied materials proved to be non-reinforcing fillers and no major property improvements were noted. None of the studied materials showed properties that could replace the most used commercial reinforcing filler, carbon black. Several possibilities as non-reinforcing filler were noted with unconventional fillers, but further research is needed.

In the experimental part, the aim was to find out properties of the selected sidestream materials in rubbers. Three different materials were compounded with natural rubber and EPDM with different quantities and compared to reference compounds. Mechanical properties such as tensile properties, tear strength, and hardness, and processability such as curing characteristics, Mooney viscosity, and The Payne effect was tested.

From the results it can be concluded that none of the studied materials worked as a reinforcing filler and thus could not replace carbon black as a filler in rubbers. Processability with all the studied materials was good or adequate. The main reason of the studied materials for not working as a reinforcing filler was their too large particle size. Some potential as a cost reducing filler was noted but further research is needed to unveil other effective properties and to determine potential applications.

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Ympäristönäkökulma nostetaan esille yhä useammin monella eri teollisuuden osa-alueella. Kestävä kehitys sekä ympäristön suojeleasiat tulee huomioida niin teollisuuden tuotantomenetelmissä kuin myös käytettävissä raaka-aineissa. Teollisuusprosessien sivuvirtojen ja erilaisten jätteiden hyödyntäminen on huomioitava nykypäivänä myös kumiteollisuudessa. Tämän työn tavoitteena oli tutkia epätavanomaisia kumien täyteaineita.

Työn teoriaosuus koostuu kumien perusteoriasta, joka helpottaa työn ymmärtämistä muilta osin, sekä katsauksesta tutkimuksiin, joissa on tutkittu erilaisten epätavallisten materiaalien käyttäytymistä kumien täyteaineina. Kumien teoriaosuus sisältää esittelyn yleisimmin käytetyistä elastomeereista, täyteaineista ja muista lisäaineista sekä perusteet kumien valmistuksesta. Kappaleessa, jossa käydään läpi jo tehtyjä tutkimuksia epätavallista täyteainesta, käsitellään laajasti monia erilaisia materiaaleja, joilla on erilaiset ominaisuudet. Pääosin kaikki tutkimukset kuitenkin osoittivat, että tutkitut materiaalit eivät toimi lujittavina täyteaineina, eikä suuria parannuksia ominaisuuksiin havaittu. Yksikään materiaaleista ei pysty korvaamaan ylivoimaisesti eniten käytetyn lujittavan täyteaineen, nokimustan, käyttöä kumien täyteaineena. Mahdollisuuksia toimia hintaa alentavana täyteaineena todettiin useilla eri materiaaleilla.

Kokeellisessa osassa tarkoituksena oli kartoittaa tiettyjen täyteaineiden vaikutuksia eri kumien ominaisuuksiin. Kolme erilaista materiaalia sekoitettiin luonnonkumin ja EPDM-kumin kanssa. Sekoituksissa käytettiin eri täyteainepitoisuuksia ja niitä verrattiin referenssisekoituksen kanssa. Mekaanisista ominaisuuksista testattiin lujuusominaisuudet, repäisyjuuus sekä kovuus, ja prosessoitavuudesta vulkanointiominaisuudet, Mooney-viskositeetti sekä Paynen efekti.

Tuloksista voidaan päätellä, että mikään testatuista materiaaleista ei toiminut lujittavan täyteaineen kaltaisesti, eikä niillä näin ollen voida korvata nokimustan käyttöä. Prosessoitavuus osoittautui kaikilla täyteaineilla hyväksi tai vähintäänkin tyydyttäväksi. Suurin yksittäinen syy täyteaineiden epälujittavaan vaikutukseen on niiden suuri partikkelikoko. Näin ollen ne eivät paranna kumituotteen mekaanisia ominaisuuksia. Kuitenkin tutkituilla materiaaleilla havaittiin potentiaalia ei-lujittavana täyteaineena, jolla voidaan alentaa tuotteiden hintaa. Jatkotutkimuksia tarvitaan joka tapauksessa, jotta muut vaikuttavat ominaisuudet saadaan selvitettyä ja mahdolliset käyttökohteet määritettyä.

PREFACE

This master's thesis work was made in Tampere University of Technology in the Department of Material Science. I would like to thank the Industrial Research Fund of Tampere University of Technology for this great opportunity. I would also like to thank UPM for such an interesting subject. It was an honour to make my master's thesis work out of this topic. Especial thanks to Kati Mustonen, who worked as a contact person from UPM and was helpful and gave valuable ideas and opinions throughout the work.

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TABLE OF CONTENTS

Abstract	i
Tiivistelmä.....	ii
Preface.....	iii
List of symbols and abbreviations	vi
1 Introduction.....	1
2 Theoretical Background	2
2.1 Rubber.....	2
2.1.1 Properties	2
2.1.2 Elastomers	3
2.1.3 Market situation.....	4
2.2 Rubber compounds.....	4
2.2.1 Fillers	4
2.2.2 Plasticizers	8
2.2.3 Protective agents.....	8
2.2.4 Vulcanizing agents	9
2.2.5 Others.....	9
2.3 Processing of rubbers.....	10
2.3.1 Mixing.....	10
2.3.2 Shaping	12
2.3.3 Vulcanization	12
3 Alternative filler materials.....	13
3.1 Ash.....	13
3.1.1 Fly ash.....	13
3.1.2 Rice husk ash.....	15
3.1.3 Other ashes	16
3.2 Sludge	18
3.2.1 Paper sludge	18
3.2.2 Marble sludge.....	19
3.3 Lignin.....	20
3.4 Cellulose	22
3.4.1 Microfibrillated cellulose (Biofibrils).....	22
3.4.2 Crystalline Cellulose.....	24
3.5 Wood flour	25
3.6 Natural fibres.....	25
3.7 Others fillers.....	27
4 Experimental.....	31
4.1 Compounding	31
4.1.1 Materials and recipes	31
4.1.2 Mixing.....	33
4.1.3 Vulcanization	36

4.2	Test Methods.....	36
4.2.1	Mooney viscosity.....	36
4.2.2	Cure characteristics.....	37
4.2.3	The Payne effect.....	38
4.2.4	Tensile properties	38
4.2.5	Tear strength.....	40
4.2.6	Hardness.....	40
4.2.7	Dynamic mechanical analysis	41
5	Results and discussion.....	42
5.1	Results of natural rubber compounds	42
5.1.1	Material A	42
5.1.2	Material S.....	45
5.1.3	Material L.....	47
5.1.4	Treatments of material A2 in NR	49
5.1.5	Comparison with pure natural rubber	51
5.2	Results of EPDM –rubber compounds	53
5.2.1	Material A	53
5.2.2	Treatments of material A2 in EPDM.....	55
5.3	Discussion	57
5.4	Business potential.....	59
6	Conclusions.....	60
	References	62
	Appendix 1: Test results.....	71

LIST OF SYMBOLS AND ABBREVIATIONS

ACM	Acrylic rubber
BR	Butadiene rubber
BRHA	Black rice husk ash
CaCO ₃	Calcium carbonate
CB	Carbon black
CBS	Cyclohexyl benzothiazolesulfenamide
CNC	Cellulose nanocrystals
CR	Chloroprene rubber
CSM	Chlorosulfonated polyethylene rubber
DMA	Dynamic mechanical analysis
ENR	Epoxidized natural rubber
EPDM	Ethylene propylene diene rubber
E'	Storage modulus
E''	Loss modulus
FPM	Fluoride rubber
FS	Fumed silica
GCC	Ground calcium carbonate
GO	Graphene oxide
IPPD	Commercial antioxidant, (<i>N</i> -phenyl- <i>N</i> -isopropyl- <i>p</i> -phenylene diamine)
IIR	Butyl rubber
IR	Polyisoprene rubber
LDH	Layered double hydroxide
MAN	Maleic anhydride
MANR	Maleic anhydride grafted natural rubber, maleated natural rubber
MAPP	<i>graft</i> -copoly(propylene/maleic anhydride) treatment
MFA	Multifunctional additive
MFC	Microfibrillated cellulose
MNR	look: MANR.
NaOH	Sodium hydroxide
NBR	Nitrile butadiene rubber
NFC	Nanofibrillated cellulose
NR	Natural rubber
phr	parts per hundred rubber
PCC	Precipitated calcium carbonate
PS	Precipitated silica
Q	Silicone rubber
RE	Red earth
RHA	Rice husk ash

SBR	Styrene butadiene rubber
SiO ₂	Silicon oxide, silica
Si69	Silane treatment agent
SMR	Standard Malaysian Rubber
Tan δ	Damping factor
T _g	Glass transition temperature
TiO ₂	Titanium dioxide
TS	Tensile strength
T _s	Tear strength
t'90	Optimum vulcanizing time
USD	United States dollar
WRHA	White rice husk ash
ZDBC	Zinc dibutyl dithiocarbamate
ZnO	Zinc oxide

1 INTRODUCTION

Rubber products have been used from the early ages so the knowledge and the researches have long history. Rubber technology is a very wide-ranging and extremely complex field of technology. There are numerous possibilities that we do not even know yet. As the technology develops new opportunities open also in rubber industries. Nowadays every field of technology is noting environmental issues as one of the most important fields of development. Environmental aspects need to be noted in used techniques as well as in used raw materials.

Many researches have been made to find new filler materials for rubbers and with them new improved properties or cost reductions. Especially the researches about waste materials as fillers for rubber compounds are interesting from the environmental point of view. If commercial fillers, such as carbon black, which manufacturing is dependent on oil, could be replaced even partly with waste materials, the environmental load would decrease dramatically.

In this study, first the basic rubber theory is explained so that the rest of the work could be more easily understood. Different kinds of elastomers, fillers and other ingredients are introduced as well as the processing of the rubbers. The main focus of the theoretical part is in the review of studies made about unconventional filler materials in rubbers. Different kinds of materials with different properties have been tested in various rubber compounds, but none of the studied materials have shown properties that could replace carbon black.

In the experimental part of the work the aim is to find out how selected unconventional filler materials work in a rubber compounds and possibly find some market value for them. The selected filler materials for the work were supplied by UPM. The elastomers used in the compounds are natural rubber (NR) and ethylene probylene diene rubber (EPDM). In addition, some treatments are performed to the filler materials based on the literature survey with the aim to improving the properties. All the compounds are tested with several different methods to determine whether the properties improved with the studied filler materials or not.

2 THEORETICAL BACKGROUND

In this chapter the basic theory behind the work is presented. Rubbers, additives and processing of rubbers are discussed and a small survey of other studies about unconventional rubber fillers is made.

2.1 Rubber

The official definition for rubber is elastomer that is in, or can be transformed into a stage where it is fundamentally insoluble to boiling solvent. In practice the word rubber is used to describe the material of a product or finished product such as rubber boots. [1]

The main component of rubber compounds is an elastomer. Often elastomers are also called rubbers even though they are just one of the components that are needed for the finished product. There are many different kinds of elastomers with different properties and they are often categorized as natural or synthetic rubbers or based on their usage to general-purpose and special rubbers. For a functional product, the wide range of additional ingredients needs to be compounded with the elastomer. Rubbers have a large range of properties and they can be altered with different elastomers, ingredients and their quantities in rubber compounds. In the following chapter, the most common elastomers and their properties are presented.

2.1.1 Properties

Elastomers are macromolecular substances that can rapidly return to almost its original size and shape after it has been exposed to deformation caused by tension [1]. Most of the rubbers have similar characteristics of what they are used for in technical point of view.

Rubbers have high resilience, thus they have ability to undergo relatively large deformations with almost full recovery from it even after being repeatedly stressed. This is the most important and utilized property of rubber. They have low hysteresis loss and thus they have small residual stress after stress relieving. Other great property is rubbers' ability to endure wear and corrosion. Additionally, they often have good chemical resistance and they are water and gas tight. Rubbers are also very flexible and they have large stretch ratio. Rubbers are also dielectric materials so they are good electric insulators. [1] [2]

From the common properties, it can be concluded that rubbers stretch, damp, seal, insulate, protect and attach [1]. Rubbers can be used in many applications, but the most significant field of industry is tyres.

2.1.2 Elastomers

The most commonly used elastomer is natural rubber (NR). It can be collected from several different plants, but its main source is a rubber tree, *Hevea brasiliensis*. In the tree, natural rubber is in latex form that can be used to manufacture thin products such as balloons. Usually, the latex is treated to solid dry rubber by coagulation. Dry rubber is normally specified according to its purity and is distributed to SMR (Standard Malaysian Rubber) –classes. The purest is SMR5 and SMR50 has the highest amount of impurities. [1] [2]

NR has excellent mechanical properties and good wear resistance. It works well at low temperatures but has limited service time at high temperatures. The main applications of NR are tyres, footwear, conveyer belts, and hoses. It is relatively affordable raw material. [1] In Table 2.1, there are presented some properties of the most commonly used rubbers.

The second most widely used rubber and the most widely used synthetic rubber is styrene butadiene rubber (SBR). It is the cheapest synthetic rubber and it is manufactured from styrene and butadiene by polymerization in water-emulsion. SBR is mostly used in tyre industries but also in rubber mats, footwear, conveyer belts, and other high wear applications. It is tough and has good wear resistance but low tolerance to oxidative environment, oils and solvents. [1] [2]

Polyisoprene (IR) is synthetic rubber that has almost the same properties and structure than NR and it is used also in similar applications. It can also be used in combination with NR or different rubbers. [1] [2]

Butadiene rubber (BR) is highly elastic and has good frost resistance but it is difficult to process and does not have good mechanical properties. It is normally compounded with other elastomers to enhance the elasticity or properties at low temperatures. [1] [2]

Ethylene propylene diene rubber (EPDM) is categorized as an elastomer for special use. Elastomers for special uses are little more expensive, but they still are used in large quantities in technical products. EPDM is a synthetic rubber that has excellent weather and ozone resistance. It has good wear and chemical resistance, and good heat endurance but poor resistance to oils. EPDM is known for its ability to be compounded with large amounts of fillers and oils without substantial deterioration of the properties. EPDM is used in different kind of gaskets, wire covers, and other applications that require good weather or ozone endurance. [1] [2]

Some other elastomers in the same category with EPDM, designed for special uses, are nitrile butadiene rubber (NBR), chloroprene rubber (CR) and butyl rubber (IIR). They all have their own special properties to suit best for certain applications. These rubbers are more expensive than general rubbers, but not as expensive as special rubbers. [1] [2]

Special rubbers are used for more demanding applications that need good chemical resilience or that are used at elevated temperatures. They are usually really

expensive and are only used when no other rubber has the same needed properties. Silicone rubber (Q), chlorosulfonated polyethylene rubber (CSM), fluoride rubber (FPM) and acrylic rubber (ACM) are all special rubbers having their own unique properties. [1] [2]

Table 2.1. Properties of selected rubbers [1]

Rubber	Tensile strength (MPa)	Hardness (Shore A)	Elongation at break (%)	Price index
NR	0-28	25-95	0-800	1
SBR	0-20	35-95	0-400	1
IR	0-28	25-95	0-800	1
EPDM	1-18	30-90	0-600	2
NBR	0-25	20-98	0-350	2
IIR	0-15	35-85	0-750	2
CR	0-25	15-90	0-800	2,5
Q	0-10	35-85	0-350	6-15

2.1.3 Market situation

Because rubbers are used in so many different applications, the usage of the rubbers is remarkable. Overall consumption of all rubber around the world was about 26 million metric tons in 2012 [3]. Natural rubbers consumption was little over 11 million metric tons in 2012 whereas synthetic rubber consumption was almost 15 million metric tons [3]. The consumption of natural rubber in Europe was about 1.3 million metric tons in 2012 [4]. The consumption of the rubbers continues increasing when population grows and living standards increase.

The prices of rubbers vary much depending on the rubber, the purity class of the rubber and oil price. The price of the natural rubber is at the moment (12/2013) around USD 2500 per tonne [3].

2.2 Rubber compounds

To manufacture durable rubber products to the markets, and gain desired properties for them, raw rubber needs ingredients, such as fillers, plasticizers, protective agents, and vulcanizing system to work as designed. Different materials and quantities are used for different properties. In this chapter, these other components of rubber compound are discussed.

2.2.1 Fillers

Fillers are used in rubbers to improve the mechanical properties or reduce the cost of the product. For this reason, the fillers are categorised in two groups; reinforcing and non-

reinforcing fillers. In some cases also semi-reinforcing fillers are mentioned. The purpose of the reinforcing filler is to improve the physical properties such as tensile strength, wear resistance and tear strength. The semi-reinforcing fillers also enhance the physical properties, but the effect is not as high. The non-reinforcing fillers are cheap materials and easily available. They are only used to reduce the cost of the final product and they do not affect the properties. [1] [5]. In general, it can be defined that smaller than 1 μm sized particles can act as reinforcing fillers. In Figure 2.1, there can be seen how reinforcing and non-reinforcing fillers affect the properties of the rubber compound.

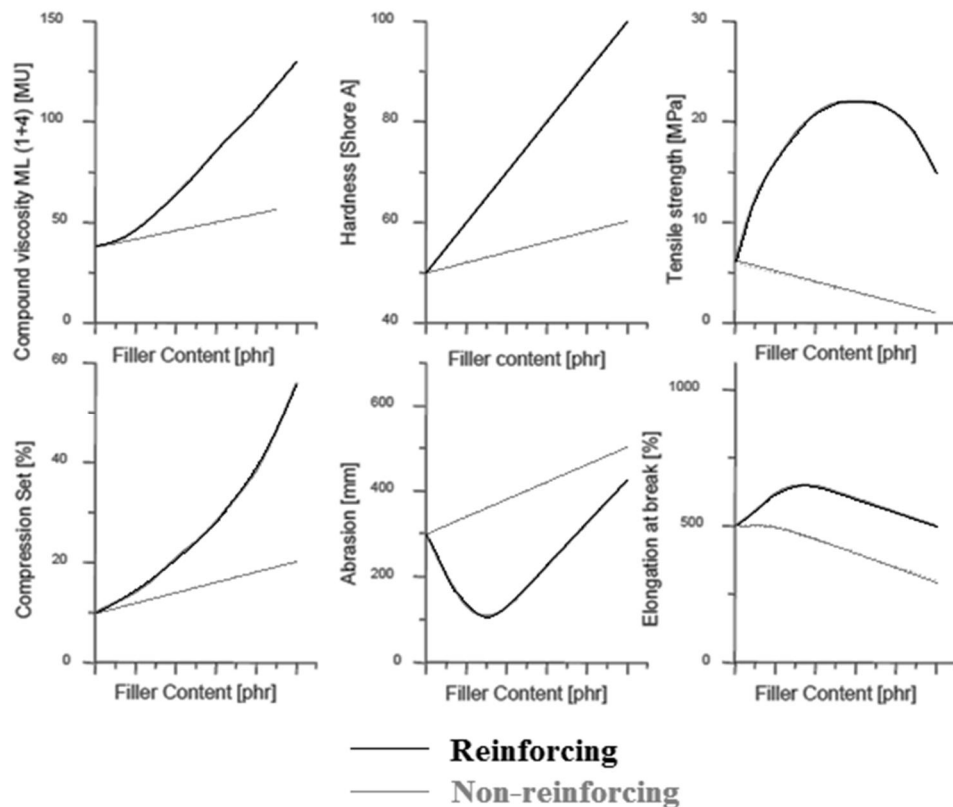


Figure 2.1. The effect of reinforcing and non-reinforcing fillers on the properties of the rubber compounds [modified: [6]]

Smaller particle sized fillers act like reinforcing fillers, and they improve the mechanical properties of the rubber compounds. Viscosity, hardness, and compression set increase almost linearly with increasing filler load, and more dramatically with reinforcing than with non-reinforcing filler. Tensile strength increases up to the point where the optimum filler load is reached and interaction with rubber matrix starts to decline. Non-reinforcing fillers decrease tensile strength from the beginning. Elongation at break increases slightly at low reinforcing filler loadings, but declines after optimum filler load is reached. Non-reinforcing fillers often reduce elongation at break. Reinforcing fillers also increase abrasion resistance up to optimum filler load.

The properties defining fillers activity are particle size, shape, structure, and surface chemistry. The smaller particle size and larger surface area means higher reinforcing effect. Generally, this kind of particle has very complex shape, having pores and cavities, due to large surface area in small particle. Surface chemistry defines how good adhesion there is between filler and rubber matrix. [1] [7] In Table 2.2, the effect of filler properties on the properties of the rubber compound is shown.

