PROCESS-DESIGN FOR DEVULCANIZATION OF WHOLE TRUCK TIRE RUBBER

by

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“Learning gives Creativity,

Creativity leads to Thinking,

Thinking provides Knowledge,

Knowledge makes you Great…”

- Dr. **A. P. J. Abdul Kalam** ,
  Former Indian President & Scientist,
  (1931-2015).

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Introduction

Interesting to know: Worldwide, app. 8.000.000 waste tire are generated annually. This is a pile 5 times around the globe or 2/3 the distance to the moon! (Saiwari, 2013)

Devulcanization, as the name says, is the reversion of the *vulcanization* process: this is the most ideal process for recycling of rubber. It is a cradle-to-cradle approach, as the devulcanized material has a high quality and a property profile close to the virgin material. In contrast to reclaimed rubber, which so far is the best recycled rubber product on the market, this material can be used in higher loadings in virgin rubber compounds; for reclaim, the quantity of recycled material is limited to a few percent in tire applications.

The core of the devulcanization process is breakdown of the sulfur network while the polymer stays intact; thus, the devulcanized material resembles the original material in structure and properties. However, there are also limitations to this approach: the material has undergone degradation to a certain extent during its first service life, influencing the properties and performance of the material. This not necessarily is a negative influence; aging for instance is slower for the recycled material than for the virgin rubber. Besides, the starting material also determines the end product: e.g. contaminations of the granulate with non-rubber components will negatively influence the properties of the devulcanizate. Furthermore, as devulcanization is a chemical process requiring a certain temperature level and shearing forces, which are non-selective concerning crosslink- and polymer breakdown, there will be a certain degree of polymer degradation as well in this process. The challenge is to shift this balance as far as possible to the side of crosslink scission, and this needs thorough fine-tuning of the devulcanization process.

In the original definition, this project was focused on the design of a devulcanization process for passenger car tires, as Rumal, the industrial partner within this project, wants to extend their product portfolio to this type of recycled rubber in the highest possible quality. However, the first setup of the process and production line was done for truck tire granulate, the standard product from Rumal. This material is mainly based on natural rubber (NR), which is less critical in devulcanization than the synthetic rubbers contained in passenger car tires. Besides the type of feedstock, the main parameters in this context are type and concentration of devulcanization aid, process oil, time temperature profile, and shearing forces. The basis for the devulcanization process is a small-scale, batch-wise process, which was developed in an earlier project within the Elastomer Technology & Engineering group at the UT. This process has to be scaled up and transferred into a continuous extruder process, including the special design of the extruder and the process parameters.

Research motivation

Why is material recycling preferred over the energy recycling ?

Lansink’s ladder (Figure 1) shows the preference of how to deal with waste, and it can easily be applied to used tires. The higher the method of processing is on the ladder, the better it is for the environment. With landfill and burning of tires without recovering energy being banned throughout Europe, re-use through retreading and reclaiming/recycling (recovering the raw materials from end of life tires) are picking up currently as seen in Figure 1. But innovations are on use of renewable raw materials, with little progress on use of old tires as a raw material in new ones.

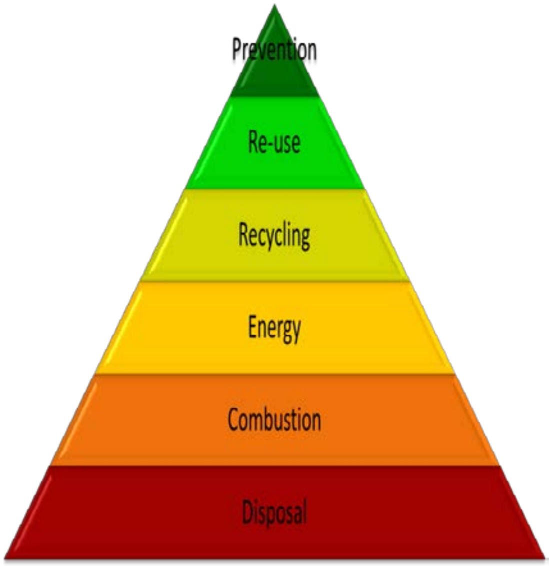

Figure 1: Lansink's Ladder **(RecyBEM, 2013)**

This is where devulcanization of waste rubber offers an opportunity to close the tire loop by putting waste tires back into new tires as shown in Figure 2. Devulcanization is the reverse of vulcanization, the process for shaping rubber and forming a stable network from the polymer chains. In the case of tires, sulfur-bonds are formed; in the devulcanization process, these bonds will selectively be broken in a thermo-chemical process. Therefore, devulcanization allows to make the highest possible quality of recycling material from tires, and enables the rubber processor to use a considerable amount of recycled rubber in new compounds while still meeting the specification for the material.

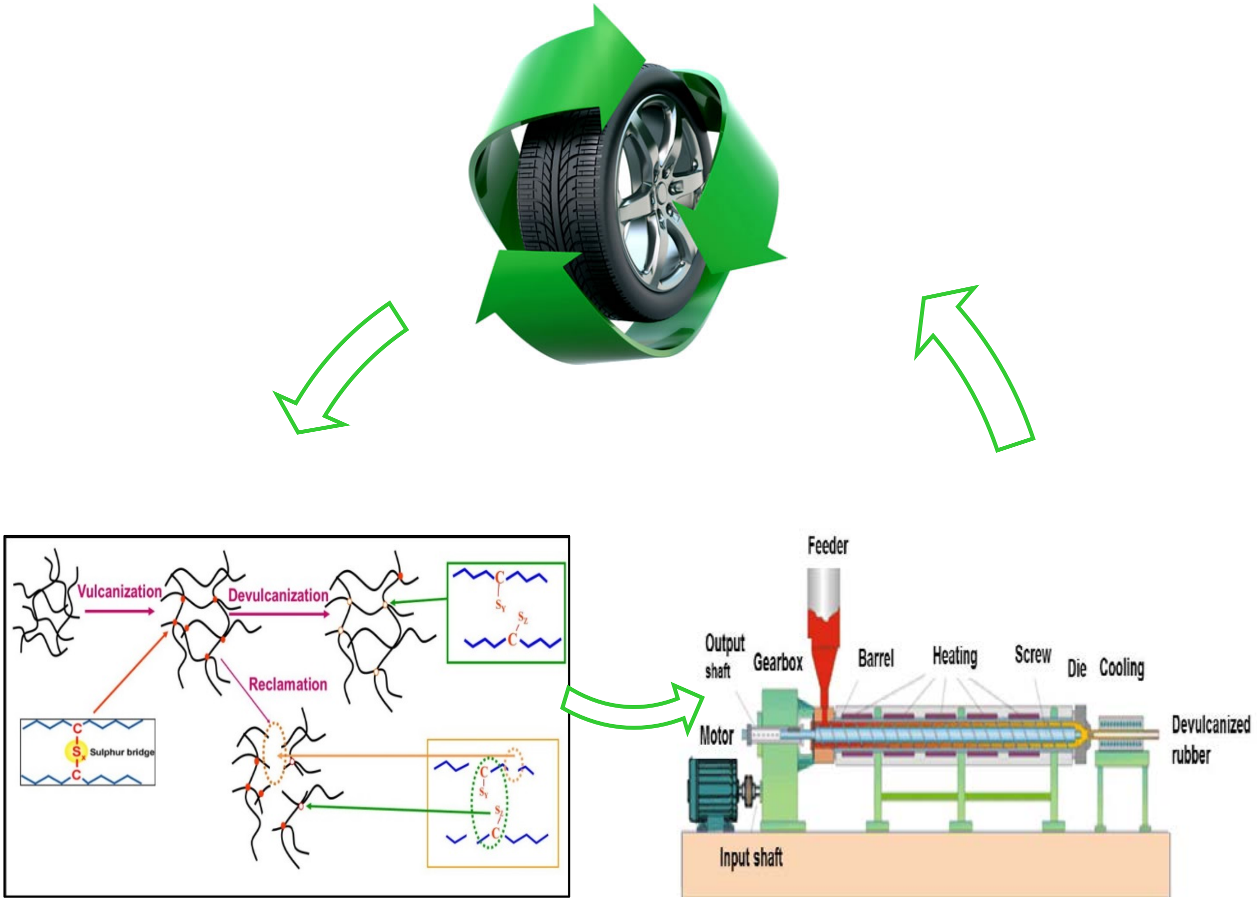

Figure 2: Closing the Tire loop **(fremoonttownship, 2015) (Saiwari, 2013) (Advancedteam, 2015)**

Objective of this thesis

This project aims at the development of an efficient and environmentally sound devulcanization processes for tire granulate. The definition of ‘efficient’ is related to the final product: The devulcanizate needs to be easy blendable with a virgin compound, and can be used in higher quantities than the current recycled rubber products. ‘Environmentally-sound’ means that the process additives should be as environmentally safe as possible.

Structure of this thesis

A literature review on recycling of tires in general, and more specific on devulcanization aids and technologies for tire polymers is given in Chapter 2.

This thesis further encompasses 4 experimental chapters:

Chapter 3: Devulcanization is a chemical process; however, the most efficient devulcanization aids are generally disulfides or mercaptans, which are expensive and have a repellant smell, thus difficult to use on industrial scale. In order to develop an environmentally-sound and efficient devulcanization process, different rubber chemicals are compared concerning their devulcanization efficiency as well as the smell of the devulcanizate. The most appropriate devulcanization aid is finally chosen for the design of the devulcanization equipment and process.

