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Masterproef

Optimization of the precision and accuracy of methods for the determination of chloroprene rubber (CR) in complex elastomer blends and technical elastom

Promotor :
Prof. dr. ir. Jozefien DE KEYZER
ir. Myriam LYNEN

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Leendert Vandenhove
Scriptie ingediend tot het behalen van de graad van master in de industriële wetenschappen: chemie

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LIST OF ABBREVIATIONS

CR:	Chloroprene Rubber
DTG:	Differential Thermogravimetric analyses
FTIR:	Fourier Transform Infrared Spectroscopy
GC/MS:	Gas Chromatography Mass Spectroscopy
IAPC:	Instrumental analysis & polymer characterization group
NBR:	Nitrile-Butadiene Rubber
NR:	Natural Rubber
Phr:	Parts per Hundred parts Rubber
SD:	Schöniger digestion
SBR:	Styrene – Butadiene Rubber
TGA:	Thermo Gravimetric analysis
UASM:	University of Applied Sciences Merseburg
Py/GC/MS:	Pyrolysis Gas Chromatography Mass Spectroscopy

ABSTRACT (English)

The Instrumental Analysis and Polymer Characterization group (IAPC) in Merseburg is specialized in the characterization of physical and chemical properties of polymers. Technical elastomers are characterized by the polymer composition and the additives used. For chloroprene rubber (CR), it is difficult to determine quantitatively the polymer-related CR content by pyrolysis GC/MS due to its inaccurate and time-consuming nature. The goal of this thesis is to combine the Schöniger digestion (SD) with Thermo gravimetric analysis (TGA) in order to determine the CR content in an elastomeric mixture.

The SD is an oxidation method used for determining the presence of chloride. The SD had to be optimized in order to accelerate the method and realise high yields of chloride. The second method, TGA, was used for the determination of the rubber amount in an elastomeric mixture. TGA was executed on pure samples and elastomeric mixtures to determine the decay steps for each material. A mathematical formula was calculated for binary and ternary elastomeric mixtures.

The results were successful. The Schöniger digestion was accelerated 2.4 times and a high yield of chloride was realized. The calculated formula from the TGA measurements had an overshoot but the results show that there is correlation between the measured and calculated values. After comparison with Pyrolysis GC/MS, results concluded that it is possible to use the combined method for an accurate CR determination.

ABSTRACT (Nederlands)

De "*Instrumental Analysis and Polymer Characterization group*" (IAPC) te Merseburg zoekt naar nieuwe mogelijkheden om de fysische en chemische eigenschappen van polymeren te karakteriseren. Technische elastomeren worden gekarakteriseerd aan de hand van de samenstelling van het polymeer en de vulstoffen. Door de lange analysetijd en beperkte nauwkeurigheid van pyrolyse GC/MS is het moeilijk om voor chloropreen rubbers (CR) het polymeer gerelateerde CR gehalte te bepalen. Het doel van deze masterproef is het combineren van de Schöniger digestion (SD) met Thermo gravimetrische analyse (TGA) om het CR gehalte in elk polymeerstaal te kunnen bepalen.

De SD is een oxidatie methode die gebruikt wordt om het chloride gehalte in een staal te bepalen. De SD diende geoptimaliseerd te worden; de procedure moet sneller doorlopen kunnen worden en er moeten hoge detectieopbrengsten aan chloride behaald worden. TGA werd gebruikt om het rubber gehalte te bepalen in een mengsel. TGA metingen werden uitgevoerd op zuivere rubbers om de verschillende degradatie stappen te karakteriseren. De metingen werden herhaald op mengsels met twee en drie rubbercomponenten. Met deze resultaten werd een wiskundig model opgesteld om onbekende mengsels te karakteriseren .

De resultaten waren succesvol. Door de optimalisatie van de SD werd de procedure 2.4 keer versneld en de opbrengst aan chloride was hoog. De degradatie stappen berekend met de experimenteel bepaalde formule zijn te hoog maar toonden aan dat er een goed verband is tussen de gemeten en berekende waarden. Door de vergelijking met Pyrolyse GC/MS, kon er besloten worden dat het mogelijk is om met de combinatie van SD en TGA het CR gehalte te bepalen in onbekende rubbermengsels.

CHAPTER 1: INTRODUCTION

The University of Applied Sciences Merseburg (UAS Merseburg) is the successor of the technical college “Carl Schorlemmer”. Founded in 1992, UAS Merseburg is a centre of education and service to the chemical industry. UAS Merseburg has now more than 2800 students and 288 employees.

The UAS Merseburg consists out of four departments: Computer Sciences & Communication systems, Engineering & Natural Sciences, Social work Media & Culture and Business Sciences. This research project will be performed in the research group Instrumental Analysis & Polymer Characterization (IAPC) in the Engineering & Natural Sciences department.

This research group’s main goal is the characterization of physical and chemical properties of polymers. The IAPC has three focuses. The first lies in the quality control and insurance of polymers for external companies all over the world. A second focus is the use and optimisation of methods to gain more insight in the composition and morphological structure of polymers. The third is the pyrolysis of polymer waste to its polyolefins monomers.

Rubber composite materials and technical elastomers are essential in all areas of industrial society. They consist of a multitude of different components that determine the chemical and mechanical properties. To know more about its application possibilities, it is important to know methods for a fast and efficient characterization.

Chloroprene rubber (CR) is a rubber well known for its good resistance to oxidation and weather ageing, stiffness and good overall properties. In comparison to other components, it is especially valuable to know the amount of CR due to its vital properties of the elastomer in the end product. [15]

The main goal of this thesis is to combine a catalogue of methods in order to determine the total and polymer-related CR content in any rubber sample. These methods have to determine the amount of CR in any elastomeric blend and the amount of chloride in the rubber part of the composition. For example, in a 30 phr (parts per 100 parts rubber) blend, the total amount of CR may end up being around 10 m%. The rest of the content consists of fillers, carbon black & oils. In a 10 m% CR the mass percentage of chloride will be about 4%. [5]

The Schöniger digestion is a method where a small sample of the polymer is wrapped in an ash-free paper and burned in a closed oxygen-filled flask containing an absorption solution. After a fixed period for complete absorption, the content of the flask will be potentiometrically titrated with $AgNO_3$ giving the chloride content released from the rubber.

The second method for the determination of CR is Thermo gravimetric analyses (TGA). TGA is an analytical technique that monitors the weight of the sample during a stepwise heating program. This method is necessary to determine the amount of rubber in technical elastomeric materials, which are often based on polymer blends and contain significant amounts of additives.

To determine the amount of CR in any elastomeric material, the SD and the TGA method are equally important. From the Schöniger digestion, the amount of chloride in a rubber sample can be determined. The TGA can determine the rubber percentage in an elastomeric material. Combined, it should be possible to determine the amount of CR in any elastomeric material.

The first step is to successfully test and optimize the SD [16] for the determination of chloride in a rubber sample. The optimization of the Schöniger digestion will be executed with pure components, to be extended in a later step to rubber mixtures. The optimization has to speed up the process of measurement and give high yields of chloride.

The focus of the Schöniger digestion will be that the obtained data will yield a meaningful evaluation of the reachable precision. Therefore the results will be statistically validated and the variation between measurements will be determined.

A standard operating procedure (SOP) for the Schöniger digestion will be written for the optimized method. This SOP will be used to perform a recovery test on various rubber mixtures and unknown elastomeric materials.

The TGA will be executed on pure components with a heating rate of 10 K/min. This is necessary to find out at which temperature the decay steps take place, which contain valuable information about the volatile components. [17] Next, a stepwise TGA will be executed on technical elastomers to determine the amount of rubber. All measurements will be taken as duplicates to result in a mathematical formula to calculate the amount of CR-rubber in any rubber-mixture. [18]

The reference method that has been used so far at the IAPC for quantitative CR determination is pyrolysis GC-MS. Pyrolysis is the process of thermal decomposition of the polymer using heat or flames [19]. This result in the exposure of volatile components, which can be measured by a gas chromatograph coupled with a mass-spectrometer. The results of the Schöniger digestion and the TGA method of the mixtures will be compared with previously obtained data from pyrolysis-GCMS.

A comparison between the two methods will confirm which of the two is the most practical and accurate. A visual overview of the catalogue is shown in figure 1.

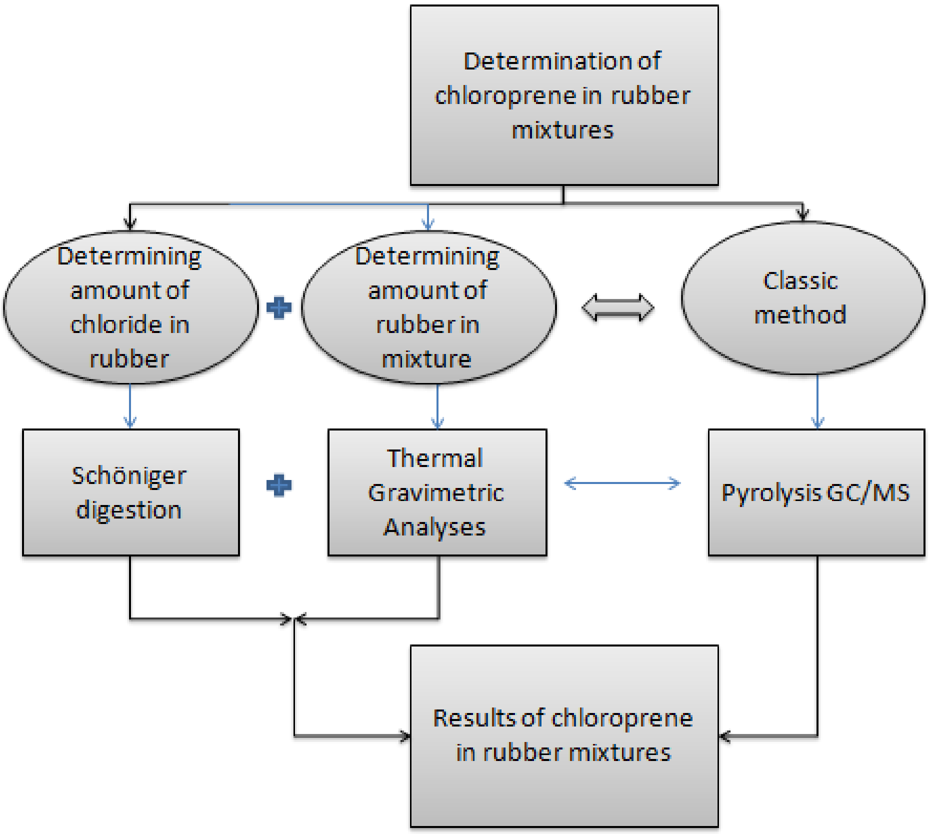

Figure 1: Overview of the determination of the amount of CR in an elastomeric mixture

CHAPTER 2: Polymer analysis principles

2.1 Introduction to Chloroprene rubber (CR)

2.1.1 General overview

Polychloroprene was first produced in 1932 under the name Duprene by Du Pont. It is a rubber that is produced by the polymerization of chloroprene monomers, resulting in a CR polymer with excellent properties and a wide variety of applications. The chemical structure of the repeating unit of polychloroprene is shown in figure 2.

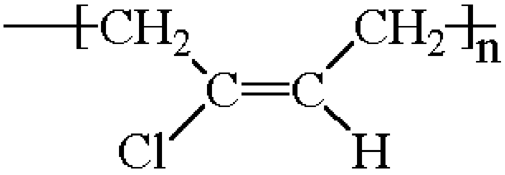

Figure 2: Chemical structure of the repeating unit of polychloroprene [1]

CR is a rubber with numerous advantageous properties. It is a versatile material with a good elasticity, well known for its overall good resistance against oil, solvents, weather ageing, heat, oxygen, ozone and flames. For this reason, CR is among the most important special rubbers in terms of quantity produced. [20] A comparison of CR with Natural rubber (NR) and Styrene – Butadiene rubber (SBR) is shown in table 1.

Table 1: Comparison Chloroprene rubber (CR), Natural rubber (NR) and Styrene – Butadiene rubber (SBR)

	CR	NR	SBR
Abrasion resistance	+	-	+
Physical properties	+	-	+
Water resistance	+	+	+
Processing	+	+	+
Flexibility	-	+	+
Heat resistance	-	+	-
Resistance to organic Materials	+	-	-
Price	-	+	+

Due to different technical and economical properties of each type of rubber, possibilities of mixing rubbers were explored. In this way, beneficial properties of different types of rubber can be combined. The resulting material is an elastomeric mixture whose characteristics are a combination of these of all the components.

Practical, the CR content of the blend ensures the beneficial technical properties of the mixture. The much cheaper NR and SBR rubbers ensure the blend is economically feasible in contrast with the expensive CR rubber.

2.1.2 Thermal degradation

When CR is heated (for example in TGA or pyrolysis GC-MS), the rubber will decompose in several steps. In the first step, starting from 340°C, HCl will be eliminated. This is an important note in CR analysis, as HCl will be eliminated from CR monomers and can interfere with techniques for characterization. The decay order of CR is shown in figure 3. Aromats are formed from the CR monomers as a result of cyclisation in the third step due to the more stable nature of aromats.

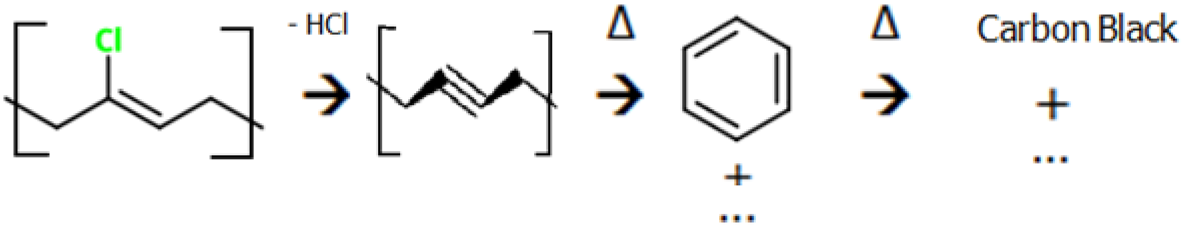

Figure 3: Visual overview of decay products, starting from CR

2.2 Analytics in polymer science

The science that studies the composition, synthesis and properties of polymers is called polymer science.

A visual overview of the disciplines of polymer sciences is shown in figure 4.

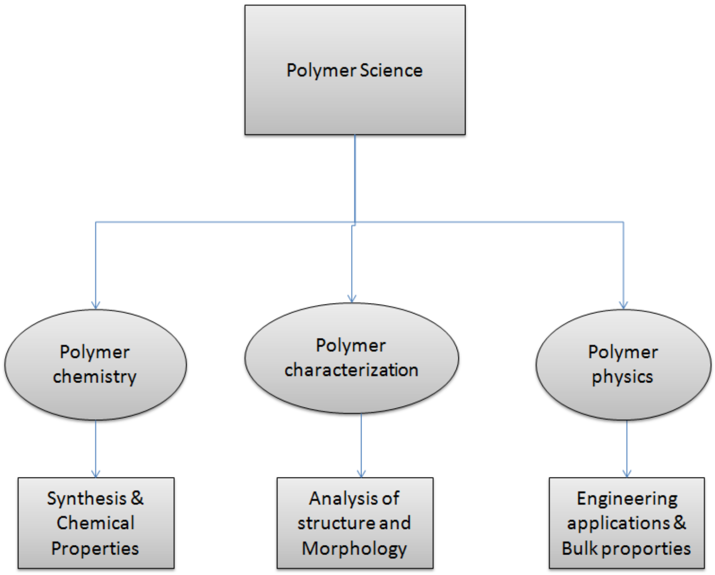

Figure 4: Overview of Polymer Science

The branch of polymer science is divided into 3 main disciplines. Polymer chemistry is concerned with the synthesis and chemical properties of polymers. The polymer physics is concerned about the engineering applications and properties of the polymer as a bulk. The last one, polymer characterization, is concerned with the analysis of the chemical structure, morphology and the determination of chemical properties in relation with compositional and structural parameters.

The analysis of elastomeric compositions is an important quality control requirement of the industry. If the correct composition of a polymer is known, the properties and behaviour of elastomeric mixtures can be explained and predicted. Various methods for the analysis of the polymer composition are developed since the rise of the rubber industry.

2.3 Methods for analysing the polymer composition in rubber

A polymer can be characterized based on its molecular mass, molecular structure, morphology, thermal - and mechanical properties. In this paragraph, an overview of existing techniques is shown.

2.3.1 Characterization based on molecular mass

The molecular mass of polymers is a distribution following a distribution curve as shown in figure 5. The principle that the molecular mass of a polymer is a distribution around an average molecular mass based on weight (M_w) or an average molecular length (M_n) is called polydispersity.

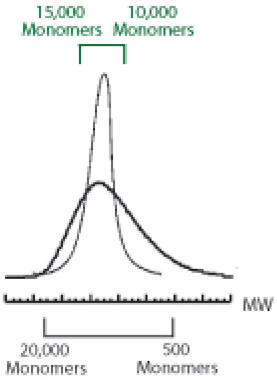

Figure 5: Molecular mass distribution in polymers [2]

Analytical techniques used to determine the molecular structure of organic compounds are also used in polymer characterization. Popular techniques to identify the molecular mass of polymers are shown in table 2.

Table 2: Examples of analytical techniques based on the molar mass distribution.

Technique	***Principle***
Viscometry	Heavier molecules ensure a higher viscosity of liquid polymers [21]
Size exclusion chromatography	Smaller molecules can penetrate more easily a stationary phase
Gel permeation chromatography	Separates polymers using a gel, depending on chemical and physical interactions.
Low- angle laser light scattering	Scattered light from the molecule is detected by a refractive index detector and compared using the Rayleigh equation

2.3.2 Characterization based on molecular structure

Spectroscopy, spectrometry and diffraction techniques are used for the characterization of the molecular structure of polymers. Popular techniques to identify the molecular structure are shown in table 3.

Table 3: Example of analytical techniques based on the molecular structure of polymers

Technique	***Principle***
Electron spin resonance spectroscopy	Electron spins are excited, absorbing a fixed amount of energy [22]
Ultraviolet-visible spectroscopy	Energy radiation of UV-Vis light results in changes between ground state and excited states of electrons within the system [23]
Infrared spectroscopy	Energy radiation of infrared light results in changes between ground state and excited states of electrons within the system
Raman Spectroscopy	Energy radiation of inelastic disturbance in changes between ground state and excited states of electrons within the system
Nuclear magnetic resonance spectroscopy	Technique based on the resonance frequency of intramolecular magnetic field around an atom
Mass spectroscopy	Measuring the mass to charge ratio of ionized molecule fragments
X-ray diffraction	Diffracted X-rays used for the determination of the molecule structure
Wet chemical analysis	Schöniger digestion, followed by chloride titration

The wet chemical analysis based on the Schöniger digestion is less conventional than the other techniques shown in table 3. Due to the detection of chloride, which is an important component of CR, the combination of the Schöniger digestion with a chloride titration is able to determine the amount of CR in an elastomeric mixture. Therefore it can be categorized under methods based on the molecular structure.

2.3.3 Characterization based on morphology

The morphology of a polymer is determined by the amount of amorphous and crystalline structures of the polymer. Material morphology is determined using modern microscopic instruments.

Examples of these techniques are Atomic Force Microscopy, Transmission Electron Microscopy, Scanning Electron Microscopy, Scanning Transmission Microscopy and X-Ray diffraction.

2.3.4 Characterization based on mechanical properties

In the characterization of mechanical properties, the tensile strength and the Young's modulus are of significant interest in the description of stress-strain properties of polymers. To characterize the mechanical properties of a polymer, there are several techniques available.

The most common technique to characterize the visco-elastic behaviour is Dynamic Mechanical Analysis (DMA), where the strain of the material is monitored under an applied sinusoidal stress. Many variants exists on the classic DMA technique. Other techniques are shown in table 4.