Table 2.2. *The effect of filler properties on rubber compound [8]*

Property	Particle size decrease	Structure increase	Dispersion increase	Interaction increase
300% Modulus	+	++	little	++
Tensile strength	++	little	+	+
Hardness	++	++	-	+
Elongation at break	-	-	++	-
Tear resistance	++	little	little	little
Hysteresis	++	+	-	-
Abrasion resistance	++	+	++	++

Carbon black is the most common reinforcing filler used in rubber products. Because of the colour of carbon black, most rubber products are black in colour. Carbon black is produced in controlled conditions by incomplete combustion or thermal decomposition of hydrocarbons [9]. It has high structure and there are different organic groups containing oxygen on the surface [9]. The particle size varies from 14 to 250 nm [10]. Depending on the production method and circumstances, different kind of properties can be achieved within carbon black. These different carbon black types have been classified by ASTM in standard D1765 and they are referred to N110- N990 [2]. The numbers refer to the particle size of the carbon black and the smaller number, the smaller particle size. In tyre industry N300 series carbon blacks are most commonly used and in technical product N550 is the most commonly used carbon black. When carbon black is compounded with rubbers the mechanical properties of the rubber compound are enhanced dramatically. In Table 2.3, there are presented some measured properties of carbon black filled rubbers gathered from different sources. [1] [7]

Table 2.3. Properties of CB filled rubbers

Composite	CB type	Filler content (phr)	Tensile strength (MPa)	Elongation at break %	Hardness (Shore A)	Ref.
NR-CB	N220	40	26.6	430	67	[11]
NR-CB	N330	50	27.0	650	63	[12]
NR-CB	N330	50	29.0	475	-	[13]
NR-CB	N330	50	36.3	324	67	[14]
NBR-CB	N765	50	15.3	450	55	[15]

Silica is the most used reinforcing white filler for rubbers. Two types of synthetic silica are used; precipitated and fumed silica. Precipitated silica (PS) is widely used in rubbers to enhance the mechanical properties and to act as bonding agent. They are manufactured from the solution of sodium silicate with acids. The average particle size of PS is 5 – 100 nm. Especially tear strength is improved in rubber compounds with the addition of PS. It has also challenged CB in tyre industries because its compounds have low rolling resistance. Fumed silica (FS) is produced by flame hydrolysis of silicon tetrachloride and the average particle size is 5 – 50 nm. Because of the hydrophilic nature, FS is not widely compatible with rubbers. With modifications it is possible to transfer it to hydrophobic form. FS are though used as reinforcing fillers in silicone rubbers. [1] [7]

Calcium carbonate (CaCO_3), also referred as whiting, is the most common non-reinforcing filler used in rubber industry. It is really cheap filler and therefore commonly used to lower products' costs. There are two types of CaCO_3 available, precipitated (PCC) and ground calcium carbonate (GCC). The most common manufacturing method is grinding a limestone and that is how GCC is produced. PCC is produced by precipitation from calcium hydroxide solution by carbonation. The properties of CaCO_3 vary quite much depending on the source and manufacturing method. PCC particles are smaller and they can be used as semi-reinforcing fillers in some cases. In general, CaCO_3 is non-reinforcing filler material in rubbers that is cheap and easy to process. It provides low hardness and compression set but it is not good for products that need to be in contact with acids because carbonate degrades easily to carbon dioxide in such environment. Common applications for CaCO_3 filled rubbers are different kinds of sealants. [1] [7]

Other fillers used in rubbers are for instance kaolin, talc, and barites. Kaolin is semi-reinforcing or non-reinforcing filler depending on particle size and it is also known as china clay. Calcinated kaolin is important filler in rubbery cable applications because it has good electric insulation properties. Particle size of talc varies and thus in some cases it can work as semi-reinforcing filler. It reduces air permeability of rubber compounds due to its laminar nature and eases the processability. Barite (BaSO_4) is mineral that can be found in limestone or clays. Barites are often used to increase the weight for example in sound insulating applications or in applications that require very

high chemical resistance. [1] [7] In Table 2.4, there are some properties of different fillers in rubbers gathered from different sources.

Table 2.4. Properties of rubbers with different fillers

Composite	Type of filler	Filler content (phr)	Tensile strength (MPa)	Elongation at break %	Hardness (Shore A)	Ref.
NR-silica	precipitated	10	23	1000	45	[12]
NR-silica	precipitated	10	22	869	41	[16]
NR-silica	precipitated	40	24	711	63	[16]
NR-silica	Hisil 233	50	29	690	-	[13]
NR-CaCO ₃	Silver W	10	11.4	616	-	[17]
NR-CaCO ₃	Silver W	40	11	579	-	[17]
NR-CaCO ₃	Kulu 5	50	18	650	48	[18]
NR-CaCO ₃	Kulu 5	100	9.5	550	55	[18]
NR-kaolin		50	19	600	49	[18]
NR-kaolin		100	14	410	55	[18]

2.2.2 Plasticizers

Plasticizers are used to make processing of rubber easier and lowering the viscosity. In addition, they reduce the hardness and the modulus of the rubber. Plasticizers are also called as softening agents. It depends on the used matrix elastomer and the wanted properties of final product which type of plasticizer should be used. [1] [7]

Mineral oils, different synthetic plasticizers such as phthalates and vegetable oils can be used as plasticizers [1]. The most commonly used plasticizers are mineral oils and they can be divided in paraffinic, naphthenic, and aromatic oils. Paraffinic oils are used with non-polar rubbers such as EPDM and IIR. Naphthenic oils are relatively affordable and they are widely compatible with non-polar and slightly polar rubbers. They are thus used as general-purpose plasticizers. Aromatic oils are cost effective and they are used with general-purpose rubbers such as NR and SBR. They are highly staining and dark in colour. The use of aromatic oils is reduced and they are tried to be replaced with other, not as harmful oils. [1] [7]

2.2.3 Protective agents

Because of the organic nature of rubbers, their properties are weakened by ozone, oxygen, light, ultraviolet light, and heat. This weakening of the properties is called aging. The product gets, depending on the rubber, for example more brittle and hard or softer and sticky. It depends on the used elastomer, filler system, vulcanizing system, product size and shape, environment, and many other different factors how the rubber

age. In general, the more rubber has free double bonds the more easily it reacts with different factors and the more easily it is aged. [1] [5]

Protective agents are used in rubber products to make them more durable to these kinds of environmental factors. Different protective agents have different effect against different factors and often several protective agents are therefore needed. Moreover, all rubbers react differently, some easier than others, to these factors, so different rubbers need different kinds of protective agents in various quantities. Some rubbers, e.g., EPDM have good weather resistance on its one and thus protective agents are needed less. [1]

The protective agents can be compounded into the rubber or they can be applied only on to the surface of the product like protective waxes. Antioxidants are used to prevent oxidation and the most typical antioxidants are amine derivatives, imidazoles and hydroquinoline [1]. Some of these chemicals also protect rubbers against ozone and are called antiozonants.

2.2.4 Vulcanizing agents

Vulcanizing of rubbers means a heat and pressure treatment of rubber with vulcanizing agents which bind rubbers molecule chains to each other in a controlled way. With this treatment, a netlike structure is formed due to the cross-linking of the elastomer. After vulcanizing process, the rubber product reaches its final properties [1].

Most common vulcanizing system is sulphur-based system. Sulphur vulcanization is a slow process and to make vulcanizing more efficient, activators and accelerators are used. Accelerators speed up the vulcanization process and make it more suitable for industrial production. In some cases, retarders or pre-vulcanization inhibitors are used to lengthen the curing time if for example more time is needed for moulding. Accelerators need activators to start working. The most commonly used activators are zinc oxide (ZnO) and stearic acid. [1] [7] [5]

Other common vulcanizing agents are peroxides and metal oxides. These are less used vulcanizing systems that are mostly used with rubbers that cannot be vulcanized with sulphur, or if sulphur is not wanted in the final product. [1] [7] [5]

2.2.5 Others

Other ingredients in rubber compounds are used to gain wanted specific properties. Generally used ingredients are peptizing agents, dispersing agents, resins, expansive agents, odours, colours, fire retardants, vulcanizing inhibitors, coupling agents, mould lubricants, and glues [1]. It depends on the product what properties and therefore ingredients are needed.

Peptizing agents are used to promote degradation and dispersing agents are used to promote dispersion. Resins improve the tack of the rubber and facilitate the compounding. Expansive agents are used when cellular rubbers are manufactured.

Rubbers tend to burn really easily if it is ignited and for this fire retardants are needed. They prevent the burning after ignition. [1]

2.3 Processing of rubbers

Components of rubber are presented in a recipe where all ingredients and their quantities are mentioned as parts per hundred rubber (phr). This means that elastomer quantity is marked as 100 units and it can contain more than one elastomer. After this other ingredients are marked as units compared to 100 units of elastomer. From this kind of recipe, the weights of all ingredients can easily be calculated and measured throughout the world to match the wanted overall weight of the compound.

The basic procedure of processing of rubbers starts with weighting the ingredients. Then they are mixed together, shaped and vulcanized. After this, some finishing such as removal of burrs can be done if necessary. In Figure 2.2, the basic process scheme is presented.

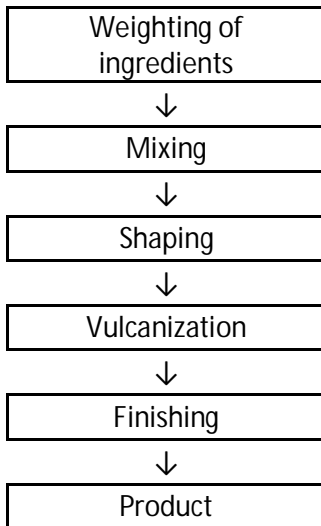


Figure 2.2. Processing scheme of rubbers

2.3.1 Mixing

After all the ingredients have been selected and measured they are mixed together as a homogenous mass. Mixing of rubber is a complex and challenging process that demands great knowledge to perform well. Firstly, the natural rubber needs to be masticated so that its viscosity is at wanted level. Mastication means cutting the polymer chains shorter with a result of decrease in viscosity. With synthetic rubbers, this phase is not needed, because their viscosity can be altered during polymerization. [1]

Secondly, the mixing of the ingredients creates homogenous mass where the wanted physical and chemical properties of the compound are achieved. During the mixing, three different processes occur simultaneously. Additive mixing combines the

originally separate ingredients together in one solid mass. Dispersive mixing breaks the components into smaller particles and makes mixing easier. This also decreases the viscosity of the mass. Distributive mixing divides the particles evenly throughout the matrix without breaking them. The blending is accomplished with shear forces that modify the mass by stretching. [1]

The most important influencing parameters of rubber compounding are recipe, batch size, fill factor, temperature, rotor speed, ram pressure, and cooling of the compound. The most important factor for successful compound is the right amount of the ingredients. If there are incorrectly weighted ingredients, the final properties will not be as designed. [1]

The mixing of the compounds can be performed in different orders and in one or multiple steps depending on the desired properties or used ingredients. If the mixing is performed in one stage, all the ingredients are mixed together during one mixing. In multiple pass mixing, the ingredients are mixed together in two or more stages. Usually, vulcanizing agents are mixed in separate mixing section to make sure that the temperature does not rise too much and start the vulcanizing process. The mixing order of all the ingredients can also be altered. In Figure 2.3, there are presented the most commonly used mixing sequences. [1] [19] [7]

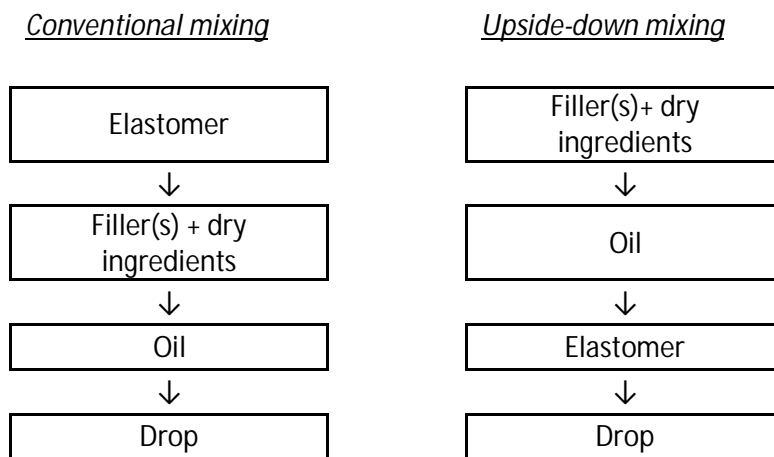


Figure 2.3. Different mixing orders of rubber compounds

In the conventional mixing method, the elastomer is added to the mixer first and masticated if needed. After this, fillers are added followed by plasticizers. The last ingredients added are vulcanizing agents. In the *upside-down* method, the elastomer is added last. This mixing method is commonly used for rubbers having high fillers contents, such as EPDM and IIR. [1] [19]

Mixing can be performed with many various machines such as open two-roll mills, internal mixers and continuous mixers. The two-roll mill has two cylinders rotating quite slowly in different directions near to each other. The distance between the cylinders and their temperature can be adjusted. Same size cylinders usually rotate in different speeds to create friction. Also different sized cylinders can be used if the same

speed is required. Either way created friction is called friction rate and usually this can be altered depending on the rubber blend. Open two-roll mills come in various sizes up to two meters long and 65 cm in diameter. Open two-roll mills are used when easy cleaning is needed, the batch size is relatively small and long mixing times are not an issue. [1] [20]

The internal mixer is used for larger batch sizes and it is easily automated. Like the name of the mixer already indicates, there is a closed chamber where the mixing takes place. Ingredients are fed to the chamber through a hopper where specially designed rotors mix them to homogenous mass. The chamber is closed by a ram and at the bottom of the chamber there is a bottom gate where the mixed mass can be dropped off. All parts of the mixer that are in contact with the rubber compound can be temperature controlled. There are two main types of internal mixers, Banbury mixer and intermeshing mixer. In the Banbury mixer, the dispersive mixing happens between the rotor and the chamber wall, when in the intermeshing mixer it happens between the rotors. [1]

Continuous mixing is well known in polymer industry and it can also be used with rubber products to create continuous products. It is also called extrusion. The principle is that material is fed from the other end and finished compound or product comes out from the other end continuously. This mixing process is suitable only a few special types of compound. [1] [19]

2.3.2 Shaping

When the ingredients have been mixed together as homogenous mass, it needs to be given its form. The shaping technique depends on the product that is being manufactured. The most common shaping technique in rubber industry is moulding. Others widely used methods are extrusion and calandering. [1]

With moulding, the products are usually very dimensionally accurate. Products manufactured with moulding include e.g., sealant rings. Car tyres are also shaped in moulds. With extrusion, continuous products can be manufactured. Calandering is used to create thin sheets and to coat fabrics with rubber. [1]

2.3.3 Vulcanization

When the shape of the product is accomplished, vulcanization can get started. Depending on the products shape and size, vulcanization can be performed in various ways either with cyclic or continuous method. The most common method is the vulcanization in mould which is a cyclic method. Other methods include autoclave, hot air, salt bath, microwave, radioactive, and infrared vulcanizing. [1]

3 ALTERNATIVE FILLER MATERIALS

To find rubber products with better properties such as mechanical, electrical, thermal, optical or processing properties with less cost new filler materials are studied. The environmental issues are also highlighted in many cases and it is nowadays a great deal to find new ways to use waste materials.

The environmental load can be reduced in two ways by substituting commercial fillers with these otherwise waste materials. Firstly, the amount of waste in landfills is reduced when these wastes can be utilized elsewhere. Secondly, the amount of virgin filler materials is reduced and non-renewable natural resources are used less.

Alternative filler materials in rubber products are widely studied. In literature, there have been reported more than 100 different reinforcing materials, but only a few of them has been commercialized and used extensively [21]. In the studies, there have been used various types of matrix rubbers and also different kinds of surface treatments which make the comparison of the results difficult. In this chapter, wide range of studies of unconventional filler materials with different rubber matrixes are investigated and summarized.

3.1 Ash

Ash is a dust-like residue left over from burning of some organic matter. Ash can be formed in many various industrial processes and their consistency can vary significantly. The most common ashes studied as fillers in rubbers are fly ash and rice husk ash.

In this chapter, different kinds of studies about ashes as rubber fillers are discussed. Different kinds of rubbers, such as NR, SBR, EBDM, and NBR, were used as matrix material. Also various surface treatments for ashes had been used to enhance the properties.

3.1.1 Fly ash

Fly ash is a waste product from thermal power stations and it is generated when pulverised coal is burned [22]. The most of the produced fly ash is disposed off as landfill which has caused problems. Fly ash is considered to be a pollutant and it causes a hazard to the environment. For this reason, many researchers have tried to find alternative applications for utilization of fly ash, construction being the most common field of study. [23]

The major chemical component of fly ash is silica (SiO_2). Other components worth of mentioning are alumina, variety of inorganic oxides, and sometimes unburned carbon. Their occurrence and concentrations vary depending on the source of the fly ash, but usually they contain about 50 % of silica. Particle size of fly ash can also have a large scale, varying from 2 μm to over 100 μm . [24] [25] [26] [16]

Natural rubber filled with fly ash has been studied by several researchers and most of the studies have some sort of treatment made for the ash [25] [16] [27] [28] [29] [18]. Without any property improving treatments, it can be noted that fly ash does not have a significant effect on the mechanical properties of rubber, due to its large particle size, and thus it works more like a cost reducing filler. This has also been observed by Alkadasi et al. [24].

Zhang et al. [30] studied different kinds of surface treatments for fly ash and their effect on natural rubber products. They used titanate (N-101), liquid paraffin, silane, aluminate and stearic acid to modify the surface properties so that it would interact more with rubber matrix. The results indicated that the best reinforcing effect in rubber, with this kind of fly ash, was achieved with titanate coupling agent treatment.

Fly ashes consist mostly of silica and for that reason numerous studies have been made about silane treated ashes. Silane coupling agents facilitate the dispersion of the filler particles into rubber matrix, which otherwise could react with accelerators and cause longer cure times [27]. Silane coupling agents improve adhesion between the mineral filler and the rubber matrix with chemical bonds and therefore improve mechanical strength along with chemical resistance of the composite [24].

Some studies have also used parts separated from the ash, such as alumina silicate by aerodynamic classification, which are used separately as filler. Kruger et al. [18] investigated how these spherical alumina silicates work in natural rubber matrix. Results indicated that spheres recovered from fly ash reduce the viscosity of natural rubber but did not affect the curing time. Physical properties were comparable with rubber compounds filled with calcium carbonate or whiting. [18]

In overall, fly ash can be considered mostly as cost reducing filler. Surface treatments enhanced the properties, but they still are poor compared to carbon black. In Table 3.1, values of some measured properties of different rubbers filled with fly ash are gathered together from varies researches. The best results can be achieved with partial replacement of commercial filler by surface treated fly ash. Some properties, such as cure time, maximum torque, and mechanical properties can be enhanced with this replacement and most importantly the cost of the product decreases [26].

Table 3.1. Properties of fly ash filled rubbers

Rubber/ filler load	Treat ment	Cure time (min)	Scorch time (min)	Max torque (dNm)	Tensile Strength (MPa)	Elongation at break (%)	Hardness (Shore A)	Ref.
NR		5.1		44.06	24	750	40	[18]
NR/ 30phr +50phr CB	Silane				15.3	460	48	[30]
NR/30phr +50phr CB	Alumi nate				17.7	607	46	[30]
NR/30phr +50phr CB	N-101				23,1	512	56	[30]
NR/30phr	Silane	5.3			17.6	782	45.5	[16]
NR/50phr		5.0	2.2	51.97	17.5	650	50	[18]
NR/100phr		5.0	2.5	51.97	10	600	55	[18]
NR/120phr	Silane	4.9			10.4	527	59	[16]
NR/130phr		4		14	5	500	55	[25]
NR/150phr		4.9	2.2	70.1	5.5	500	65	[18]

3.1.2 Rice husk ash

Rice husk ash (RHA) is a waste product from electrical power plants, where rice husks are burned to generate energy, and it primarily consists of amorphous silica and residual carbon black [31]. There are two different types of rice husk ash, white rice husk ash (WRHA) which consists around 96 % of silica and black rice husk ash (BRHA) which has lower silica content, around 54 % [32]. The type of rice husk ash depends on burning process and the amount of left over carbon black. Particle size varies from 2 μm to 36 μm , average size being around 5 μm .

Costa et al. [33] compared the processability of WRHA and BRHA compounded with NR to two commercial fillers, silica and carbon black. The results showed that the properties with WRHA were better and closer to results with carbon black than with BRHA. Figure 3.1, shows the maximum torque values at 150°C with different filler loading of tested fillers. The maximum torque of unfilled natural rubber was in this case measured to be 41.6 dNm. The figure shows that the properties of WRHA and BRHA can be compared to the properties of silica, but not to carbon black. Higher filler loadings increased also maximum torque. The curing times of both ash compounds were

very similar with CB compound. WRHA illustrated the shortest cure times and with increasing filler loadings, the cure time decreased.

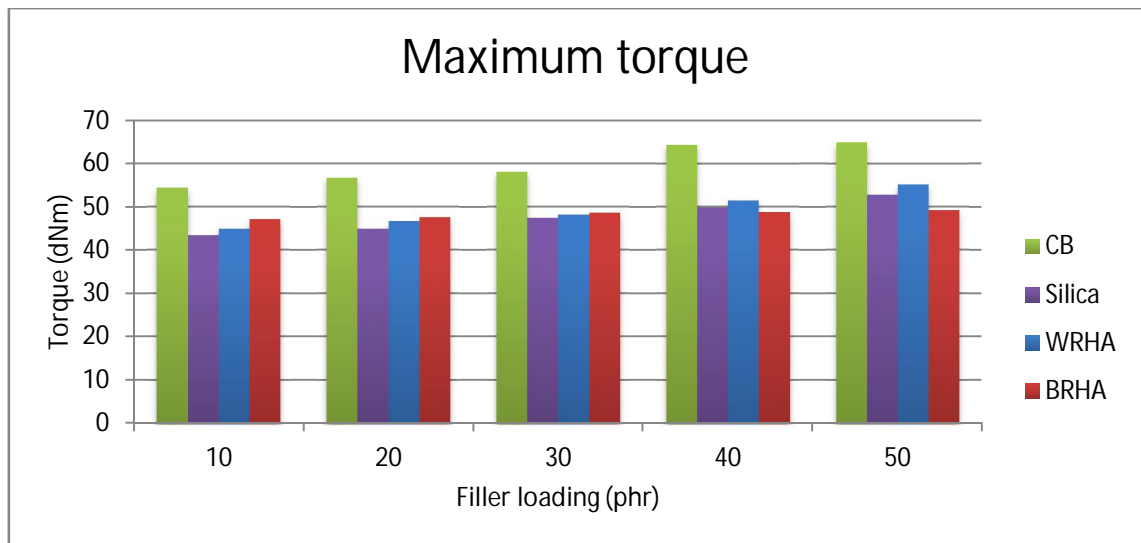


Figure 3.1. Maximum torque values of NR with different fillers at 150°C [33]

The influence of RHA on mechanical properties of NR was studied by Arayapraneet et al. [31]. They noticed that RHA increased hardness but decreased viscosity, tensile and tear strength compared to pure NR. Compared to compounds with CB as filler, all the values were lower. In addition, RHA shortened curing times compared to pure NR, but the trend was similar to curing times of the compounds containing CB.