Chapter 4: The devulcanization process was scaled up to a continuous extruder process with a capacity of around 25 kg/h using a Planetary Roller Extruder. In this first series of trials, the integral process was elaborated. However, this approach did not result in a stable, robust process and a stable and high-quality product, but a number of important design rules were elaborated.

Chapter 5: The approach was changed, and in this series of trials, the setup of the planetary extruder was elaborated module by module. This allowed to study the effect of the different components of the extruder and the parameters much more precisely and to better control the process step by step. A study on instantaneously mixing the devulcanization system with the Ground Truck tire Rubber in the extruder was performed to avoid a pre-blending step. The outcome of this trial session was a global process design in terms of choice of spindles, temperature profile, applied shearing forces, and residence time as defined for an extruder setup with 5 to 6 modules.
A third trial session was done for the fine-tuning of the process parameters in the last period of the PDEng project. The analysis of these materials and the conclusions for the process were not available in time for the main part of the thesis; therefore this information is added in Appendix 3 later on.

Chapter 6: An application study was performed using the Ground Truck tire Rubber and Devulcanized Rubber Compound in blends with virgin Natural Rubber to compare the properties in terms of

- Rheology: Complex viscosity and Mooney viscosity
- Curing activity: Scorch and curing time as well as after-cure performance
- Stress strain properties: Tensile strength and elongation at break, as well as moduli
- Dynamic mechanical properties: Storage and loss moduli, which are important in determining the usage of devulcanized rubber in new tire compounding

Finally, the conclusions for the devulcanization process design as well as suggestions for further study are summarized in Chapter 7.

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Recycling of tires with special emphasis on devulcanization aids and technologies

Introduction

Rubber Products are a vital part of everyday living. In homes, hospitals, hotels, offices, laboratories, construction and production facilities, rubber applications are so amazingly broad, but astonishingly comparatively few people are aware how dependent we are on this remarkable material.

Within this very wide array of applications, the transport area accounts for more than 75% of the rubber applications. (ETRMA, 2013/2014)This strong link between transport and rubber is not only tires, but a wide number of parts and components used in transport of goods and materials such as hoses, pipes, sealings, vibration damping, etc. Other application areas are floorings, engine mountings, V belts, fan belts, etc. Furthermore, the rubber industry contributes significantly to improving the sustainability of transport through its infrastructure as rubber added to the road surface can help making it more silent, durable and safe. As even most of the shoes we walk in have a rubber component, it is obvious to state that:

NO RUBBER = NO TRANSPORT ! (ETRMA, 2013/2014)

Tires establish the contact between the vehicle and the road. The most important tasks for the tire are carrying the weight of the vehicle, providing comfort and transferring forces (i.e., traction, braking).

During its service life, the tire consumes more energy than the raw material production, tire fabrication or recycling, so the best sectors for energy savings are:

1. Reduction of rolling resistance and the carbon foot print by enhancing fuel efficiency
2. Reducing the tire weight by e.g. by using highly reinforcing nanofillers

But as a responsible tire maker, the industry should also take care of the tire after its service life.

What happens to our tires at the end of their life cycle?

First the term end-of-life tires (ELT) needs to be defined. A tire is considered at the end of its life when it can not longer be used on vehicles (after having been retreaded or regrooved). All tires including passenger car, truck, airplane, two-wheel and off-the-road tires result in ELTs; however, the bulk of ELTs results from car and truck tires. Figure 1 shows the evolution of recovery routes of tires since 1996.

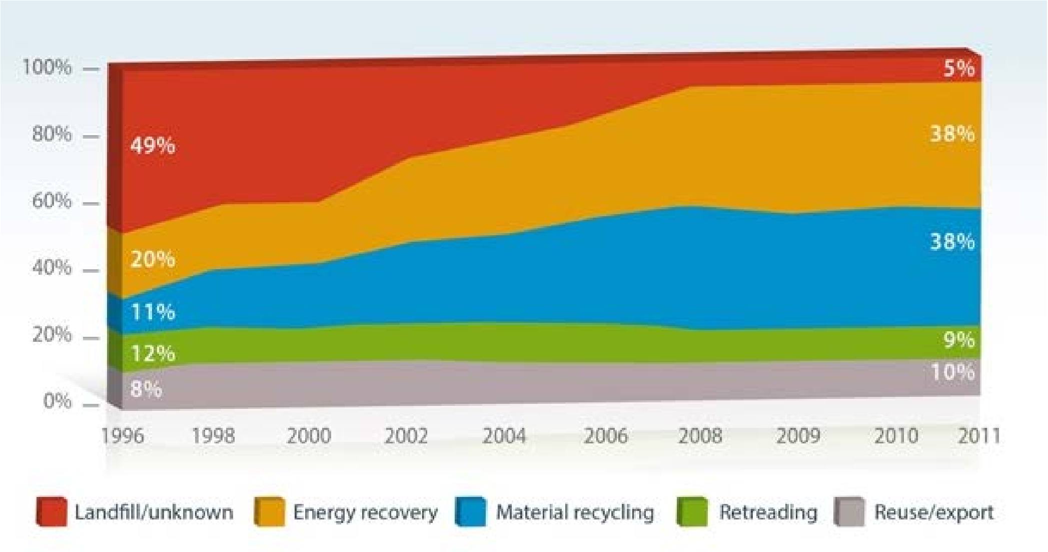

Figure 1: Different recovery routes **(European Tyre and Rubber Manufacturers Association, 2016)**

Off-the-road (OTR) and to some extent truck tires are even more difficult to dispose of than car tires. They are extremely cumbersome, difficult to move, and obviously specialized centers for giant tire disposal cannot be found at every corner. However, OTR and truck tires are mostly made of natural rubber, which makes them attractive for material recycling.

In a tire recycling facility,

1. loose tire components are separated (rim, tube, valve);
2. tires are cut into smaller pieces for better compaction in official storage areas;
3. rubber parts are crushed into granular form;
4. tires are used for producing Tire Derived Fuel (TDF);
5. steel is separated from the granulated rubber with the help of magnets and fibers by gravity separation ;
6. steel and granulated rubber are resold as recycled materials.

End of life tires are reused for two main applications: material recycling (material recovery) and fuel for generating energy (energy recovery).

Why recycle tires/rubber?

Recycling of polymers has been a hot topic for decades, with plastics recycling always topping the charts, leaving the rubber recycling behind. Rubber recycling is indeed far more difficult compared to plastics recycling due to its high molecular weight and thermosetting nature. Recycling of rubber is the need of the hour considering the rapid depletion of resources such as e.g. crude oil and zinc ore, two components absolutely necessary for the production of rubber. Besides, the growing industrialization leads to countless incidents of land, air, and water resources being contaminated with toxic materials and other pollutants originating from waste, threatening humans and ecological systems with serious health risks. Tire form a risk if they are illegally stored in large dumps, and especially when they catch fire like recently in Spain (CBCnews, 2016). The environment forms the background where all life forms sprout and grow. It is affected mostly by the natural calamities such as the earthquakes, floods etc. But in recent times with the advancement of science and technology, man-made polymers with high end properties and stability have started to create problems. In a very short span of time, accumulation of such materials is one of the biggest threat to the environment as nature failed to absorb the accumulated limited resources i.e., polymeric waste.

It is high time that the companies consider the triple bottom line: PEOPLE, PLANET, PROFIT as shown in Figure 2, rather than profits alone (reRUBBER, 2016).

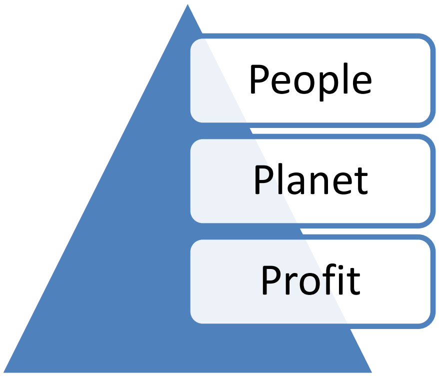

Figure 2: PPP model **(reRUBBER, 2016)**

The world's population is growing. Urban and middle class populations are growing even faster. And people's aspirations and the number of vehicles on the road are increasing day by day. This is depleting the earth's resources fast and creating uncertainty about sustainability, which depends upon the reduction of waste, and increase of reuse and recycling. Rubber production requires a significant amount of petroleum and carbon black, and is an energy-intensive process: Generally 20 liters of oil is required to produce the feedstock materials for a tire, and 8 liters of oil is required to produce 1 passenger car tire from these materials. (RubberManufacturersAssociation, 2016)

Within the past period, rubber consumption and the production rate of the rubber industry have been increasing in parallel to rapid industrialization and civilization. The current world rubber production is 26,702,000 tons (natural & synthetic rubber) as shown in Figure 3 (MalaysianRubberBoard, 2015) and there is no doubt that the global rubber production nor the consumption is going to decrease in the future. But the question arises: What can be the use of these rubber products once they are discarded? Since the polymeric materials do not decompose easily, disposal of waste polymers is a major environmental concern.