Table 4: Example of analytical techniques based on the mechanical properties

Viscometry	Viscosity is measured with a stepped or constant shear rate
Rheometry	Measured property is a function of the flow conditions
Pendulum Hardness	Measuring the hardness of a polymer using a pendulum

2.3.5 Characterization based on thermal properties

In most cases of polymer characterization, thermal analysis is used. Thermal analysis is based on the characterization of the polymer based on heat properties and categorizes the major part of analytical techniques in polymer characterization.

Hereby is Differential Scanning Calorimetry (DSC) the most popular technique. In DSC, the difference in the amount of heat required to increase the temperature of a sample and a reference is measured.

In Thermo gravimetric analysis (TGA), the mass of the sample is measured during a constant stepwise heating program. The TGA will be discussed in the next paragraph.

2.4 TGA execution principles

An overview of the TGA-apparatus is shown in figure 6.

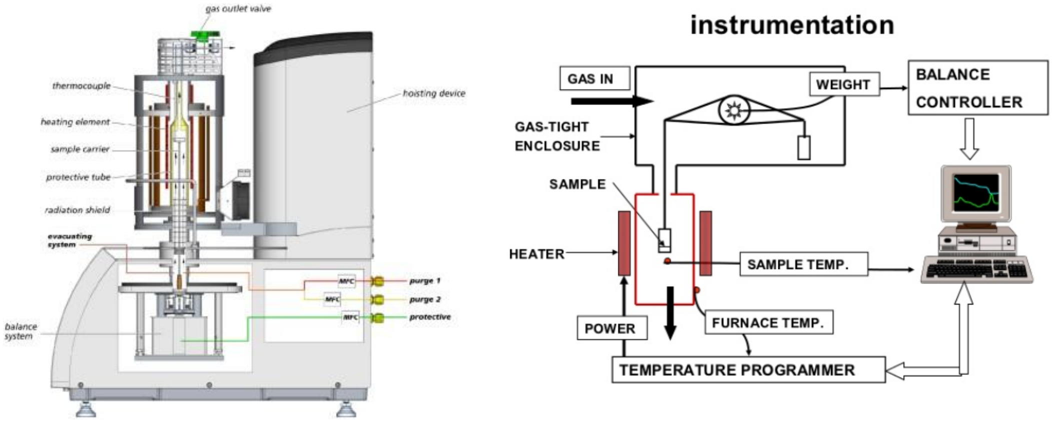

Figure 6: Overview of the TGA- apparatus [3]

The TGA equipment consists of a microbalance, a heater, a temperature programmer, a balance controller and a switching box. The temperature programmer provides a linear increase of the temperature while the microbalance monitors the weight of the sample during the measurement. The TGA apparatus has two gas inlets. One for the Nitrogen, which is the gas stream in the early stage of the measurement. And one for the oxygen, which is the gas stream in the later stage of the measurement and ensures the oxidation of the sample.

TGA analyzes the percentage of carbon black, non-combustibles and all volatile components present in the sample which are set free at a given temperature. The amount of carbon black and non-combustibles are obtained by switching to oxygen in a later stage of the measurement. The non-combustibles are shown by the remaining weight percentage at the end of the measurement. The output of a TGA measurement is shown as an illustration in figure 7.

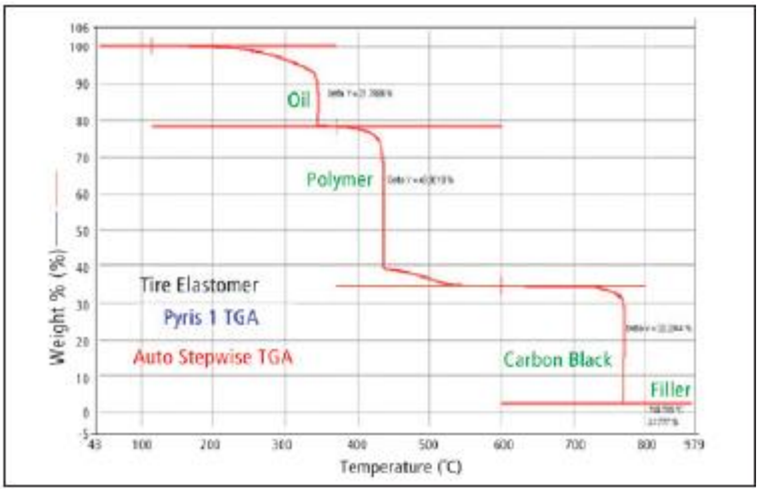

Figure 7: Example of a TGA decay-curve [4]

The Y-axis (figure 5.) represents the weight of the sample in function of the temperature. Sometimes, the time instead of the temperature is shown on the X-axis. These two can easily be transformed in each other as the temperature increases due to the linear temperature program. The TGA curve shows that with an increase in temperature, the weight of the sample decreases. Volatile components are set free from the sample which results in a mass reduction. The location and the height of the steps depend on the type of rubber, the composition and the level of vulcanization. Table 5 shows an exemplary evaluation of the steps of this TGA curve.

Table 5: Decay steps of an SBR (SBR 1090) TGA curve

Temperature range (C)	*Mass reduction of the sample (%)*	*Component loss (in general)*	*Component loss (specific)*
20° - 312.9°	5.0	Most volatile components	Oligomers/ Unpolymerized residues/Oil
312.9° - 413°	14.3	More thermolabile components	Lightest parts of the decay products
413° - 599°	79.9	More thermostabile components	More heavy fragments of the decay products
599° - 900	0.7	Pyrolysis products	Carbon black
Residual mass	0.2	Rest mass	Fillers/Ashes

The TGA curve has several steps. The first step occurs due to the vaporization of oligomers and unpolymerized residues from the production process. This step is not always visible in TGA results, as the only components in this decay step are the lightest components that are not always present in every elastomeric mixture. Examples of these components are monomers, oligomers and auxiliaries.

In the second step, the more thermolabile components of the rubber will vaporize. The decay in the third step of the TGA curve represents the more thermostabile components in comparison with the second step. The last step shows the carbon black percentage of the sample. This carbon black can be a result from the pyrolysis of the rubber itself or could be added as a filler for optimizing an elastomeric mixture. The carbon black added can result in several problems for chloroprene rubber, as described in the next paragraph. The residual mass at the end of the curve shows the percentage of fillers and ashes in the sample.

When analysing complex elastomeric mixtures, several problems can occur as described in the next paragraph.

2.5 Problems and recommendations for TGA- analysis in elastomeric mixtures

Two common problems in the TGA analysis of elastomeric mixtures are discussed. A third one is typical for CR containing rubbers.

A first problem is the difficulty in determining the oil and elastomeric part of the mixture in cases where their volatilization temperature range overlaps. These components often oxidize and evaporate together. After consulting several published works that studied this problem, isothermal TG together with the use of “High Resolution” TG equipment is recommended. [24]

> *“The addition of high resolution capability to TGA not only provides improved resolution for better interpretation of weight loss and evolved gas results, but it also provides additional flexibility for determining valuable and reliable kinetic information.”* [25]

Due to the sufficiency of normal TGA equipment in this research, TGA measurements are conducted using conventional TGA equipment.

A second problem concerns the determination of the carbon residue which originated from the components and the carbon black which was additionally added in the compound. Carbon black is added in an elastomeric mixture to increase the resistance against UV and abrasiveness. These carbon black components often oxidize together, which makes it difficult to determine which part of the carbon black originates from the rubber and which part is additionally added.

A third problem is that chloride containing rubbers will release hydrochloric acid (HCl) during heating, as a result of pyrolysis. This HCl can react with other constituents, which will lower the amount that can be detected in the sample and interferes with the measurements. After the HCl is eliminated, cyclisation occurs as shown in figure 6.

When analyzing chloride containing rubbers, it is important to keep the presence of HCl in mind, to avoid interference with measurements.

In general, small amounts of carbon black are formed during pyrolysis of NR and SBR rubbers. Mass percentages vary from 0 to 2%. However, with chloride containing rubbers such as chloroprene, relatively large amounts of carbon black are formed during the pyrolysis program. The mass percentages of carbon black can be up to 20%. This results in a more difficult determination of the filler carbon black in these polymers. An example of the TGA curve determining the carbon black using different heating rates is shown in figure 8.

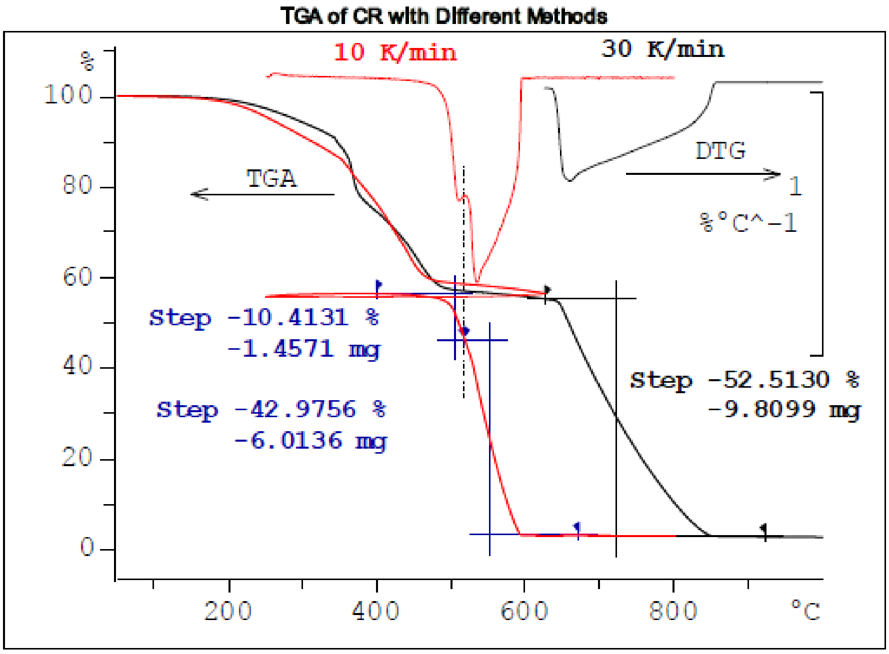

Figure 8: TGA analysis using different heating rates (10 K/min & 30 K/min) [5]

When measuring at a heating rate of 30K/min, combustion takes place in one step. Therefore, the carbon black formed during pyrolysis cannot be distinguished from the carbon black added as filler. In contrast, when heating at a rate of 10K/min, the carbon black from the filler burns a little later than the pyrolytic carbon black of the CR. In this case, the curve shows a distinct difference in the shoulder that can be separated using TGA analysis.

Therefore, a slow heating rate of 10 K/min has to be chosen when the analysis of carbon black is executed on chloride containing rubbers.

CHAPTER 3: The determination of Chloride-ions: the Schöniger digestion

3.1 History and overview of the method

The Schöniger digestion is a method developed in 1892 by Hempel. Originally, the technique was developed to determine the sulphur amount in coals. The sample was placed in a platinum-gauze and ignited by electrical current in a 10 litre flask. The sulphate formed by the oxidation process was determined gravimetrically [6]

The Schöniger digestion can be used to determine the amount of sulphur, phosphor and halogens in organic samples. The organic sample is burned in an oxygen rich atmosphere which will result in the release of the volatile inorganic components. When chloride is present in the sample, HCl will be released and can be determined.

3.2 Oxidation process

The ignition of the sample ensures the volatiles are set free in the flask. For this reason, the flask is sealed from the environment as shown in figure 9a. These volatiles need to be absorbed in the liquids present in the oxidation flask. The kind of absorption liquid depends on the components that need to be determined. The sample is folded in a filtration paper as shown in figure 9b. The wrapped sample is attached to the gauze before it seals of the flask. After ignition, the gasses need a fixed time to ensure complete absorption in the absorption liquid.

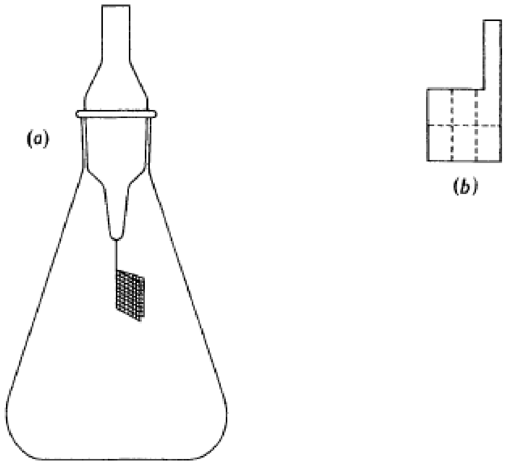

Figure 9: Oxidation flask & paper [6]

3.3 Determination of the component

In the last stage, it is necessary to determine the amount of component released from the sample in the absorption liquid. Various methods can be used for the determination. As an example, the precipitation titration of chloride using $AgNO_3$ is explained in the next section.

3.4 Precipitation titration of chloride using $AgNO_3$

In the determination of chloride using a precipitation titration with $AgNO_3$, the chloride present in the absorption solution forms an insoluble salt AgCl. The amount of chloride can be determined using a precipitation titration. If for example, the precipitation titration of sodiumchloride using $AgNO_3$ is executed, the following reaction occurs. (figure 10)

$$AgNO_3 + NaCl \rightarrow AgCl \downarrow + NaNO_3$$

Figure 10: Argentometric titration of NaCl using $AgNO_3$ [7]

The silvernitrate reacts with the sodiumchloride, forming insoluble silverchloride and soluble sodiumnitrate. If the amount of silverchloride that precipitates is determined, the reaction stochiometrics shows that the same amount of silvernitrate is added to the solution to reach the equivalence point. The equivalence point can be determined by the use of potentiometry.

In the potentiometric titration, instead of using an indicator, the potential is measured across the analyte. A condition for potentiometric titration is that the analyte has to be an electrolyte to ensure there is a potential difference between the measuring electrode and the indicator electrode. The potential is in relationship with the activity of the ions in the solution between the two electrodes according to the Nernst equation as shown in figure 11.

$$U = U_0 + \frac{2.303 * R * T}{z * F} * \log a_M$$

Figure 11: Nernst equation [8]

When silvernitrate is added to the solution, chloride ions will precipitate and thus are removed from the solution. When the end-point is reached, there is a change of potential between the two electrodes of approximately 100 mV. This change of potential is detected using a Volt meter. [26]

CHAPTER 4: Pyrolysis GC/MS & IR spectroscopy

4.1 Pyrolysis GC/MS (Py /GC/MS)

Pyrolysis gas chromatography mass spectrometry (Py/GC/MS) is a method used for the characterisation of all types of macromolecules. [27] By combination of three techniques, it is possible to analyse all types of polymeric materials included those that are compounded as co-polymers, are cross-linked, contain fillers or are completely insoluble. [9] The pyrolysis method breaks the sample in smaller molecules after which the gas chromatograph is responsible for the separation of the different fragments. In the last step, mass spectroscopy ensures the identification of the pyrolysis products.

In the first step, pyrolysis breaks down the large, complex molecules into smaller, more analytically useful fragments by the use of thermal energy. This takes place in an inert atmosphere or vacuum, where the sample is rapidly heated between 600 and 1200 °C. GC can only analyse components which may evaporate. Polymers can't be vaporized, so the pyrolyses breaks the polymer down in depolymerised pyrolysis products that can be analysed using a GC. The temperature and heating rate depends on the application and the type of sample. A flow chart for the determination of the pyrolysis temperature is shown in figure 12.

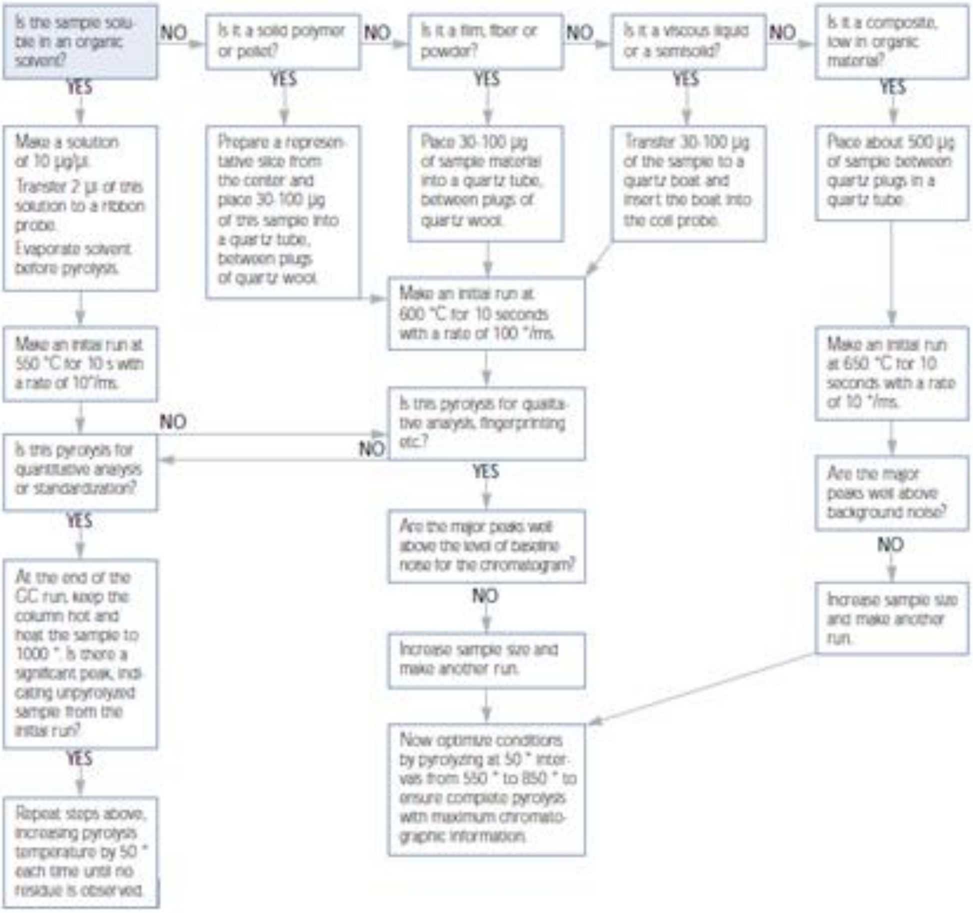

Figure 12: Flow chart for the determination of the pyrolysis temperature. [9]

When the energy applied to the molecule exceeds the energy of the specific bonds, those bonds will break.

These fragments are passed through the GC for a separation based on the affinity of the pyrolysis product for the stationary and mobile phase. The separation of the pyrolysis products ensures that in the next step, all fragments can be identified separately and no interference of products occurs.

In the last step, the identification of the fragments, mass spectrometry (MS) is used. MS is a technique that identifies the type and amount of chemicals by measuring the mass to charge ratio. When the molecules arrive in the mass spectrometer, high energetic electrons interact with atoms or molecules in the gas phase to produce ions. The accelerated ionized molecules end up in the detector where a mass spectrum is drawn. An example of the mass spectrum of styrene is shown in figure 13.

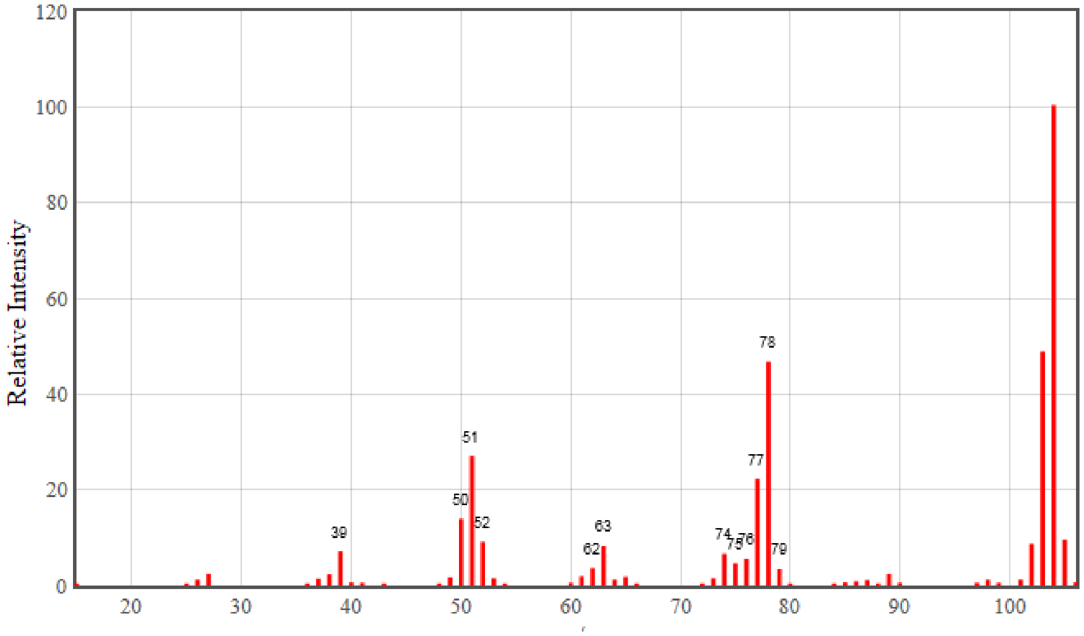

Figure 13: Mass spectrum of polystyrene, electron impact ionization [28]

The axis (figure 13) show the percentage present in the sample in function of the mass to charge ratio. The mass spectrum shows the presence and abundance of the fragment detected. This is valuable information for determining the content of the sample.