WRHA with mean particle size of 5.4 μm was compounded with NR at different filler loadings. Elongation at break, tensile and tear strength decreased while hardness increased with increasing filler loadings. Compared to pure NR, the tensile and tear strength though were noted to have higher values with filler loads of 10 and 20 phr. Silane coupling agent was noted to increase the cure rate and improve the mechanical properties of natural rubber filled with WRHA. Also multifunctional additive (diamine salt of fatty acid of general structure), MFA, was noted to improve same properties. [32]

In overall, it can be concluded that RHA does not work as a reinforcing filler, even though it improved some mechanical properties slightly compared to pure NR and the properties could be enhanced with suitable treatments. If the properties are compared to CB filled rubbers, the mechanical properties are weaker. Small amounts of RHA could be used as cost reducing filler and in applications where mechanical properties are not the main criteria.

3.1.3 Other ashes

Bagasse fibre ash is a waste product from combusting of bagasse. The ash is mostly composed of silica and particle size range from 45 μm to 150 μm . It was found out that

with bagasse fibre ash the tensile strength of rubber compounds was lower compared to precipitated silica and carbon black filled rubbers. This was due to the poor dispersion level of the ash and an aggregation of silica particles. Better results were achieved when commercial fillers were partly replaced by bagasse fibre ash. When the amount of bagasse fibre ash did not exceed 15 phr and 75 % of all filler material it was shown that there was no significant effect on the mechanical properties. [34]

Oil palm ash is considered as waste that comes from combustion of oil palms. A few studies have investigated its properties in natural rubber. Ooi et al. [35] found that scorch and cure times decreased with increasing oil palm ash loadings whereas cure rate index increased. Maximum torque, tensile strength, and hardness increased with increasing filler loadings compared to pure natural rubber. The tensile strength of the reference compound with no filler was 21.8 MPa and the highest value achieved with oil palm ash was 25.2 MPa with optimum filler content of 1 phr. The investigated filler loads were from 0.5 to 9 phr.

In their other work Ooi et al. [12] compared the properties of oil palms ash filled rubber to rubbers filled with commercial filler, silica and carbon black. The results indicate that the properties of oil palm ash are comparable with precipitated silica. Figure 3.2, illustrates the mechanical properties of pure natural rubber, oil palm ash, silica, and carbon black filled rubber. The contents of the fillers were quite different and they were determined to be optimum loadings, with oil palm ash only 1 phr, silica 10 phr and carbon black 50 phr. The highest tensile strength was measured with carbon black, and it was 26 MPa. Tensile strength of oil palm ash was 25 MPa and silica 23 MPa. Elongation at break was increased with oil palm ash whereas silica and carbon black reduced it compared to pure natural rubber. With oil palm ash the hardness did not change much compared to NR (around 40 ShoreA), whereas the hardness of carbon black was around 65 ShoreA.

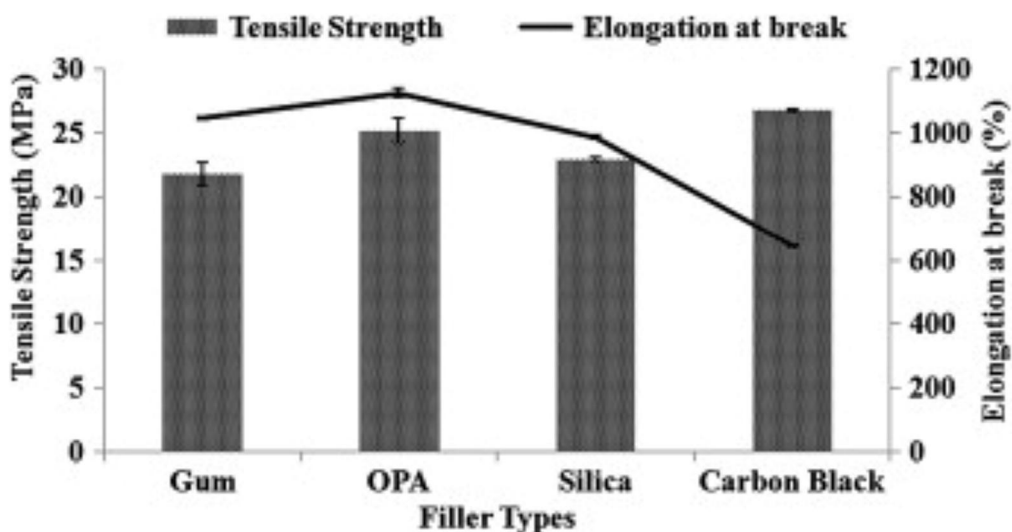


Figure 3.2. Mechanical properties of NR filled with different fillers [12]

3.2 Sludge

Sludge can be defined as a mixture of solid particles in a liquid matrix. The size of the solid particles is not defined and the texture of the sludge can vary much. The word can be used to describe many kinds of liquid matters with different kind of solid substance such as mud, slime, sewage, or paper sludge. It is usually a by-product of different industrial processes.

In this chapter, different kinds of sludges tested as filler for rubber are discussed. Natural rubber is used as matrix elastomer in the compounds. Also chemically treated rubbers such maleic anhydride grafted and epoxidized natural rubber are used in the studies.

3.2.1 Paper sludge

Paper sludge is a by-product of pulp and paper industries and is mostly composed of cellulosic and inorganic materials [36]. It must be dried and ground before the use as a filler in rubber products. With different sieves, the particle size can be obtained constant, even if the size varies a lot from 63 μm to 300 μm . The particle size is relatively large for being reinforcing filler.

Ismail et al. [37] studied paper sludge filled natural rubber at different filler loadings and with and without maleic anhydride grafted natural rubber (MANR). MANR was added to the compound in small amount, 5 phr, and it acted as a coupling agent. Results showed that with increasing filler loadings, the scorch and cure time decreased, but maximum torque, viscosity and tan delta increased. The mechanical properties such as tensile strength and elongation at break decreased with increasing filler loadings whereas tensile modulus increased. With addition of MANR to the compound the rubber filler interaction improved, and thus curing and scorch time was extended and tensile properties enhanced. Viscous torque and tan delta values decreased, but for maximum torque values there were no effect noted with the addition of MANR.

In the other research, Ismail et al. [38] studied how replacement of commercial fillers, carbon black and silica, by paper sludge affect the properties of natural rubber composites. They tested pure paper sludge, silica and carbon black with a quantity of 30 phr. Different mixtures of fillers were also tested with quantities of 20 phr paper sludge with 10phr carbon black and 10 phr paper sludge with 20 phr carbon black. Same mixtures were tested with silica. Cure and scorch times were significantly higher with silica than with carbon black and paper sludge. Incorporating paper sludge with silica the curing times were decreased, but with carbon black there was not much change in the curing times. Paper sludge had the lowest maximum torque, thus it increased when carbon black or silica were incorporated. With decreasing loading of paper sludge and increasing loading of carbon black, the tensile strength, modulus, and elongation at break increased. Silica did not have the same effect when its quantity increased. Fatigue

life decreased with both commercial fillers with increasing paper sludge replacement loads.

Ismail et al. [39] also studied the fatigue life properties of paper sludge filled epoxidized natural rubber (ENR) and maleated natural rubber (MANR) with different filler loadings. It was noted that ENR-paper sludge composite had better fatigue life than non-epoxidized natural rubber. Incorporating MANR to ENR/paper sludge composite the fatigue life increased even more. Higher fatigue life is due to better interaction between rubber matrix and paper sludge filler.

Results from these studies indicate that paper sludge is not a reinforcing filler on its own, but it can be used to reduce cost together with commercial fillers in some less demanding applications. With different kinds of additives and treatments the properties of the composite can be enhanced.

3.2.2 Marble sludge

Marble sludge is a by-product from marble processing industries where the marble stones are cut and polished. Before the sludge can be used as filler, it needs to be dried, ground and sieved to a constant particle size. The studied particle sizes varied from 10 μm to 75 μm . Marble powders' main component is calcium carbonate. In addition, it contains magnesium carbonate and small quantities of silicates and metal oxides. [40]

Ahmed et al. [40] tested marble sludge as filler for natural rubber with different particle sizes and different filler loadings. In Figure 3.3, there is a graph from collected values that shows how tensile strength changes with different filler loadings with different particle sizes. It can be noted that tensile strength increases with all particle sizes with increasing filler loadings until 70 phr filler load and decreases after that. It can also be noted that particle size has little effect on the tensile strength. In the work [40] the results of tear strength followed similar trend and the maximum tear strength, 24 N/mm, is obtained with 10 μm particle size and 70 phr filler loading. Elongation at break was reduced with increasing marble sludge loading, whereas hardness and stress at 100%, 200%, and 300% elongation increased. Resilience and swelling ratio decreased and compression set, abrasion loss, shear modulus, and chemical cross-link density increased with higher filler loads.

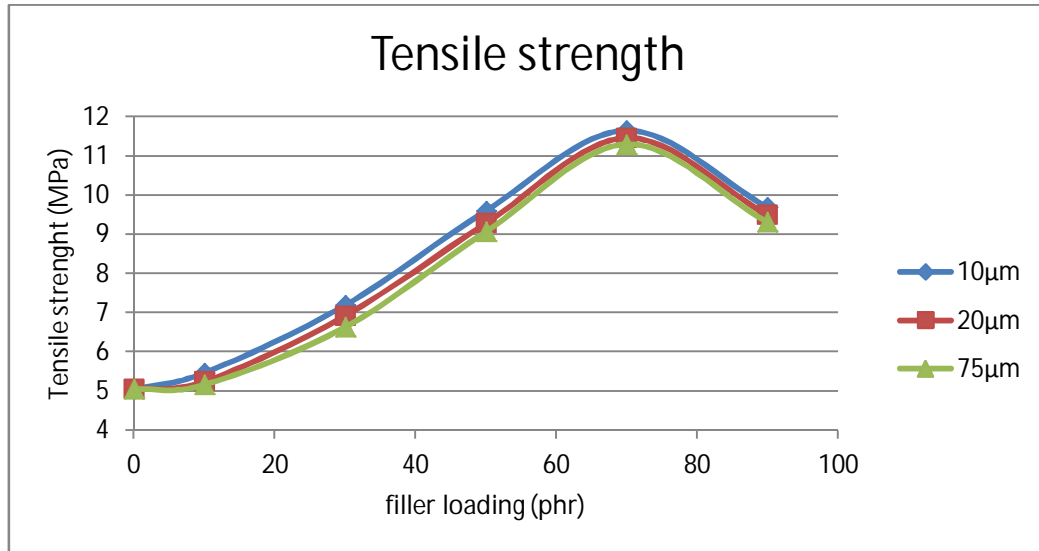


Figure 3.3. Tensile strengths of marble sludge filled NR with different filler loadings and particle sizes [40]

In other study Ahmed et al. [41] partially substituted marble sludge by carbon black and rice husk derived silica and used these mixtures as filler in natural rubber. Results indicate that replacing some of the marble sludge with either carbon black or with silica, tensile strength, modulus, tear strength and hardness increases. From these studies, it can be concluded that marble sludge could be used as non-reinforcing filler for rubbers or it could be used as co-filler with commercial fillers for better properties. With smaller particle size better reinforcing properties could be achieved.

3.3 Lignin

Lignin is natural polymer that can be found in plants where it acts as stabilizer against mechanical, environmental and biochemical stresses [11]. It is a three-dimensional amorphous polymer and is composed of phenyl propane units with carbonyl, hydroxyl and methoxyl substitutions. Lignin is mostly obtained from pulp and paper industries and it is often used as fuel for the process. The most common pulp processes are sulphite process producing sulphite lignin, and kraft process that produce thioglignin. Also sulphur-free lignin can be obtained from, for example, the Organocell and Alcell processes. [42]. Also soda pulping process can be used to produce soda lignin [43].

Botros et al. [43] studied how soda lignin and thioglignin affected the properties of natural rubber composites. The results showed that with both lignins the cure and scorch times were shorter and maximum torque higher compared to pure natural rubber. Tensile strength and elongation at break were lower with lignin filled natural rubber, but both lignin composites had better thermal stability than pure natural rubber. Thioglignin had the best thermal stability with filler loading of 20 phr.

Kosiková et al. [42] studied the effect of sulphur-free lignin filled natural rubber. Unlike soda and thioglignin, sulphur-free lignin improved the mechanical properties and

had minor effect on the cure characteristics, compared with unfilled natural rubber. Tensile strength, 100% modulus, and elongation at break increased significantly with addition of lignin, but it had just slight effect on hardness. In Figure 3.4, there are presented some mechanical properties as a function of filler load. In the study, the tensile strength of pure natural rubber was measured to be less than 2 MPa, which normally is around 20 MPa [44]. The tested pure NR was vulcanized in 150°C and 20 MPa for 9.5 minutes.

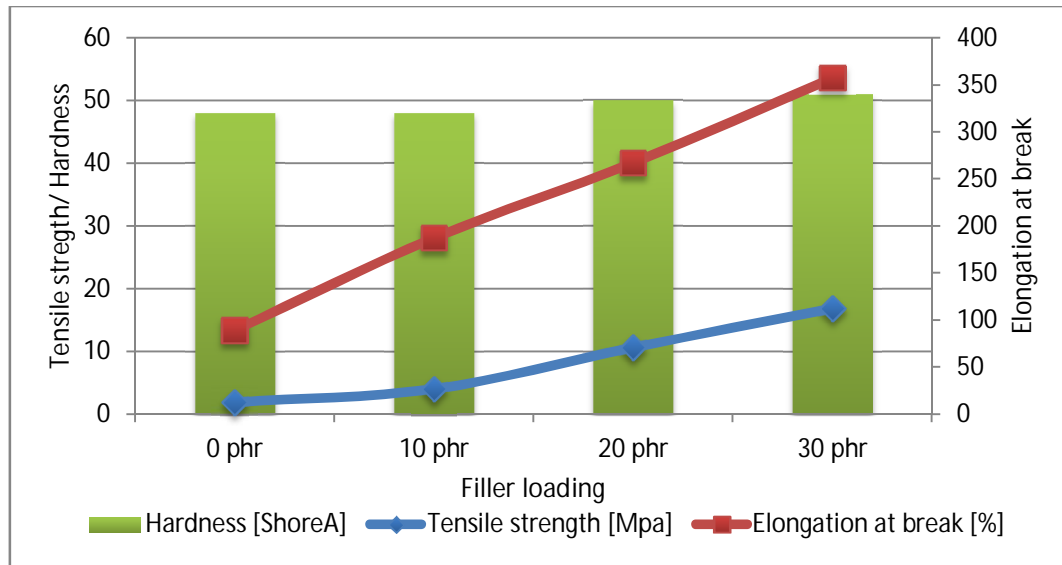


Figure 3.4. Mechanical properties of lignin filled NR with different filler loadings [42]

With styrene butadiene rubber (SBR) sulphur-free lignin was found to be dispersible in the rubber by dry mixing and it did have effect on the cure characteristics [45]. In their other study, Kosiková et al. [45] tested the properties of sulphur-free lignin in SBR and noted that the addition of lignin increased cure time but scorch time started to decrease above 5 phr lignin. Tensile strength was measured to be highest, around 5 MPa, with filler load of 60 phr when pure SBR was measured to be around 2.5 MPa. Elongation at break was highest with filler loading of 50 phr, around 250%.

Gregorova et al. [11] studied the stabilizing effect of lignin in carbon black filled natural rubber composites. They compared small lignin loadings to commercial antioxidant known as IPPD (*N*-phenyl-*N*-isopropyl-*p*-phenylene diamine). All the compounds had 40 phr of carbon black and the lignin and IPPD amount was varied. The results indicated that lignin had little effect on the cure characteristics and mechanical properties. The cure time was increased with lignin loading of 2 phr by half a minute and with other compounds decreased less than that. Tensile strength was slightly decreased with all lignin compounds and the difference was largest, 2.8 MPa, with compound that had lignin 4 phr. Measured value for reference was 26.6 MPa. Lignin did though act as antioxidant during thermal aging of carbon black filled natural rubber

composite but not quite efficiently than IPPD. There is still potential for lignin as antioxidant in natural rubber and carbon black composites.

Lignin can also be used to enhance other fillers' properties. Xiao et al. [46] used lignin to enhance the dispersion of layered double hydroxide (LDH) to SBR matrix. The complex of lignin and LDH was synthesized by *in situ* method and compounded with SBR. LDH content was kept constant, 30 phr with all the compounds. The results showed that combining lignin with LDH enhanced mechanical properties of the rubber composites significantly. Tensile strength, elongation at break, 300% modulus, and hardness increased with increasing lignin loading. At the highest lignin loading, 15 phr lignin, tensile strength was 10.9 MPa whereas without lignin it was 4.0 MPa. Moreover, the cure time and maximum torque increased with increasing lignin loading but scorch time decreased. Compared to pure SBR all the compounds had lower cure and scorch times. [46]

Setua et al. [15] incorporated benzoyl peroxide modified lignin powder and hexamine into nitrile rubber (NBR) and compared the results with pure NBR, unmodified lignin and carbon black. Both, lignin and modified lignin, made the rubber compound harder compared to pure and carbon black filled NBR, but the mechanical properties were measured to decrease with both lignins. The properties of modified lignin were slightly higher than with unmodified lignin. In addition, modified lignin had improving effect on the thermal stability compared to carbon black. Also resistance to oil and fuel was noted to be better with lignin composites than with pure or carbon black filler NBR.

3.4 Cellulose

Cellulose is a biopolymer, linear homopolysaccharide, and it is the main building component of wood. Cellulose fibres are composed of smaller fibres called microfibrils which have amorphous and crystalline parts. Depending on the separation technique mainly two different types of nanocellulose can be created, microfibrillated or crystalline cellulose. [47]

In this chapter, celluloses used in rubber compounds are discussed. Many studies have compounded cellulose fillers with latex form natural rubber. It is possibly easier to process rubber and cellulose fillers in that way, but the results are not comparable with other materials compounded with bulk NR.

3.4.1 Microfibrillated cellulose (Biofibrils)

Microfibrillated cellulose (MFC) is created from cellulose fibres with mechanical treatment where cellulose fibres are grounded to smaller fibres. Depending on the application, they can be used to make products tougher, lighter or thinner [48]. It has several names in literature such as fibril cellulose, cellulose microfibril, microfibrillar cellulose, and nanofibrillated cellulose (NFC). Dimensions of MFC range from 20 to 60

nm in diameter and several micrometers in length. It has both amorphous and crystalline parts and it presents a web-like structure. [47]

Researchers have studied MFC with unvulcanised and vulcanized natural rubber latex [49] [50] [51] [52]. The results of both compounds show that MFC increased mechanical properties. Table 3.2, shows gathered results from different articles. It was also noted that with nanoparticles addition, the stiffness increased above glass transition temperature [50]. Visakh et al. [51] discovered that MFC decreased the uptake of aromatic solvents of natural rubber composites even at low concentrations.

Table 3.2. Properties of NR with different loadings of MFC

Rubber +filler content	Tensile strength (MPa)	Young modulus (MPa)	Elongation at break (%)	Vulcanized/unvulcanized	Ref.
NR	0.56	0.5	576	unvulcanized	[49]
NR	1.6	1.3	912	vulcanized	[52]
NR-MFC 1% wt	0.7	1.27	209	unvulcanized	[50]
NR-MFC 2.5% wt	3.1	2.7	477	unvulcanized	[52]
NR-MFC 5% wt	4.2	3.8	325	unvulcanized	[52]
NR-MFC 5% wt	2.17	35.46	13.8	unvulcanized	[50]
NR-MFC 6% wt	2.3	102	5.9	unvulcanized	[49]
NR-MFC 7.5% wt	6.6	5.7	205	unvulcanized	[52]
NR-MFC 10% wt	5.99	172	6.65	unvulcanized	[50]
NR-MFC 15% wt	6.26	233	3.95	unvulcanized	[50]
NR-MFC 10% wt	9.1	7.2	101	unvulcanized	[52]
NR-MFC 2.5% wt	5.2	4.2	576	vulcanized	[52]
NR-MFC 5% wt	6.8	6.3	413	vulcanized	[52]
NR-MFC 7.5% wt	9.8	8.1	275	vulcanized	[52]
NR-MFC 10% wt	12.2	9.6	144	vulcanized	[52]

3.4.2 Crystalline Cellulose

Crystalline cellulose, also referred as cellulose nanocrystals (CNC), nanocrystalline cellulose, cellulose whiskers, cellulose microcrystallites, microcrystals, microfibrils, or rod-like colloidal particles, are obtained from cellulose fibres by chemical treatment. The main process of treatments is based on strong acid hydrolysis which attacks the amorphous parts of the cellulose, leaving only the more resistant crystalline parts left. [47] Typically the length of CNC particles is around 200-400 nm [50].

Many researchers have studied the properties of CNC incorporated with NR latex [49] [50] [51] [53]. Like MFC, also CNC had improving effect on the mechanical properties of natural rubber composites. In Table 3.3, there are results collected from different studies. Crystalline cellulose composites were also discovered to decrease aromatic solvent uptake [51] and increase stiffness above glass transition temperature [50] just like MFC, but not as effectively. Visakh et al. [53] found out that no microscaled aggregation occurred with dispersion of CNC in natural rubber. Mechanical properties increased with increasing filler loadings and also thermal stability increased, indicating good filler-rubber interaction.