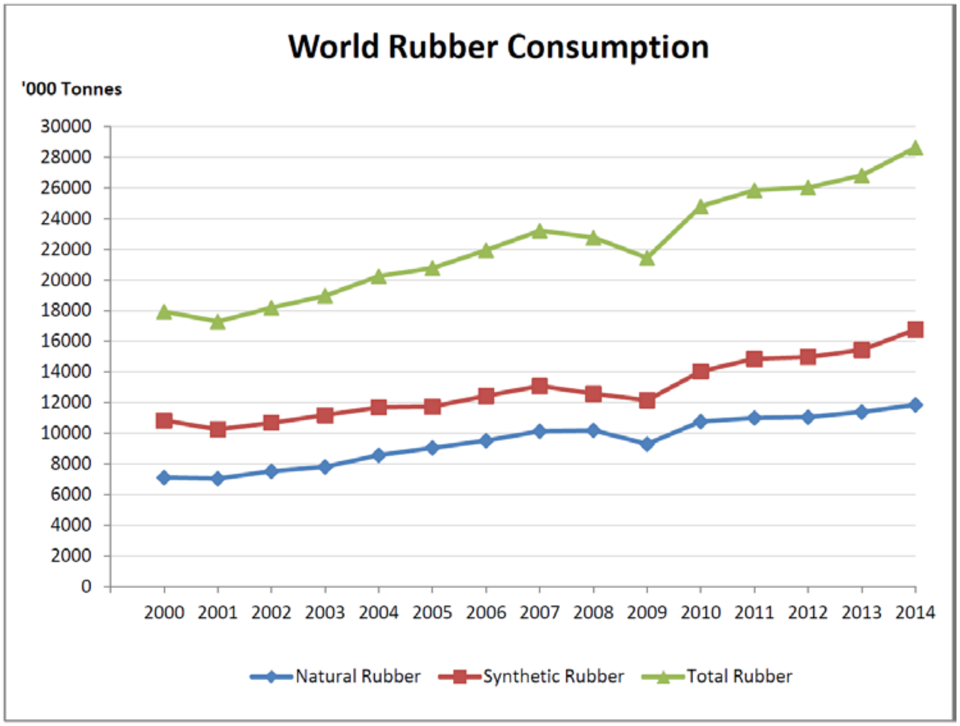

Figure 3: World rubber production statistics **(MalaysianRubberBoard, 2015)**

1. Environmental Impact of Scrap Tires

Approximately 1.4 billion tires are produced worldwide annually. 1 billion tires are disposed of yearly for thermal and material recycling and it is estimated that 0.4 billion waste tires are currently in stockpiles and landfills (Martinez, 2013). Due to the complexity of rubber recycling and the lack or markets for recycled tires and rubber, waste tires were and are still dumped in open landfills creating health hazards.

Health hazards of tire disposal:

Hazards of tire disposal (reRUBBER, 2016) are represented in Figure 4.

- Tires take up landfill space where it is still allowed to store them. As land is becoming more and more scarce and as there is a fee introduced for discarding of tires, this will lead to illegal dumping. It causes socio-economic segregation as tires typically are dumped in low income areas. The large sites for stockpiling waste tires are often hazardous for health as they act as breeding ground for mosquitos by holding water for a longer period of time and cause diseases like west nile virus and LaCrosse encephalitis (Moon, 2015). Besides, rodents and insects live in tire stock piles.
- There is a great risk of fire as tires contain flammable components, and dumping sites also leak methane gas and other greenhouse gases which is obviously not good for the environment.
- Besides, tires in landfills have led to worker injury and death. With the amount of negative space in tires, as they are compressed with more waste, they have a tendency to rebound to the surface, leading to instability and falling onto workers.

Figure 4: Environmental impacts of scrap tires **(reRUBBER, 2016)**

Fire Hazards:

Tires contain flammable and toxic materials, like carbon, sulfur, polymers, oil. The risk for tire stockpile ignition is due to the 75% void space in scrap tire stockpiles which makes it difficult to either quench the fire with water or cut off the oxygen supply. If they catch fire, this is hard to extinguish because the tires have high energy contents: (Palma A, 2002). Open burning of tires produces many toxic gases, which are extremely harmful for the environment and human health. The burning of tires releases benzene, polycyclic aromatic hydrocarbons (PAH), dioxins and furans (Energyjustice, 2015). The PAHs are fat-soluble and not easily degradable in the environment and may accumulate in living organisms (HA oils in automotive tyres, 2003). Burning of tires also pollutes the soil and ground water.

Economic impact of scrap tires

Burning granular rubber generates the same thermal power as the best coal quality. Besides, it does not generate heavy metal emissions into the atmosphere. In this sense, waste tires could be the answer to Europe's decreasing coal production and large coal imports saving a lot of foreign exchanges, and avoiding that the tire material finally has to be discarded. Besides, thousands of jobs are created by recycling of rubber.

What does the law say?

Recycled tires are gaining wider acceptance due to the increase of raw material prices and growing environmental awareness among governments, manufacturers and consumers. In 2012, the European Union has made the payment of an "environmental contribution" mandatory covering the cost of tire collection and of an environmentally-sound disposal/reuse procedure**,** in such a way that this kind of waste is not going to be accumulated in landfills or burnt in the surroundings throughout Europe. Countries adopt different approaches in the management of ELTs. Within the EU, there are three different systems for managing ELTs today (Taverne, 2010):

- Producer responsibility
- Tax system
- Free market system

Producer Responsibility:

According to EC directive 2000/53/EC, which introduces the principle of producer responsibility, the car manufacturers are responsible for treating the end-of-life vehicles making the rubber industry also accountable for their manufactured tires at their end-of-life.

In the purchase invoice, a tire disposal contribution is added, which varies on the tire application and its weight. This contribution paid by the user covers the complete cost necessary for end-of-life tire handling: collection from tire dealers or repair shops, transport to special storage centers, recycling and recuperation operations.

Disposal operations are entrusted to an independent organization working at a national level, acknowledged by all tire manufacturers and importers operating in the country. This allows absolute transparency towards the final user, who can clearly see on the purchase invoices the sum paid for tire disposal; however, the consumer cannot control where the money is spent on. This system is economically very suitable on the long run for resolving end of life tire arising's and also to achieve 100% recycling.

The following EU countries have adopted this system: Belgium, Estonia, Finland, France, Greece, Hungary, Italy, the Netherlands, Norway, Poland, Portugal, Romania, Slovenia, Spain, Sweden and Turkey.

Tax system:

In this system, every country is responsible for implementing the tax on tire manufacturers for their tire production, which the tire companies subsequently charge to the customer. Hence the state is responsible for collaborating with the non-profit organizations for recovery of end of life tires.

The following States have adopted the Tax System: Denmark and Slovak Republic.

Free market system:

The last system is a middle course between the first two options: it is neither the State dealing with worn tires nor a single appointed organization. There are several companies authorized to deal with tire disposal operating on the market in full compliance with the set of legal requirements, but are not designated to be responsible. This system facilitates the cooperation between tire manufacturers and companies dealing with tire disposal leading to partnerships and agreements easing the recuperation process.

The countries which are already operating under a free market system are Austria, Bulgaria, Croatia, Germany, Ireland and Switzerland. (Taverne, 2010)

Different methods of recycling of waste tires:

The different methods of tire recycling are tabulated in Table 1.

Table 1: Different methods of tire recycling

Repeated use (generally for Truck tires)	Re-grooving
	Retreading
Energy recycling	Incineration
Feedstock recycling	Pyrolysis
	Gasification
	Hydrogenation
	Syn gas generation
Material recycling	Shredding
	Grinding
	Surface activation of ground rubber
	Reclaiming
	Devulcanization

The recycling paths making use of the material will be discussed in the following.

Repeated use of Tires:

The established model in the developed world for a truck fleet manager is to buy good quality tires and run them for 18 – 24 months, clocking up around 10,000 km/month. Then the tires are dismounted and sent for reprocessing. That re-processing might be re-grooving, where a layer of rubber is cut out from the bottom of the tread groove to make the grooves deeper, or it might be a full retread. This cycle is repeated a number of times, giving a single carcass three, four or even five lives. Managed this way, a good quality carcass combined with regular maintenance and careful processing can clock up something like 1 million km before it has to be scrapped (Shaw, 2015).

The cost of a retreaded tire can be from 30-50% less than a new tire. The usage of retreaded tires also reduces the CO_2 emissions into the atmosphere. The tire carcass needs to be in a good condition for retreading. With the upcoming of radial tires with steel belted carcasses, the tire carcass integrity is extended. However, high labor costs, tougher safety regulations and cheap imports hurt the retreading business. Mostly medium- and heavy-duty truck tires, off-the-road vehicles, and aircraft tires are retreaded. Retreading of passenger car tires is not common, as there is no market for it due to the impression of the customers that these tires are unsafe, seeing truck tire treads on the highways. Besides, the decline in cost of purchasing new passenger tires also limits the market for retreaded tires in general. (MacHillop, 2002).

For retreading, initially the old tread of the tire is removed by a process called buffing (Figure 5) to create a flat surface on which new tread is vulcanized.

Figure 5: Tire buffing **(Shaw, 2015)**

Retreading is of two types (Vrakking, 2016), namely:

1. Hot retreading
2. Cold retreading

Hot Retreading:

In the hot retreading process, an unvulcanized rubber sheet is applied to the buffed tire/carcass and then it is vulcanized in a heating press. The hot retreading process is done at 150^0C for truck tires and 180^0C for passenger car tires. The shortcoming of this process is that it involves using separate molds for every tread size demanding high capital investment.

Cold Retreading:

In the cold retreading process, the pre-cured tread is applied onto the buffed tire/carcass with the help of an adhesive. The cold retreading process involves less investment compared to hot retreading and does not degrade the tire by subjecting the whole tire structure to curing temperatures.

Pyrolysis:

Pyrolysis is the process of breaking down the organic chemical bonds by heating in an oxygen-free environment. It is also known as destructive distillation, thermal de-polymerization, thermal cracking, carbonization and coking. Pyrolysis of tires produces three products, namely gas, oil and char. Product yields depend on the processing parameters rather than on the process type (J. Dodds, 1983).