4.2 IR -spectroscopy

IR spectroscopy is due to its high information content and simple execution, a commonly used technique in research and industry. It uses the infrared part of the electromagnetic spectrum. IR is a technique that makes it possible to determine both the structure and the composition of molecules.

Infrared radiation is mainly thermal energy. It induces stronger molecular vibrations in covalent bonds. Covalent bonds of molecules are not rigid and vibrate at room temperature in a variety of ways. By the absorption of Infrared light, transitions between vibrational energy states are induced.

The position of an infrared absorption band is determined by the mass of the atoms and the type of the bond. The strength of absorption increases with increasing polarity of the vibrating bonds. A paper from A. Barth explains that;

> *"The absorption of infrared radiation excites vibrational transitions of molecules. In the mid- and far-infrared spectral regions this is generally the case when the frequencies of light and vibration are equal and when the molecular dipole moment changes during the vibration. Since vibrational frequency and probability of absorption depend on the strength and polarity of the vibrating bonds, they are influenced by intra- and intermolecular effects. The approximate position of an infrared absorption band is determined by the vibrating masses and the type of bond (single, double, triple), the exact position by electron withdrawing or donating effects of the intra- and intermolecular environment and by coupling with other vibrations. The strength of absorption increases with increasing polarity of the vibrating bonds."* [28]

Each atomic bond vibrates in several motions. Individual bonds can absorb more than one IR frequency. Each peak of the IR spectrum represents a specific vibration of a bond. Vibrations can be categorized according to the way the bond of the molecule moves. The motion possibilities are shown in figure 14.

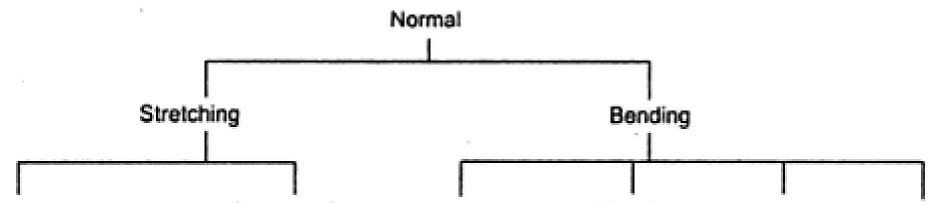

Figure 14: Vibrational possibilities of molecule bonds [11]

In the IR instrument, the beam splitter splits the IR beam in two parts. The first part is directed to the sample and the second part counts as a reference. Due to the presence of the molecules, the fraction with the same frequency as the vibrational frequency of the bond, is absorbed. Hereafter, the intensity of the light is determined by the intensity emitted (I_0)

divided by the observed intensity (I). This is the transmittance. The transmittance can be calculated using the following formula.

$$T = I/I_0$$

The output is available as an IR spectrum. The IR spectrum of formaldehyde is shown in figure 15.

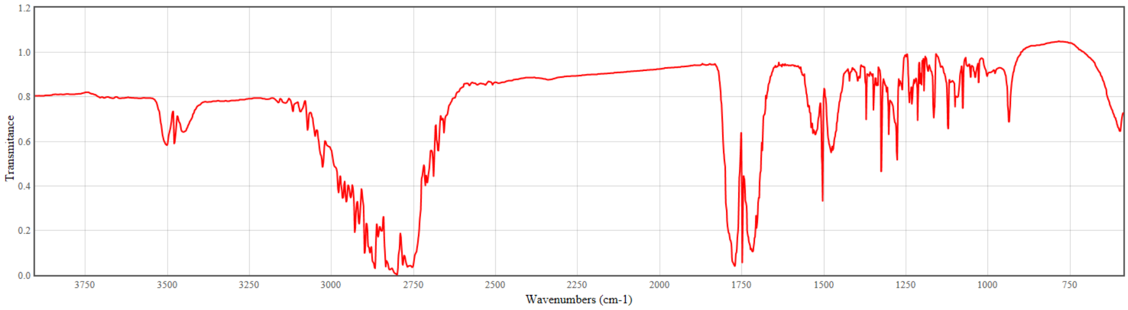

Figure 15: The IR spectrum of formaldehyde [12]

CHAPTER 5: Material & Methods

To determine the amount of CR in any elastomeric material, the Schöniger digestion and the TGA method are equally important. From the Schöniger digestion, the amount of chloride in a rubber sample can be determined. The TGA can determine the rubber percentage in an elastomeric material. Combined, it should be possible to determine the amount of CR in any elastomeric material.

5.1 CR rubbers and elastomeric components

The chloroprene rubbers used for the testing and optimization of the SD for chloride determination are Neoprene W and Skyprene B-30. The datasheets of both materials are enclosed as an attachment and general properties are shown in table 6.

Table 6: General properties of CR (Skyprene B-30 and Neoprene W)

Property	*Skyprene B-30*	*Neoprene W*
Mooney Viscosity	39 ± 4	49 ± 2
Color	White	White, silver gray
Gel content	/	/
Specific gravity	1.20 ± 0.04	1.23
Odor	Characteristic	Mild, characteristic

For testing the combined method on elastomeric mixtures, blends were made using SBR and NR. The datasheets of these materials are also enclosed as an attachment and a brief overview of these properties is shown in table 7.

Table 7: General properties of NR (RMA IX) and SBR (1500)

Property	*NR (RNA IX)*	*SBR (1500)*
Mooney Viscosity	40 -65	46 - 58
Color	Black, brown	Black
Gel content	/	/
Specific gravity	1,13	1,17

For the analysis of the binary rubber mixtures, samples of 56g were made. In order to make the binary mixtures, the following amount of pure components need to be mixed as shown in table 8.

Table 8: Composition of the NR/SBR mixtures

Mass percentage NR/SBR (%)	*Amount of NR (g)*	*Amount of SBR (g)*
10/90	5.6	50.4
20/80	11.2	44.8
30/70	16.8	39.2
40/60	22.4	33.6
50/50	28.0	28.0
60/40	33.6	22.4
70/30	39.2	16.8
80/20	44.8	11.2
90/10	50.4	5.6

These pure materials had to be homogeneously mixed in order to have good overall properties at any location in the material. The manufacturing of the mixtures is described in the next paragraph.

5.2 Manufacturing of the NR/SBR mixtures

In the first step of the manufacturing of the mixtures, the NR and SBR pure components were mixed with the Plasticorder PL 2000. The Plasticorder ensures a homogeneous and isothermal mixture of both components. After this, the material is rolled using the Walzwerk Polymix in order to unify both components. This Plasticorder PL 2000 and technical specifications are shown in figure 16.

System	Plasticorder PL 2000 (Fa. Brabender)
Allgemeine Maschinenparameter	- Leistung 6,5 kW - Drehmoment max. 400 Nm - Drehzahl 5-120 U/min
Spezialausrüstungen	- Messkneter Umlaufthermostat beheizt (max. 200°C) Walzenkneter W 50 (Kammervolumen 60 ccm) Nockenkneter N 50 (Kammervolumen 75 ccm, pneumatisch verschließbarer Einfüllschacht, Drehzahlverhältnis linke zur rechten Schaufel 3:2) - Messkneter elektrisch beheizt (max. 400°C) Walzenkneter W 50 HT (Kammervolumen 60 ccm, Drehzahlverhältnis 2:3) Walzenkneter W 350 HT (Kammervolumen 370 ccm, Drehzahlverhältnis 3:2)
Ergebnisse	- Aufnahme der Drehmoment-Zeit- und Temperatur-Zeit-Diagramme für die Mischungsherstellung - Reproduzierbare Ermittlung der Black Incorporation Time (BIT) nach Cotten - Bereitstellung der ASCII-Files dieser Untersuchungen - Erstellung temperaturkorrigierter Drehmoment-Zeit-Kurven und Ermittlung des Eigenschafts-Erhaltungsgrades

Figure 16: Plasticorder PL 2000, Brabander for mixing of NR and SBR

The NR/SBR amounts of table 8 were added in the machine at 60°C. The time necessary to ensure complete and homogeneous mixing was 10 minutes.

To ensure a complete homogeneous material, the elastomeric mixture was rolled 3 times. The roller used for this application is the Walzwerk Polymix type 110L. The laboratory Mill and specifications are shown in figure 17.

VEB Spezialmaschinenbau
46 Wittenberg Lutherstadt
Hergestellt in der DDR

zeugnistyp	K 408
GL Nr.	
zeugnis-Reg-Nr.	1038/04
aujahr	1973
chl.-Nr.ELN	183/03/210
Masse kg	800
TKO	

Figure 17: Walzwerk Polymix type 110L and specifications

After the rolling of the technical elastomer, the material was homogeneous in order to execute an accurate characterization using the Schöniger digestion and TGA.

5.3 The Schöniger digestion

The Schöniger digestion has been conducted on the instrument Mikro K by Elementar. In the first step, the Schöniger digestion is optimized and used for the determination of chloride in the pure CR samples. From the information of the pure CR samples, the optimized method can be used for CR determination in elastomeric mixtures and technical elastomeric materials. An overview of the laboratory equipment and chemicals necessary for one successful execution of the Schöniger digestion is shown in table 9.

Table 9: Equipment and chemicals for the Schöniger digestion

Equipment	***Amount***
Analytical balance (Sartorius CPA 225 D)	1
Schöniger combustion flask	1
Digestion instrument (Mikro K by Elementar)	1
Filter paper (Grade 2, Whatman)	1
Beaker (250 ml)	2
pH meter (Microprocessor pH meter pH 539)	1
Automatic stirrer (Mini MR standard IKA labor technik)	1
Automatic potentiometric titrator (Mettler Toledo T-50)	1
Flask with cover (100ml)	1
Meaurement pipet (20 ml)	1
Droplet pipet (2 ml)	1
Chemicals	***Amount***
H_2O_2 (30% m/V)	10 drops
NaOH (1M)	± 5 ml
H_2O	100 ml
O_2	*
$AgNO_3$ (0.01 M)	1000 ml

* A couple of seconds blowing pure O_2 in the Schöniger combustion flask before sealing ensures complete combustion of the polymer sample.

5.3.1 Description of the optimized procedure and materials

A homogeneous CR sample of 50 mg is taken and analytically weighted by the Sartorius CPA 225 D.

In the first step of the procedure, the sample is wrapped in the filter paper (grade 2, Whatman) cutted in the following dimensions as shown in figure 18.

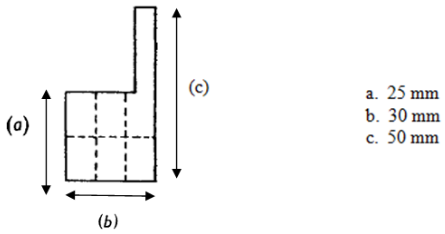

Figure 18: Dimensions of the ash free paper, Schöniger digestion [13]

When the sample is folded in the paper with the fuse protruding, it is attached into the gauze of the combustion flask. The stripe of paper has to be in touch with the platinum wire to ensure ignition of the sample.

Next, the combustion flask is filled with 10 drops of 30% m/V H_2O_2 and 8 ml H_2O. Before the gauze seals the combustion flask, pure oxygen is blown in the flask for 30 seconds to ensure complete combustion. The flask is then installed upside-down as shown in figure 19. The sample is ignited by pressing the combustion button on the instrument (Mikro K by Elementar).

Figure 19: Installation of the Schöniger flask in the combustion device (Mikro K, Elementar)

After 10 minutes to ensure complete absorption of the HCl, the combustion flask is shaken to ensure that all the HCl that is present in the flask dissolves in the 30% H_2O_2 absorption solution.

The content of the flask is analytically poured in a beaker and neutralized using 1.0 M NaOH while stirring the solution automatically using the Mini MR standard. The pH is continuously measured using the pH meter; Microprocessor pH meter pH 539. Neutralisation stops when pH is between 6 and 8.

In the last step, the chloride amount is determined by an argentometric titration using 0.01 M $AgNO_3$. It is important to keep in mind to choose a suitable titration volume to ensure the chloride amount is above the lower detection limit of the titration device. The automatic titrator (Mettler Toledo T-50), is shown in figure 20. After 30 minutes, one complete Schöniger digestion is executed.

Figure 20: Automatic potentiometric titrator (Mettler Toledo T-50)

5.4 Equipment for TGA measurements

The TGA measurements were conducted using the TGA device, TG 209 F1 from Netzsch. The TG 209 F1 is shown in figure 21.

Figure 21: TG 209 F1, Netzsch

First, a sample between 10 and 20 mg is taken using the analytical balance. The sample is put in an alumina crucible for TGA determination.

The software used for TGA analysis is *"Proteus, Analysis"* developed by Netzsch. Before starting the measurement, it is advised to press on the *"purge gass"* button in the software interface. This ensures that accurate peaks are drawn in the beginning of the measurement. Right before starting the measurement, the analytical balance in the machine has to be put on "*tarra"* to ensure the balance is calibrated to zero.

For TGA measurements, The machine heats the sample from 20°C to 900°C using a heating rate of 10 K/min. At 600°C, purge gasses are switched from nitrogen to oxygen. After 105 minutes, one TGA measurement is completed.

5.5 Fourier transform Infrared spectroscopy (FTIR)

The IR spectroscopic characterization of the composition of the CR rubbers was conducted on a FTIR spectrometer Nicolet Avatar 360. The apparatus is shown in figure 22. IR spectra were recorded in the spectral range between 4000 and 400 cm^{-1} with a resolution of 8 cm^{-1} using a single beam diamond attenuated total reflection cell (Golden Gate).

Figure 22: Avatar 360 FTIR from Nicolet [14]

CHAPTER 6: Results & discussion

6.1 CR rubbers

6.1.1 IR spectra of the pure components

To have an overview of the general composition of the CR rubbers, IR spectra were taken from both CR's. The IR spectra of Skyprene B-30 and Neoprene W with wavenumbers of the maxima of the absorption bands are shown in figure 23 and 24.

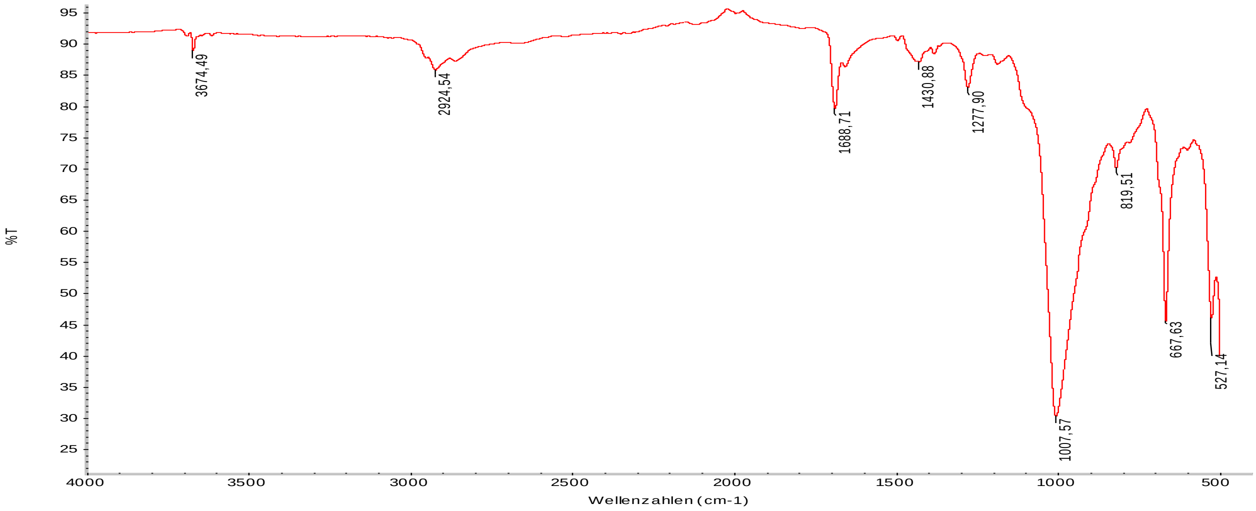

Figure 23: IR spectrum of Skyprene B-30 with band numbers.

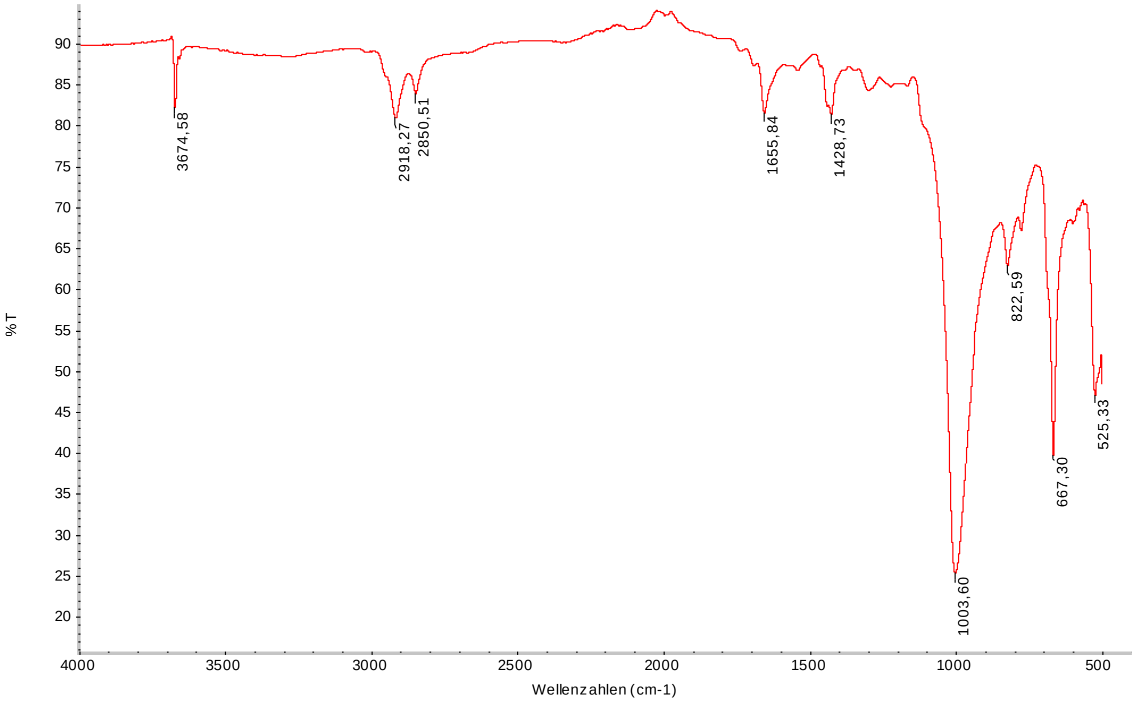

Figure 24: IR spectrum of Neoprene W with band numbers

An overview of the identification of the most important band numbers is shown in table 10. Important note has to be made about the Si-O bending vibration, which is seen at 1007,57 cm^{-1}. This implies the presence of talc in the rubber sample.