Table 3.3. Properties of NR with different loadings of CNC

Rubber +filler content	Tensile strength (MPa)	Young modulus (MPa)	Elongation at break (%)	Vulcanized/unvulcanized	Ref.
NR	0.56	0.5	576	unvulcanized	[49]
NR	9.2	1.7	554	vulcanized	[53]
NR-CNC 1% wt	0.86	1.7	408	unvulcanized	[50]
NR-CNC 5% wt	2.71	8.4	231	unvulcanized	[50]
NR-CNC 6% wt	5.1	109	364	unvulcanized	[49]
NR-CNC 10% wt	8.93	118	16	unvulcanized	[50]
NR-CNC 15% wt	12.15	187	14	unvulcanized	[50]
NR-CNC 2.5% wt	14	2.6	539	vulcanized	[53]
NR-CNC 5% wt	14.5	3.0	477	vulcanized	[53]
NR-CNC 10% wt	17.3	3.8	455	vulcanized	[53]

3.5 Wood flour

Wood flour is lignocellulosic material composed of small wood fibres [54]. Depending on the grinding and sieving, the fibre length varies from 75 μm to 1 mm.

It has been noted [54] [55] [56] [57] that with increasing wood flour loadings tensile strength and elongation at break decrease but tensile modulus and hardness increase regardless of the matrix rubber used. For these observations, unmodified wood flour can be ascribed as inert rubber filler [57]. The cure and scorch time were noted to decrease with increasing filler loadings [54] [57] and fatigue life was noted to be reduced [55].

Different kinds of surface treatments have been tested for wood flour to improve the properties. Mansour et al. [58] used sodium hydroxide (NaOH), maleic anhydride (MAN), MAN-glycidyl methacrylate, and silane coupling agent treatments and SBR/polystyrene blend as a matrix. It was noted that the treatments increased the mechanical properties such as stress at yield, and rupture. MAN-glycidyl methacrylate treatment gave the highest values. Curing times were longer with all the treatment compounds than without treatments.

Corona treatment of fillers with NBR matrix was used by Vladkova et al. [59] and they noted that with 40 phr loading of corona treated wood flour, tensile strength increased about 48% and elongation at break about 35% compared to untreated wood flour.

MAPP (*graft-copoly(propylene/maleic anhydride)*) treatment were used by Sameni et al. [60] with blend of natural rubber, liquid natural rubber and polypropylene. With MAPP treatment, the tensile strength and Young's modulus were noted to be higher than without the treatment.

Albano et al. [61] investigated how different surface treatments of coconut flour filler effected on thermal degradation of NBR. They used NaOH, acetic anhydride ($(\text{CH}_3\text{CO})_2$), sulphuric acid (H_2SO_4), titanate (Lica 12) and zirconate (NZ12) as coupling agents. They noted that the thermal stability of NBR increased with increasing coconut flour loading and the increase was even more dramatic with zirconate treatment.

In overall, wood flour can be thought as non-reinforcing filler without treatments. Some treatments enhance the properties, but not significantly. In general, the particle size is too large for wood flour to be active, reinforcing filler material.

3.6 Natural fibres

Natural fibres come from many different sources and have really different properties, shapes, and sizes. They all have potential to work as reinforcing filler because of their fibrous nature. In this chapter, some studies of these natural fibres as unconventional rubber filler are discussed.

Bamboo fibre reinforced natural rubber was studied by Ismail et al. [62] with and without bonding agent. Bamboo fibre decreased the vulcanizing time and increased viscosity compared to unfilled reference compound and the compound with bonding agent had even more dramatic change in the values. Mechanical properties, such as tear and tensile strength decreased with increasing filler loads but the decrease was not that high when the bonding agent was used. Tensile modulus and hardness increased with increasing filler loads with and without the bonding agent. It can be noted that the bonding agent enhanced the mechanical properties of bamboo fibre in NR matrix, but it still does not work as reinforcing filler.

Oil palm fibre with NaOH treatment and different bonding agents, such as phenol and resorsinol formaldehyde, silica, and hexatetramin, were compounded with natural rubber. The average diameter of the fibres was 0.1 mm and length 10 mm. Tensile strength, tear strength, and elongation at break were decreased and modulus and hardness increased with increase of the oil palm fibre. The NaOH treatment of the fibre increased other mechanical properties except elongation at break compared un-treated compounds. The presence of bonding agents affected the mechanical properties of NR in the same way the NaOH treatment did. Curing time shortened with increasing filler loads, but the presence of bonding agents increased the curing times notably. [63]

Macro- and microfibres of oil palm in NR was investigated by Joseph et al. [64]. Diameters of macrofibres varied between 194-279 μm and microfibres had 5-20 μm diameter. After cleaning, washing, drying, and cutting, the microfibres were treated with different kinds of chemicals to modify the surface chemistry. It was noted that with addition of fibres, the storage modulus increased and was even more affected by silane coupling agent treated microfibres. $\tan \delta$, that is also named as damping factor and it illustrates the relation between loss and storage modulus, decreased with all the fillers thus the damping properties were weakened by the filler. In overall, the silane coupling agent treated microfibres had the best dynamic properties due to the smaller particle size and chemically improved compatibility. However, it can be said that oil palm fibres do not work as reinforcing filler, but it can be used in less demanding applications.

Sisal fibres are known to be the strongest natural fibres used in polymeric materials [65]. Kumar et al. [66] investigated how sisal fibres affect the properties of SBR compound. It was noted that tensile strength in longitudinal direction and hardness was increased whereas elongation at break decreased with increasing filler loadings. The decrease in elongation at break was dramatic even with first addition of 5 phr filler loading. The value of pure SBR was 400% in longitudinal direction and 80% with 5 phr filler load. The descent was more discreet after the first addition of sisal fibres. Tensile strength was increased also in transverse direction at 35 phr filler loading. They also investigated how the fibre length affected the properties and noted that with 2 mm long fibres the strengthening was lowest, better with 10 mm long fibres, and the best with 6 mm long fibres. The diameter of the fibres varied between 100 and 300 μm .

Sisal fibres and oil palm fibres in NR was noted to have better properties in longitudinal direction than in transverse direction. The addition of these fibres increased the tensile strength up to 30 phr load. Tear strength decreased first but with loading of 30 phr it increased. After that the tear strength decreased to the same level than before the 30 phr addition. In addition, torque and modulus increased. Curing time was slightly shortened by increasing filler content. Thus, these fibres could be used as oriented reinforcement in rubber matrix. [67]

3.7 Others fillers

There can be found numerous studies about fillers in rubber compounds and almost from every material you could imagine. Some materials have been studied more than others and by several researchers. In this chapter, some of the less studied materials that are found to be worth mentioning are presented. Source criticism needs to be remembered when only one research has been made about a subject.

Crushed cuttlebone as a filler of NR have been studied by Poompradub et al. [17]. Cuttlebone was found to be composed mainly of calcium carbonate and chitin. Average particle size was 19.5 μm . The compounds were vulcanized using peroxide and it was noted that cuttlebone did not prevent the reaction. With comparison to commercial CaCO_3 it was noted that cuttlebone as a filler had very similar effect on the mechanical properties. Dynamic mechanical analysis (DMA) also indicated that cuttlebone compound had good mechanical properties. The maximum tensile strength of cuttlebone was measured to be 13.2 MPa with 40 phr filler loading and 11.5 MPa with 20 phr CaCO_3 . In overall, the cuttlebone could be considered to be used as commercial CaCO_3 in basis of its properties.

The properties of chitosan and chitin in rubber compounds have also been investigated. Chitosan is a linear polymer obtained from chitin and they can be found primary in exoskeletons [68]. In comparison with unfilled NR, it was noted that chitosan powder, with average particle size of 90 μm , decreased vulcanizing time, tensile strength, and elongation at break but increased maximum torque and tensile modulus [68]. It was also noted that rubber-filler interaction decreased with increasing filler loadings [68]. Chitin however was treated in to nano sized whiskers with average length of 240 nm and compounded with latex NR [69]. It was noted that chitin decreased tensile strength and elongation at break, and increased tensile modulus compared to unfilled NR [69]. The processing technique had major influence on the mechanical properties, but in overall chitin did not act as reinforcing filler [69].

Rheological and curing characteristics of cassava starch filled NR and maleated NR (MNR) was studied by Nakason et al. [70]. In their research, it was noted that the Mooney viscosity increased with increasing cassava starch loadings with both rubbers, but was higher with MNR. Cure time was increased with increasing filler loadings and

with all MNR compound they were approximately 10 min longer than with untreated NR. Mechanical properties were not tested in the study.

Maize starch compounded with NR was studied by Khalaf et al. [71]. They noted that with addition of maize starch to the compound, the mechanical properties were decreased, cure time was longer, and maximum torque decreased with increasing filler loading. These property changes could possibly be partly explained with the compound structures. The compounds were executed so that when maize starch load increased, NR load decreased and their combined load was in all compounds 100 phr and so the results show that the mechanical properties decrease due to decrease of NR.

Ahmad et al. [72] have studied how oil palm empty fruit bunch works as an electrical tree inhibitor in silicone rubber. The fruit bunch was sieved and dried before use and the mean particle size was 32 μm . They used 1 weight % filling rate and referred it into non-filler rubber. It was noted that with filled rubber, the electrical tree was shorter than with non-filled rubber. The average length of the tree with non-filled rubber was 1.45 mm and with filled about 0.85 mm thus the fruit bunch shortened the length about 0.5 mm. The filler prevented the extension of the trees by acting as a barrier. Fruit bunch could expand the lifetime of electrical insulations, but further studies are needed.

Peanut shell powder has been compounded with natural rubber with different particle sizes, filler loadings, and treatments. The used particle sizes were 0-45 μm and 45-90 μm . It was noted that cure time decreased with increasing filler loading while maximum torque increased. Mechanical properties was noted to decrease with increasing filler load, but with 10 phr filler load the tensile strength was higher than with non-filled rubber. The best overall results with mechanical properties were achieved with alkali treated filler with particle size 0-45 μm . Peanut shell powder could be used in small quantities as semi reinforcing filler. [73]

Bagasse waste with particle sizes 300 nm, 125 nm, 75 nm, and smaller than 75 nm, was studied in natural rubber and styrene-butadiene rubber. Mechanical properties were noted to be rather good compared to commercial fillers. The stress and strain at yield and rupture was increased with both rubbers. For example the stress at yield of unfilled reference compound was 5.2 MPa, with 50 phr high abrasion furnace carbon black 11.2 MPa and with 30phr smaller than 75 nm particle size bagasse 36.3 MPa. The results were noted to be best at compounds with 30 phr smaller than 75 nm particle size bagasse waste. [74]

Red earth was compounded with natural rubber by Osabohien et al. [14] and the potential as reinforcing filler was investigated. The used red earth was first dried, ground, and sieved through 75 nm sized mesh. Pure NR and NR with CB (N330) was used as reference compound. It was noted that red earth increased the mechanical properties significantly compared to pure NR but not as much as CB. Some of the results can be seen in Table 3.4. The best results were measured with compound containing 50 phr red earth. The processability of red earth compounds was noted to be

comparable to CB filled compounds. Replacing CB by red earth in different quantities showed good results in mechanical properties. With 10 phr replacement the compound did not endure major decreases in mechanical properties, thus the red earth could be used as cost reducing filler together with CB. [14]

Table 3.4. Properties of NR with red earth (RE) and carbon black (CB) at different filler loadings [14]

Rubber/ filler load	Tensile strength [MPa]	Elongation at break [%]	Modulus, 100% elongation [MPa]	Curing time [s]
NR	9.98	835.4	0.86	43.8
NR/ 10 phr RE	14.72	655.5	0.93	46.2
NR/ 50 phr RE	24.66	498.3	1.33	52.8
NR/ 10 phr CB	19.74	603.2	1.02	44.2
NR/ 50 phr CB	36.28	324.2	3.42	41.8
NR/ 10 phr RE /40 phr CB	34.42	272.1	3.84	32.4
NR/ 20 phr RE/ 30 phr CB	33.48	281.2	3.49	33.0

Lime kiln dust was compounded with NR at different quantities. CaCO₃, silica, and CB filled NR were used as reference compounds. It was noted that the tensile strength and tear strength was decreased whereas Young's modulus and hardness increased with increasing filler loadings. However, modulus and hardness were lower than with reference fillers. Mooney viscosity was measured to be lower than commercial filler, but increased with increasing filler loads. Curing time was decreased with increasing filler load and was shorter than other fillers except for CB compounds. Processability was noted to be as good as or better than the commercial fillers. In overall, lime kiln dust worked more like CaCO₃ and it could be used as cost reducing, non-reinforcing filler. [75]

Titanium dioxide, TiO₂, compounded in small amounts (1, 2.5 and 5 phr) with NR was noted to increase the elongation at break and decrease tensile modulus with increasing filler loads. When compounded with EPDM rubber, the tensile modulus was first increased compared to pure EPDM, but decreased with increasing filler loads. Elongation at break was first decreased and increased with increasing filler loads. The vulcanizing time was extended by TiO₂ in both rubbers. EPDM and compound containing half of NR and half of EPDM were noted to be thermally more stable with TiO₂ filler. [76]

The influence of hard magnetic strontium ferrite with CB (N550) as a filler in NR/BR blend was studied. Blends with different amounts of ferrite and CB in different ratio to rubber matrix were compounded. Tensile strength was noted to decrease with increasing amount of ferrite and elongation at break decreased due to increasing overall filler content. Hardness was influenced by the CB amount in the compound and it was increased with increasing CB loads. The curing times were not influenced by the ferrite and CB content. The remanent magnetization was noted to be linearly dependent on the mass fraction of ferrite content. [77]

Silane (bis(triethoxysilylpropyl)tetrasulfide) treated graphene oxide (GO) was studied as a low filler content in natural rubber compound. It was noted that the treatment of GO had major influence on the mechanical properties. For example the measured value of tensile strength for treated GO filled NR with filler loading of 0.3 weight % was 14.7 MPa and for untreated about 9.6 MPa with filler load of 0.5 weight %. Treated GO increased the tensile strength about 100%, tensile modulus 66% and reduced the air permeability 48% only with 0.3 weight % filler load compared to pure NR compound. Thus, GO could be used in rubber applications for improving mechanical and gas barrier properties. [78]

4 EXPERIMENTAL

In the present work, the aim was to find out how selected unconventional filler materials work in rubber compounds. The goal was to find a potential market for some of these tested materials. NR and EPDM were used as matrix materials. Also different surface treatments were studied for some of the fillers. The rubber composites were tested and the results are discussed.

4.1 Compounding

Compounding of the materials was performed in Sastamala and vulcanization took place at Hervanta, both in the facilities of Tampere University of Technology (TUT). The methods and some of the materials were tested as introduction prior to the real test phase to make the procedure more familiar. The mixing of the rubbers went well as planned excluding the maleic anhydride (MAN) treated EPDM compound.

4.1.1 Materials and recipes

The materials and their quantities in the compounds were selected to correspond to real recipes in industry. Sidestream materials and their surface treatments were selected on the basis of the literature survey and discussions with UPM. Each compound had their own recipe and overall there were 34 different mixings.

Tables 4.1, 4.2, and 4.3 represent all the recipes used in the work. The values in the tables are in parts per hundred rubber (phr). The studied sidestream materials are referred as A1, A2, A3, S1, S2, L1, and L2. The A1, A2, and A3 are of the same material but have different particle size. The mean particle sizes are discussed further. S1 and S2 are of the same material but they are manufactured with a different method as well as are the materials L1 and L2. Different amounts of CB were replaced with these other fillers and the names of the compounds refer to the amount of the unconventional fillers. For example the NR compound with 10 phr material A1 and 40 phr CB is named NR_A1_10. With the treatments, the name of the compounds refers to the used treatment substance, where Sta refers to stearic acid, si refers to silane, and M refers to maleic anhydride. All the compounds containing treated fillers have CB and the selected sidestream material at a fifty-fifty ratio.

As reference compounds pure NR, CB filled NR, EPDM with CB and EPDM with CaCO₃ were used. All filled NR compounds had the same amount of filler, 50 phr. In EPDM compounds, the filler amount was 200 phr. Only the relation of studied materials and CB was changed.

Table 4.3. Recipes for EPDM compounds. Units are in phr.

	EPDM_ CB	EPDM_ CaCO3	EPDM_ A1	EPDM_ A1	EPDM_ A1	EPDM_ A2	EPDM_ A2	EPDM_ A2	EPDM_ A2_Sta	EPDM_ A2_Si	EPDM_ A2_M
EPDM	100	100	100	100	100	100	100	100	100	100	100
CaCO3		200									
CB	200		160	100		160	100		100	100	100
A1			40	100	200						
A2						40	100	200	100	100	100
Silane										10	
MAN											5
ZnO	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	10	2	2
ZDBC	2	2	2	2	2	2	2	2	2	2	2
CBS	1	1	1	1	1	1	1	1	1	1	1
Sulphur	1	1	1	1	1	1	1	1	1	1	1
Oil	60	60	60	60	60	60	60	60	60	60	60

The used CB type was N550 in all the compounds. NR used was SMR5 and EPDM was Keltan 512. The oils used in NR and EPDM compounds were Nytex 810 and N-par 20, respectively. In all the compounds, there were used zinc oxide (ZnO) and stearic acid as activators and cyclohexyl benzothiazolesulfenamide (CBS) as an accelerator. In the EPDM compounds, there were also used zinc dibutyl dithiocarbamate (ZDBC) as an accelerator. All the compounds used sulphur as a vulcanizing agent. For silane treatment bis(triethoxysilylpropyl)tetrasulfide from Evonik industries (Si69) was used.

4.1.2 Mixing

Mixing was performed in intermeshing mixer, Krupp Elastomertechnik GK 1.5 E (Figure 4.1.), and on an open two-roll mill (Figure 4.2.). In the first step, other ingredients except curatives were mixed in the intermeshing mixer. Then the compound was transferred to the two-roll mill where the curatives were added and rough rubber sheet created. The mixing was performed in stages to get the best possible outcome. All NR compounds had the same kind of mixing order and timing (conventional mixing) and for EPDM compounds a different procedure (upside-down mixing) were used.



Figure 4.1. Intermeshing mixer used for compounding rubbers



Figure 4.2. Two roll mill used for compounding rubbers

The fill factor of the intermeshing mixing chamber was 70% with all the compounds. Temperature was 50°C at the beginning of the mixing process and the rotor speed was kept at 60 rph. For some surface treatments different parameters were used, but they are mentioned in each case separately. Temperature rose during the mixing to around 120°C. In this work, the dumping of the rubber compound took place according to time, not temperature which is often in practise.

The mixing sequence of NR compounds was as follows. First, the rubber was added into the mixer and it was masticated for one and a half minute on its own to make it softer and easier to mix with ingredients. After mastication, filler or fillers were added into the mixer and mixed with NR for one minute. After this the activators, stearic acid and zinc oxide, and oil were added. The overall mixing time was 6 minutes. After this

the lump of rubber (Figure 4.3. a.) was transferred to the two-roll mill where vulcanizing agents, sulphur and CBS, were mixed into the rubber. From the two-roll mill the rubber compounds came out as rough sheets (Figure 4.3. b).

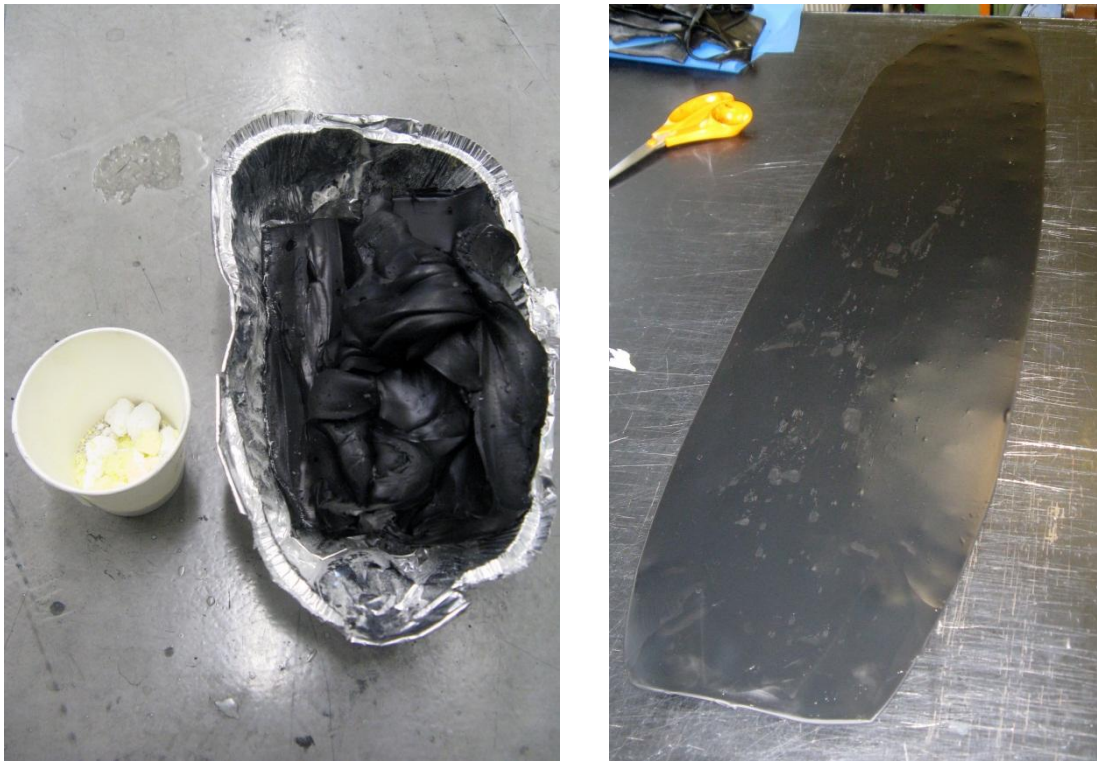


Figure 4.3. a) Rubber lump from internal mixer.

b) Rough rubber sheet from two roll mill.

EPDM rubber compounds were mixed in different order. First the fillers, oil and activators, ZnO and stearic acid, were added in to the mixer and mixed together for 30 seconds. After this the EPDM was added, and the whole compound was mixed overall for 4 and half minutes. The mixing in the two-roll mill was performed in the same way with NR compounds. In Figure 4.4, there is illustrated the mixing scheme of both rubber compounds.