Products from pyrolysis process are according to (J. Dodds, 1983):

Gas: Most of the gas produced is used back in the pyrolysis process as a heat source, but the remainder of the gas having high heating value cannot be marketed as pipeline gas because of an excessive carbon monoxide content. It contains low molecular weight paraffins and olefins, hydrogen, carbon monoxide and hydrogen sulfide.

Liquid: The gaseous and liquid products are separated within the process, depending on the condensation temperature used to separate liquids from gas. The difference between the gaseous and liquid products is that the gas contains most of the hydrocarbons having a carbon number of five and lower, and the liquid product has most of the hydrocarbons with a carbon number of six and higher.

The liquid products consist mostly of aromatic hydrocarbons with 26% by weight of either benzene or toluene and the remaining part being high molecular weight aromatics. The benzene and toluene could be separated from the liquid product with sufficient purity to be used as petrochemical feedstocks, and the heavy oil fraction can be used as extender oil for rubbers according to Dodds. (J. Dodds, 1983)

Char: The solid product, char, consists of carbon, silica, ash, sulfur, nonvolatile hydrocarbons, zinc sulfide, zinc oxide and/or metallic zinc with some iron and titanium dioxide (Resource Recovery and Waste Reduction, 1977). Many works are being done to recover carbon black form char as it is considered a high-value market. But the carbon black produced from char is comparable to Semi-Reinforcing Furnace (SRF) blacks (K. P. Raman, 1981), which does not improve reinforcement; it rather helps in improving the tack for tire building compounds. However, another interesting point is that High-Abrasion Furnace blacks are used only in treads, and most of the tread is worn out in a scrap tire, so the quest to recover the char as carbon black higher than SRF seems to be questionable.

The inferior properties of the char are due to the

- Ash content (up to 15% by weight)
- Solid hydrocarbons
- Particle size (distribution)

Elastomers are compounded with inorganic materials, including sulfur, zinc oxide, clay fillers, calcium and magnesium carbonates, silicates as well as a variety of inorganic pigment materials; all these components are present in the char. An acid leaching reduces the ash content and upgrades the char. Solid hydrocarbons are removed by pyrolyzing at higher temperatures or by toluene extraction, and particle size reduction is used to increase the surface area. But even after different post-treatments, pyrolyzed carbon black doesn’t reinforce the rubber, as the surface reactivity of the carbon black is lost due to extra heat history seen during pyrolysis (Sons).

So drawbacks of pyrolysis are:

- Low quality products, which prevents direct use for high-quality products
- Upgrading the pyrolysis products is difficult and cost intensive

Material recovery:

Shredding/ grinding:

Tires which are not able to be retreaded, mostly undergo a shredding or grinding process. Shredding reduces almost 75 percent of the volume of the waste tires. For shredding, generally 19.2 KWh energy is required to shred 1000 Kg of waste tires (S. Ogilvie, 2004). Shredded tires are used for different applications depending upon the size of the shredded rubber, but the cost of shredding increases significantly, as the shred size decreases. Shredding produces particles in cm–size, which can be used as tire chips for power generation like in cement kilns as tire derived fuel (TDF). Subsequently, these tire chips undergo a series of granulations or comminutions to produce crumb rubber in mm-size. Size reduction allows steel removal by magnetic separation, and fiber removal by gravity separation, as shown in Figure 6.

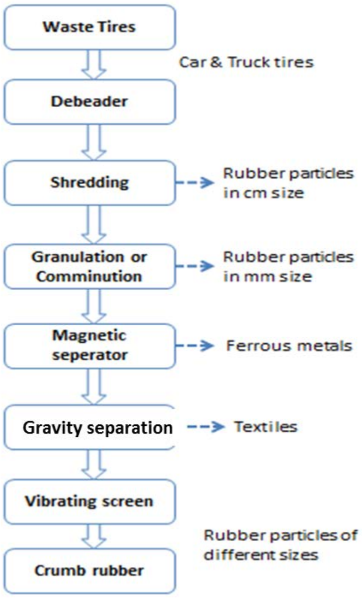

Figure 6: Schematic of scrap tire processing **(Ni-Bin Chang, 2015)**

The three different grinding processes used in practice are ambient, cryogenic and wet-ambient grinding (Mackillop, 2002). In the ambient process, the waste rubber is ground in an ambient mill, whereas during the cryogenic process, rubber is immersed in liquid nitrogen where it is cooled down to a temperature below the glass transition point. In this brittle state, the rubber is then pulverizing into fine particles. Considering the cost of inexpensive tire rubbers, the cost for the high quantities of expensive liquid nitrogen required to freeze the rubber makes it less attractive (LaGrone, 1986). However, it is the only way to produce very fine powders for reuse in high quality products like tires.

Application of whole and particulate tires:

Table 2 shows different applications of whole and particulate tire rubbers.

Table 2: Application of whole and particulate tire rubbers

	Selected Uses
Whole Tires	Artificial reefs Coastal defense Construction bales Erosion control
Shreds and Chips	Landfill applications Horse riding tracks & arenas Thermal insulation Roadway filter drains
Granulate and Powders	Sport surfaces Noise barriers Rubberized bitumen Paving blocks Roofing & insulation materials Train & tram rail crossings Artificial turf Road furniture & signposting Porous drainage pipes Footwear Running tracks Children’s play areas

The use of recycled rubber powder from tires in the bitumen used in road surfaces has proven not only to reduce noise, but also to enhance other asphalt performances such as durability of the asphalt pavements, the reduction of maintenance costs and improved friction, minimization of hydroplaning with reduced splash and spray during rainstorms (ETRMA, 2013/2014).

There was a problem reported because of the zinc content in tires which might percolate into the ground water stream, initiated when synthetic turf was used for soccer fields. However, it is not particularly toxic to humans. In fact, zinc is an essential and beneficial element in the human metabolism that may be consumed at 10 mg/L of drinking water with no harmful side effects. However, fresh water organisms (i.e., algae, minnows, trout) have exhibited a reduction in reproduction fecundity at zinc concentrations of 0.1 mg/L (Fritschel, 1983). Therefore, the release of zinc to an aquatic system may result in adverse impacts to the environment.

The California Office of Environmental Health Hazard Assessment (OEHHA) investigated the potential health risks to children from playground surfaces made from recycled tires. Tire rubber, which besides natural and synthetic rubber also contains phthalates in plasticizers (chemicals that affect hormones), polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) and other chemicals known or suspected to cause adverse health effects (Llompart M, 2012). Researchers mimicked the child's stomach and placed 10 grams of tire shreds in it for 21 hours at a temperature of 37^0C. Results showed that a single incident of eating or touching the tire crumbs doesn't hurt a child's health, but repeated exposure does. One of the PAH's being chrysene was higher than the risk level established by OEHHA, which could subsequently result in chances of developing cancer in the child (CalRecycle, 2007). Other components were mostly irritants – substances which cause a body's reaction, out of which 24% were respiratory irritants that can cause asthma symptoms, 37% can cause skin irritations and 27% can irritate eyes (Environmental and Human Health, 2016).

DEVULCANIZATION AIDS and technologies for tire polymers

VULCANIZATION

Rubber in its natural form it is rather unstable: at higher temperatures, it starts to flow and degrade, and if it is too cold, it becomes rigid and brittle. Raw rubber is an entanglement of high molecular weight hydrocarbon chains, which flows and does not retain its shape. The key invention for rubber to initiate an industrial revolution was the process of vulcanization, which permanently links the elastomer chains. Only this made it possible to use them as e.g. seals and gaskets in machines, which made the machines more durable. Earlier, the only way to seal the small gap between moving machine parts was to use leather soaked in oil. This practice was acceptable only at moderate pressures, but above a certain point, machine designers were forced to compromise between extra friction generated by the tight packing and greater leakage of steam. This problem was solved by using vulcanized rubber. Vulcanized rubber could be formed in any shape and dimension, it accepts moderate to large deformations under load and recovers quickly to original dimensions, once the load is removed. These qualities combined with high durability and lack of stickiness were effective for sealing material.

As early as 1839, Charles Goodyear in America and Thomas Hancock in England discovered that by heating a mixture of natural rubber (NR) and sulfur to 130 - 140^{o}C, an elastic, non-sticky material with good mechanical strength and insoluble in all solvents resulted, which did not soften any more when heated. The phenomenon was called hot vulcanization. Later, cold vulcanization at room temperature in the presence of sulfur chloride (S_2Cl_2) was discovered as well (History.com, 2016). From a chemical point of view, vulcanization is a crosslinking process as illustrated in Figure 7. After vulcanization, the rubber holds its characteristics both in summer as well as in winter, making rubber a commodity to be used.

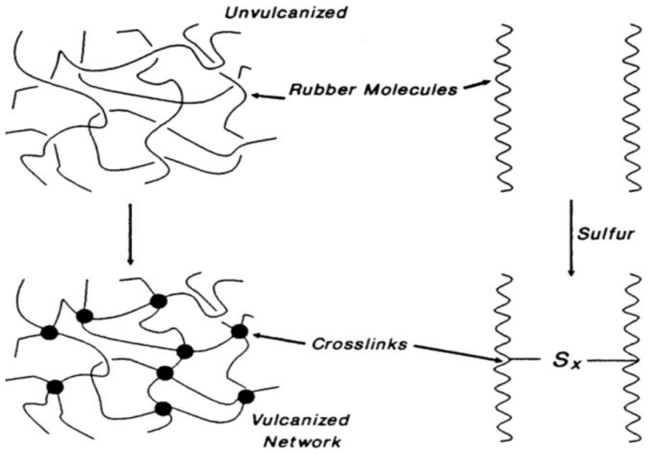

Figure 7: Network formation **(James E. Mark, 1994)**

Figure 8 is a schematic of the bonds formed in a vulcanization process, in which sulfur links the rubber molecules to form a crosslinked network. These chemical bonds are formed by a group of sulfur atoms or a single sulfur atom as shown in Figure 2, carbon-carbon bonds, an organic radical, an anionic cluster or a polyvalent metal ion (nawi780, 2016).