Table 10: Identification of the band numbers of Neoprene W

Band number (cm^{-1})	***Bond***	***Vibration***
667,63	C-Cl	Stretch
819,51	C-Cl	Stretch
1007,57	Si-O	Bend
1666,71	O-H	Bend
	C = O	Stretch
2900	C-H	Stretch
3500	O-H	Stretch

Although there are no O-H bonds present in the CR samples, H_2O is present in the air around the sample, this results in the detection of a O-H bend. To compare the homogeneity of the compound on the inner and outer side of the Neoprene W samples, spectra were taken from the middle and the outer side of the sample. These spectra are shown in figure 25.

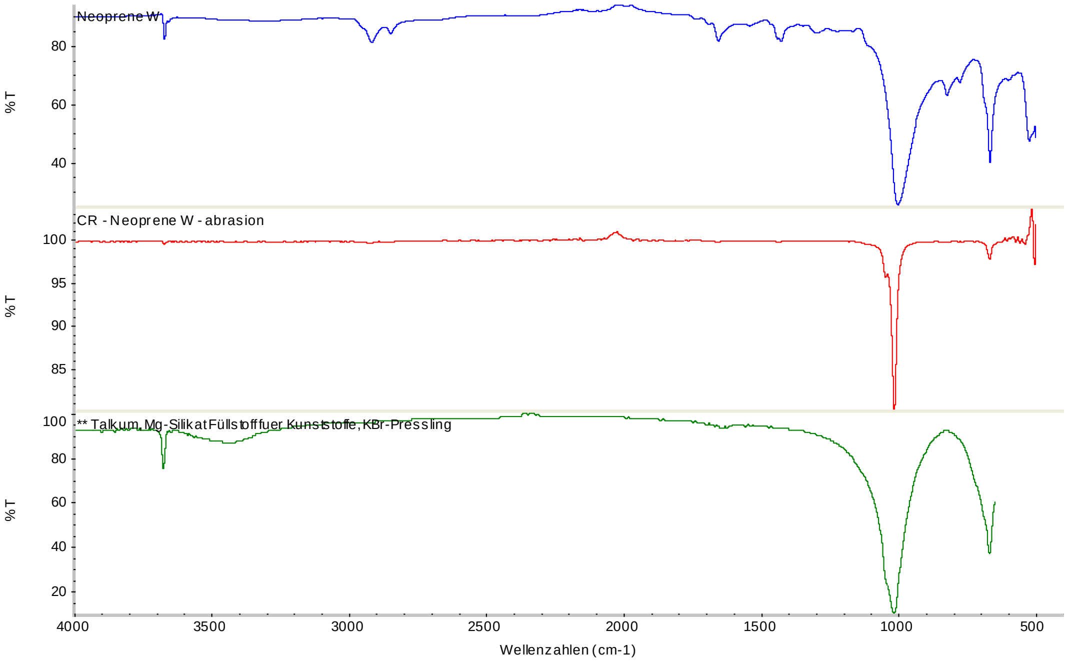

Figure 25: Comparison of inner and outer side of the IR spectra of Neoprene W

Results show the presence of talc on the outer side and the abrasion of the sample. The Si-O peak at 1007 cm^{-1} shows the amount of talc on the outer side of the sample is greater than on the inner side of the sample.

6.1.2 Schöniger digestion

The percentage of chloride, measured experimentally, has to be divided by the efficiency factor of the Schöniger digestion. Due to experimental circumstances like the combustion of the CR sample, incomplete absorption and apparatus detection limits, the efficiency of the SD is in the range of 80%. The efficiency factor can vary in different experimental circumstances. Therefore the efficiency factor of the SD in these circumstances was calculated.

The efficiency factor can be calculated by the use of the molecule structure of pure CR. The mass percentage in pure CR can be calculated according to the molecule structure and is 40%. If the experimental yield is divided by the theoretical percentage, the efficiency factor under these experimental circumstances is calculated at 78 ± 0,5 %.

In the first step, the accuracy and precision of the Schöniger digestion was determined. A 10-fold repetition of the Schöniger digestion was executed on two different pure CR samples. The results are shown in figure 26.

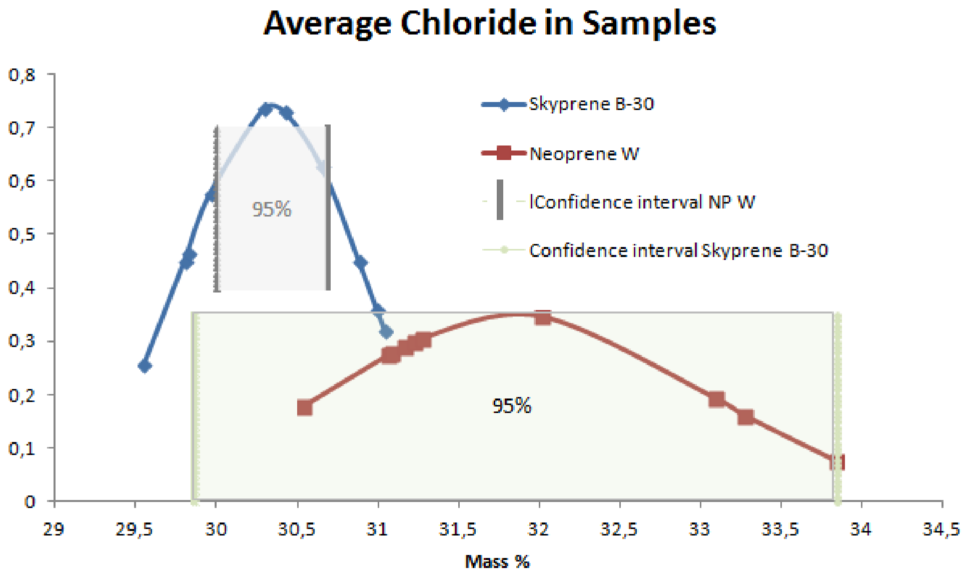

Figure 26: Statistical overview of CR (Skyprene B - 30 and Neoprene W)

The mass percentage of chloride in both CR rubbers is slightly different. This is due to different talc percentages in the samples. Different talc percentages slightly influences the mass % chloride in the sample.

Results show that the confidence interval of the Neoprene W is broader than this of the Skyprene B-30. The trustworthiness of every single measurement is examined in the plot of a 10 fold repetition of the SD on CR(B -30) and CR(Neoprene W). The measurement to measurement variation of the 10 fold repetition on both materials is shown in figure 27 and 28.

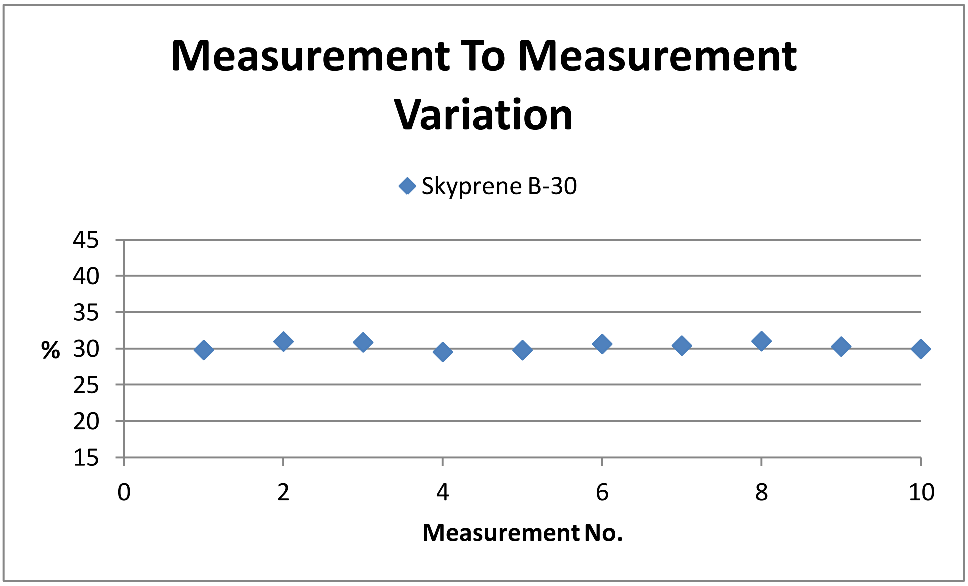

Figure 27: Measurement to measurement variation Skyprene B-30

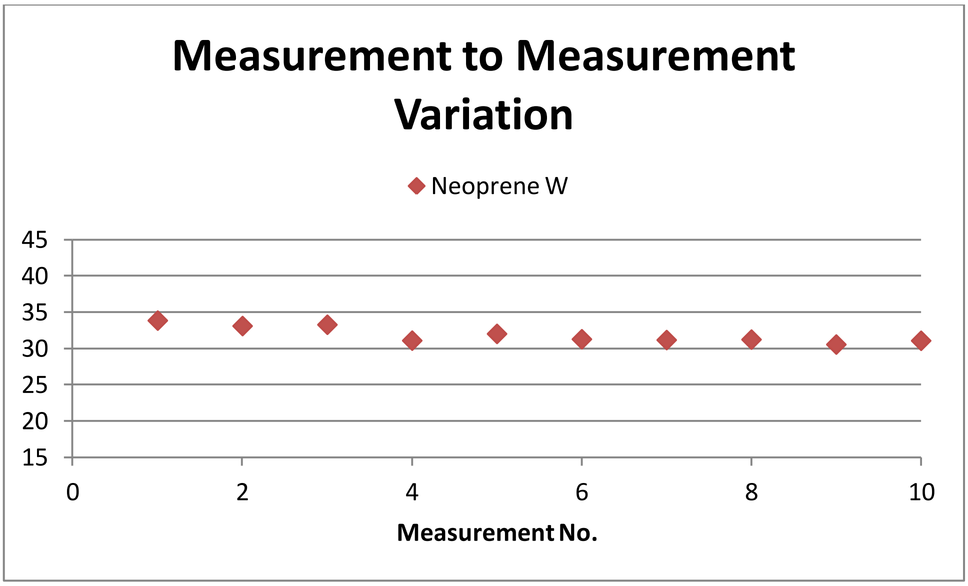

Figure 28: Measurement to measurement variation Neoprene W

The measurement to measurement variation shows that fluctuations between measurements are limited. The optimized SD was executed with stable results. The statistical documentation of the measurement to measurement variation on both methods is shown in table 11.

Table 11: Statistical validation of Skyprene B-30 and Neoprene W

	Skyprene B-30	***Neoprene W***
Average chloride (%)	30.34	31.85
Stdev	0.54	1.14
n	10	10
Confidence Coëfficient	1.96	1.96
Margin of error	0.34	1.99
Upper Bound	30.68	33.84
Lower Bound	30.00	29.86
Max	31.04	33.84
Min	29.55	30.54
Range	1.49	3.3

Results show that the measurement to measurement variation of the Schöniger digestion is stable but a difference in accuracy is present. This difference is caused by choosing the same value as a prediction value for the calculation of the accuracy. The average chloride percentage of both materials is slightly different. This is due to a different chloride percentage in both rubber materials. The same prediction value and a slightly different chloride percentage in both materials results in a different accuracy value. Therefore the variation in chloride average between the two materials is not due to measurement variations. The margin of error on both materials is acceptable and the difference between the minimum and the maximum measured on both materials is small.

6.1.3 TGA output

In the analysis of the TGA output, the decay steps have to be determined the same way for every sample. In order to do this, the peak separation is determined by the separation of the peaks using the DTG curves of the pure CR rubbers (Neoprene W & Skyprene B-30). An average of the separation temperatures of each step is made. This average temperature in the decay steps is used in the TGA analysis of every sample in order to be able to compare the decay steps. The separation of the peaks on B-30 and is showed in figure 29 and 30.

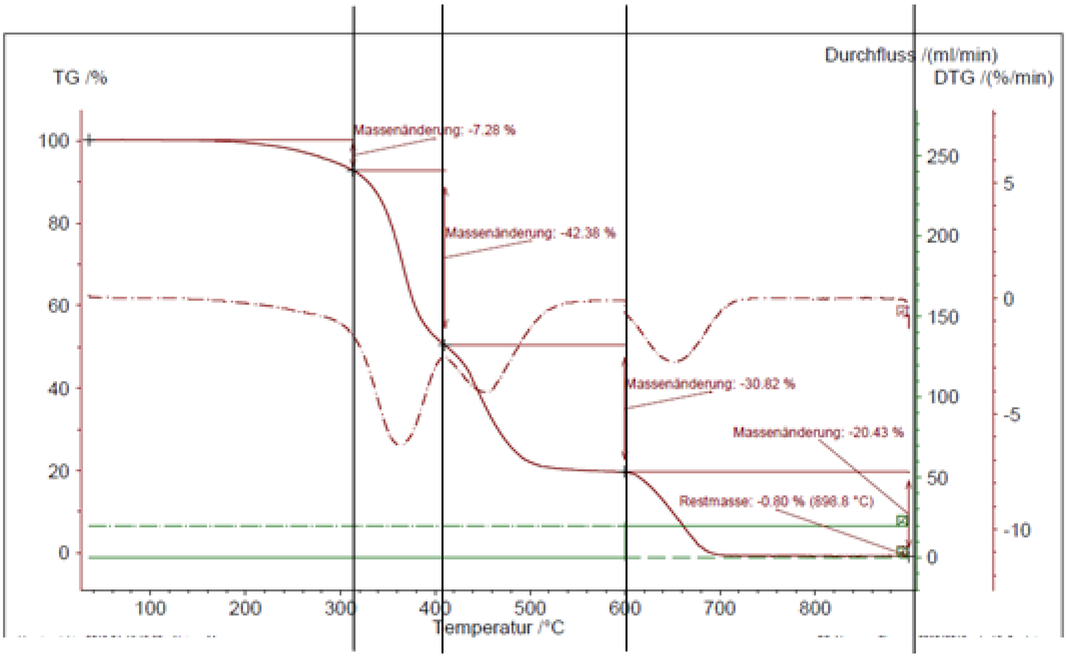

Figure 29: TGA & DTG curve to determine the boundaries for Skyprene B-30

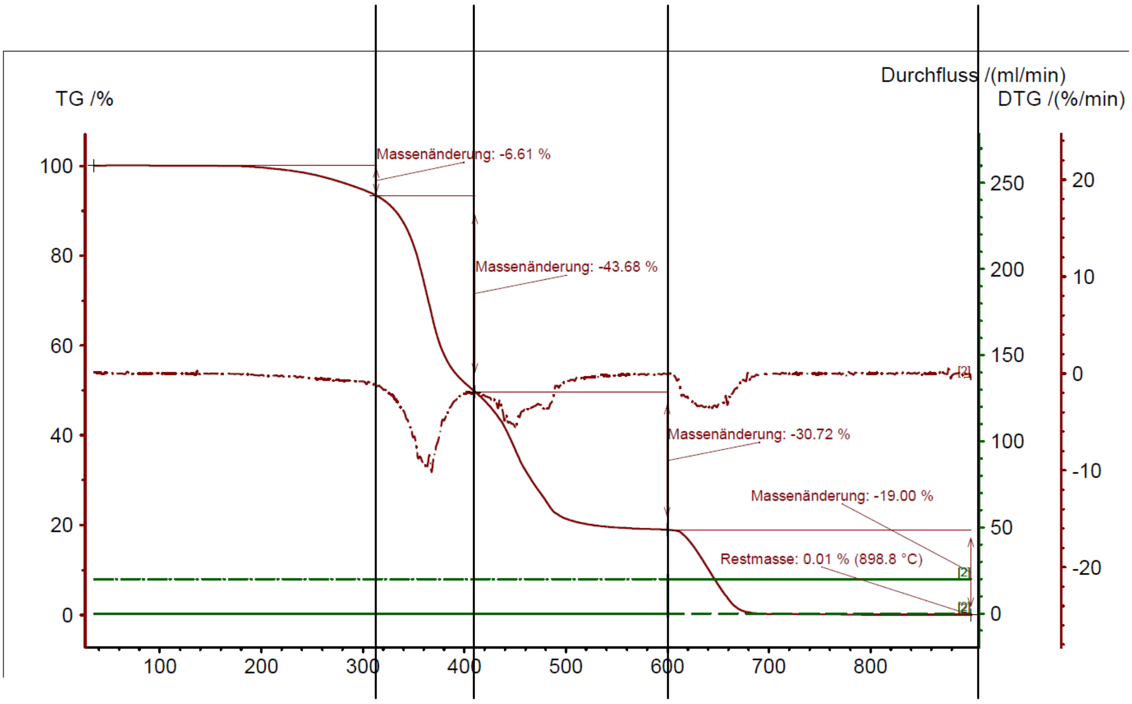

Figure 30: TGA & DTG curve to determine the boundaries for Neoprene W

The DTG curve shows the location of the borders for the separation of the TGA peaks to determine the decay steps. All DTG peaks have to be separated in order to use the right borders for TGA analysis. The borders are chosen that the whole peak drop of the DTG curve is in the region.The regions and results for the decay steps are shown in table 12.

Special note has to be made for 2 peak drops. The first is the peak drop of carbon black, which is slightly higher for B-30. and the second is the peak drop of the thermolabile component, which is slightly lower for B-30. This proves the results of the SD measurements that there is a slightly higher m% of chloride in the Neoprene W than in the Skyprene B-30.

Table 12: Results of the m% decay of CR rubbers

Peak	**1 (%)** **(0°-313°)**	**2 (%)** **(313° - 410,2°)**	**3 (%)** **(410,2° - 599,9°)**	**4 (%)** **(599,9° - end)**	**5 (%)**	**Sum (%)**
Comp.	*Volatile*	*Thermolabile*	*More Thermostabile*	*Carbon black*	*Res. mass*	*Total*
B-30	6.8	42.4	29.3	20.4	1.1	100
B-30	7.2	41.7	30.3	20.0	0.8	100
W	6.6	43.7	30.7	19.0	0.0	100
W	6.6	43.1	30.4	19.6	0.2	100
AVG	6.8	42.7	30.2	19.7	0.5	100

Mean values of the TGA output will be used for the determination of the carbon black mass %, the simulation of the TGA output and the determination of the CR Phr amount in the elastomeric mixtures.

6.2 NR, SBR and Nitrile rubber (NBR)

In order to simulate a formula for the rubber percentage present in an elastomeric mixture, TGA measurements were executed on NR (RMA IX), SBR (SBR 1500) and NBR (NBR 3445F) pure rubber samples. In the determination of the decay steps, the same boundaries determined in the CR-TGA output were used. An overview of the decay steps are shown in table 13.

Table 13: Results of the m% decay for pure rubber components

Peak	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)	Sum (%)
Comp.	*Volatile*	*Thermolabile*	*More Thermostabile*	*Carbon black*	*Res. Mass*	*Total*
NR	3.1	80.6	15.4	0.5	0.4	100
NBR	1.1	11.3	77.4	8.8	1.4	100
SBR 4602	5.2	15.4	78.5	0.6	0.4	100
SBR 1500	0.5	5.4	94.4	0	0.7	100

6.3 NR/SBR mixtures

6.3.1 TGA executed on binary elastomeric mixtures

TGA measurements were executed on two types of NR/SBR mixtures in order to compare the calculated formula with experimental values. All samples were taken as duplicates and values were rescaled to 100%. An overview of the TGA output of the NR/SBR mixtures is shown in table 14 (SBR 1500) and table 15 (SBR 4602).