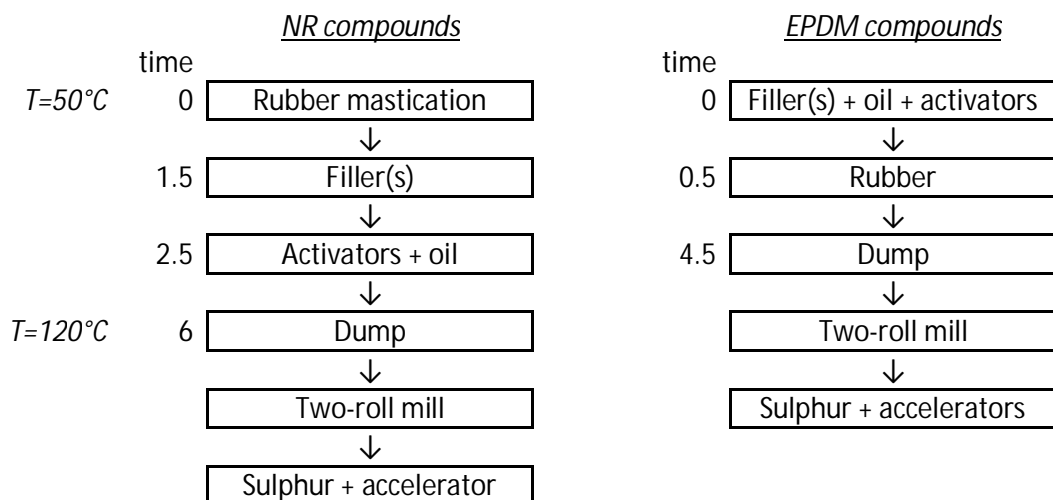


Figure 4.4. Mixing scheme of the compounds

The surface treatments were performed in intermeshing mixer. Stearic acid compounds were mixed like the compounds without treatments. Silane was added together with material A2 and mixed for a while before the addition of carbon black. Other ingredients were added as described earlier. The speed of the rotors was increased to increase the temperature up to 140°C and the compounds were also mixed a little bit longer, with NR compounds overall for 8 minutes and with EPDM for 5.5 minutes to complete silanization. The MAN was added after mastication of NR and mixed for 4 minutes. The rotor speed was also increased during the treatment to increase the temperature. During the NR treatment temperature only increased to around 95°C even when the rotors speed was at maximum. This was possibly due to too small a fill factor. Other ingredients were added after that normally. Overall mixing time was longer than without the treatment. EPDM rubber was mixed with MAN for 5 minutes prior the compounding with other ingredients. After the treatment the mixing was performed as the non-treated compounds. The EPDM rubber acted unexpectedly with MAN and some of the rubber was not able to be added to the compound. This is why the final compound contained more sulphur than the other compounds and thus the results of it are not comparable.

4.1.3 Vulcanization

The rubber compounds were vulcanized at TUT in a large heated press. Two different moulds with thicknesses of 2 mm and 1 mm were used, to prepare thin sheets of the rubbers for different tests. All the compounds were vulcanized after one week of the compounding and tests for vulcanized rubbers were performed next day.

Each rubber compound had its own unique vulcanizing time which was measured prior to the vulcanization. The times are discussed further in chapter 5. Vulcanization temperature was 150°C for natural rubber compounds and 160°C for EPDM compounds. The compression force was held in 120 kN with 2 mm thick sheets and around 150 kN with 1 mm thick sheets.

4.2 Test Methods

After compounding of the rubbers, different tests were performed to find out the established properties. Some measurements were performed before vulcanizing of the rubber and some after it. In overall, the tests succeeded as planned without problems and the results are considered to be reliable.

4.2.1 Mooney viscosity

Mooney viscosity was measured in Mooney viscometer (MV2000) from Alpha Technologies (Figure 4.5.). Mooney viscosity is named after its developer and the unit for Mooney viscosity is Mooney unit. This testing method is established practice in

rubber industry even though it is not compatible with viscosities measured with other devices.



Figure 4.5. Mooney viscometer

Viscosity was measured from the rubber without vulcanizing agents and for that there was a small section of rubber cut from the two-roll mill before the vulcanizing agents were added. The viscosities of the NR compounds were tested in 100°C and the EPDM compounds in 125°C. The overall testing time for both rubbers was 5 minutes containing a preheating time for one minute and the 4 minute test. Each compound was measured at least two times and even more if there were any change between these first two measurements.

4.2.2 Cure characteristics

Cure characteristics were measured with Advanced Polymer Analyzer (APA2000) from Alpha Technologies (Figure 4.6.). Optimum cure times (t'_{90}) scorch times and torque values were measured during the same test for all the samples. Scorch times were measured from the point where the torque reaches 2 dNm. t'_{90} is the time where vulcanizing is 90% completed.



Figure 4.6. Advanced Polymer Analyzer

Round samples were cut with cutting press from the rough rubber sheet. For NR compounds, the test was performed in 150°C for 25 minutes. For EPDM compounds the temperature was 160°C and the testing time 20 minutes. Only one measurement was made for every compound.

4.2.3 The Payne effect

The Payne effect illustrates the interaction between the filler particles in a rubber matrix. It is a special type of stress-strain behaviour of filled rubbers and it has been named after the researcher of the effect. It is measured as a storage modulus as a function of the strain. The filler particles form a network in the rubber matrix that increases the modulus. Smaller Payne effect values result from poorer filler-filler interaction. When strain is applied, the filler-filler network breaks after critical amplitude is reached and the modulus decreases. [5]

The Payne effect was measured also with the APA2000 -device at 100°C, from unvulcanized rubber. Every compound was measured three times and average values were calculated to the modulus values as a function of the strain. The Payne effect value was calculated as a change of the modulus within strains of 0.28 – 140.2 %.

4.2.4 Tensile properties

Tensile properties were measured with Messphysik tensile testing machine that can be seen in Figure 4.7. The tests were performed according to ISO 37, 2005. In the study,

the dump-bell, type 4, test pieces were used and they were die-cut with sharp mould from 1 mm thick vulcanized sheets. According to the standard, the test length can be 10 ± 0.5 mm and the thickness 1.0 ± 0.1 mm [79]. All the test pieces were standard in length, but some variation was noted in the thickness. The tensile strength, TS , is calculated from equation

$$TS = \frac{F_m}{Wt}$$

where F_m is the maximum force measured in newtons, W is the width and t is the thickness of the narrow portion of the die in millimetres. According to the equation, the tensile strength is higher with thinner test pieces if the maximum force is the same. Thickness variation is noted in the calculations.



Figure 4.7. Messphysik tensile testing machine

For every compound, at least five parallel measurements were made for lower uncertainty. There were slight problems with the saving of the results and with test pieces breaking elsewhere than from the narrow section, thus some compounds were needed to be tested more than five times. The results are nevertheless reliable and comparable. All compounds were tested for tensile strength, elongation at break and stress at 100% and 300% elongation.

4.2.5 Tear strength

Tear test were performed also with Messphysik tensile testing machine according to ISO 34-1, 1994. The trouser shaped test pieces were used in this study. The pieces were cut from the 2 mm thick vulcanized rubber sheets with sharp mould. Tear strength, T_s , was calculated from the measured maximum force with equation

$$T_s = \frac{F}{d}$$

where F is the maximum force and d is the medium thickness of the test piece measured from the end of the slit. Some variations were noted in the thickness of the pieces, but this was taken into account in the calculations.

With tear strength measurements the same data saving problem occurred than with tensile testing. Also, the test pieces tend to broke towards the sides and not straight to the end from the slit. The reliability is discussed further in results.

4.2.6 Hardness

Hardness of the samples was measured according to ASTM D2240-05 in normal laboratory conditions. As a tester device, the AFFRI Hardness tester was used (Figure 4.8.) Three layers of 2 mm rubber sheets were stacked to ensure at least 6 mm thick layers.

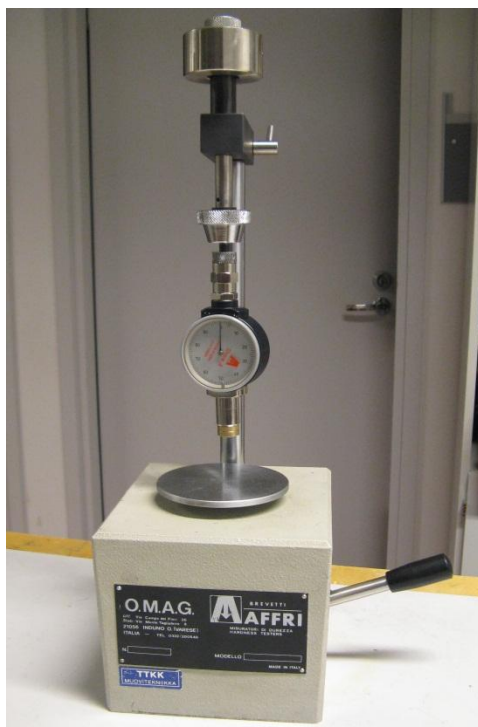


Figure 4.8. AFFRI Hardness tester

The hardness was measured at least five times for every compound from different spots that had at least 1 cm distance to each other and to the edges of the test piece. The values of the hardness were read after 15 seconds. The average values of five measurements were calculated.

4.2.7 Dynamic mechanical analysis

As an extra test, a dynamic mechanical analysis (DMA) was performed for selected compounds; NR_CB, NR_A2_10, NR_A2_25 and NR_A2_50. With DMA test viscoelastic behaviour of rubbers can be investigated. From the tests, the values of storage modulus (E') and damping factor ($\tan \delta$) are discussed in the results. $\tan \delta$ is the relation of loss modulus (E'') and storage modulus (E''/E'). The $\tan \delta$ value illustrates the damping properties of the rubber compound and also glass transition temperature (T_g) can be defined from the peak of $\tan \delta$ curve. [20]

Small test pieces with length of 20 mm were cut from the 2 mm thick vulcanized sheets. The DMA tests were performed with Perkin Elmer Pyris Diamond -machine at temperatures from -80°C to $+80^\circ\text{C}$. The heating rate was 3 K/min, frequency 1.0 Hz and amplitude 20 μm .

5 RESULTS AND DISCUSSION

In this chapter, all the results of the tests are presented and discussed. Because of the large amount of the samples and tests, the results are divided into categories according to the used elastomer and filler material to make comparison easier. In addition, contemplations of the possibilities for these tested filler materials in real markets are included.

5.1 Results of natural rubber compounds

In this chapter, the results of natural rubber compounds are presented and discussed. The chapters are divided according to the studied filler materials. Results of each compound are discussed separately and compared to the reference compound. Also the results of the treated compounds are dealt separately.

In mechanical properties charts, the values of hardness, tensile and tear strength columns are read from the left side axis and elongation at break line from the right side axis. In processability charts, the values of scorch and vulcanizing times and maximum torque columns are read from the left axis and the Mooney viscosity and the Payne effect from the right side axis. All units can be seen from the legend bar.

5.1.1 Material A

Material A was tested in three different particle sizes. The mean particle size of material A1 was 10 μm , material A2 4 μm and material A3 2 μm . Materials A1 and A2 were tested with filler loadings of 10, 25 and 50 phr, but material A3 only at 50 phr loading. All the results are gathered into Table 1 in Appendix 1.

Mechanical properties; tensile strength, tear strength, hardness, and elongation at break are presented in Figure 5.1. It can be seen from the figure that increasing material A loadings decrease the tensile strength and the hardness whereas elongation at break increases. In addition, tear strength decreases with increasing material A content, but with both A1 and A2 materials the tear strength is slightly higher at 10 phr load than that of the reference compound. The decreases in strengths are due to poorer filler-rubber interaction compared to CB. This lack of interaction affect also elongation at break by increasing it, as the filler does not form bonds with rubber and the polymer chains has more free space to move.

Stress at 100% and 300% elongation was also measured for the compounds. The values can be seen in the Table 1 in Appendix 1. All the values decreased with increasing replacement loads and were smaller compared to reference compound.

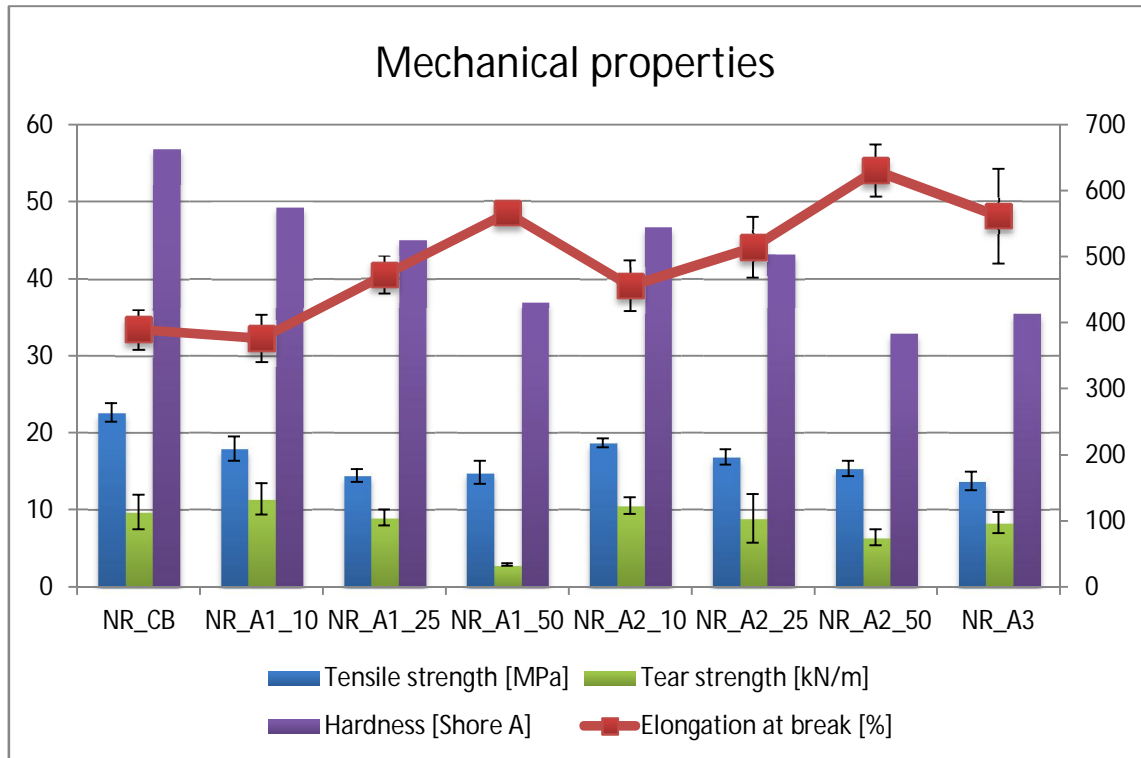


Figure 5.1. Mechanical properties of material A compounds

The processing properties; scorch time, optimum vulcanizing time ($t'90$), maximum torque, Mooney viscosity and the Payne effect are presented in Figure 5.2. It can be seen from the figure that with increasing CB replacement loadings $t'90$, maximum torque, viscosity and the Payne effect decrease. From decreasing Payne effect it can be concluded that the filler-filler interaction is poorer with material A than CB. Compared to the reference value, material A increases the viscosity when 10 phr of CB is replaced by it but decrease at higher material A loadings. Scorch time has slightly increasing trend with increasing material A loads, but with all the compounds the time is shorter than with reference and the variation is relatively small.

The material A had high pH. This could be one of the reasons for shorter curing times with the compounds. Other properties are unlikely affected by it, but it must be taken in to consideration in further exams and when selecting applications for these kinds of compounds.

Stress at 100% and 300% elongation of the compounds was also measured and the values can be seen in the Table 1 in Appendix 1. All the values decreased with increasing replacement loads and were smaller compared to the reference compound.

The particle size had no or little effect on the properties. The most notable dissimilarity is in tear strength where compound NR_A1_50 show lower value compared to compounds NR_A2_50 and NR_A3_50. This could be due to unsuccessful measuring of compound NR_A1_50. In overall, even the smallest particle size of the material A was too large to work as reinforcing filler.

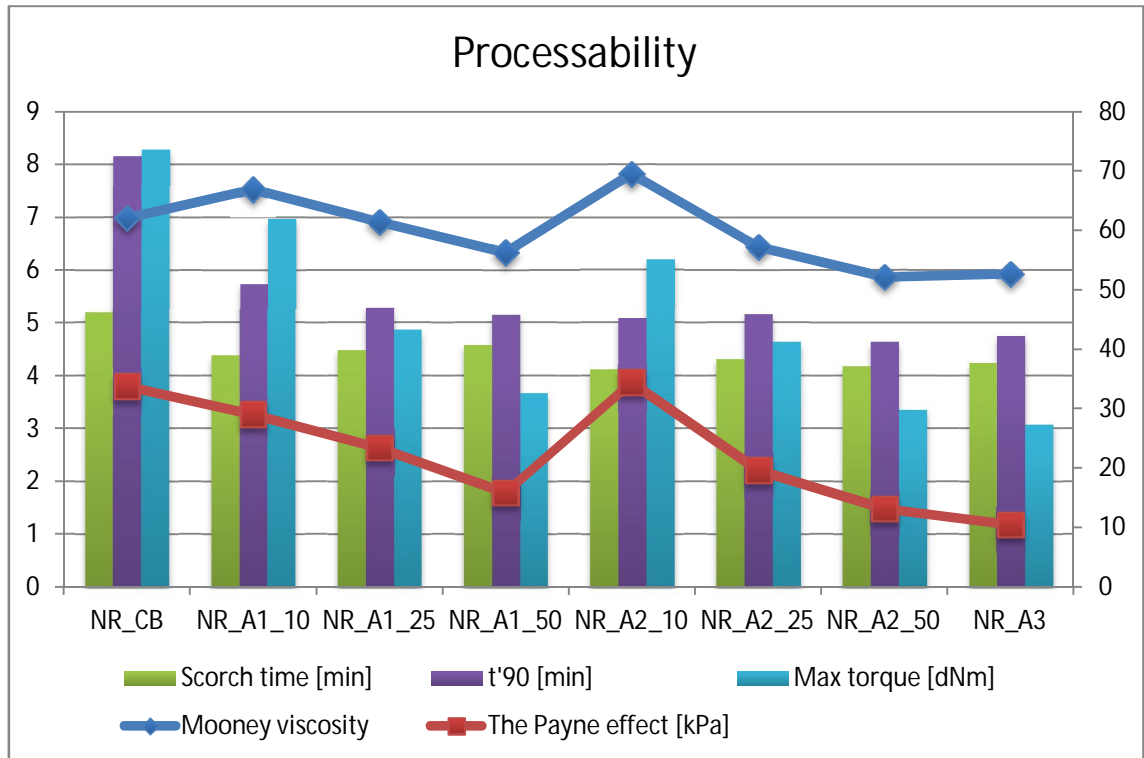


Figure 5.2. Processability of material A compounds

An extra DMA tests were performed to compounds NR_CB, NR_A2_10, NR_A2_25 and NR_A2_50. In Figure 5.3, the storage modulus as a function of temperature is presented. It can be noticed that with increasing material A2 loading the storage modulus decreases. At lower temperatures the compound NR_A2_25 shows the highest values of storage modulus, but it is decreased the most dramatically between temperatures -60°C and -50°C .

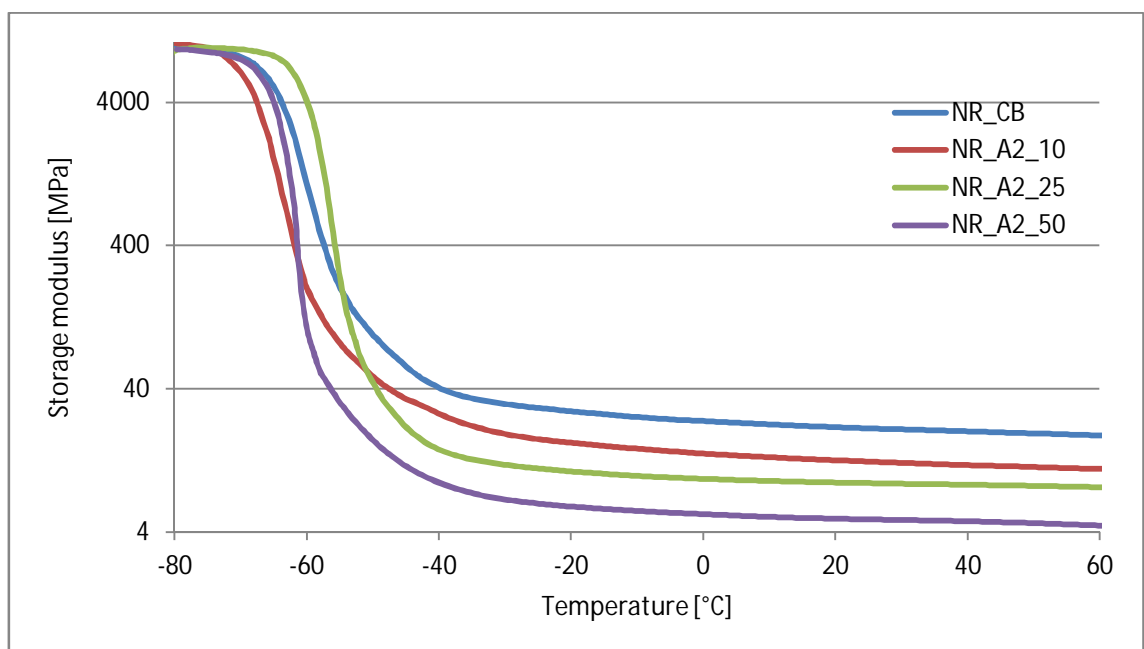


Figure 5.3. Storage modulus of selected compounds at different temperatures

In Figure 5.4, the values of $\tan \delta$ are presented at different temperatures. It can be seen that size of peaks of $\tan \delta$ curve increase with increasing material A2 loading. At room temperature, the differences are not significant. The T_g values can be defined from the peaks of $\tan \delta$ curve, and they are shown in the figure 5.4.