During vulcanization with sulfur or any other curing agent, rubber is converted into a thermoset system that is crosslinked, with a molecular weight (MW) between each crosslink of approximately 10,000 Dalton. This gives rubber its unique properties, i.e., excellent flexibility, high elasticity and very good energy absorption. Elastomer transformation from plastic to elastic state, lack of solubility in organic solvents, limited swelling ability, as well as modification of certain important physio-mechanical properties like tensile strength, elasticity, elasticity modulus, relative and plastic elongation, plastic compression, heat evolution, swelling stability, permeability to gases, resistance to low temperatures, can be explained by the presence of these crosslinks. The vulcanization process is irreversible at standard atmospheric conditions.

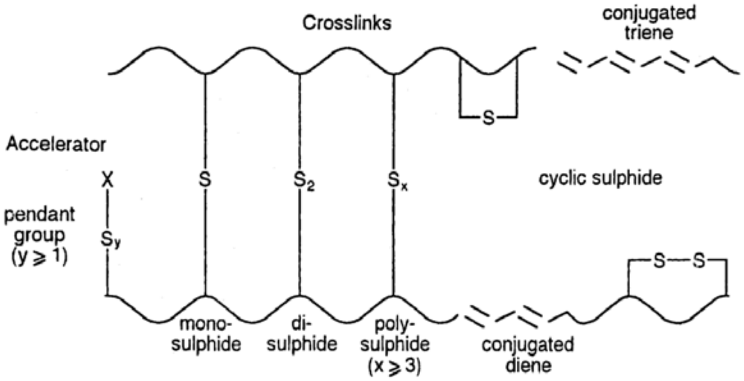

Figure 8: Different sulfur crosslinks **(nawi780, 2016)**

The length of sulfur crosslinks affects the physical properties: the longer the crosslinks such as polysulfide crosslinks, the higher the tensile and tear strength, and the higher the fatigue properties for e.g. tires. Shorter crosslinks improve thermal and oxidative stability and result in low compression set for e.g. oil seals and O-rings.

Elastomers differ concerning their ease of vulcanization as the highly unsaturated ones cure faster. For example, the curing tendency decreases for the following polymers:

Natural rubber > Styrene Butadiene Rubber > Ethylene Propylene Diene Rubber

As a result, the amount of sulfur and accelerator used to cure various rubbers varies. For a Conventional Vulcanization system (CV system), Natural Rubber is cured using 2.5 parts per hundred rubber (phr) of sulfur and 0.7 phr of sulfonamide accelerator. By comparison, Styrene Butadiene Rubber is cured with less sulfur (1.8 phr) and more accelerator (1.5 phr) (J.L. Zelibor, 2013).

RECLAIMING OF RUBBER

The rubber recycling industry started shortly after Goodyear obtained the patent for vulcanization of natural rubber with sulfur (Ball, 1947). The traditional ways of recycling are grinding and reclaiming, that is replasticizing, of the rubber.

Reclaimed rubber is generated by the application of heat to ground vulcanized rubber, which results in a soft, plastic (i.e., processable) state due to substantial depolymerization. The degree of plasticity introduced by the reclaiming process enables it to be blended with virgin rubber easily. The main reason for using reclaimed rubber is to reduce the cost and to improve the processing characteristics. It mixes faster than virgin rubber because all the fillers of the original product are already incorporated and hence the power consumed and processing temperature for mixing are less. The remaining three-dimensional structure of the thus recycled rubber increases the green strength, reduces the nerve (so less die swell and shrinkage), and also imparts gauge stability to the calendared and extruded stocks. Reclaimed rubber blends also reduce cure blistering as surface roughness of the reclaimed rubber particles provide a path for the air to escape.

Reclaiming benefits can also be reaped during compounding as well, as it requires little or no new carbon black for new compound preparation, so the carbon dioxide emissions during virgin carbon black manufacture can be avoided. Reclaim rubber poses higher aging resistance as it suffered oxidation and mechanical flexing during its first life cycle, and a high degree of mechanical shearing during the reclaiming process. So the compounds with reclaimed rubber require no or less antioxidants. Due to its higher thermal stability, the reclaimed rubber has less tendency to revert. Reclaimed rubber when blended, usually possess a low scorch time and cure time, faster cure rate and high rheometric torque due to the presence of curing additives in the reclaimed rubber which are partly active, and also due to the chemical devulcanization aids affecting the curing reaction. Higher hardness and modulus are due to a higher number of crosslinks. The tear strength increases, as the crack propagation length is longer: the crack passes around the surface of recycled rubber particles in case of blends with reclaimed rubber, as this interface is in general the weakest spot. Besides, energy dissipation occurs on the interface around the reclaim particles. Tack and penetration of rubber into textile cord is improved, as during reclaiming the viscosity is reduced due to molecular breakdown, making the material to flow easier. But lower mechanical properties like tensile properties are caused by degradation of polymeric chains: the average length of the rubber chains is reduced during reclaiming, which is limiting its practical usage in tire compounds. A higher proportion of reclaimed rubber results in increased stiffness and causes brittle failure. The addition of reclaimto virgin compounds generally increases hysteresis loss. Hysteresis refers to the amount of energy lost by a rubber after being stretched or compressed. Unreturned energy is converted primarily into heat and directly increases the heat build-up and rolling resistance of the rubber. With increased hysteresis loss, rolling resistance also increases, resulting in greater fuel consumption. This is due to the increase in the number of dangling chain ends as a result of chain modifications, making into difficult to use reclaimed rubber in tread compounds of tires.

While compounding the reclaimed rubber with virgin rubber, even if it is the same type of compound, the properties will change since the recycled rubber has already undergone a whole life cycle resulting in aging of the material. In addition, polymer-filler interaction is different since it is formed during mixing which the recycled rubber has to undergo twice. And also, the curing system for a blend of reclaimed rubber and virgin rubber needs to be adjusted since the former still contains partially active curing additives (Marvin Myhre, 2012).

Addition of reclaimed rubber to NR reduces the chance of strain-induced crystallization, which in turn reduces crack and fatigue resistance and also mileage when used in a tire tread. It also reduces tire durability and longevity and increases the rolling resistance. The reduction in properties will lead to an increased tire replacement frequency and an increased annual scrap tire disposal rate. Therefore reclaim or crumb rubber utilized in compounding of new tires will not serve the purpose of cradle-to-cradle loops. The use of reclaimed or crumb rubber is limited due to the property mismatch between the recycled and virgin rubber and a weak bond between recycled and virgin rubber, while a devulcanizate is attached by stronger chemical and physical-chemical bonding. Only the latter can opens the possibility for cradle-to-cradle loops with an appreciable amount of recycled rubber in the future.

DEVULCANIZATION VS RECLAIMING

The main difference that distinguishes an elastomer from a thermoplastic material is the crosslinking between polymer chains, which is fundamental to confer its peculiar mechanical properties (elasticity), but in turn it causes the loss of material’s thermoplastic behavior which is essential for recycling.

Devulcanization of cured rubber is the process of selectively cleaving, either totally or partially, the crosslinks between polymer chains, with depolymerization (i.e., main chain cleavage) and main chain modification being minimized. This operation also restores the thermoplastic behavior of the material, allowing it to be processed again. Reclaiming is an uncontrolled breakdown of the network, which includes both, depolymerization and devulcanization, resulting in extensive polymer scission and highly branched chain segments with a broader molecular weight distribution (Figure 9).

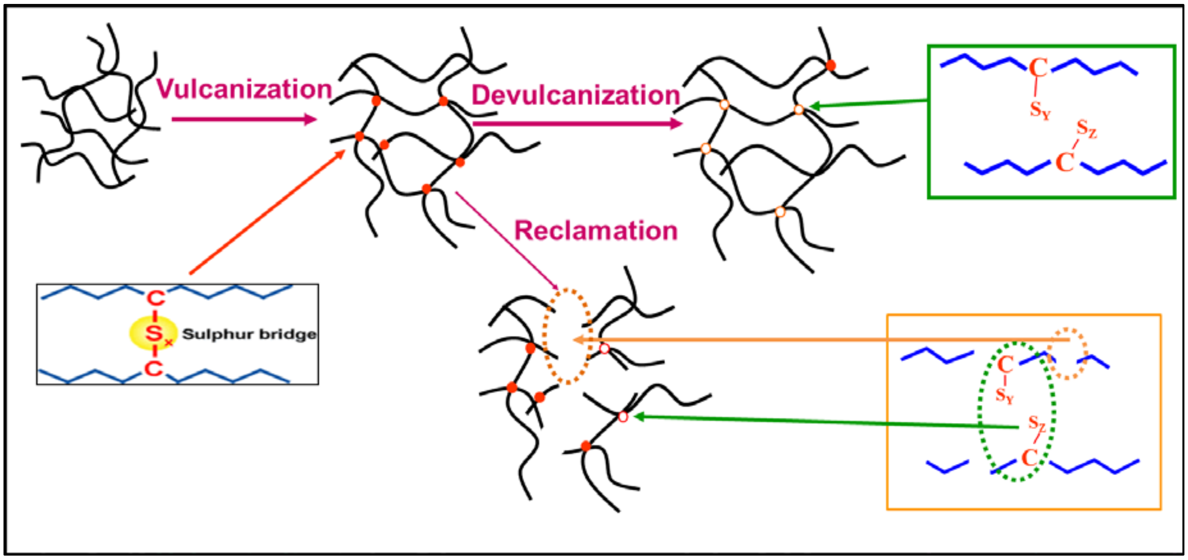

Figure 9: Devulcanization Vs Reclaiming **(Saiwari, 2013)**

The double bonds located in the molecular chain allow both, vulcanization and thermal rupture as well. The presence of double bonds directs the thermal rupture to the β-carbon location relative to the double bond (Figure 10) (J. Dodds, 1983).