Table 14: Results of the measured m% decay for binary elastomeric mixtures, NR (RMA IX) and SBR (SBR 1500)

Peak	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)	Sum (%)
NR/ SBR	*Volatile*	*Thermolabile*	*More Thermostabile*	*Carbon black*	*Res. Mass*	*Total*
10/90	0.6	10.3	88.0	0.5	0.5	100
20/80	0.7	13.9	84.6	0.3	0.5	100
30/70	0.1	20.7	77.9	0.4	0.8	100
40/60	1.2	26.0	71.4	0.5	0.8	100
50/50	1.6	33.8	63.7	0.5	0.4	100
60/40	1.2	41.5	56.1	0.5	0.7	100
70/30	1.8	52.5	44.7	0.2	0.8	100
80/20	1.8	61.8	34.7	0.5	1.2	100
90/10	1.9	70.3	24.8	0.1	2.9	100

Table 15: Results of the measured m% decay steps binary elastomeric mixtures, NR (RMA IX) and SBR (SBR 4602)

Peak	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)	Sum (%)
NR/ SBR	*Volatile*	*Thermolabile*	*More Thermostabile*	*Carbon black*	*Res. mass*	*Total*
10/90	4.6	18.4	75.9	0.4	0.7	100
20/80	5.1	24.7	69.1	0.6	0.4	100
30/70	4.5	29.4	64.7	0.6	0.8	100
40/60	4.7	35.6	58.2	0.6	0.9	100
50/50	4.5	43.5	50.8	0.8	0.4	100
60/40	4.5	51.6	43.0	0.6	0.3	100
70/30	4.2	57.0	37.6	0.8	0.4	100
80/20	3.4	65.1	30.4	0.8	0.5	100
90/10	3.4	73.7	22.0	0.6	0.3	100

The TGA results for the binary NR/SBR mixtures on two different kinds of SBR show there are small differences between TGA output depending on the type of SBR is used. This has to be kept in mind when simulating a formula for CR determination of TGA measurements.

6.3.2 Simulation of TGA formula based on pure NR/SBR samples

A formula is calculated based on the decay steps of pure samples to test if it is possible to simulate TGA decay steps of mixtures. The formula is calculated for all NR/SBR mixtures. An example of the calculation for the 70/30 is shown. These calculated values are compared with the measured values of table 15. The principle is the same for all NR/SBR mixtures. An overview of the input necessary to simulate the decay steps is shown in table 16. The values of NR and SBR were taken from table 13.

Table 16: Overview of the measured input for decay step calculation

Peak	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)	Sum (%)
Comp.	*Volatile*	*Thermolabile*	*More Thermostabile*	*Carbon black*	*Res. mass*	*Total*
NR/SBR 70/30	1.8	52.5	44.7	0.2	0.8	100
SBR	0.5	5.4	93.4	0.0	0.7	100
NR	3.1	80.6	15.4	0.5	0.4	100

The mass % NR/SBR mixture exists out both NR and SBR. The mass percentage of the volatile component (column 1) of the mixture is calculated with the following formula:

$$M\%\ Volatile\ comp. mixture = (Volatile\ comp. NR * Mass\%\ NR) + (Volatile\ comp. SBR * Mass\ \%\ SBR)$$

Applied on the 70/30 mass % elastomeric mixture, the % of the volatile component is:

$$M\%\ Volatile\ comp. mixture = (3.09 * 0.7) + (0.53 * 0.3) = \ 2.3$$

According to the calculated formula, the mass percentage decay of the volatile components is 2,3%. This shows an overshoot in comparison with the measured value, as shown in table 16.

When this formula is applied to all decay steps of the 70/30 mixture. All decay steps are calculated as a simulation of the 70/30 m% mixture. The decay steps of the 70/30 m% mixtures are shown in table 17.

Table 17: Calculated decay steps for the 70/30 m% mixture

Peak	**1 (%)**	**2 (%)**	**3 (%)**	**4 (%)**	**5 (%)**	**Sum (%)**
Comp.	*Volatile*	*Thermolabile*	*More Thermostabile*	*Carbon black*	*Res. mass*	*Total*
NR/SBR 70/30	2.3	58.1	38.8	0.3	0.5	100

If the formula is applied to every NR/SBR mixtures, values are calculated as shown in table 18 and table 19.

Table 18: Calculated decay steps for binary elastomeric mixtures, NR (RMA IX) and SBR (SBR 4602)

Peak	**1**	**2**	**3**	**4**	**5**	**Sum**
NR/ SBR	*Volatile*	*Thermolabile*	*More Thermostabile*	*Carbon black*	*Res. mass*	*Total*
10/90	0.8	12.9	85.6	0,1	0.7	100
20/80	1.0	20.4	77.8	0.1	0.6	100
30/70	1.3	28.0	70.0	0.2	0.6	100
40/60	1.6	35.5	62.2	0.2	0.6	100
50/50	1.8	43.0	54.4	0.3	0.6	100
60/40	2.1	50.5	46.6	0.3	0.5	100
70/30	2.3	58.0	38.8	0.3	0.5	100
80/20	2.6	65.6	31.0	0.4	0.5	100
90/10	2.8	73.1	23.2	0.4	0.5	100

Table 19: Calculated decay steps for binary elastomeric mixtures, NR (RMA IX) and SBR (SBR 1500)

Peak	1	2	3	4	5	Sum
NR/ SBR	*Volatile*	*Thermolabile*	*More Thermostabile*	*Carbon black*	*Res. mass*	*Total*
10/90	4.9	21.5	72.3	0.6	0.8	100
20/80	4.7	28.0	66.0	0.6	0.8	100
30/70	4.5	34.6	59.7	0.5	0.7	100
40/60	4.3	41.2	53.3	0.5	0.7	100
50/50	4.1	47.8	47.0	0.5	0.7	100
60/40	3.9	54.3	40.7	0.5	0.6	100
70/30	3.7	60.9	34.4	0.5	0.6	100
80/20	3.5	67.5	28.0	0.5	0.5	100
90/10	3.3	74.1	21.7	0.5	0.5	100

These decay steps can be compared with the experimental decay steps from table 14 and table 15. If the calculated steps for the binary mixtures are compared with the experimental measured steps, a correlation between the measured and calculated values are observed, though the calculated formula has an overshoot.

6.4 Recovery on the ternary elastomeric mixtures

6.4.1 Schöniger digestion

The optimized Schöniger digestion was executed on ternary elastomeric mixtures in order to test the method on samples containing a fixed amount of CR. The measured chloride is divided by the efficiency factor of the SD (0.78) to calculate the percentage of chloride present in the rubber. An example of the rescaling for the 20/50/30 mixture is shown using the following formula:

$$12.6\ \% = \frac{9.8\ \%}{78\%}$$

An overview of the chloride determination before and after rescaling of the ternary elastomeric mixtures are shown in table 20.

Table 20: Overview results Schöniger digestion on ternary mixtures

Mixture (NR/SBR/CR)	*Chloride determined (%)*	*Rescaled chloride (Efficiency factor SD) (%)*
20/50/30	9.8	12.6
40/20/40	11.7	15.0
50/20/30	9.0	11.6
60/20/20	5.0	6.5
60/30/10	2.6	3.4

When this value is divided by the chloride percentage in pure CR rubber, the amount of CR in the sample is calculated. The CR rubber percentage can be calculated according to the following formula;

$$\%\ CR = \frac{Rescaled\ chloride\ \%}{Chloride\ \%\ in\ pure\ rubber}$$

When the formula is applied to the 20/50/30 mixture, the formula can be written as:

$$\%\ CR = \frac{9.8}{0.78 * 40} = 31.0\ \%$$

In the elastomeric mixture that contains 30 m% CR, a CR percentage of 31.0 m% was calculated.

If this formula is applied to all NR/SBR/CR ternary elastomeric mixtures, the CR percentage is calculated. The results are shown in table 21.

Table 21: Results of the recovery of the chloride percentage in the ternary elastomeric mixtures.

Mixture (NR/SBR/CR)	*Theoretical CR (%)*	*CR calculated (%)*
20/50/30	30	31.0
40/20/40	40	37.5
50/20/30	30	29.0
60/20/20	20	17.9
60/30/10	10	8.4

The CR percentage can be plotted against the percentage of chloride determined. This graphic is shown in figure 31.

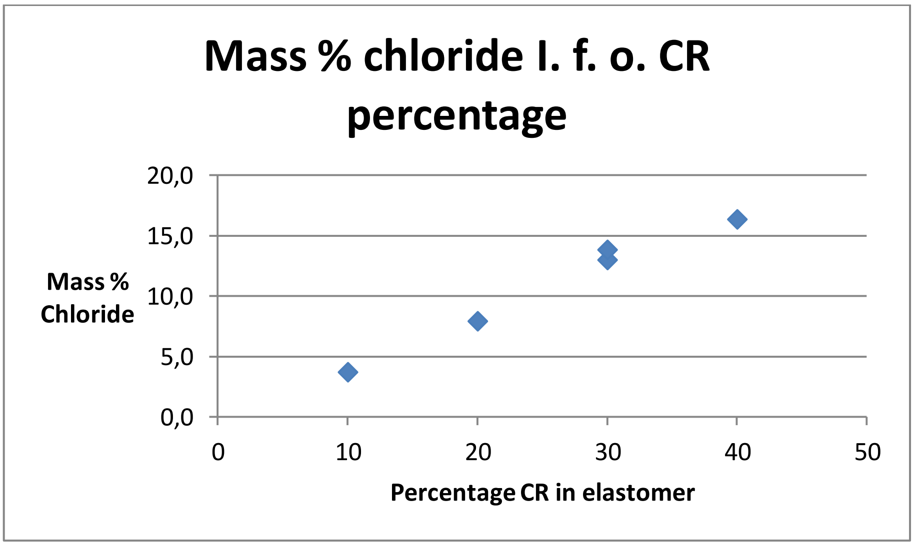

Figure 31: m% chloride in function of CR percentage for ternary elastomeric mixtures

Results visualise the correlation between the chloride detected and the CR percentage calculated according the formula. This graphic can be used as a visual inspection for the chloride determination of the unknown samples.

6.4.2 TGA

To test the recovery of the TGA- formula on the ternary elastomeric mixtures, TGA measurements were executed. An overview of the decay steps are shown in table 22.

Table 22: Results of the measured m% decay for ternary elastomeric mixtures

Peak	1	2	3	4	5	Sum
NR/ SBR/ CR	*Volatile*	*Thermolabile*	*More Thermostabile*	*Carbon black*	*Res. mass*	*Total*
20/50/30	3.1	29.8	61.8	5.2	0.1	100
40/20/40	4.1	42.3	46.0	7.0	0.5	100
50/20/30	4.6	45.2	44.0	5.3	0.9	100
60/20/20	3.1	47.5	44.8	3.7	0.9	100
60/30/10	2.3	44.7	50.4	2.0	0.5	100

Table 22 shows a correlation between the CR content of the elastomeric mixture and the 4th decay step. This implies that carbon black is formed due to CR in the elastomeric mixture.

6.5 Testing the optimized method on unknown samples

6.5.1 Schöniger digestion on unknown samples

In order to test the combined method, the optimized method and CR calculation were executed on 3 unknown samples. Sample 1 and 2 were ternary elastomers and sample 3 was a technical elastomeric material. The results of this execution was compared with pyrolysis GC/MS. In the first step, the Schöniger digestion was executed and the following results were found, as shown in table 23.

Table 23: Results of the Schöniger digestion in the unknown samples

Unknown mixture (NR/SBR/CR)	*Chloride determined (%)*	*CR calculated (%)*
1	8.3	19.6
2	17.2	40.5
3	4.0	9.8

The unknown sample can be compared with the graphic plotted from the unknown mixtures as a visual inspection. This visual inspections are shown in figure 32, 33 and 34.

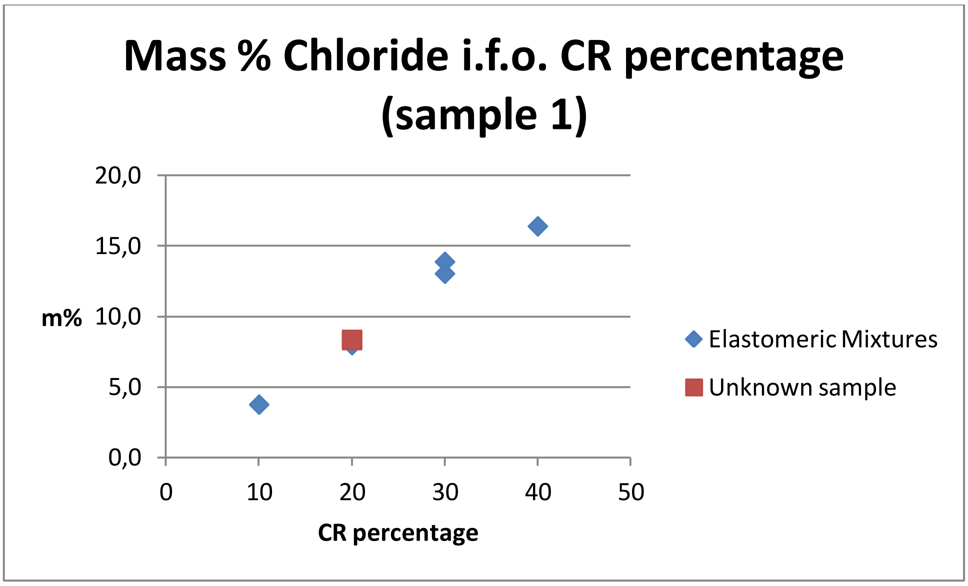

Figure 32: m% chloride in function of CR percentage for sample 1

Visual inspection of sample 1 shows a CR percentage of 10%.

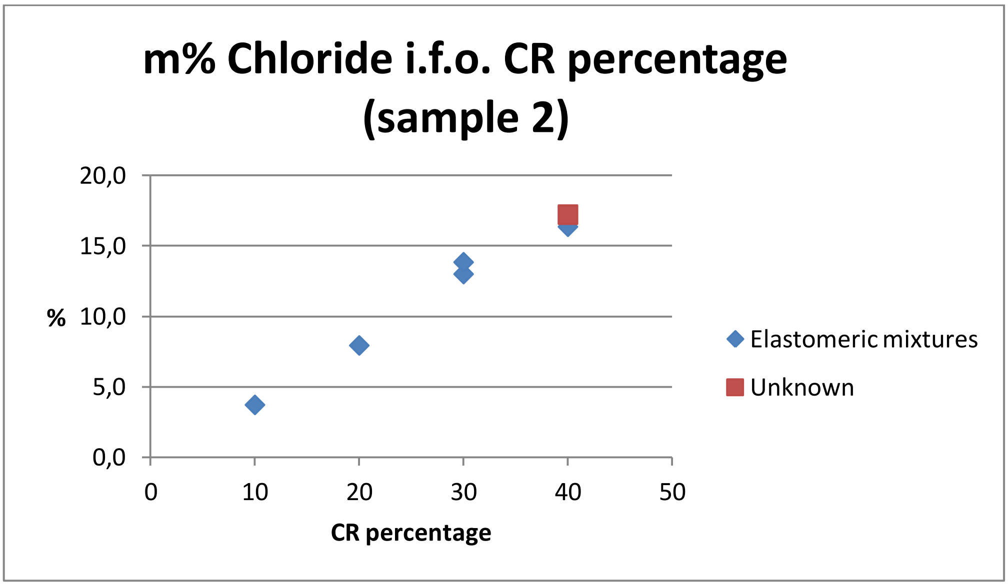

Figure 33: m% chloride in function of CR percentage for sample 2

Visual inspection of sample 2 shows a CR percentage of 40%.

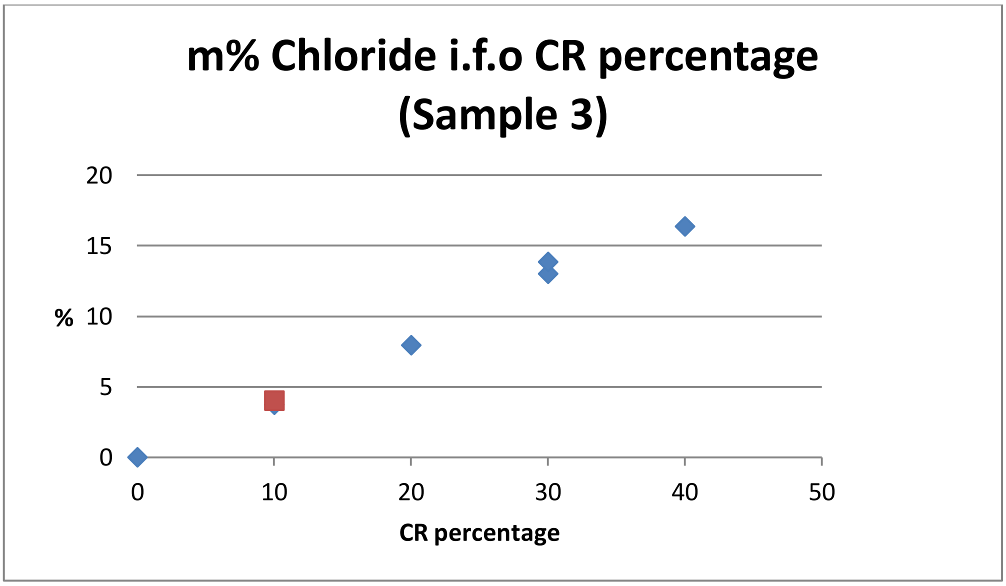

Figure 34: m% chloride in function of CR percentage for sample 3

Visual inspection of sample 3 shows a CR percentage of 10%.

In the next step the CR percentage is determined by the combination of methods. Out the TGA decay step of pure CR, the result of the mass % of carbon black was 19.7% (table 12). The CR percentages calculated by the SD of sample 1, 2 and 3 were respectively 19.6, 40.6 and 4.0. The carbon black resulting from the pyrolysis of the CR amount in the elastomeric mixture can be calculated according to the following formula:

$$\text{CB \% in mixture} = \text{CB\% of pure CR} * \text{mass\% of CR in mixture}$$

Applied on sample 1, 2 and 3 the carbon black % from pure CR can be calculated. Results are shown in table 24.

Table 24: Carbon black due to CR in unknown elastomeric mixtures

Unknown mixture (NR/SBR/CR)	***CR (%)***	***Carbon black from CR(%)***
1 (C)	19.6	3.9
2 (D)	40.6	8.0
3 (B)	9.8	1.9

6.5.2 Calculation of the recovery of carbon black in sample 1.

In the ternary elastomeric mixtures (1 & 2), the recovery of carbon black can be determined. In the previous section, the carbon black content originated from the CR component in the mixture was calculated. As explained, the carbon black can be determined as the 4th step in the TGA output. If the amount of carbon black due to the pure CR component is added with the amount which originates from the NR and SBR content in the mixture. The recovery of carbon black can be calculated.

The CR measured in sample C is 19.6 %. As the unknown samples originate from the ternary elastomers used in this research, the amount of NR is 60% and SBR is 20%. The TGA output of sample 1 is shown in table 25.

Table 25: Results of the measured m% decay for unknown sample 1

	A (%)	**B (%)**	**C (%)**	**D (%)**	**Res. Mass (%)**	**Sum (%)**
AVG	3.1	45.9	45.5	4.1	1.4	100

Out of decay step B & C of the pure samples NR and SBR, and the amount of NR and SBR in the rubber mixture, the recovery of the carbon black can be calculated:

$\text{CB}\ \%\ \text{in mixture due to NR or SBR} = \text{CB}\%\ \text{pure sample} * \text{mass}\%\ \ \text{in mixture}$

$60\ \% * 0.47\ \% = \ \ 0.28\%$ CB originates from NR

$20\ \% * 0.63\ \% \ = \ \ 0.13\%$ originates from SBR

The recovery of carbon black can be determined by taking the sum of the calculated carbon black amounts.

$\text{Total CB} = \text{CB}\%\ (\text{NR}) + \text{CB}\%\ (\text{SBR}) + \ \text{CB}\%\ (\text{CR})$

$4.28\ \% \quad = \ 0.28\ \% \qquad + \ \ 0.13\ \% \qquad + \ 3.87\%$

This can be compared with the 4th decay step of the TGA output of mixture 1. The calculated carbon black has a correlation with the measured carbon black, as shown in table 26.

Table 26: Comparison between measured and calculated carbon black values in sample 1

Measured carbon black (%)	Calculated carbon black (%)
4.1	4.3

6.5.3 Calculation of the recovery of carbon black in sample 2.

The same procedure used for the determination of CB in sample 1 is used for the determination of CB in sample 2. Out of the results of the SD (table 23), the CR measured in sample 2 is 40.55%. As the unknown samples originate from the ternary elastomers used in this research, the amount of NR is 40% and SBR is 20%. The TGA output of sample 2 is shown in table 27.