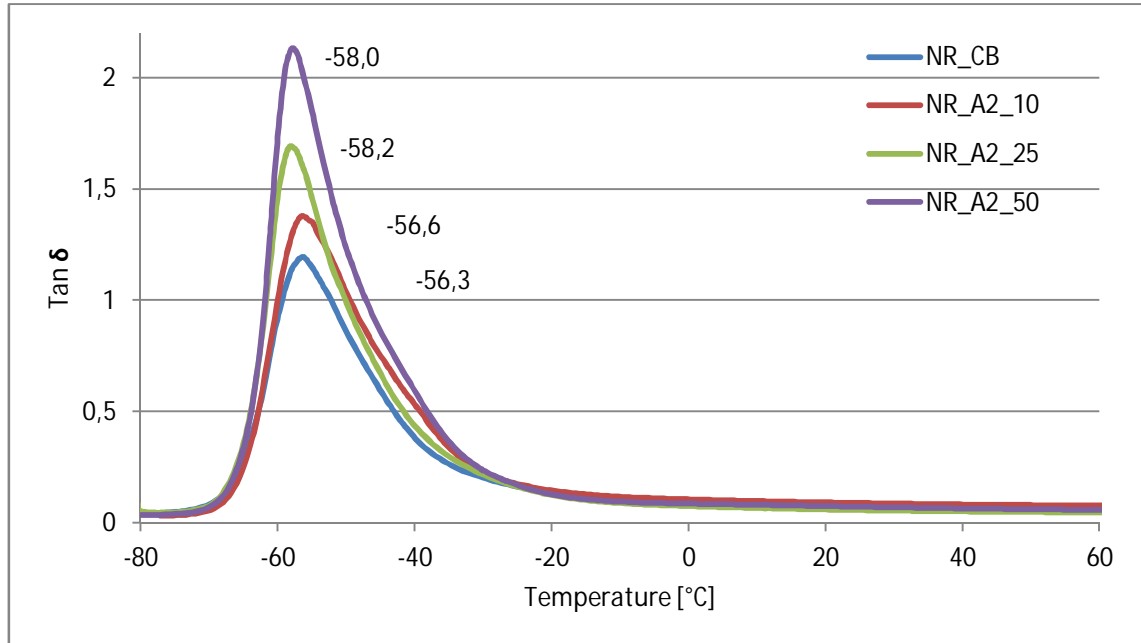


Figure 5.4. Tan delta values of selected compounds in different temperatures

5.1.2 Material S

Two different types of material S were studied. Material S1 was used to replace CB with loadings of 10, 25, and 50 phr and material S2 only with 50 phr. MAN treatment was also performed to material S1 with loading of 25 phr. All the test results can be seen in Table 2 in Appendix 1. Mechanical properties are presented in Figure 5.5.

It can be seen from the figure that the tensile and the tear strength decrease with increasing material S loads, but compared to reference the tear strength is higher with the compounds containing material S and CB. The hardness decreases with S/CB compounds, but increases with the compound containing only material S as filler. Elongation at break acts the same way than hardness, first decreasing and then with compound NR_S1_50 increasing, but having even higher value than the reference compound. MAN treatment does not improve the mechanical properties of NR_S1_25 compound. Material S2 has very similar properties than S1.

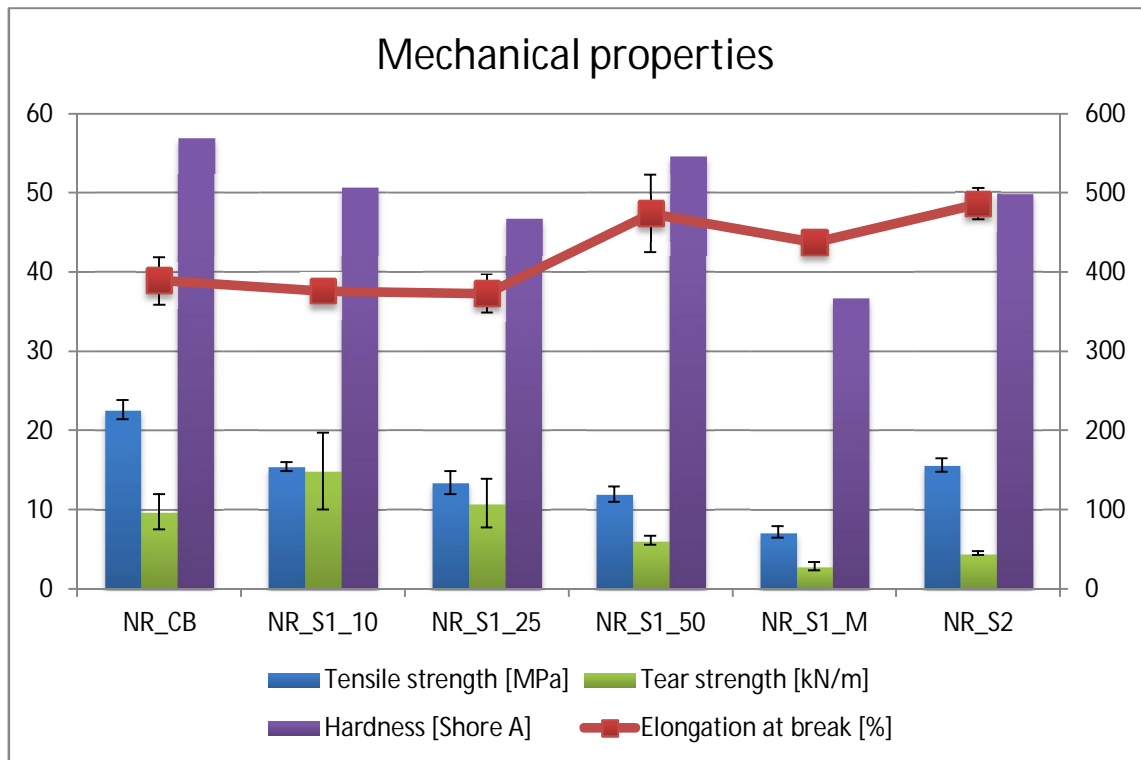


Figure 5.5. Mechanical properties of material S compounds

The processing properties are presented in Figure 5.6. It can be seen from the figure that maximum torque, viscosity and the Payne effect decrease with increasing material S content. Scorch and t'_{90} times are shorter than reference with all compounds except NR_S1_M because of the treatment. The longest curing and scorch time with untreated material S compounds was noted to be on compound NR_S1_25, and with 10 phr and 50 phr the times were almost equivalent.

Stress at 100% and 300% elongation was also measured and the results can be seen in Table 2 in Appendix 1. All the values were smaller than with reference compound NR_CB. The decrease was linear with increasing material S load. With materials S1 and S2 there were no major difference between the values.

The tested treatment can be noted to be useless because the treatment causes the vulcanizing time to increase dramatically. The increase in t'_{90} is partly due to the absorption of the accelerators by the MAN treatment. The mechanical properties also were noted to decrease due to the treatment, thus it is not worth using.

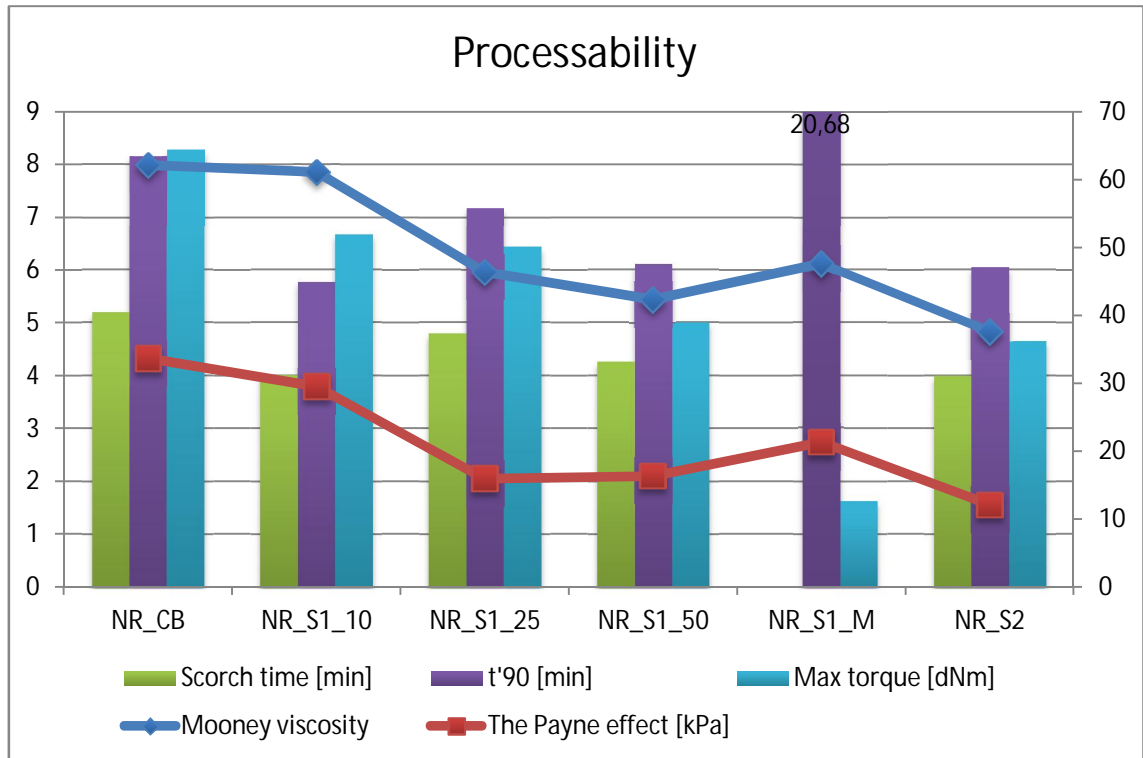


Figure 5.6. Processability of material S compounds

The material S was noted to be slightly fibrous. This could be seen from the tensile test and the tear test samples after testing. This property could be the reason for the large divergence in some of the tear strength results. The tensile strength and tear strength was tested only in the milling direction and with these compounds it would have been good to make test also in transverse direction. If the filler is oriented in the rubber compound it shows better mechanical properties in oriented direction and this could be worth of testing.

The particle size of the material S was nevertheless too large for it to work as reinforcing filler and replace carbon black. On basis of the studied properties some possibilities are as a cost reducing filler along with commercial fillers. If the fibrous nature of the filler could be utilized, these materials could have potential in some applications that require reinforcement in one direction.

5.1.3 Material L

Material L was tested as two different materials, L1 and L2, both with all three replacement quantities. No treatments were used for the materials. All the results can be seen in Table 3 in Appendix 1.

Mechanical properties can be seen in Figure 5.7. Hardness and tensile strength can be noticed to decrease with larger material L amounts. Tear strength tends also to decrease, but compared to the reference, the tear strength of the compounds NR_L1_10 and NR_L2_25 are slightly higher. Compound NR_L2_25 has also slightly higher tear strength than the compound NR_L2_10. However, the uncertainty of the results is

relatively high and the differences fit inside the error bars. Elongation at break increases compared to reference with all the compounds containing material L. With material L2 the elongation at break increases linearly with increasing L2 amount, but with material L1 the lowest value is on compound NR_L1_25. The differences between the compounds L1 and L2 are relatively small, but L2 compounds are somewhat harder than L1 compounds. The tear strength has the largest difference between the compounds with 25 phr CB replaced. Rubber-filler interaction is noticed to be weaker also with material L compared to CB due to the decrease in strength and increase in elongation at break.

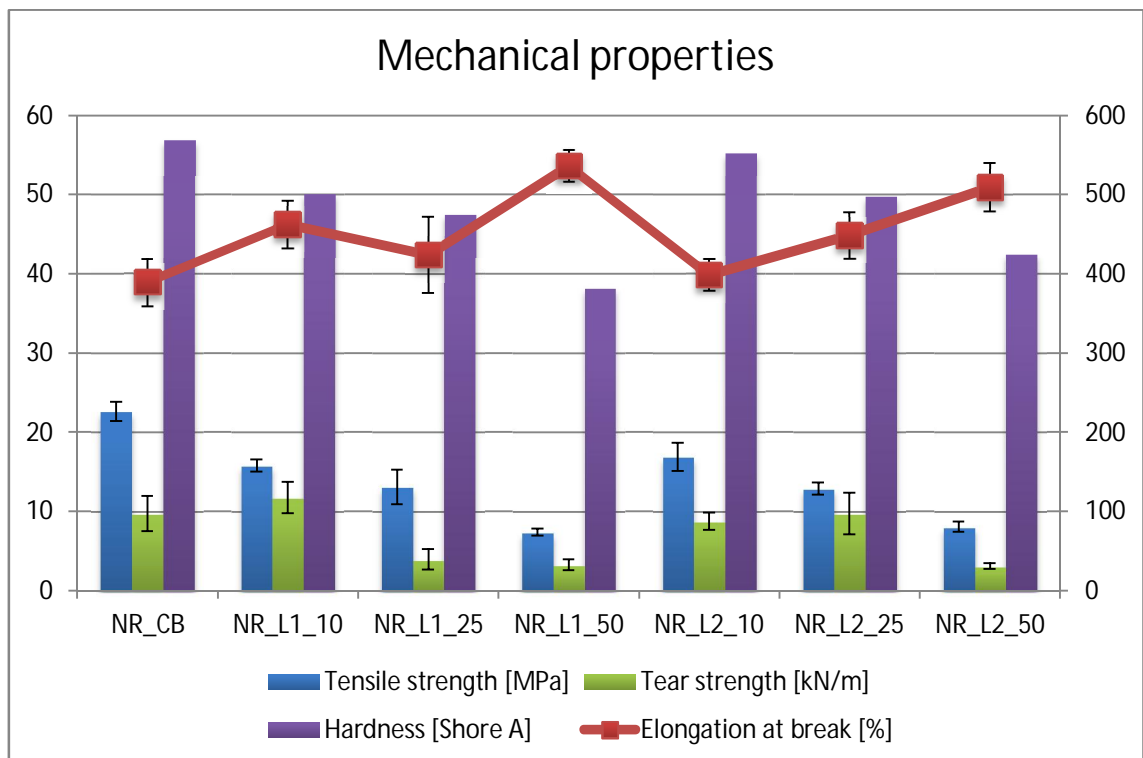


Figure 5.7. Mechanical properties of material L compounds

The processability of material L is presented in Figure 5.8. Maximum torque and the Payne effect decrease when the amount of material L increases. Viscosity also increases with higher replacement loads, but compared to the reference compound, the NR_L1_10 compound has higher viscosity. Vulcanizing and scorch time increase with larger L amounts, but only the compounds that do not contain any CB have longer curing times than the reference. The difference between the L1 and L2 compounds are minor.

The results of tested stress at 100% and 300% elongation can be seen in Table 3 in Appendix 1. All the values were smaller than with reference compound NR_CB. The both modules decrease with increasing material L loading. With material L1 the values were little higher than with L2 compounds. With both compounds there was larger decrease after CB was left out from the compound.

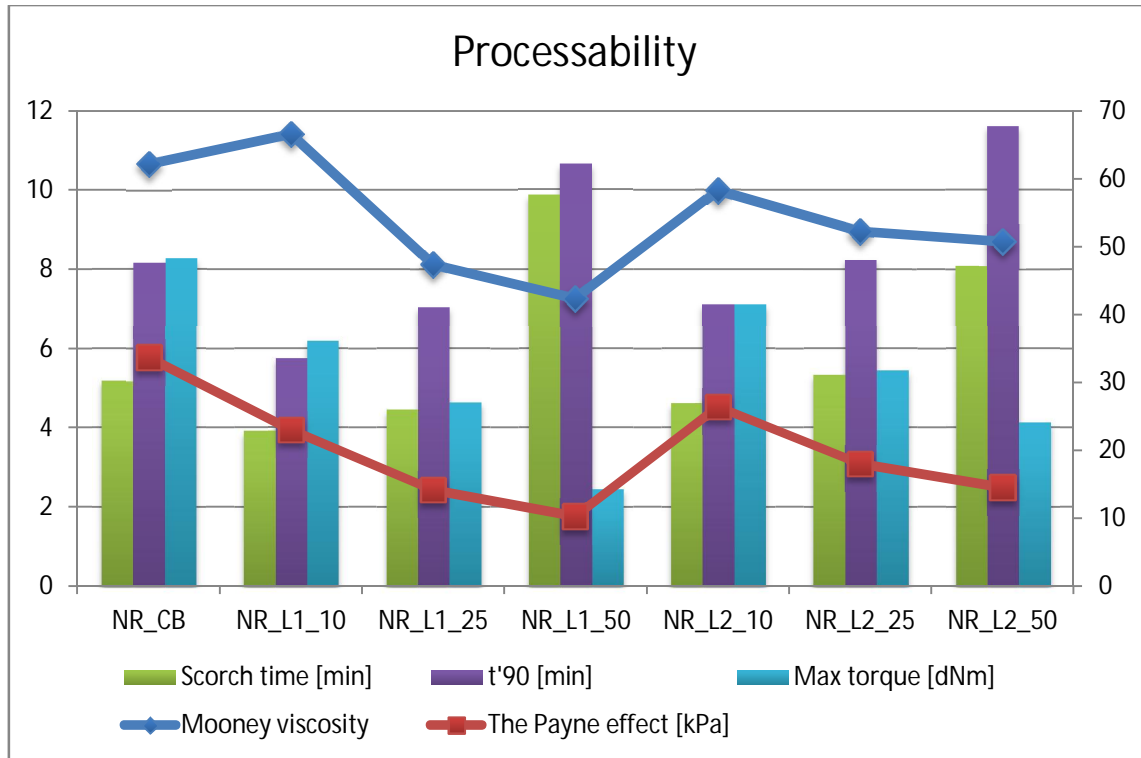


Figure 5.8. Processability of material L compounds

No major difference was noted with the properties of materials L1 and L2 compounds. The particle size of both materials L was too large for them to work as reinforcing fillers. The results show that material L could be used as non-reinforcing filler.

5.1.4 Treatments of material A2 in NR

Three treatments were performed to material A2; stearic acid, silane and maleic anhydride treatments. All the results are gathered into Table 4 in Appendix 1. Mechanical properties can be seen in Figure 5.9. Tensile and tear strength decrease with all the treatments. Hardness is hardly affected by stearic acid treatment, but other treatments decrease it. Elongation at break decreases with stearic acid and MAN treatments, but increases with silane treatment.

Processability of these treated compounds is presented in Figure 5.10. Stearic acid and silane treated compounds show no or really small difference in scorch and vulcanizing times. MAN treatment increases the scorch and vulcanizing times dramatically partly due to the absorption of accelerators. Maximum torque and viscosity decrease slightly with silane and MAN treatments whereas with stearic acid treatment these values are little higher. The Payne effect has unnoticeable change caused by the treatments so the filler-filler interaction is not affected by them.

Stress at 100% and 300% elongation was also measured and the results can be seen in Table 4 in Appendix 1. With stearic acid and MAN treatment the chance of the

stress was minor compared to untreated compound, but with silane treatment the values were decreased.