-CH2-CH=CH**(α)**-CH2**(β)**-

Figure 10: Type of carbon atoms in the polybutadiene structure

Tobolsky (Tobolsky, 1965) and Ono (Ono, 1979) have pointed out the mechanisms that can potentially cleave the sulfur crosslinks without damaging the rubber molecules themselves. Three mechanisms are associated with the different chemical bonds present in the sulfur crosslinks and the rubber molecules, namely:

1. Differences in the bond energies

Table 3: Bond energies for sulfur crosslinks in rubber **(E. Finnazzi, 2011)**

Bond location in crosslinked rubber	**Bond type**	**Bond energies (kJ/mol)**
Di- and polysulfidic crosslinks	S-S, S-(S)$_n$-S	270
Monosulfidic crosslinks	C-S-C	310
Main chain bonds in rubber molecules	C-C	370

From Table 3, it is apparent that sulfur-sulfur and carbon-sulfur bonds have lower bond dissociation energies, so they will be broken more easily than the main chain carbon-carbon bonds in the rubber molecules, when sufficient heat is applied to the crosslinked rubber.

2. Differences in the shear stiffness

Table 4: Elastic constants for sulfur crosslinks in rubber **(Finazzi, 2011)**

Bond location in crosslinked rubber	**Bond type**	**Elastic constant, K (N/m)**
Di- and polysulfidic crosslinks	S-S, S-(S)$_n$-S	~3
Monosulfidic crosslinks	C-S-C	Intermediate value
Main chain bonds in rubber molecules	C-C	~100

The spring or elastic constant (Table 4) is a measure of the elasticity of a spring: the lower its value, the lower the stiffness of the bond, and the lower the force needed to extend the spring. Bonds having a lower elastic constant (i.e., elastic constants of S-S bonds are

1/30th of the constants of C-C Bonds) will be more extended compared to bonds with a higher constant like e.g. C-C bonds, and the former tend to break more easily upon the application of shear force to the crosslinked rubber.

3. Differences in the chemical reactivity

The reactivity of covalent bonds differs due to variations in its chemical properties and atomic structures. This difference in reactivity can be exploited by using devulcanizing aids which are used to specifically target the sulfur-sulfur and sulfur-carbon bonds. The devulcanization aids also function as “radical scavengers”, which react with the free radicals generated from bond scission in the polymeric network and prevent them from recombining.

DEVULCANIZATION AIDS:

Reclaim has the plasticity of an unvulcanized rubber compound, however, the molecular weight is reduced so reclaim compounds have poorer physical properties mainly caused by the intense physical forces and thermal load applied in this process. Under severe shear and high temperatures, various reactions occur during the reclaiming process, causing main chain and crosslink scission. However, the use of devulcanization aids which are effective in low concentrations, introduces new pathways for a more effective and selective crosslink scission and faster devulcanization.

The functionalities of chemical devulcanization aids are (Marvin Myhre, 2012):

- Initiation of the cleavage of sulfur crosslinks
- Radical scavenging: reacts with the free radicals generated by C-C, C-S and S-S bond cleavage and prevents recombination of the molecules
- Gel prevention by acting as a radical acceptor

Organic devulcanization aids are divided into two categories based on the working mechanism (Forrest, 2014):

- Reaction with free radicals to prevent reformation of crosslinks, e.g., disulfides, thiols and phenolic compounds
- Cleavage of sulfur crosslinks by a nucleophilic mechanism, e.g., amines and their derivatives

A large number of chemical devulcanization aids were developed for natural as well as synthetic rubbers. Some examples of chemical devulcanization aids are diphenyl disulphide, dibenzyl disulfide, diamyl disulfide (Canada Patentnr. 456,789, 1949) (US Patentnr. 2,494,593, 1949), bis(alkoxy aryl) disulfides (Canada Patentnr. 2,469,529, 1949), butyl mercaptan and thiophenols (Switzerland Patentnr. 215,952, 1948) (US Patentnr. 2,415,449, 1947), xylene thiols (Canada Patentnr. 452,085, 1948) (US Patentnr. 2,408,296, 1946) and other mercaptans (US Patentnr. 2,211,592, 1940).

Knorr (Knorr, 1994) studied the reaction of diaryl disulfide with natural and synthetic rubber waste. In this process, the finely ground rubber mixed with reclaim oil and disulphides (Aktiplast 6) was heated in saturated steam at a temperature of 150–180^{0}C. 2-mercaptobenzothiazole was found to be an effective reagent for the reclamation of waste powder rubber (H. Okamoto, 1979). Anderson (US Patentnr. 4,554,675, 1985) patented the reclamation of sulfur-vulcanized rubber in the presence of oil, water vapor and aryl disulfide in a temperature range from 175^{0}C to 195^{0}C and a pressure in the range of about 230-260 psi for about 3 to 4 hours. Here, aryl disulfide is a mixture of disulfides, namely diphenyl disulfide, dicresyl disulfide and dixylyl disulfide. De and coworkers (De. D, 1997) (De. D M. S., 1999) used an ecologically friendly renewable resource material known as RRM. The constituents are diallyl disulfides (majorly), different monosulfides, disulfides, polysulfides and thiol compounds. De and coworkers (De. D D. A., 2006) used as a multifunctional reclaiming chemical for example tetra methyl thiuram disulfide, for reclamation of ground tire rubber. It is important to note that the thiuram disulfides used as a devulcanization aid are merely produced from secondary amines. Most of the secondary amines have been shown to produce nitrosamines, which are known to be carcinogens (Eisenbrand, 1984). Swapan Kumar Mandal et al., (Mandal. S. K, 2012) have used safe tetra benzyl thiuram disulfide as devulcanization aid for the devulcanization of ground tire rubber in the presence of spindle oil.

Myhre et al. (Marvin Myhre, 2012) suggested that the reactivity of sulfur radicals, which are formed via the cleavage of S-S bonds, determines the efficiency of the rubber devulcanization process. A lower bond dissociation energy of disulfides gives higher efficiency. The bond dissociation energies of the S-S bonds of the different disulfide compounds follow the order (Yi-Meng Yang, 2015):

Aliphatic disulfides ~ disulfides containing heteroatom substituents > bis (para-substituted phenyl) disulfane ~ multi-substituted diphenyl disulphides

The conjugation between the S—S bond and the α-substituted unsaturated groups favor the S—S bond cleavage. And electron-withdrawing groups (i.e. —NO_2, —CN, —CF_3) disfavor the

S—S bond cleavage due to the formation of the instable electron-deficient S radical center, while the electron-donating groups (such as—NH_2,—NMe_2) tend to facilitate radical formation.

DEVULCANIZATION OILS:

The oil plays several roles in the devulcanization process, such as increasing the plasticity of the devulcanized rubber and preventing sol formation by acting as a radical acceptor, but it also is accelerating the oxidation of the rubber (Kawasaki et al, 1979) . The mechanism is such that addition of oil actually swells the rubber which increases the spacing between the rubber chains for the devulcanization aid to be more accessible. This in turn increases the devulcanization efficiency of the rubber. The oils generally have active double bonds or methylene groups in the molecules, through which they are more easily oxidized than the rubber molecule. It is assumed that these activated molecules formed by the auto-oxidation reaction accelerate the oxidation of the rubber (Myhre M, 2012). In a devulcanization process, the common organic solvents, e.g., toluene, benzene and cyclohexane, were used. However, these solvents are volatile, flammable, difficult to remove after the reaction and associated with toxicity related issues. Supercritical fluids were considered to be the best substitutes for harmful solvents in terms of cost, non-flammability and non-toxicity, and can be removed easily from the polymer at the end of the process by releasing pressure. (Meysami, 2012)

The oil is chosen on the basis of high compatibility with the rubber and devulcanization aid. For instance MBTS dissolves easily in aromatic oil because it has an aromatic structure similar to the oil (S Ostad Movahed et al, 2014). Generally aromatic and naphthenic oils are used. A high boiling point oil is preferred to prevent evaporation of the oil during the devulcanization process.

Problems of devulcanization:

- The process of converting a threedimensional, insoluble and infusible thermoset structure to a one-dimensional soft, plastic, low modulus and processable thermoplastic is the real challenge in devulcanization. Since tires are designed to withstand harsh mechanical and weather conditions as ozone, light and bacteria, the tire rubber is difficult to recycle and to further process.

- The quality of devulcanization of single rubbers is higher than that of devulcanized multiple rubbers, therefore tires, made of different rubbers and compounds and consisting of several ingredients as shown in Table 5, are difficult to recycle.