Table 27: Results of the measured m% decay for unknown sample 2

	A	B	C	D	Res. masse	Sum
AVG	4.6	49.2	36.1	9.1	1.0	100

Out of decay step B & C of the pure samples NR and SBR, and the amount of NR and SBR in the rubber mixture, the recovery of the carbon black can be calculated:

$\text{CB \% in mixture due to NR or SBR or CR} = \text{CB\% pure sample} * \text{mass\% in mixture}$

$40.55\,\% * 19.77\,\% = 8.02\,\%$ CB originates from CR

$40\,\% * 0.47\,\% = 0.19\,\%$ CB originates from NR

$20\,\% * 0.63\,\% = 0.13\,\%$ originates from SBR

The recovery of carbon black can be determined by taking the sum of the calculated carbon black amounts.

$\text{CB\% (NR)} + \text{CB\% (SBR)} + \text{CB\% (CR)} = \text{Total CB (mixture)}$

$0.19\,\% + 0.13\,\% + 8.02\,\% = 8.34\,\%$

This can be compared with the 4th decay step of the TGA output of mixture 2 (table 27). The calculated carbon black has a correlation with the measured carbon black in the sample, as shown in table 28.

Table 28 : Comparison between measured and calculated carbon black in sample 2

Measured carbon black (%)	Calculated carbon black (%)
9.1	8.3

6.5.4 Simulation of decay steps B and C due to CR, NR and SBR on sample 1

In the next step, decay step B and C are calculated using compositional percentages. The TGA decay steps B and C for pure CR are shown in table 29. Mixture C consist out of 60% NR and 20% SBR.

Table 29: m% decay, step B and C for pure CR

B (%)	C (%)
42.7	30.2

The recovery on sample 1 will be tested by calculating the decay steps and comparing them with table 29. Decay step B & C due to CR can be calculated using the following formulas:

$$\%\ \text{decay step B due to pure CR} \ * \ \text{mass\% in mixture} = \text{B \% in mixture due to CR}$$

$$42.71\ \% \quad * \quad 19.57\ \% \quad = \quad 8.36\ \%\ \text{decay in B due to CR}$$

$$\%\ \text{decay step C due to pure CR} \ * \text{mass\% in mixture} = \text{C \% in mixture due to CR}$$

$$30.18\ \% \quad * \quad 19.57\ \% \quad = \quad 5.91\ \%\ \text{decay in C due to CR}$$

Table 30: m% decay, step B and C for pure NR and SBR

	B	C
NR	80.6	15.4
SBR	15.4	78.5

Decay steps B and C will be calculated for the mixtures and compared with the decay steps B and C in the mixture. Mixture 1 consist out of 60% NR and 20% SBR.

$$\text{Decay step B due to pure NR} \ * \ \text{mass\% in mixture} = \text{B \% due to NR in mixture}$$
$$80.6\ \% \quad * \ 60\ \% \quad = \ 48.4\ \%$$

$$\text{Decay step B due to pure SBR} \ * \text{mass\% in mixture} = \text{B \% due to SBR in mixture}$$
$$15.4\ \% \quad * \ 20\ \% \quad = \ 3.1\ \%$$

$$\text{Decay step C due to pure NR} \ * \ \text{mass\% in mixture} = \text{C \% due to NR in mixture}$$
$$15.4\ \% \quad * \ 60\ \% \quad = \ 9.2\ \%$$

$$\text{Decay step C due to pure SBR} \ * \text{mass\% in mixture} = \text{C \% due to SBR in mixture}$$
$$78.4\ \% \quad * \ 20\ \% \quad = \ 15.7\ \%$$

The recovery of step B and C can be determined by taking the sum of the calculated decay amounts of B and C.

$$\text{B\% (NR)} + \text{B\% (SBR)} + \text{B\% (CR)} = \text{Total B(mixture)}$$

$$48.4\,\% \;+\; 3.1\,\% \;+\; 8.4\,\% \;=59.9\,\%$$

$$\text{C\% (NR)} + \text{C\% (SBR)} + \text{C\% (CR)} = \text{Total C(mixture)}$$

$$9.2\,\% \;+\; 15.7\,\% + 5.9\,\% \;=30.8\,\%$$

This can be compared with decay step B and C of the TGA output of mixture 1. The calculated decay in B and C can be compared with the measured B and C, as shown in table 31.

Table 31: Comparison between measured and calculated m% decay steps B & C for sample 1

	Measured decay B	**Calculated decay B**	**Measured decay C**	**Calculated decay C**
Unknown C	45.9	59.8	45.5	30.8

The mathematical correlation of the decay steps for sample 1 has an overshoot on decay step B and an undershoot on decay step C.

6.5.5 <u>Simulation of decay steps B and C due to CR, NR and SBR on sample D</u>

For the simulation of the decay steps B and C on sample D, the same procedure as in 5.5.4 can be used. Mixture 2 consist out of 40% NR and 20% SBR.

The recovery on sample 2 will be tested by calculating the decay steps and comparing them with table 29.

Decay step B & C due to CR can be calculated using the following formulas:

$$\text{\% B due to pure CR} * \text{mass\% in mixture} = \text{B \% in mixture due to CR}$$

$$42.7\,\% \quad * \quad 40.5\,\% \quad = \quad 17.3\,\% \text{ decay in B due to CR}$$

$$\text{\% C due to pure CR} * \text{mass\% in mixture} = \text{C \% in mixture due to CR}$$

$$30.2\,\% \quad * \quad 40.5\,\% \quad = \quad 12.2\,\% \text{ decay in C due to CR}$$

If the calculated value of B and C from CR is retracted from the measured B and C in the mixture, the remaining amount of step B and step C originates from NR and SBR. The recovery of step B and step C can be determined. The decay values of step B and C of pure NR and SBR were shown in table 30.

$$\text{Decay step B due to pure NR} * \text{mass\% in mixture} = \text{B \% due to NR in mixture}$$
$$80.6\,\% \quad * \; 40\,\% \quad = \; 32.3\,\%$$

$$\text{Decay step B due to pure SBR} * \text{mass\% in mixture} = \text{B \% due to SBR in mixture}$$
$$15.4\,\% \quad * \; 20\,\% \quad = \; 3.0\,\%$$

$$\text{Decay step C due to pure NR} * \text{mass\% in mixture} = \text{C \% due to NR in mixture}$$
$$15.4\,\% \quad * \; 40\,\% \quad = \; 48.4\,\%$$

$$\text{Decay step C due to pure SBR } * \text{mass\% in mixture} = \text{C \% due to SBR in mixture}$$
$$78.5\ \% \quad * \ 20\ \% \quad = \ 15.7\ \%$$

The recovery of step B and C can be determined by taking the sum of the calculated decay amounts of 2.

$$\text{B\% (NR)} + \text{B\% (SBR)} + \text{B\% (CR)} = \text{Total calculated decay step B(mixture)}$$

$$\text{C\% (NR)} + \text{C\% (SBR)} + \text{C\% (CR)} = \text{Total calculated decay step C(mixture)}$$

$$For\ B\!: \ 32.3\ \% \ + \ 3.0\ \% \ + \ 17.3\ \% \ = 52.6\ \%$$

$$For\ C\!: \ 6.2\ \% \ + \ 15.7\ \% \ + \ 12.2\ \% \ = 34.1\ \%$$

This can be compared with decay step B of the TGA output of mixture D. The calculated carbon black has a correlation with the measured carbon black in the sample, as shown in table 31.

Table 32: Comparison between measured and calculated m% decay steps B & C for sample 2

	Measured decay B	Calculated decay B	Measured decay C	Calculated decay C
Unknown D	49.2	52.6	36.1	34.1

The mathematical correlation of the decay steps for sample D is a good estimation for decay step B and C of sample 2.

6.5.6 Determination of the CR Phr amount in a technical elastomer (sample 3)

The CR percentage calculated in sample 3 was 9,8% (table 23). As this is a technical elastomer, the only rubber component which produces significant amounts of carbon black is CR. The remaining carbon black is added as a filler.

To calculate the Phr amount of CR in the technical elastomer, the carbon black which originates from the filler has to be determined.

The carbon black from the CR rubber can be calculated according to the following formula:

$$\text{CR measured } * \text{CB in pure CR} = \text{Carbon black generated by CR (\%)}$$

$$9.8\ \% \quad * \quad 19.8\ \% \quad = 1.9\ \%$$

The TGA output of sample 3 is shown in table 33.

Table 33: Measured m% decay for sample 3

	A (%)	*B (%)*	*C (%)*	*D (%)*	*Res. Mass (%)*	*Sum*
Unknown Sample B	3.0	23.8	22.5	38.2	12.5	100

The percentage carbon black from the filler can be calculated by extracting the carbon black from the CR from the total amount of carbon black from sample 3.

$$38.2\ \% \qquad - \qquad 1.9\ \% \qquad = 36.3\ \%$$

The total sum of polymer in this technical elastomer can be calculated by taking the sum of step B, C and the carbon black produced by CR.

$$\text{Decay step B} + \text{Decay step C} + \text{ CB from CR} = \%\text{ of polymer in the technical elastomer}$$

$$23.8\ \% \qquad + 22.5\ \% \qquad + \ 1.9\ \% \qquad = 46.3\ \%$$

The amount of fillers is the rest of the polymer and can be calculated by extracting the polymer percentage from 100%.

$$100\ \% - 46.3\ \% = 53.7\ \%$$

The CR content in Phr can be calculated by dividing the CR percentage by the rubber percentage in the elastomer.

$$\%\ \text{Phr} = \frac{9.8}{46.3}(\%) = 21.1\ \%$$

The CR content expressed in Phr is 21.1 %

The results of the SD show the amount of CR in an elastomeric mixture. The TGA measurements determine the amount of carbon black and the amount of polymer in the mixture. The polymer related CR percentage (Phr) was determined by combining both methods. These results are compared with Pyrolysis GC/MS in order to make a conclusion on the combined method for CR polymer characterization.

6.6 Comparison of the optimized method with Pyrolysis GC/MS

The results are compared with previously obtained Pyrolysis GC/MS results. These results were plotted in a calibration curve. When a sample of an elastomeric mixture of 80% NR and 20% CR is taken for Pyrolysis GC/MS analysis, the pyrolysis chromatogram is shown in figure 35.

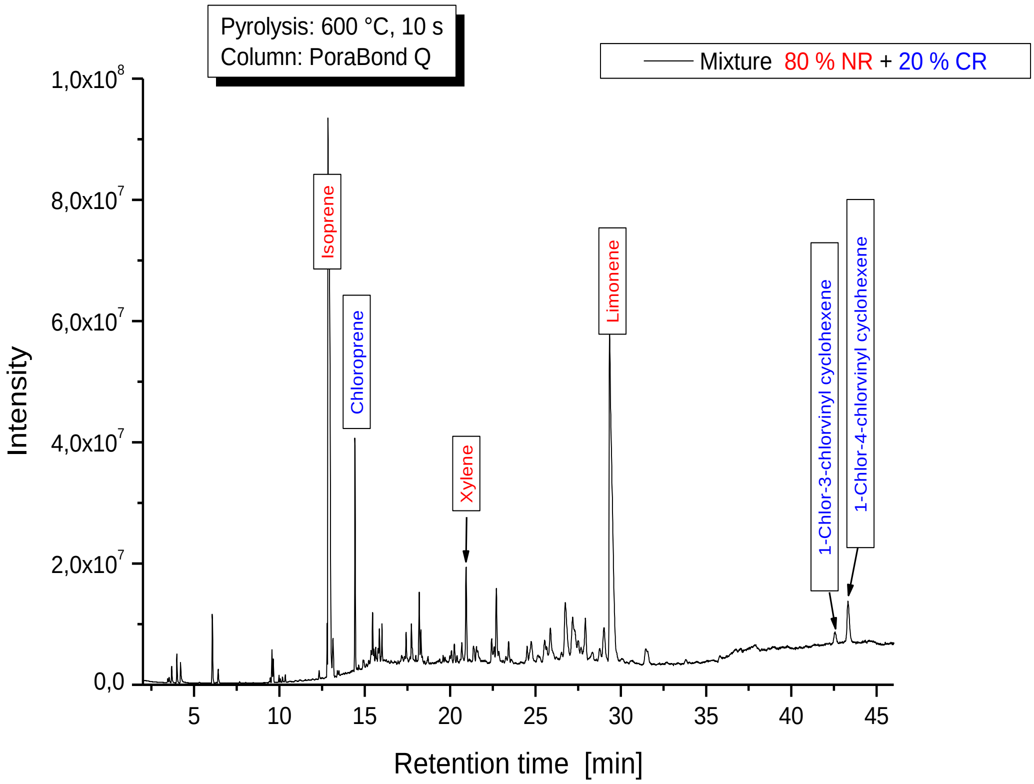

Figure 35: Pyrolysis chromatogram of a 80% NR, 20% CR binary mixture

The area under each peak describes the abundance of the component present in the sample. The content of the unknown samples were externally tested and the results are shown in the calibration curve. The calibration curve is shown in figure 36.

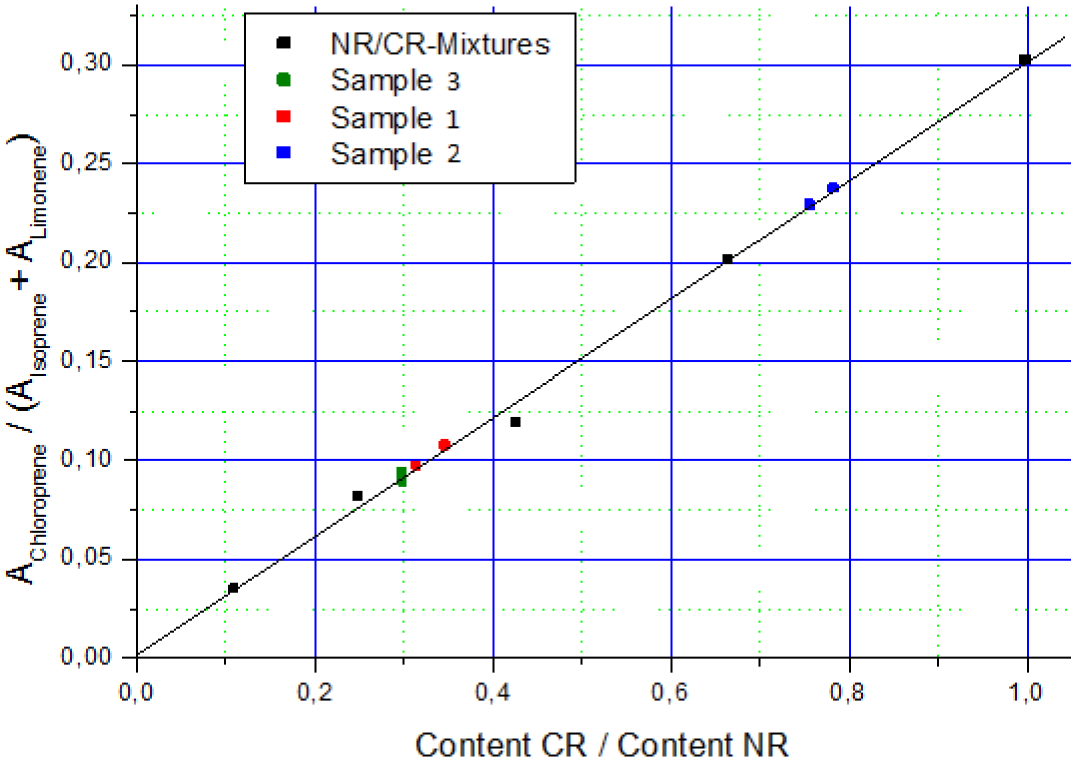

Figure 36: Calibration curve of the NR/SBR/CR ternary mixtures and unknown samples

In order to check the recovery of the CR determination. The CR content, measured with both methods, has to be compared. The CR content determined by Pyrolysis GC/MS can be calculated by the use of the calibration curve. The fracture of the area's under the pyrolysis peaks (CR and NR) can be taken out the chromatogram (figure 35) and represent the value of the abscis of the sample on figure 36. By the use of the calibration curve, the ordinate represents the fractures of the content CR on the content NR. The values of sample 1, 2 and 3 are shown in table 34.

Table 34: Fractures of the CR and NR content, based on FTIR, in the technical elastomer (3) and ternary elastomeric mixtures (1 & 2)

Sample	$\frac{\boldsymbol{Content\ CR}}{\boldsymbol{Content\ NR}}$
3	0.30
1	0.33
2	0.78

For the technical elastomer (3), the polymer related CR content can be calculated using two equations with two unknown variables. The first equation is the fracture of the CR content on the NR content.

$$\frac{Content\ CR}{Content\ NR} = 0.3$$

The second equation is based on the fact that the total polymer content in the technical elastomer consists out of NR and CR.

$$[NR] + [CR] = 1$$

If these two equations are combined, the polymer related CR content can be calculated.

$$[CR] = 0.23$$

The polymer related CR content for both methods for the technical elastomer (3) is shown in table 35.

Table 35: Comparison of the polymer related CR content determined by the combined method and Pyrolysis GC/MS

CR content (SD + TGA)	*CR content (Pyrolysis GC/MS)*
21.1	23

The CR content determined by the combination of the SD and TGA is slightly lower than this determined by Pyrolysis GC/MS. The combined method gives an accurate estimation of the CR content for technical elastomeric materials.

For the ternary elastomeric mixtures (C and D), the fracture of the CR content with the NR content can be examined by the calibration curve (figure 36).

For sample 1:

$$\frac{Content\ CR}{Content\ NR} = 0.3$$

For sample 2:

$$\frac{Content\ CR}{Content\ NR} = 0.78$$

The ternary elastomeric mixtures consist out of NR, SBR and CR, the second equation necessary for the calculation of the m% CR is:

$$[NR] + [SBR] + [CR] = 1$$

The SBR component in the ternary mixture is determined by comparing figure 32 and 33 with the ternary elastomeric mixtures in table 22.

$$[SBR] = 0.20$$

The CR content for sample 1 and 2 is:

For sample 1:

$$[CR] = 0.184$$

For sample 2:

$$[CR] = 0.350$$

The results of the CR determination on the ternary elastomeric mixtures with the combined method are compared with the results of the Pyrolysis GC/MS method. This is shown in table 36.

Table 36: Comparison of the CR determination on the ternary elastomeric mixtures with the combined method and Pyrolysis GC/MS

Sample m% (NR/SBR/CR)	***CR content (SD + TGA) %***	***CR content (Pyrolysis GC/MS) %***
1 (60/20/20)	19.6	18.4
2 (40/20/40)	40.6	35.0

Table 36 shows that the CR content determined with the combined method is more closely to the theoretical m% then in case determined with Pyrolysis GC/MS.

CHAPTER 7: Conclusions & Outlook

The goal of this thesis was to combine the Schöniger digestion with TGA in order to determine the CR amount in any complex elastomer. In order to reach this goal, several steps were taken.

First, the Schöniger digestion was optimized for the purpose of determining the chloride amount in rubbers. This optimization was executed on pure CR samples. After the optimization, the Schöniger digestion was accelerated 2.4 times, gave stable results and high yields of chloride (79%). The TGA output on the pure samples showed the temperatures necessary for TGA decay step determination in the next stages of the research.

The second step involved TGA measurements on binary elastomeric mixtures using the temperatures determined by TGA execution on the pure samples. This in order to find a correlation between TGA results of pure samples and TGA results of binary mixtures. A correlation between calculated values of the mixtures, based on the pure components, and the measured values was examined. Due to a severe overshoot, the formula can't be used for an accurate determination of the CR content. Further research is advised.

In the third step, both the SD and TGA were executed on ternary elastomeric mixtures in order to check the recovery of CR on ternary elastomers. The m% CR was determined very accurately and a correlation was examined between the m% of CR and the fourth decay step of TGA. This implied that in ternary elastomeric mixtures, a vast amount of carbon black originated from CR.

The fourth step included a recovery test on two unknown ternary elastomers and an unknown technical elastomeric material. In the testing of the unknown elastomeric mixtures, the CR recovery was determined accurately and it was possible to simulate the carbon black amount using the TGA formula based on the elastomeric components. For the unknown technical elastomeric material, it was possible to determine the polymer related CR amount in an accurate way. A correlation was also found between simulated TGA decay steps (B and C) and calculated values.