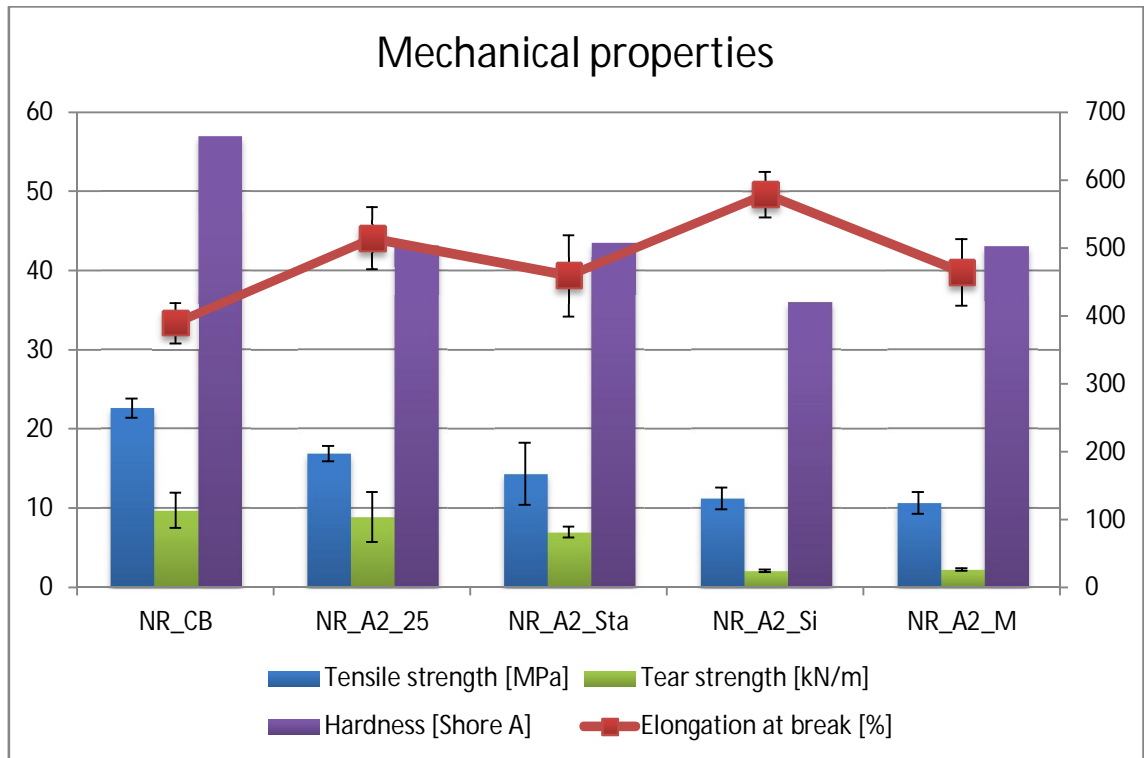


Figure 5.9. Mechanical properties of treated A2 compounds

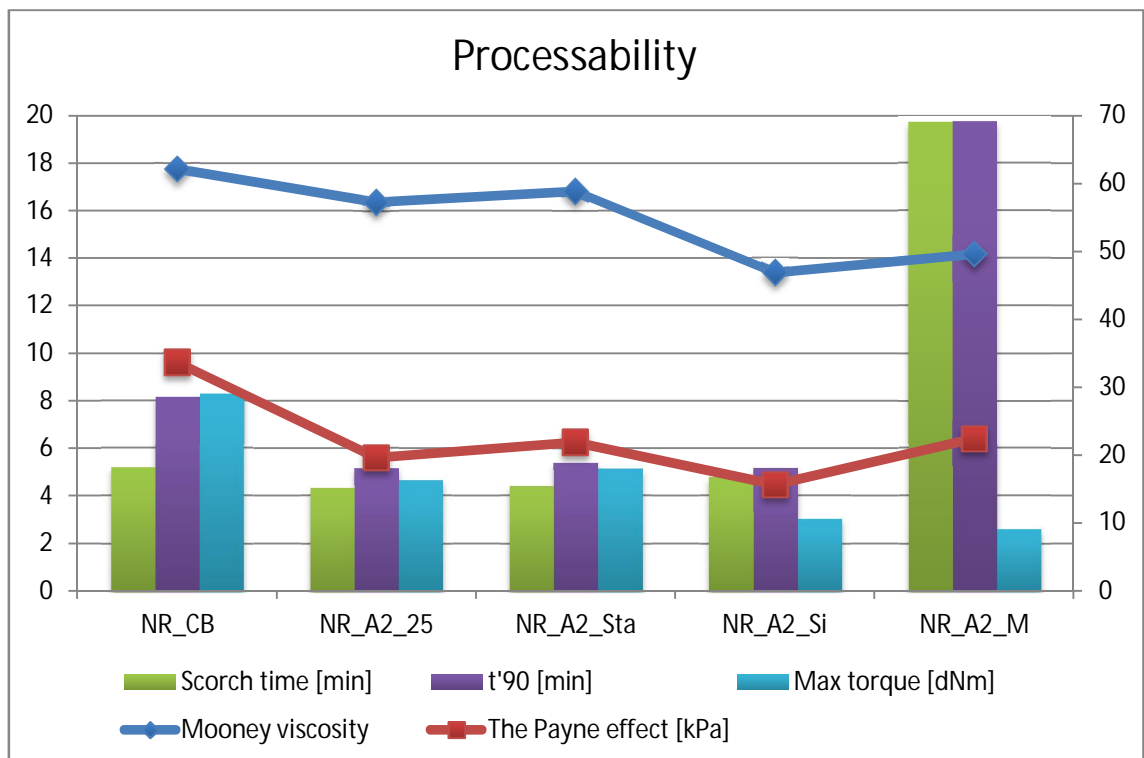


Figure 5.10. Processability of treated A2 compounds

In overall, the properties of the treated compounds were weaker and thus not preferable. The treatments reduced the rubber-filler interaction. Processability also declined. Thus, it would not be profitable to use these kinds of treatments in these kinds of compounds without further development.

5.1.5 Comparison with pure natural rubber

Comparison between pure NR compound and all the compounds, that have only one filler material, have been made. The comparison was made to find out how the fillers affect the properties of pure NR and if there could be a potential as a non-reinforcing filler. All the results have been gathered into Table 5 in Appendix 1. The results of the NR_CB compound are also included to the illustrating figures so that the results of all the compounds having only one filler material can be easily compared.

The mechanical properties of the compounds are presented in Figure 5.11. All compounds show decrease in tensile strength and almost all compounds have smaller tear strength than pure NR. Only NR_A3_50 shows slightly higher value in tear strength. The hardness decreases with all A compounds and increase with material S compounds. With material L1 the hardness is slightly smaller, and with L2 slightly higher than pure NR compound. Elongation at break increases with material A, and decreases with material S, while material L shows unnoticeable difference. In stretch, NR starts to crystallizes and thus have good strength. The decrease in strengths with studied fillers can be caused by the fillers' reducing effect of natural rubber's crystallization in stretch.

Comparison of processability is shown in Figure 5.12. It can obviously be seen that scorch times and cure times of material A and S compounds are more than half shorter than pure NR. The difference between material L compounds and pure NR is not that significant. Maximum torque shows only little variation between the compounds when material S shows the highest values. Compounds NR_A3 and NR_L1_50 are the only compounds having slightly lower maximum torque than pure NR. Mooney viscosity is higher with all the compounds compared to pure NR and the compound NR_S2 has the closest value to the reference. The Payne effect cannot be referred to pure NR because without any filler the value of it will be zero.

The values of stress at 100% and 300% elongation can be seen in Table 5 in Appendix 1. With materials A and L the difference was very small compared to pure NR and with materials S moderate increase was noted.

With material A the overall difference to pure NR compound is the smallest. Thus, the material A could be considered to be the most potential material for cost reducing, non-reinforcing filler.

The tested NR compound was vulcanized after 6 months from compounding on the basis of new measured cure time, and the mechanical properties were tested a day after that. This could have affected the measured mechanical properties. The processing properties were tested after the compounding so they are not affected by the long storing time.

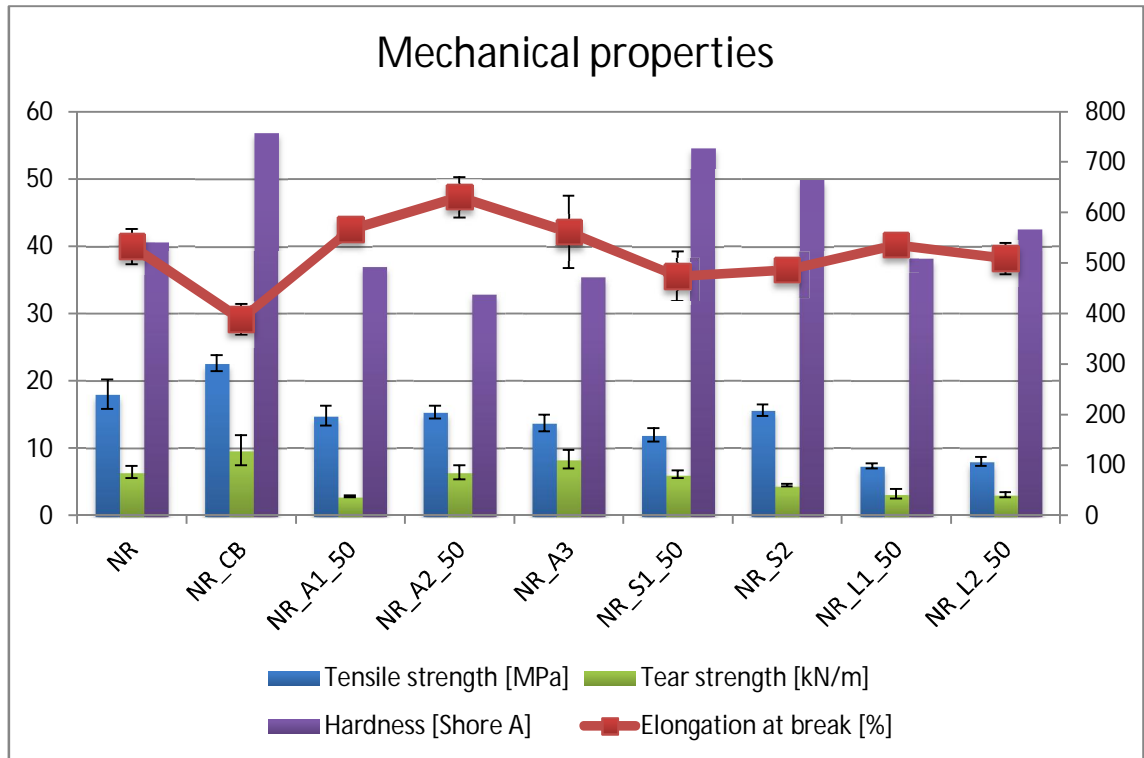


Figure 5.11. Comparison of mechanical properties

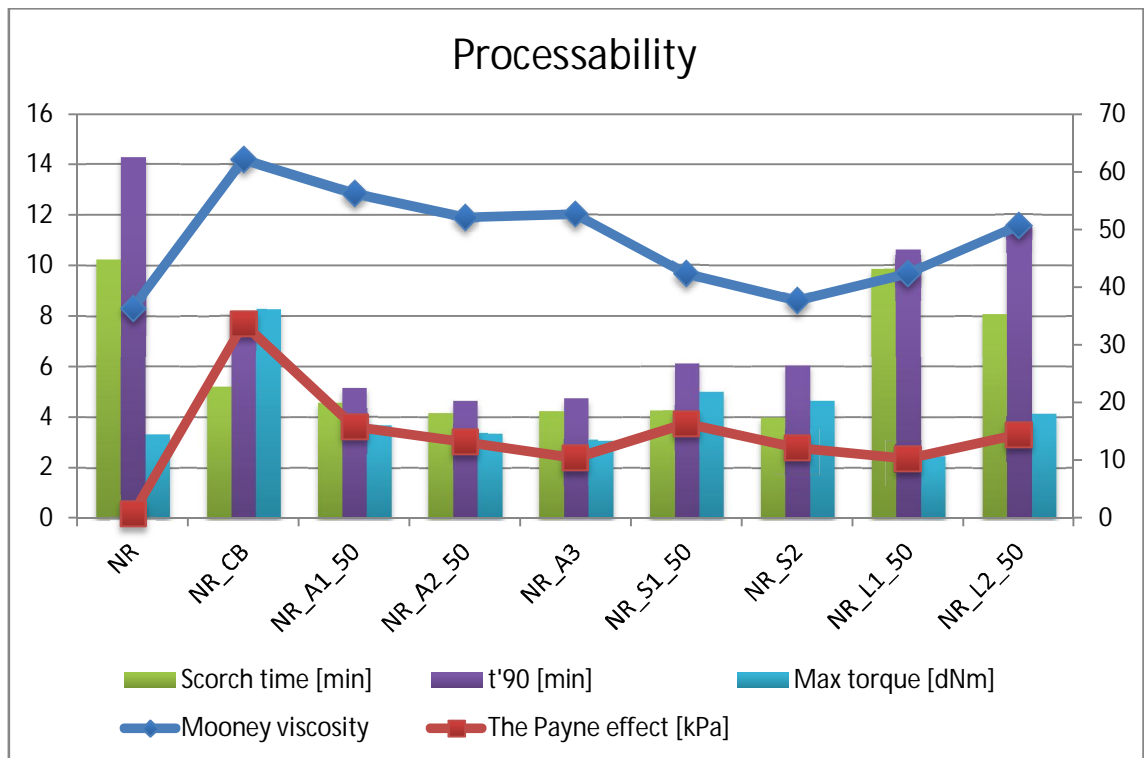


Figure 5.12. Comparison of processability

5.2 Results of EPDM –rubber compounds

In this chapter, the results of EPDM compounds are presented and discussed. The chapters are divided to untreated material A and treated material A2. Results of each material are discussed separately and compared to the reference compound and the results of the treated compounds are dealt separately.

In all the mechanical properties charts, the values of hardness, tensile and tear strength columns are read from the left side axis and elongation at break line from the right side axis. In processability charts, the values of scorch and vulcanizing times and maximum torque columns are read from the left axis and the Mooney viscosity and the Payne effect from the right side axis. All units can be seen from the legend bar. The scaling of the axis are fitted so that the legibility would be as good as possible and some significantly large values are left out and shown only as number.

5.2.1 Material A

Materials A1 and A2 were compounded to EPDM with CB replacement quantities of 40, 100 and 200 phr. All the results can be seen in Table 6 in Appendix 1. The mechanical properties are presented in Figure 5.13. Tensile strength of all material A compounds is lower than with either reference compounds. The highest values are measured with 25 phr compounds. The same trend can be seen with tear strength however the values are higher than reference compounds excluding compounds with 40 phr material A loads. Hardness decrease with increasing material A loads and all the values are lower than EPDM_CB compound and higher than EPDM_CaCO₃ compound. Elongation at break increases with increasing material A loads and all the values are smaller than EPDM_CaCO₃. Compared to EPDM_CB compound the compounds with 40 phr material A load have slightly lower elongation at break values and all the other compounds notably higher. The decreasing strengths and increasing elongation at break is due to poorer rubber-filler interaction, and less bonds between the filler and rubber is formed compared to CB.

Processability of EPDM compounds can be seen in Figure 5.14. The vulcanizing and scorch times increase with increasing material A load whereas maximum torque and the Payne effect decreases. Viscosity of compound EPDM_CB was not able to be measured because it was higher than the used equipment could measure. Also the viscosity value of compound EPDM_A1_40 was not able to be measured due to some malfunction of the machine. It nevertheless can be assumed that with increasing material A loads the viscosity decreased and the values were lower than EPDM_CB compound and higher than EPDM_CaCO₃. With the compound EPDM_A2_200 the scorch time is measured incorrectly to be longer than the optimum vulcanizing time. This is due to the low torque trough out the performed test.

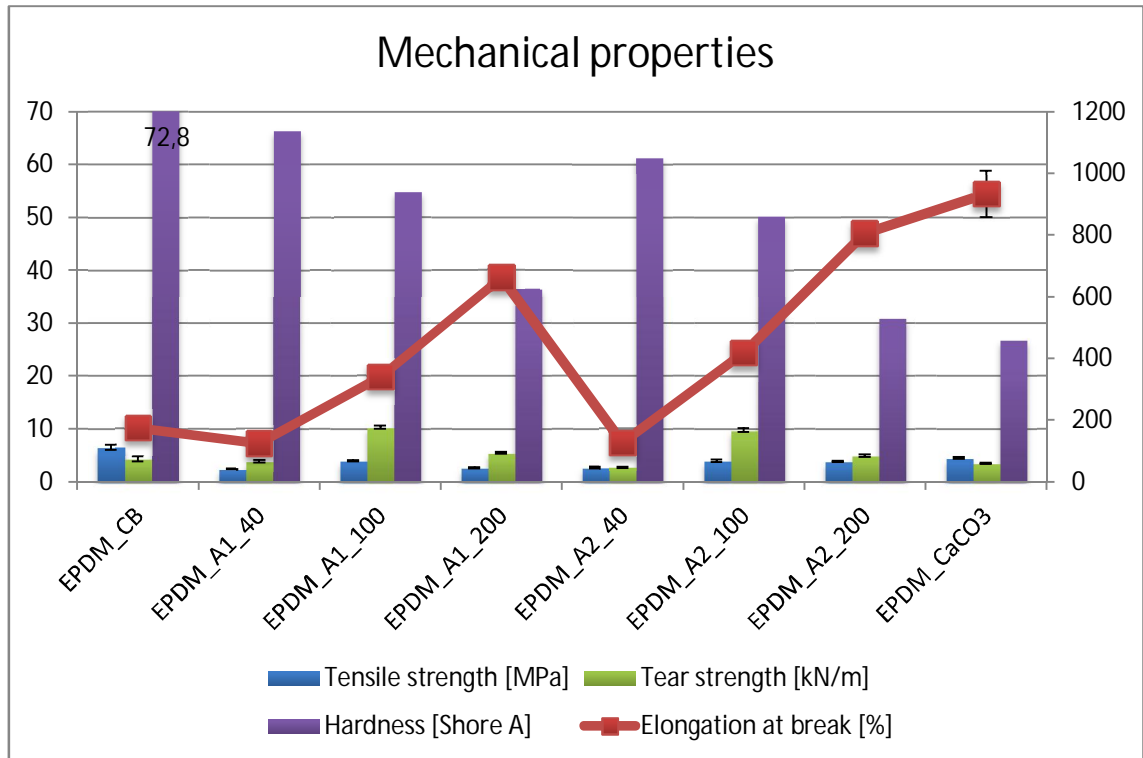


Figure 5.13. Mechanical properties of EPDM compounds

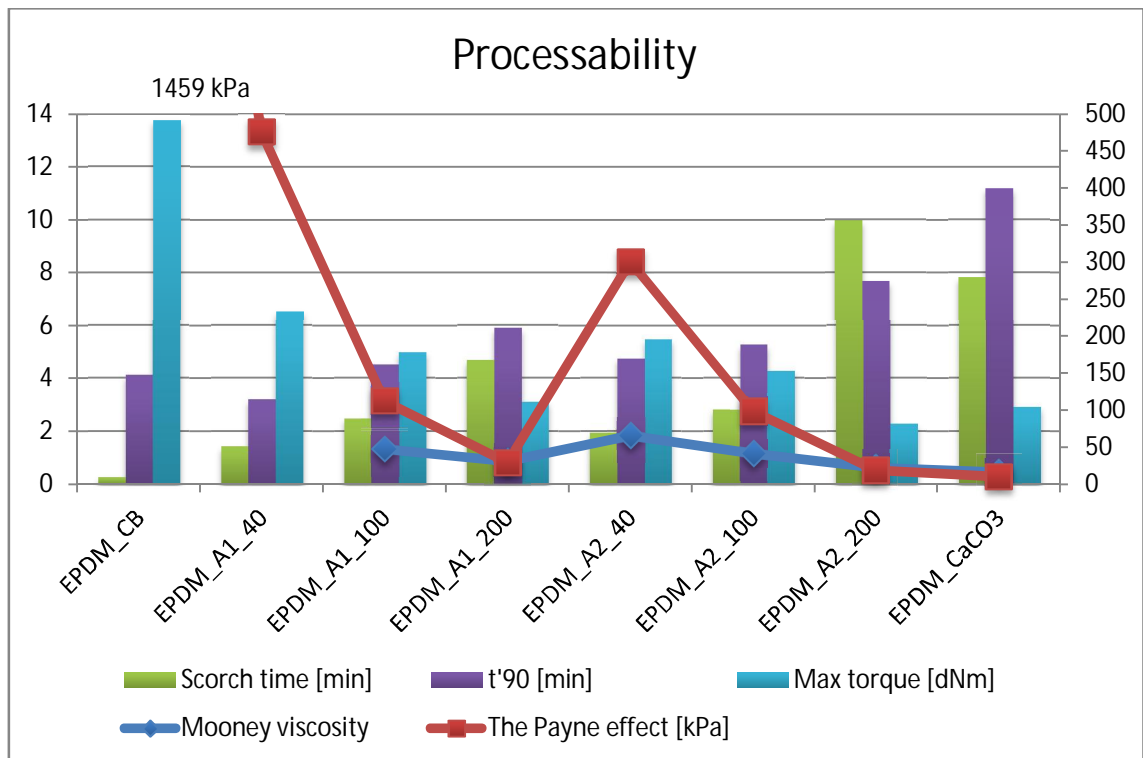


Figure 5.14. Processability of EPDM compounds

The values of stress at 100% and 300% elongation can be seen in Table 6 in Appendix 1. The values of stress at 100% elongation with the studied compounds are lower than EPDM_CB compound, but higher than EPDM_CaCO₃. The values

decreased with increasing material A loadings. For compounds EPDM_CB and both compounds having 40 phr material A, the stress at 300% elongation could not be determined because they did not stretch so far. The other compounds with material A had larger values than compound EPDM_CaCO₃ and the values decreased with increasing material A loadings.

From the results it can be concluded that material A works very similarly in EPDM than CaCO₃. Curing time is shorter than CaCO₃ compound due to the high pH nature of material A. It can thus be said that material A can be used as non-reinforcing filler and to reduce the cost of EPDM products.

5.2.2 Treatments of material A2 in EPDM

Material A2 was also compounded to EPDM with three different treatments; stearic acid, silane and maleic anhydride. The results are gathered in to Table 7 in Appendix 1. In the results also the compound EPDM_CB is shown to make comparison easier. The results of the compound EPDM_A2_M are also incorporated to the table and figures further, but it is not comparable with the other treated compounds and thus it is not discussed in the results.

The mechanical properties are presented in Figure 5.15. It can be seen that tensile strength and hardness decrease with both, stearic acid and silane treatments compared to EPDM_A2_100 compound. Tear strength decreases with both treatments and the decrease is more significant with silane treatment. Elongation at break shows nearly any difference with stearic acid treatment but decrease quite a lot with silane treatments.

Figure 5.16, shows the processing properties of the treatment compounds. Cure time and maximum torque decrease with stearic acid treatment but otherwise it shows hardly any changes in the processability compared to EPDM_A2_100 compound. Silane treatment decreases maximum torque and increase the curing time significantly due to the absorption of accelerators. Viscosity and the Payne effect also slightly decrease with silane treatment. Scorch times of stearic acid and silane treatment compounds were not able to be determined because the vulcanizing curve did not show clear section where the crosslinking started.

Stress at 100% and 300% elongation was also measured for the treated compounds and results can be seen in Table 7 in Appendix 1. Stearic acid and silane treatments decreased the stress at 100% elongation compared to untreated compound. Only the stearic acid compound showed the value of 300% elongation and it was almost half of the value of un-treated compound.

In overall, it can be concluded that none of the used treatments improved any of the mechanical properties and the processability is deteriorated. Thus, these kinds of treatments with this kind of materials are not worth using without further development.