Table 5: Composition of Tires **(Rubber Manufacturers Association, 2004)**

Truck Tire	**Constituents**
Natural rubber	27%
Synthetic rubber	14%
Carbon black	28%
Steel	14-15%
Fabric (polyester, nylon), fillers, accelerators, antiozonants, zinc oxide, stearic acid, antioxidant, wax, processing chemicals, sulfur	16-17%

This leads to the following problems:

- Presence of free sulfur can negatively influence the devulcanization process, as the sulfur can be involved in a (re)crosslinking process.
- Shortened crosslinks due to network maturations during the service life, as the polysulphidic crosslinks are transformed into mono- and disulphides during tire use.
- Broken crosslinks, end capped during devulcanization and not participating in re-vulcanization.
- Anti-oxidants from the discarded rubber impact the devulcanization process as they act as free radical acceptors.
- Carbon black known for its anti-aging properties, absorbs free radicals.
- Most so-called devulcanization techniques give rubber powders with a chemically partially activated surface, as for example chemical and mechanical devulcanization are considered to be surface devulcanization technologies (CalRecovery, 2004).
- Radial tires use a rather sophisticated rubber compounding; as the devulcanized rubber does not have the same physical or mechanical properties as the virgin rubber compound, so the compounding has to be fine-tuned again.

- Devulcanized rubber blended with virgin rubber tends to increase rolling resistance as well as heat build-up: polymeric chains are cut in the process leading to branched polymer formation with a higher number of chain ends and thus an increased viscous part.

Some of the disadvantages of using the devulcanization aids:

- Requires the time-consuming extra step of mixing the devulcanization aids with ground tire crumb.
- Requires relatively high temperature for activation, which leads to more energy consumption and can also degrade the rubber.
- Impart unpleasant odor.
- During processing, vapors are released, which need to be treated before releasing it into the ambient atmosphere.
- Health and safety concerns associated with them.
- A short reaction period leads to insufficient diffusion into the rubber particles, which results in surface devulcanization rather than bulk devulcanization. This can be offset by fine grinding of the cured rubber which in turn will increase the cost of manufacturing of the ground tire rubber.
- Most devulcanization aids are relatively expensive.
- Grinding has an effect on the absorption of devulcanization aids and oil: A smaller particle size permits a more uniform distribution of devulcanization aids.
- In a blend of SBR and NR, SBR particles absorb devulcanization aids at a slower rate than Natural Rubber, resulting in an uneven distribution of additives results.

Devulcanization techniques in the market:

The Toyota process, (K. Fukumori, 2006) based on the shear flow reaction control technology, is used to selectively break down the crosslinks in ethylene-propylene-diene rubber (EPDM) without the use of devulcanization aids. The process is carried out in a modular screw type reactor (i.e., twin screw extruder) as shown in the Figure 11, where the rubber waste is finely ground and heated to devulcanization temperature quickly in the first pulverization zone. In the devulcanization zone, the residence time is adjusted such that the complete devulcanization reaction takes place.

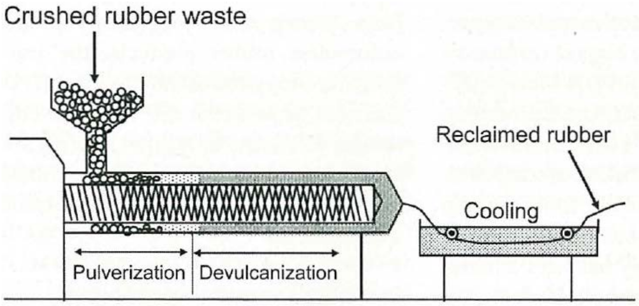

Figure 11: Schematic illustration of the reactor in the Toyota process **(K. Fukumori, 2006)**

From Figure 12, it can be seen that there is a small difference in the bond dissociation energy of the C-C, C-S, S-S bonds. Hence, with simple heating it is difficult to cleave the bonds selectively. However, with regard to the elastic constant k for these bonds, the k-value for the S-S bonds can be estimated to be about 1/30th of the C-C bonds enabling it to selectively cleave the bonds, as mentioned before in Table 4.

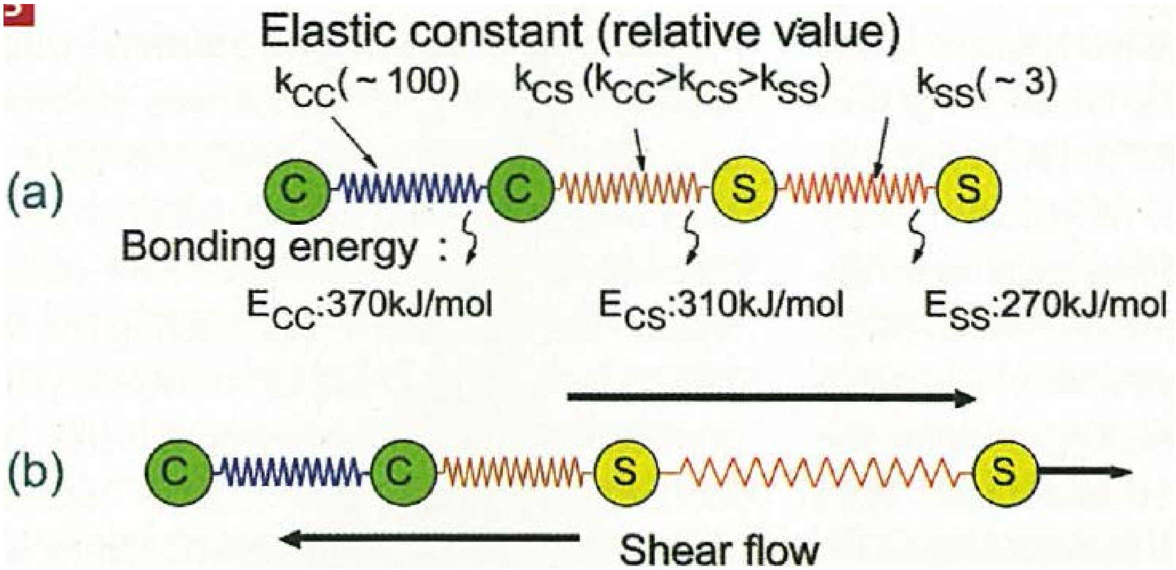

Figure 12: Breakage of crosslinks in high shear flow: (a) model for the network chain;

(b) deformation of the network chain (particularly, S-S bonds) by shearing **(K. Fukumori, 2006)**

The characteristic odor of devulcanized rubber may limit its end use. Hence a deodorization procedure was employed, in which high pressurized water was injected into a barrel. The deodorization mechanism is schematically shown in Figure 13, odorous components in the rubber compound are trapped in the high pressured water vapor and removed efficiently through the vents with vacuum pumps. (K. Fukumori, 2006)

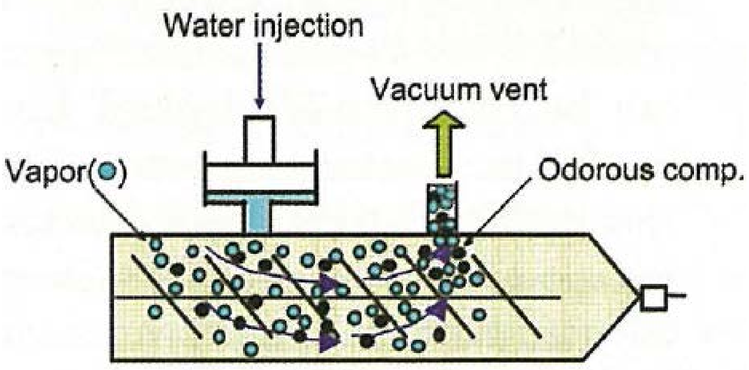

Figure 13: Deodorization mechanism **(K. Fukumori, 2006)**

The Delink process (Patent No. US005770632A, 1998) makes use of the relatively poor thermal stability of diene rubbers by employing a chemical activator system that is capable of devulcanizing rubber through a proton exchange mechanism at relatively low temperatures (preferably below 50^0C). The general devulcanization mechanism of the Delink process is given in Figure 14. The chemical devulcanization substance known as De-Vulc, is comprised of the zinc salt of thiocarbamates such as zinc dimethyl dithiocarbamate (ZDMC) and 2-mercaptobenzothiazole (MBT) or derivatives thereof, in a molar ratio in the range of 1:10 to 1:12. The accelerators are boosted by activators, preferably zinc oxide and stearic acid. Sulfur may be additionally added to the mixture. The De-Vulc mixture was blended with tire crumbs in a concentration of 6 parts per 100 parts of rubber crumb in an open mill for 7-10 minutes. The advantage of using the Delink process is that no re-compounding for vulcanization is required as the residual chemicals enable it to be revulcanized at standard curing temperatures.