The results of the fourth step were compared with Pyrolysis GC/MS results on the same elastomers in order to compare the combined method with a reference method. On the ternary elastomeric materials, the combined method made a more accurate CR determination in comparison with the Pyrolysis GC/MS based on the theoretical CR percentage.

Therefore, it can be concluded that CR determination in elastomeric mixtures is possible with a combination of the Schöniger digestion and TGA.

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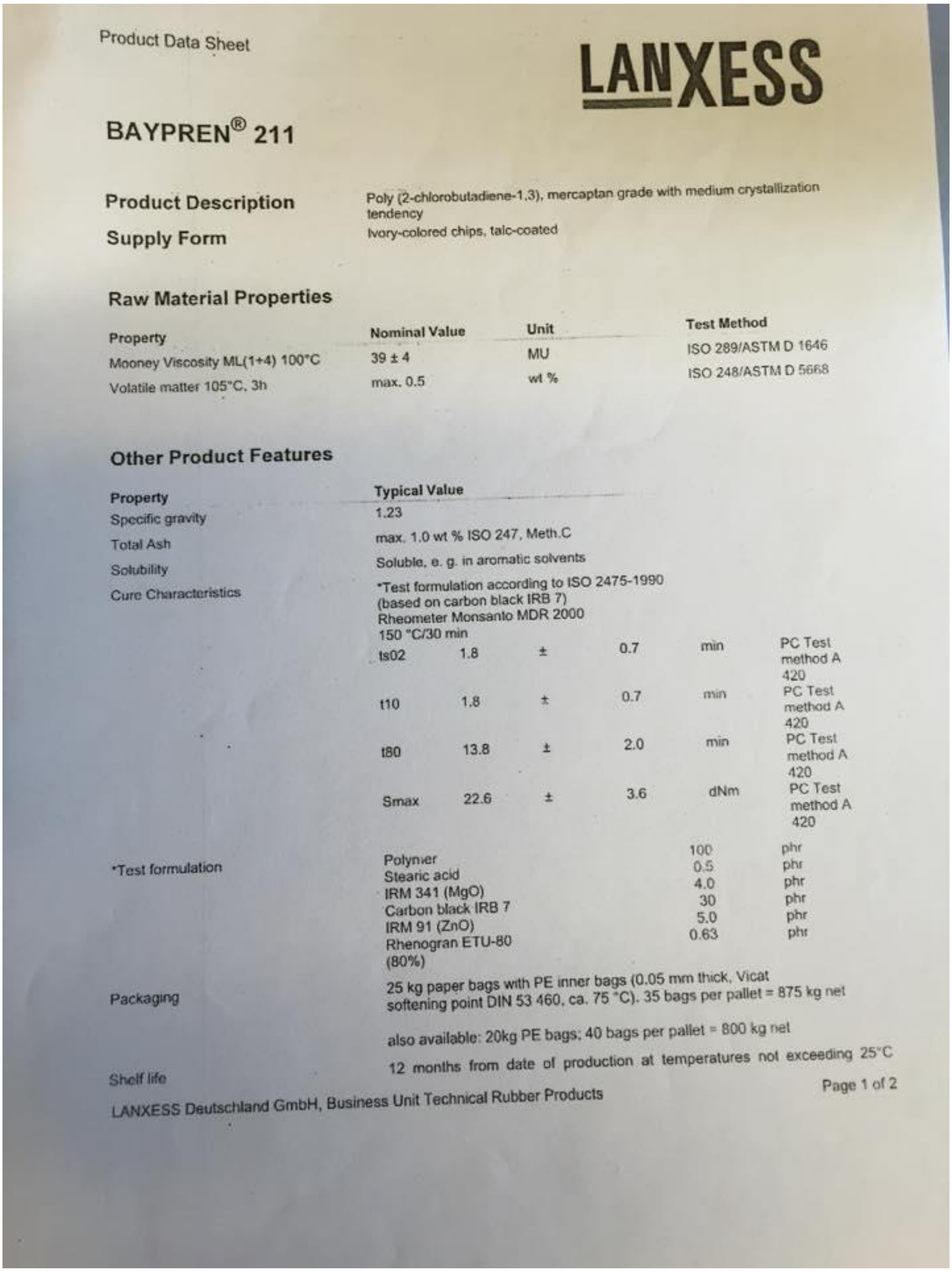
APPENDICES

Datasheets NR, SBR, NBR, CR



Product Data Sheet

LANXESS

BAYPREN® 211

Product Description	Poly (2-chlorobutadiene-1,3), mercaptan grade with medium crystallization tendency
Supply Form	Ivory-colored chips, talc-coated

Raw Material Properties

Property	Nominal Value	Unit	Test Method
Mooney Viscosity ML(1+4) 100°C	39 ± 4	MU	ISO 289/ASTM D 1646
Volatile matter 105°C, 3h	max. 0.5	wt %	ISO 248/ASTM D 5668

Other Product Features

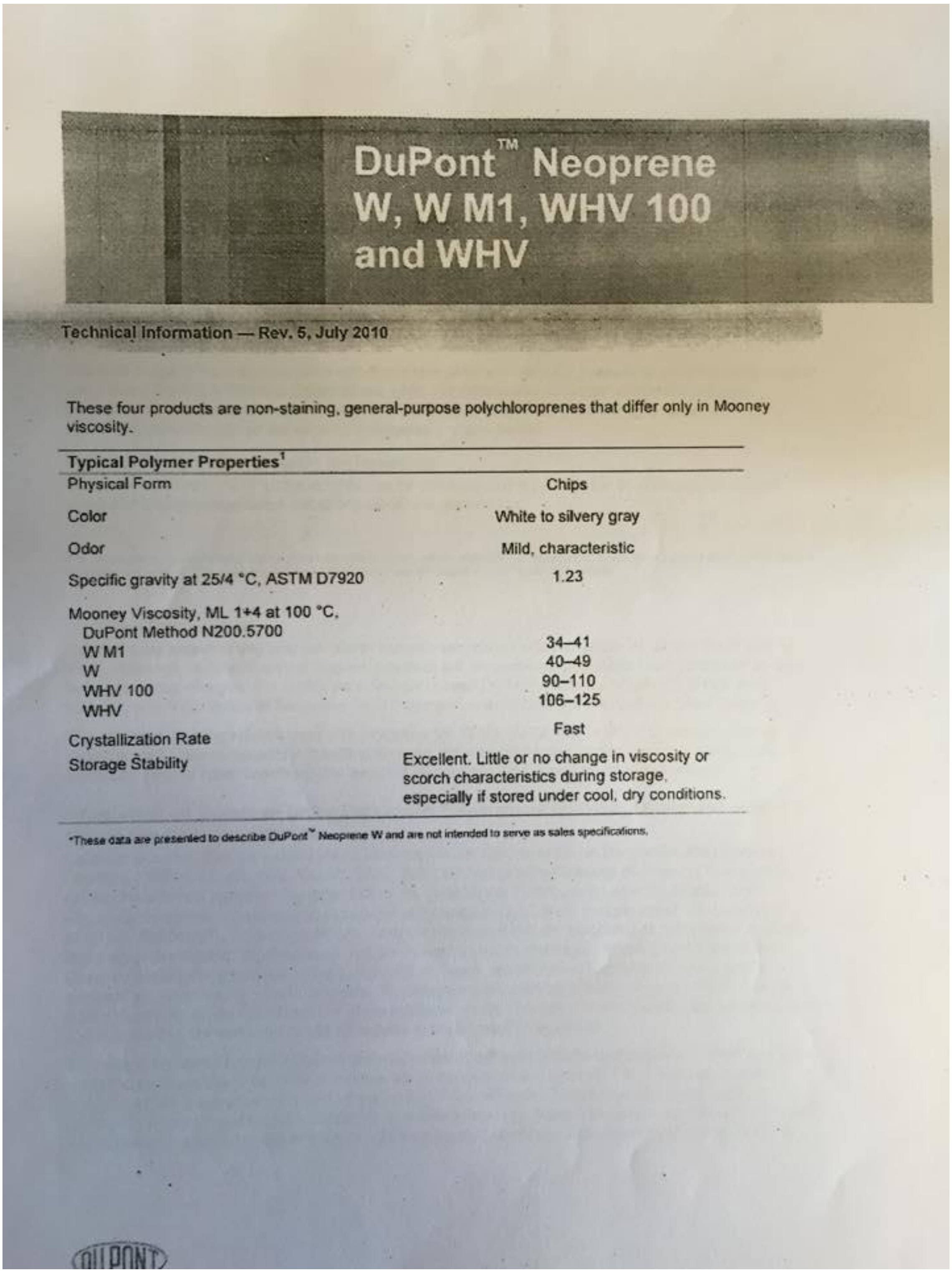
Property	Typical Value				
Specific gravity	1.23				
Total Ash	max. 1.0 wt % ISO 247, Meth.C				
Solubility	Soluble, e. g. in aromatic solvents				
Cure Characteristics	*Test formulation according to ISO 2475-1990 (based on carbon black IRB 7) Rheometer Monsanto MDR 2000 150 °C/30 min				
	ts02	1.8	± 0.7	min	PC Test method A 420
	t10	1.8	± 0.7	min	PC Test method A 420
	t80	13.8	± 2.0	min	PC Test method A 420
	Smax	22.6	± 3.6	dNm	PC Test method A 420

*Test formulation			
	Polymer	100	phr
	Stearic acid	0.5	phr
	IRM 341 (MgO)	4.0	phr
	Carbon black IRB 7	30	phr
	IRM 91 (ZnO)	5.0	phr
	Rhenogran ETU-80 (80%)	0.63	phr

Packaging	25 kg paper bags with PE inner bags (0.05 mm thick, Vicat softening point DIN 53 460, ca. 75 °C). 35 bags per pallet = 875 kg net also available: 20kg PE bags; 40 bags per pallet = 800 kg net
Shelf life	12 months from date of production at temperatures not exceeding 25°C

LANXESS Deutschland GmbH, Business Unit Technical Rubber Products

Page 1 of 2



DuPont™ Neoprene W, W M1, WHV 100 and WHV

Technical Information — Rev. 5, July 2010

These four products are non-staining, general-purpose polychloroprenes that differ only in Mooney viscosity.

Typical Polymer Properties[1]	
Physical Form	Chips
Color	White to silvery gray
Odor	Mild, characteristic
Specific gravity at 25/4 °C, ASTM D7920	1.23
Mooney Viscosity, ML 1+4 at 100 °C, DuPont Method N200.5700	
W M1	34–41
W	40–49
WHV 100	90–110
WHV	106–125
Crystallization Rate	Fast
Storage Stability	Excellent. Little or no change in viscosity or scorch characteristics during storage, especially if stored under cool, dry conditions.

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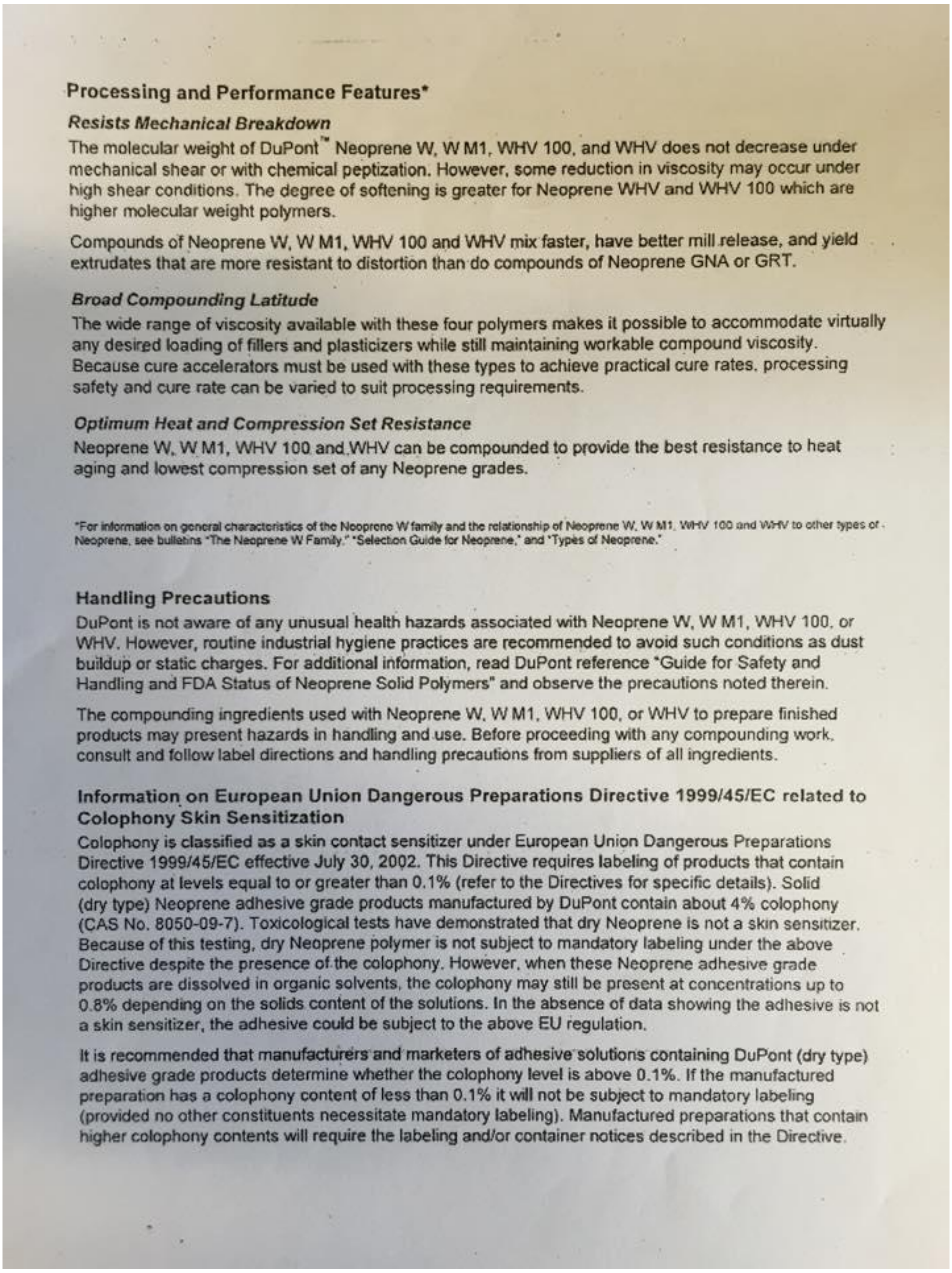
[1] These data are presented to describe DuPont™ Neoprene W and are not intended to serve as sales specifications.



Processing and Performance Features*

Resists Mechanical Breakdown

The molecular weight of DuPont™ Neoprene W, W M1, WHV 100, and WHV does not decrease under mechanical shear or with chemical peptization. However, some reduction in viscosity may occur under high shear conditions. The degree of softening is greater for Neoprene WHV and WHV 100 which are higher molecular weight polymers.

Compounds of Neoprene W, W M1, WHV 100 and WHV mix faster, have better mill release, and yield extrudates that are more resistant to distortion than do compounds of Neoprene GNA or GRT.

Broad Compounding Latitude

The wide range of viscosity available with these four polymers makes it possible to accommodate virtually any desired loading of fillers and plasticizers while still maintaining workable compound viscosity. Because cure accelerators must be used with these types to achieve practical cure rates, processing safety and cure rate can be varied to suit processing requirements.

Optimum Heat and Compression Set Resistance

Neoprene W, W M1, WHV 100 and WHV can be compounded to provide the best resistance to heat aging and lowest compression set of any Neoprene grades.

*For information on general characteristics of the Neoprene W family and the relationship of Neoprene W, W M1, WHV 100 and WHV to other types of Neoprene, see bulletins "The Neoprene W Family," "Selection Guide for Neoprene," and "Types of Neoprene."

Handling Precautions

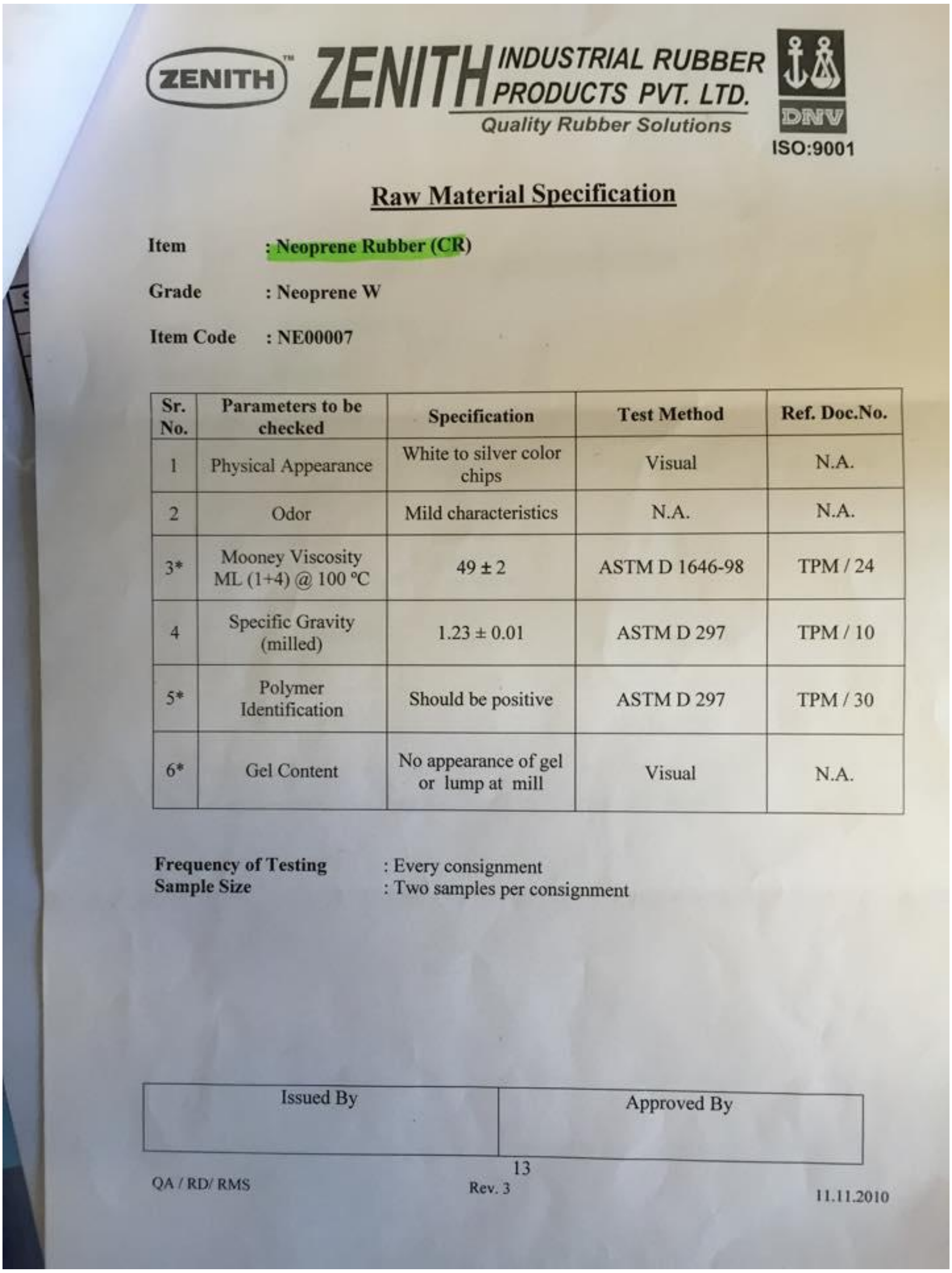
DuPont is not aware of any unusual health hazards associated with Neoprene W, W M1, WHV 100, or WHV. However, routine industrial hygiene practices are recommended to avoid such conditions as dust buildup or static charges. For additional information, read DuPont reference "Guide for Safety and Handling and FDA Status of Neoprene Solid Polymers" and observe the precautions noted therein.