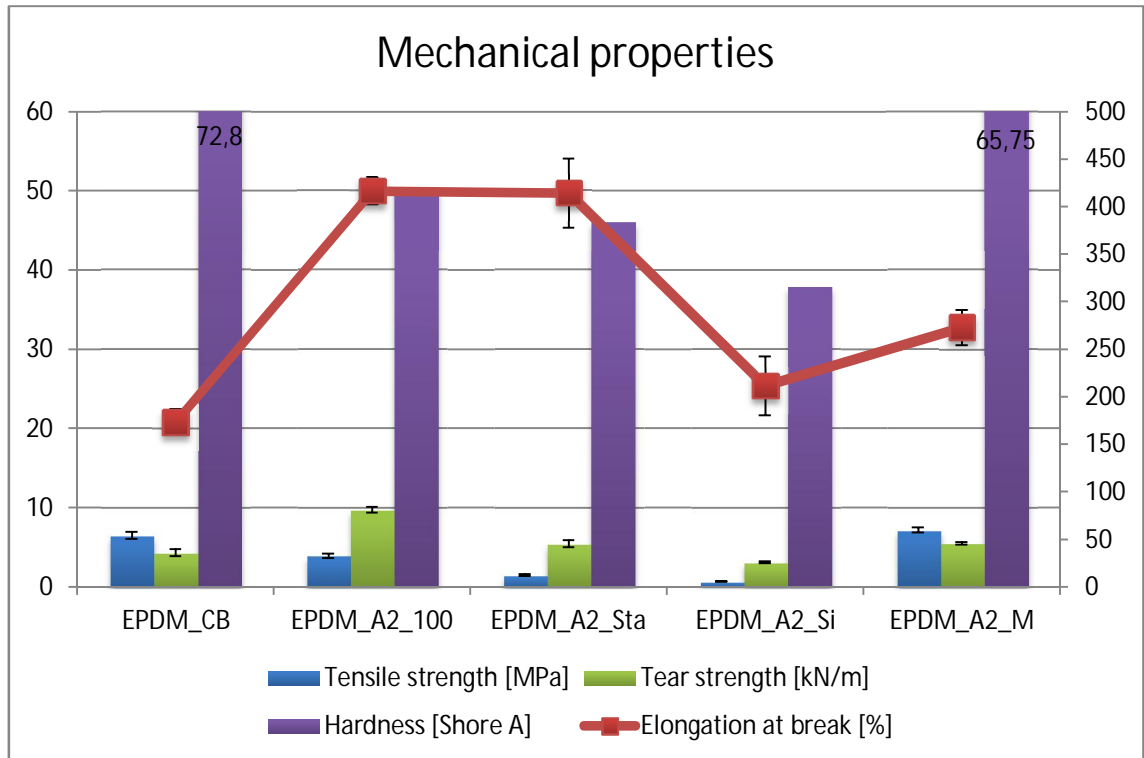


Figure 5.15. Mechanical properties of treated A2 compounds

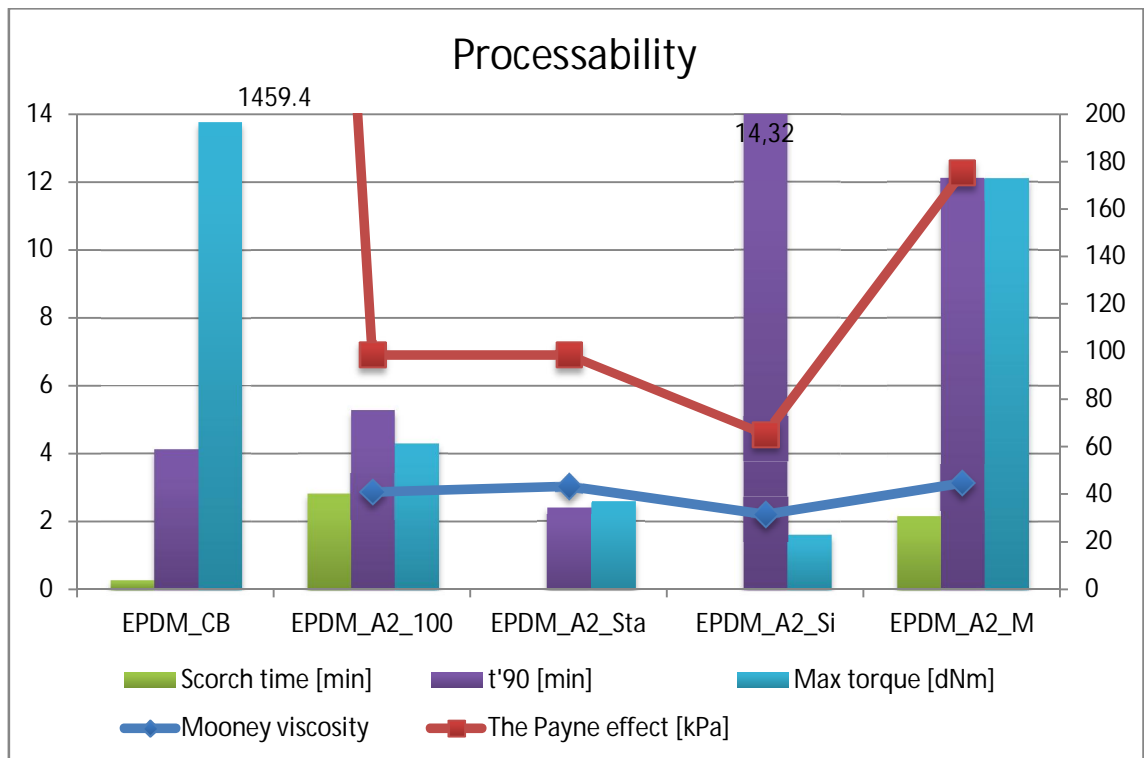


Figure 5.16. Processability of treated A2 compounds

5.3 Discussion

All the studied filler materials showed rather good processability properties and because all the compounds could be prepared for this research, processability is not the restrictive factor. The worst processability in NR compounds was noted with the MAN treatments, partially due to its unsuitability with substances having high pH. In addition, the other properties were also weak so the compounds with MAN treatment are not a potential subject for further research.

In Table 5.1, there is made a comparison of the compounds containing only one filler. The tested properties are compared to reference compound NR_CB in percent. The colours are selected so that the values having lighter colours have slight difference to the reference, and the darker colours mean larger difference. Four shades of both colours are used. With processing properties the green colour means smaller value than the reference and red means higher. With mechanical properties it is the other way around, so that green is for larger values and red for smaller. It is totally dependent of the final product what kinds of properties are desirable so the colours do not necessarily represent the goodness or the badness of the results.

In most cases, especially with reinforcing fillers the mechanical properties are wanted to be enhanced. This is why the mechanical properties are red if the value is smaller than the reference in the table. Moreover, the processing needs to be fast and easy so that the compound is suitable for a large-scale industry. This why the processability values in the table are green if the values are smaller than the reference.

Table 5.1. Comparison of studied filler materials

	Mooney	Payne effect	Scorch time	Curing time	Max torque	Tensile strengt h	Elongat ion at break	Tear strengt h	ShoreA hardne ss	100% Modulu s	300% Modul us
NR_CB	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %
NR_A1_50	90.6 %	46.8 %	88.1 %	63.2 %	44.5 %	65.6 %	145.5 %	29.6 %	65.0 %	16.3 %	14.2 %
NR_A2_50	83.9 %	39.0 %	80.4 %	57.0 %	40.6 %	67.9 %	162.0 %	66.4 %	57.8 %	13.8 %	10.1 %
NR_A3	84.9 %	30.8 %	81.5 %	58.2 %	37.3 %	60.8 %	144.3 %	86.0 %	62.4 %	14.2 %	12.9 %
NR_S1_50	68.2 %	48.4 %	82.1 %	74.9 %	60.6 %	52.9 %	121.7 %	62.9 %	96.0 %	43.5 %	27.2 %
NR_S2	60.6 %	35.9 %	76.9 %	74.1 %	56.3 %	69.1 %	124.9 %	46.3 %	87.7 %	48.6 %	31.9 %
NR_L1_50	68.1 %	30.4 %	190.0 %	130.5 %	29.7 %	32.6 %	137.7 %	33.4 %	67.1 %	18.1 %	11.7 %
NR_L2_50	81.6 %	43.0 %	155.8 %	142.4 %	50.0 %	35.5 %	130.9 %	31.9 %	74.7 %	20.7 %	13.5 %

The values of the studied material compounds are very similar compared to each other and the change from the reference compound roughly the same size. None of the compounds show superior properties.

The most interesting material was material A because it was definitely the cheapest filler material studied, and the properties were better or close to the other studied materials. Especially material A1 is interesting for further studies, because there was no significant difference between the properties of other A materials, and A1 was the cheapest one of them. With material A the mechanical properties in both rubbers, NR and EPDM, did not deteriorate markedly. In Table 5.2, there are all the measured properties of material A and NR compounds compared to NR_CB compound in percent. The compounds with the lightest colours are the closest to the reference compound. It can clearly be seen that with increasing material A loading the properties are changed more from the reference values.

Table 5.2. Comparison of the material A compounds properties to reference compound

	Mooney	Payne effect	Scorch time	Curing time	Max torque	Tensile strength	Elongation at break	Tear strength	ShoreA hardness	100% Modulus	300% Modulus
NR_CB	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %
NR_A1_10	107.8 %	86.1 %	84.4 %	70.5 %	84.2 %	79.4 %	96.8 %	117.5 %	86.7 %	66.0 %	77.6 %
NR_A1_25	98.9 %	69.3 %	86.3 %	65.0 %	58.9 %	64.0 %	121.3 %	92.6 %	79.1 %	28.1 %	36.1 %
NR_A1_50	90.6 %	46.8 %	88.1 %	63.2 %	44.5 %	65.6 %	145.5 %	29.6 %	65.0 %	16.3 %	14.2 %
NR_A2_10	111.9 %	102.0 %	79.4 %	62.4 %	74.9 %	82.7 %	117.1 %	108.7 %	82.1 %	48.5 %	58.7 %
NR_A2_25	92.1 %	58.2 %	83.1 %	63.4 %	56.1 %	74.6 %	132.1 %	91.4 %	75.9 %	26.7 %	35.0 %
NR_A2_50	83.9 %	39.0 %	80.4 %	57.0 %	40.6 %	67.9 %	162.0 %	66.4 %	57.8 %	13.8 %	10.1 %
NR_A3	84.9 %	30.8 %	81.5 %	58.2 %	37.3 %	60.8 %	144.3 %	86.0 %	62.4 %	14.2 %	12.9 %

From the table it can be seen that the biggest difference between the properties of A1 and A2 is in the tear strength with compounds having 50 phr of material A. The drop also from the compound NR_A1_25 is rather big. Even if there were some error with the tear strength measuring, it can be said that tear strength is somewhat improved with decreasing particle size but decreased with increasing material A load.

EPDM compounds did not show improvements in mechanical properties compared to CB reference, but they all have adequate processing properties. The studied

materials A1 and A2 acted a lot like the non-reinforcing commercial filler CaCO_3 . The treatments did not have an improving effect on the compounds. It would be worth studying if material A could be used in some applications having EPDM matrix and non-reinforcing fillers.

5.4 Business potential

Carbon black is the most used reinforcing filler in rubbers. The overall world consumption is almost 10 million metric tons and about 90% of the carbon black is used in rubber products [9]. The tyre industry consumes around 65% of the CB used for rubbers. The share of Europe is around 20% of the total world consumption [80]. The price of CB is highly dependent on the purity class, particle size, and oil price. The prices vary somewhere around 700 to 1300 USD per ton (12/2013) [81] [82].

Calcium carbonate is mostly used in paper industry and the total world consumption was 73 million metric tons in 2011 from which 60 million metric tons was ground CaCO_3 and 14 million metric tons of precipitated CaCO_3 . Rubber industries use around 5 to 7 million metric tons of CaCO_3 . The price varies a lot depending for example on the purity and particle size and is somewhere around 26 - 550 USD per ton. [83]

From these numbers it can be seen that the market for rubber fillers is quite wide ranging. There is large potential for many sorts of fillers with different properties. For the studied filler materials, the best market would be as a non-reinforcing filler and for reducing the cost of rubber products. If these studied sidestream materials could replace the conventional filler materials even with small section it would be really ecological and cost effective.

The properties indicate that especially material A could be used in some applications that do not need high reinforcement, such as seals and gaskets. These applications often use CaCO_3 as a filler, so material A could be a substitutive material for these kinds of applications.

6 CONCLUSIONS

The goal of the study was to investigate unconventional filler materials. In the theoretical part, a wide range of studied materials and their properties were introduced. Some materials had been investigated more than others and by several researchers, and some had only one study made about the subject. In some cases, the reliability of the results was a little questionable because the studies were made only by one researcher or there was only one research made. In my opinion the selected articles are trustworthy, yet the final decision of whether to believe in all the articles or not is left to the reader to decide.

In the experimental part, three different materials, A, S, and L, were tested with natural rubber and EPDM compounds. Three different kinds of treatments of material A were studied in both elastomers to improve compatibility of rubber and filler. Mechanical and processing properties were determined for all the compounds.

All the studied materials proved not to work as reinforcing fillers as they did not improve the mechanical properties. However, the processability was good or adequate with all the compounds, thus these materials could be used in industrial scaled rubber products as non-reinforcing fillers to decrease the price of the rubber product.

The main reason for the decrease in the mechanical properties with all the studied materials was the large particle size of the fillers. In addition, the decrease in strengths was influenced by the poor rubber-filler interaction. Elongation at break was increased also due to the decreased polymer-filler interaction. The replacement of CB with studied materials decreased the rubber-CB interaction and the polymer chains could move more easily past each other when the other fillers did not form as much bonds with the rubber matrix.

The tested treatments did not improve the properties and they complicated the processability. The used amounts of the treatment chemicals were selected based on the literature survey. It is highly unlikely that with other quantities the properties would improve remarkably with these treatments, thus they are not worth of testing further with these materials. Other treatments could be tested with these materials but before that the exact chemical composition of the materials should be in knowledge. After this the best treatment could be selected based on the chemical compatibility.

To work as non-reinforcing fillers, and to reduce the costs of the product, the materials need to be as inexpensive as possible. From the results it can be seen that the properties between the studied materials do not vary significantly. The material A1 is the cheapest one from the studied materials. This would, in other words, be the most potential material for further investigations as a non-reinforcing filler material.

More research is needed to determine other properties of these rubber compounds such as ageing, wear and chemical resistance etc. Also compounding the studied materials with other elastomers could be worth studying. These other properties and different kinds of compounds can open other possibilities in applications that do not need excellent mechanical properties.

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APPENDIX 1: TEST RESULTS

In the tables all the results of all the compounds are presented. The results of reference compounds are highlighted with orange colour.

Table 1. Results of NR and material A compounds.

	Mooney	Payne effect	Scorch time	Curing time	Max torque	Tensile strength	Elongation at break	Tear strength	ShoreA hardness	100% Modulus	300% Modulus
	ML(1+4))100	kPa	min	min	dNm	MPa	%	kN/m		MPa	MPa
NR_CB	62.1	33.7	5.2	8.2	8.3	22.6	389	9.7	57	3.9	16.6
NR_A1_10	67.0	29.0	4.4	5.8	7.0	18.0	377	11.4	49	2.6	12.9
NR_A1_25	61.4	23.3	4.5	5.3	4.9	14.5	472	9.0	45	1.1	6.0
NR_A1_50	56.2	15.8	4.6	5.2	3.7	14.8	566	2.9	37	0.6	2.4
NR_A2_10	69.5	34.4	4.1	5.1	6.2	18.7	456	10.5	47	1.9	9.8
NR_A2_25	57.2	19.6	4.3	5.2	4.6	16.9	514	8.9	43	1.0	5.8
NR_A2_50	52.1	13.2	4.2	4.7	3.4	15.4	630	6.4	33	0.5	1.7
NR_A3	52.7	10.4	4.2	4.8	3.1	13.7	561	8.3	36	0.6	2.2

Table 2. Results of NR and material S compounds.

	Mooney	Payne effect	Scorch time	Curing time	Max torque	Tensile strength	Elongation at break	Tear strength	ShoreA hardness	100% Modulus	300% Modulus
	ML(1+4))100	kPa	min	min	dNm	MPa	%	kN/m		MPa	MPa
NR_CB	62.1	33.7	5.2	8.2	8.3	22.6	389	9.7	57	3.9	16.6
NR_S1_10	61.1	29.5	4.0	5.8	6.7	15.4	375	14.8	51	2.2	11.0
NR_S1_25	46.4	15.9	4.8	7.2	6.4	13.4	373	10.8	47	2.0	9.1
NR_S1_50	42.4	16.3	4.3	6.1	5.0	12.0	474	6.1	55	1.7	4.5
NR_S1_M	47.6	21.3	-	20.7	1.6	7.2	437	2.8	37	0.9	3.8
NR_S2	37.7	12.1	4.0	6.1	4.7	15.6	486	4.5	50	1.9	5.3

Table 3. Results of NR and material L compounds.

	Mooney	Payne effect	Scorch time	Curing time	Max torque	Tensile strength	Elongation at break	Tear strength	ShoreA hardness	100% Modulus	300% Modulus
	ML(1+4))100	kPa	min	min	dNm	MPa	%	kN/m		MPa	MPa
NR_CB	62.1	33.7	5.2	8.2	8.3	22.6	389	9.7	57	3.9	16.6
NR_L1_10	66.6	23.0	3.9	5.8	6.2	15.8	462	11.7	50	1.4	7.5
NR_L1_25	47.3	14.2	4.5	7.1	4.6	13.1	424	3.9	48	1.3	6.7
NR_L1_50	42.3	10.2	9.9	10.7	2.5	7.4	536	3.2	38	0.7	1.9
NR_L2_10	58.3	26.4	4.6	7.1	7.1	16.9	399	8.8	55	2.3	11.2
NR_L2_25	52.2	18.0	5.3	8.3	5.4	12.9	449	9.7	50	1.3	6.0
NR_L2_50	50.7	14.5	8.1	11.6	4.1	8.0	509	3.1	43	0.8	2.2

Table 4. Results of treated NR compounds.

	Mooney	Payne effect	Scorch time	Curing time	Max torque	Tensile strength	Elongation at break	Tear strength	ShoreA hardness	100% Modulus	300% Modulus
	ML(1+4))100	kPa	min	min	dNm	MPa	%	kN/m		MPa	MPa
NR_CB	62.1	33.7	5.2	8.2	8.3	22.6	389	9.7	57	3.9	16.6
NR_A2_25	57.2	19.6	4.3	5.2	4.6	16.9	514	8.9	43	1.0	5.8
NR_A2_Sta	58.8	21.9	4.4	5.4	5.1	14.3	459	7.0	44	1.1	5.7
NR_A2_Si	46.9	15.7	4.8	5.2	3.0	11.2	579	2.1	36	0.7	3.0
NR_A2_M	49.6	22.4	19.7	19.7	2.6	10.6	464	2.2	43	1.1	5.2

Table 5. Results compared to pure NR.

	Mooney	Payne effect	Scorch time	Curing time	Max torque	Tensile strength	Elongation at break	Tear strength	ShoreA hardness	100% Modulus	300% Modulus
	ML(1+4))100	kPa	min	min	dNm	MPa	%	kN/m		MPa	MPa
NR	36.3	0.8	10.3	14.3	3.3	18.0	533	6.5	41	0.7	2.2
NR_CB	62.1	33.7	5.2	8.2	8.3	22.6	389	9.7	57	3.9	16.6
NR_A1_50	56.2	15.8	4.6	5.2	3.7	14.8	566	2.9	37	0.6	2.4
NR_A2_50	52.1	13.2	4.2	4.7	3.4	15.4	630	6.4	33	0.5	1.7
NR_A3	52.7	10.4	4.2	4.8	3.1	13.7	561	8.3	36	0.6	2.2
NR_DS_50	42.4	16.3	4.3	6.1	5.0	12.0	474	6.1	55	1.7	4.5
NR_MF	37.7	12.1	4.0	6.1	4.7	15.6	486	4.5	50	1.9	5.3
NR_L1_50	42.3	10.2	9.9	10.7	2.5	7.4	536	3.2	38	0.7	1.9
NR_L2_50	50.7	14.5	8.1	11.6	4.1	8.0	509	3.1	43	0.8	2.2

Table 6. Results of EPDM compounds.

	Mooney	Payne effect	Scorch time	Curing time	Max torque	Tensile strength	Elongation at break	Tear strength	ShoreA hardness	100% Modulus	300% Modulus
	ML(1+4) ₁₂₅	kPa	min	min	dNm	MPa	%	kN/m		MPa	MPa
EPDM CB	-	1459.5	0.3	4.1	13.8	6.5	173	4.3	73	4.4	0.0
EPDM CaCO ₃	16.5	9.9	7.8	11.2	2.9	4.5	933	3.5	27	0.3	0.4
EPDM A1_40	-	475.1	1.4	3.2	6.5	2.4	123	3.9	66	2.4	0.0
EPDM A1_100	47.4	112.4	2.5	4.5	5.0	4.0	339	10.3	55	1.4	3.7
EPDM A1_200	31.0	28.8	4.7	5.9	3.1	2.6	661	5.5	37	0.5	1.0
EPDM A2_40	65.3	300.9	2.0	4.7	5.5	2.7	126	2.7	61	2.6	0.0
EPDM A2_100	40.9	98.6	2.8	5.3	4.3	3.9	417	9.7	50	1.2	3.1
EPDM A2_200	22.4	18.8	10.0	7.7	2.3	3.9	804	4.9	31	0.4	0.7

Table 7. Results of treated EPDM compounds.

	Mooney	Payne effect	Scorch time	Curing time	Max torque	Tensile strength	Elongation at break	Tear strength	ShoreA hardness	100% Modulus	300% Modulus
	ML(1+4) ₁₂₅	kPa	min	min	dNm	MPa	%	kN/m		MPa	MPa
EPDM CB	-	1459.5	0.3	4.1	13.8	6.5	173	4.3	73	4.4	0.0
EPDM A2_100	40.9	98.6	2.8	5.3	4.3	3.9	417	9.7	50	1.2	3.1
EPDM A2_Sta	43.4	98.5	-	2.4	2.6	1.5	414	5.5	46	0.9	1.4
EPDM A2_Si	31.4	65.2	-	14.3	1.6	0.7	212	3.1	38	0.6	0.0
EPDM A2_M	44.7	175.0	2.2	12.1	12.1	7.2	273	5.5	66	3.8	0.0