The compounding ingredients used with Neoprene W, W M1, WHV 100, or WHV to prepare finished products may present hazards in handling and use. Before proceeding with any compounding work, consult and follow label directions and handling precautions from suppliers of all ingredients.

Information on European Union Dangerous Preparations Directive 1999/45/EC related to Colophony Skin Sensitization

Colophony is classified as a skin contact sensitizer under European Union Dangerous Preparations Directive 1999/45/EC effective July 30, 2002. This Directive requires labeling of products that contain colophony at levels equal to or greater than 0.1% (refer to the Directives for specific details). Solid (dry type) Neoprene adhesive grade products manufactured by DuPont contain about 4% colophony (CAS No. 8050-09-7). Toxicological tests have demonstrated that dry Neoprene is not a skin sensitizer. Because of this testing, dry Neoprene polymer is not subject to mandatory labeling under the above Directive despite the presence of the colophony. However, when these Neoprene adhesive grade products are dissolved in organic solvents, the colophony may still be present at concentrations up to 0.8% depending on the solids content of the solutions. In the absence of data showing the adhesive is not a skin sensitizer, the adhesive could be subject to the above EU regulation.

It is recommended that manufacturers and marketers of adhesive solutions containing DuPont (dry type) adhesive grade products determine whether the colophony level is above 0.1%. If the manufactured preparation has a colophony content of less than 0.1% it will not be subject to mandatory labeling (provided no other constituents necessitate mandatory labeling). Manufactured preparations that contain higher colophony contents will require the labeling and/or container notices described in the Directive.



ZENITH ZENITH INDUSTRIAL RUBBER PRODUCTS PVT. LTD.
Quality Rubber Solutions
DNV
ISO:9001

Raw Material Specification

Item : **Neoprene Rubber (CR)**

Grade : **Neoprene W**

Item Code : **NE00007**

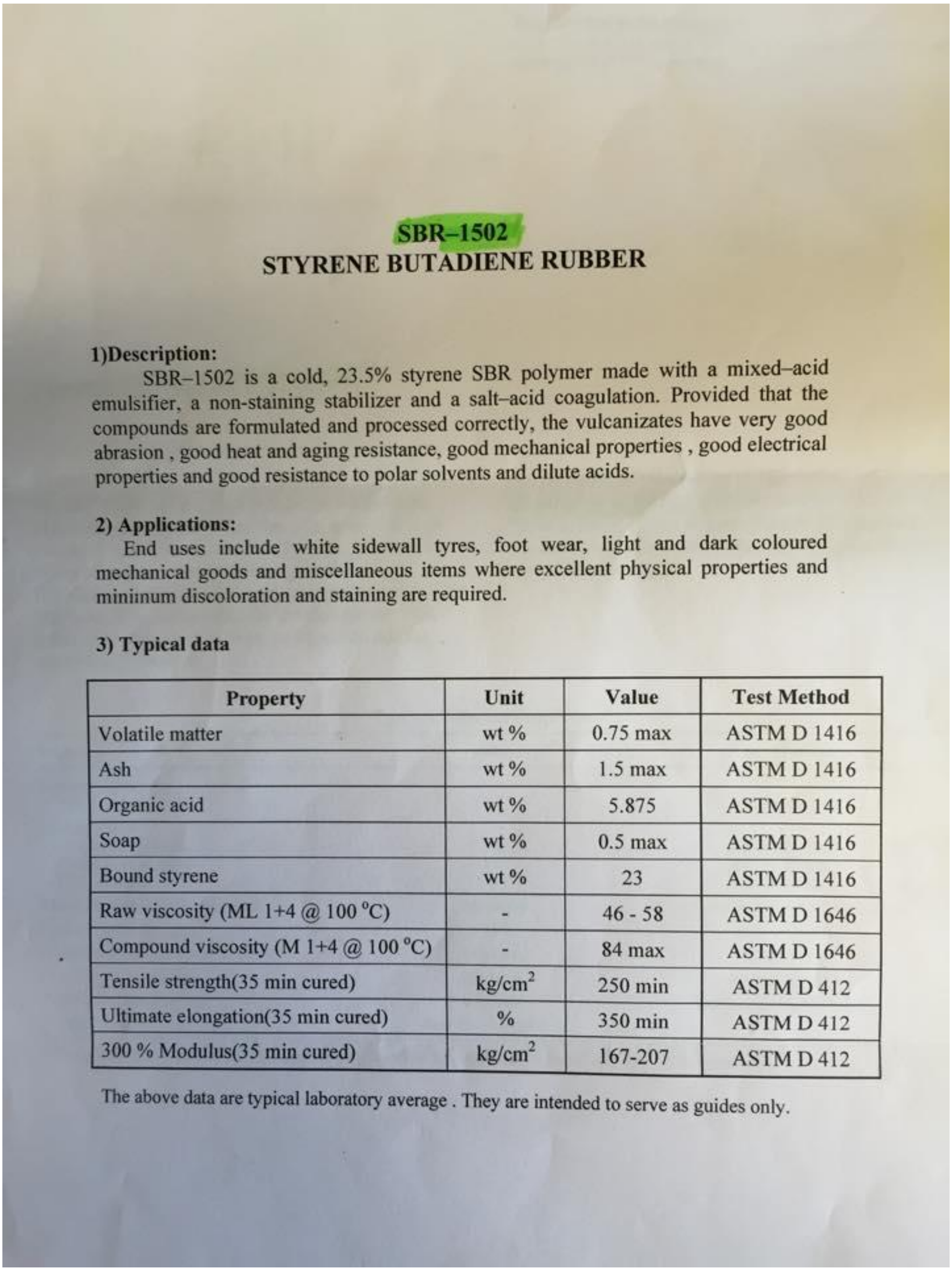
Sr. No.	Parameters to be checked	Specification	Test Method	Ref. Doc.No.
1	Physical Appearance	White to silver color chips	Visual	N.A.
2	Odor	Mild characteristics	N.A.	N.A.
3*	Mooney Viscosity ML (1+4) @ 100 °C	49 ± 2	ASTM D 1646-98	TPM / 24
4	Specific Gravity (milled)	1.23 ± 0.01	ASTM D 297	TPM / 10
5*	Polymer Identification	Should be positive	ASTM D 297	TPM / 30
6*	Gel Content	No appearance of gel or lump at mill	Visual	N.A.

Frequency of Testing	: Every consignment
Sample Size	: Two samples per consignment

Issued By	Approved By

13

QA / RD/ RMS
Rev. 3
11.11.2010



SBR–1502
STYRENE BUTADIENE RUBBER

1)Description:

SBR–1502 is a cold, 23.5% styrene SBR polymer made with a mixed–acid emulsifier, a non-staining stabilizer and a salt–acid coagulation. Provided that the compounds are formulated and processed correctly, the vulcanizates have very good abrasion , good heat and aging resistance, good mechanical properties , good electrical properties and good resistance to polar solvents and dilute acids.

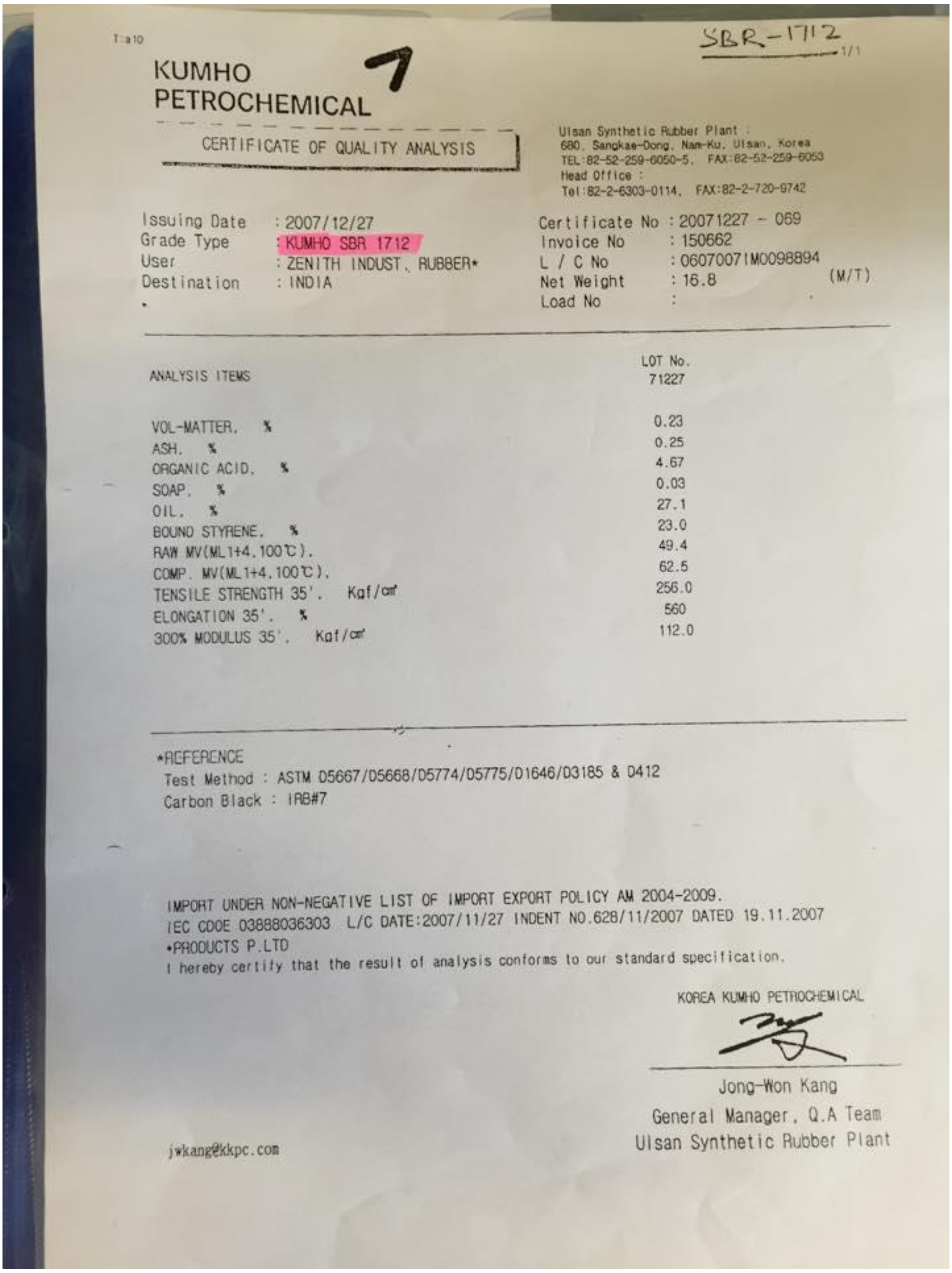
2) Applications:

End uses include white sidewall tyres, foot wear, light and dark coloured mechanical goods and miscellaneous items where excellent physical properties and minimum discoloration and staining are required.

3) Typical data

Property	Unit	Value	Test Method
Volatile matter	wt %	0.75 max	ASTM D 1416
Ash	wt %	1.5 max	ASTM D 1416
Organic acid	wt %	5.875	ASTM D 1416
Soap	wt %	0.5 max	ASTM D 1416
Bound styrene	wt %	23	ASTM D 1416
Raw viscosity (ML 1+4 @ 100 °C)	-	46 - 58	ASTM D 1646
Compound viscosity (M 1+4 @ 100 °C)	-	84 max	ASTM D 1646
Tensile strength(35 min cured)	kg/cm^2	250 min	ASTM D 412
Ultimate elongation(35 min cured)	%	350 min	ASTM D 412
300 % Modulus(35 min cured)	kg/cm^2	167-207	ASTM D 412

The above data are typical laboratory average . They are intended to serve as guides only.



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SBR-1712

1/1

7

KUMHO
PETROCHEMICAL

CERTIFICATE OF QUALITY ANALYSIS

Ulsan Synthetic Rubber Plant :
680, Sangkae-Dong, Nam-Ku, Ulsan, Korea
TEL:82-52-259-6050-5, FAX:82-52-259-6053
Head Office :
Tel:82-2-6303-0114, FAX:82-2-720-9742

Issuing Date : 2007/12/27
Grade Type : KUMHO SBR 1712
User : ZENITH INDUST, RUBBER*
Destination : INDIA

Certificate No : 20071227 - 069
Invoice No : 150662
L / C No : 06070071M0098894
Net Weight : 16.8 (M/T)
Load No :

ANALYSIS ITEMS	LOT No. 71227
VOL-MATTER, %	0.23
ASH, %	0.25
ORGANIC ACID, %	4.67
SOAP, %	0.03
OIL, %	27.1
BOUND STYRENE, %	23.0
RAW MV(ML1+4, 100℃),	49.4
COMP. MV(ML1+4, 100℃),	62.5
TENSILE STRENGTH 35', Kgf/㎠	256.0
ELONGATION 35', %	560
300% MODULUS 35', Kgf/㎠	112.0

*REFERENCE
Test Method : ASTM D5667/D5668/D5774/D5775/D1646/D3185 & D412
Carbon Black : IRB#7

IMPORT UNDER NON-NEGATIVE LIST OF IMPORT EXPORT POLICY AM 2004-2009.
IEC CODE 03888036303 L/C DATE:2007/11/27 INDENT NO.628/11/2007 DATED 19.11.2007
*PRODUCTS P.LTD
I hereby certify that the result of analysis conforms to our standard specification.

KOREA KUMHO PETROCHEMICAL

Jong-Won Kang
General Manager, Q.A Team
Ulsan Synthetic Rubber Plant

jwkang@kkpc.com

Standard Operating Procedure

Schöniger digestion Execution

1.0 Purpose

This procedure describes how to execute the Schöniger digestion on a sample of chloroprene rubber.

2.0 Method Summary

The Schöniger digestion is a method of elemental analysis and allows quantitative determination of elemental chlorine, nitrogen and sulfur in a sample. The Schöniger digestion consist of three parts. The incineration of the sample, afterwhich the combustion products will be absorbed in a mixture of peroxide and water. The neutralization of the solution and a potentiometric titration using 0.01M $AgNO_3$ to determine the amount of elements in the sample.

3.0 When it should be performed:

Calibration should be performed at least on a weekly basis, after cleaning or if the readings become unsteady.

4.0 Equipment

pH meter, calibrated and ready for use

Schöniger oxidation flask

Filter paper, cutted (see below)

Solutions: 30% H_2O_2 ; Demineralized water; 1M NaOH, 0.01M $AgNO_3$.

Sample of chloroprene rubber: 50mg

Pipet 50 ml

Measurement flask 10 ml

Droplet pipets

Beakers

Magnetic stirrer

5.0 Preparation

Cut the filter paper in the following form

1. To correctly execute the Schöniger oxidation it’s important the filterpaper which is used in step 1, has the following dimensions

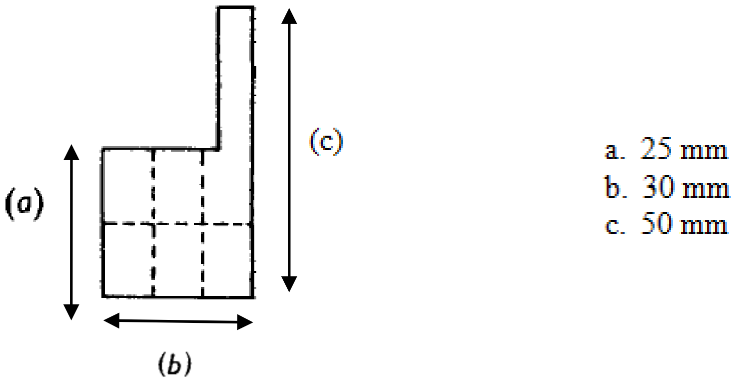

Figure 1: Schöniger paper

Switching the meter on

Press the ON/OFF key to power up your meter. All the LCD segments display for a few seconds as the meter goes through a self-diagnostic test. The LCD then switches into pH measurement mode.

Before use: remove the electrode soaker bottle. If the electrode has been stored dry, condition the glass bulb by soaking it in tap water for 30 minutes. This hydrates the

glass bulb if the electrode is too dry, or has not been used for a long period of time.

Procedure

1. Complete the **Schöniger preparation Sheet Appendix 1.**
2. Make sure to begin with a blanc test of the procedure to measure the amount of chloride in the filter paper.
3. Pore 10 ml 30% H_2O_2 and 8 ml H_2O_{demin} into a clean, dry Schöninger flask.

4. Carefully fold the 50 mg chloroprene rubber sample in the paper and clamp it, with the fuse protruding, into the gauze. It's important that the stripe of paper is in touch with the platinum wire.

5. Blow oxygen in the Schöniger flask for 30 seconds. This ensures complete combustion.

6. The apparatus needs to be installed upside-down. See figure 2.

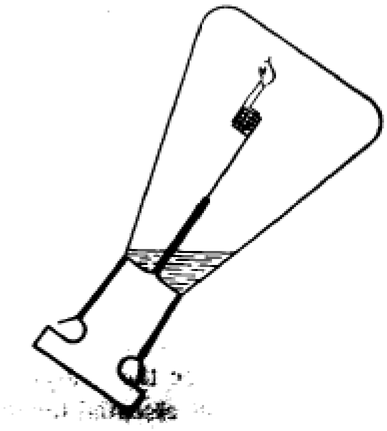

Figure 2: Installation Schöniger device

7. Step away from the instrument. Lower the safety glass for safe combustion.

8. Ignite the sample by pressing on the button. Wait 10 minutes for the reaction to complete.

9. Remove the flask from the Schöniger device, shake vigorously with the closed flask to dissolve all volatile components in the peroxide and water solution.

10. Pore the content of the flask in a 250 ml beaker. Rinse the flask carefully with H_2O_{demin}.

    <u>Note: It's important to ringe the flask analytically. Every drop of chloride needs to be transferred into the beaker.</u>

11. Measure the pH in the beaker, do it while stirring, Add drop wise 1M NaOH until a pH between 6 and 8 is measured.

12. Bring the content of the beaker in a 100 ml flask. Add water until dimension line is reached. Homogenise the content.

13. Take a sample of 10 ml of the previous solution and put it in the beaker of the pH meter. Add water to ensure all electrodes are immersed.

14. Do a potentiometric titration with 0.01M $AgNO_3$

15. Repeat step 12 & 13 for two times.

After measuring

1. Rinse the electrode and reference junction in deionized water.

2. Store the electrode as for best results, keep the pH bulb wet. Store the pH bulb in the electrode soaker bottle filled with electrode storage solution. Or you can store the electrode in a pH 4 buffer with 1/100 part saturated KCl. Other pH buffers are also suitable for storage. **NEVER use deionized water for storage.**

Electrode cleaning

1. Because your pH electrode is susceptible to dirt and contamination from the AgCl precipitates., clean it every one to three weeks depending on extent and condition of use.

2. Clean the electrode in a mild detergent solution. Wipe the probe with a soft tissue paper. Avoid touching the glass membrane with your fingers.

3. Wash thoroughly in tap water and then in distilled water.

4. Recalibrate your meter after cleaning the electrode.

Special Cleaning Tip

Salt deposit: dissolve the deposit by immersing the electrode in tap water for ten to fifteen minutes. Then thoroughly rinse with distilled water.

Schöniger Method

Chloride mass (blanc) : ___________________________

Mass Sample : ___________________________

Ashes after combustion?

☐ Yes

☐ No

Drops NaOH : ___________________________

pH after NaOH: ___________________________

Measurement	Volume (ml)	Mass (mg)
1.		
2.		
3.		

Damages : ☐ None

☐ Type of damage ___________________________

____

Evaluation :

☐ Test passes

☐ Test not passed ☐ returned to Lab Instructor

Date : ________________________ **Examiner :** ________________________

Auteursrechtelijke overeenkomst

Ik/wij verlenen het wereldwijde auteursrecht voor de ingediende eindverhandeling:
Optimization of the precision and accuracy of methods for the determination of chloroprene rubber (CR) in complex elastomer blends and technical elastomeric materials

Richting: **master in de industriële wetenschappen: chemie**
Jaar: **2015**

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Datum: **17/06/2015**