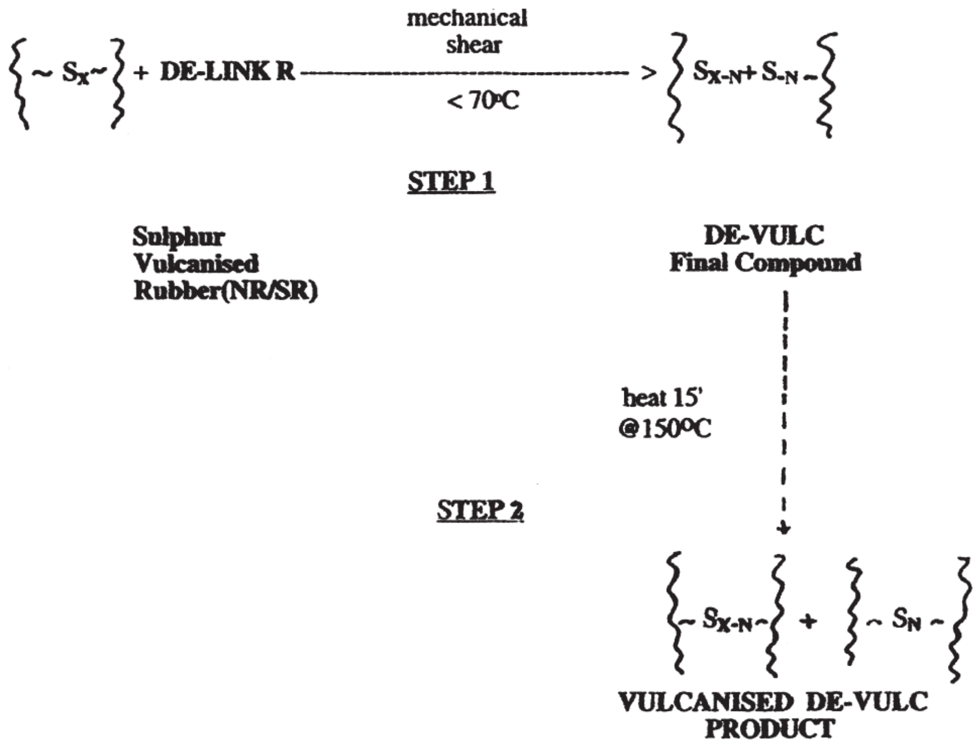

Figure 14: De-Vulc devulcanization mechanism **(U. S. Ishaiku, 1999)**

The Israeli company Levgum has patented a chemical devulcanization process (Patent No. US 6831109 B1, 2004) where the additive is said to be derived from the agricultural industry. The chemical modifier system consists of two substances, in which the first chemical substance is mono-, di- or tri-substituted urea, and generates protons by the formation of an organic cation and amine and thus initiate a proton exchange with the polymer structure of a pre-stressed cured elastomer. The second chemical substance is a dicarboxylic acid with 2-4 carbon atoms in the main chain, which acts as a promoter for the dissociation of the first chemical substance, urea, and also as an acceptor of amine. The molar ratio of urea to acid ranges from 0.5:1 to about 2.5:1 and the blend is prepared by simple dry mixing. The modified system ranging from about 0.25 to 4.0% of the quantity of waste tire crumb is added in a two roll mill at a narrowing nip gap and room temperature for about 7-12 min.

Equipment for devulcanization

Functional Principle of Planetary Roller Extruder (Gerdon, 2012)

The planetary roller extruder was first developed in the Fifties of the last Century by Mr. Wittrock. Previously the extruder was primarily used for compounding of instable materials like PVC. Meanwhile the application spectrum of the planetary roller extruder has been extended in all fields where gentle compounding with precise temperature control is required. This technique was exploited for the devulcanization of elastomers where only the sulfur chains need to be targeted leaving the carbon chains of the material intact.

The planetary roller extruder essentially consists of the feed part, the heatable-coolable cylinder assembly, the heatable-coolable central spindle and the planetary spindles as shown in Figure 15.

The cylinder assembly and the central spindle are toothed in a helix angle of -45°. The planetary spindles have a helix angle of 45° and thus can be screwed between cylinder assembly and central spindle. Depending on the size of the planetary roller extruder and the material requirements, the planetary roller extruder can be equipped with 3 – 24 planetary spindles.

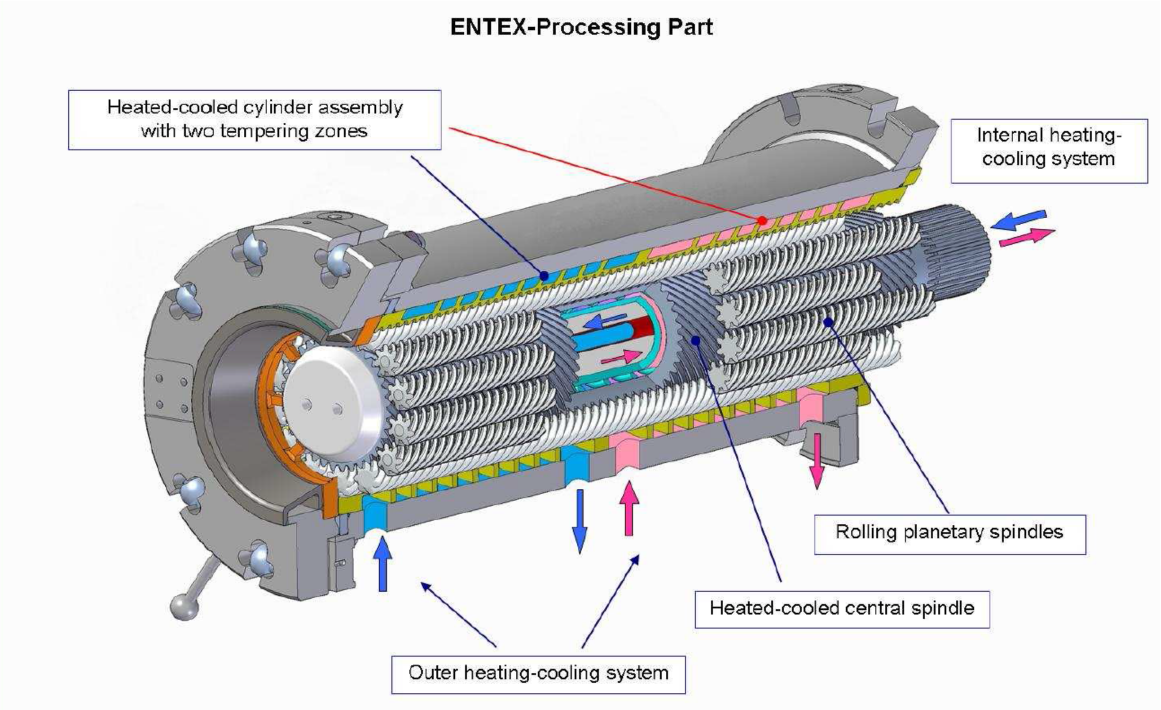

Figure 15: Schematic presentation of a planetary roller extruder

The tooth angle is a compromise of the rolling effect and material transport. At a tooth angle of 0^0, the material will be rolled out, but will not be transported. At a toothing of 90^0, the planetary spindles are again functioning like a rolling element. But at twisted gearing of 45^0, the radial forces catch the material, roll it out and the axial forces accelerate the material.

The good mixing effect of the planetary roller extruder is achieved primarily by the constant renewal of the surface and also by the constant material exchange between the kneading stocks.

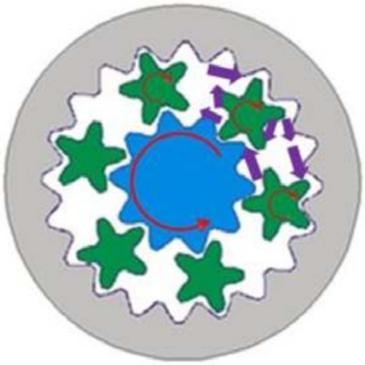

Figure 16: Schematic presentation of the material behavior in the processing part

The kneading stock (large arrows in Figure 16) will be caught, as already described, by the planetary spindles and rolled out. Due to the constant rolling out, additionally new heat exchanging surfaces occur. Thereby the heat transfer will be influenced positively and the homogeneity of the melt increases. This combination of rolling out and renewal of the surface provides a high degree of laminar mixing. However, it must be noted that the flow speed inside of the kneading stock is higher than at the surface. Thus, it must be ensured that the material only leaves the planetary roller extruder when it is also sufficiently plastified at the surface of the kneading stock.

The Planetary spindles define how well a material will be rolled out and how much shear needs to be applied to the material. The conventional spindles as shown in Figure 17 are planetary spindles with a continuous toothing. Due to this, they are ideally suited to catch and to plastify pulverized materials. The continuous toothing provides a low dwell time of the material, and this is a reason to use such a planetary spindle for PVC processing. The disadvantage of using such a spindle is that catching hard granulates is difficult.

Figure 17: Conventional spindle

The transversal mixing or Igel spindle (Figure 18) was first used to increase the cross-mixing in the material. Due to grooves present in the spindle, the transport of the material is decelerated and dwell time is increased. Moreover, the material can flow unhindered through the grooves and join another kneading stock, thereby increasing cross-mixing. The transversal mixing spindle is used in applications where the material needs to be cooled, which can be explained by a higher dwell time and larger surface area than the nap spindles.

Figure 18: Transversal mixing or Igel spindle

The nap spindle as shown in Figure 19 is used for plastifying the granulate or platelet type raw materials. Due to the counter toothing in the lands, a leakage flow occurs, which reduces the capability of pressure build-up and thus increases the dwell time. Thereby the heat energy has more time to permeate the material. The nap spindles are used in those ranges in which the material will be molten and/or high dispersion qualities must be achieved. In the nap planetary spindle, the cross mixing is increased considerably due to the interruptions in the toothing.

Figure 19: Nap spindle

The transport and drying spindles (TT-3 spindles, Figure 20) are conventional spindles, at which individual teeth have been removed. Due to the removal of the toothings, the number of meshings will be reduced and the material will not be sheared so strongly. This results in a reduction of temperature of the material at the same speed and throughput. The outcome of this is that the speed can be increased without exceeding a critical point with regard to the temperature at which the material would decompose.

Figure 2: TT-3 spindle

The larger surface provided by these spindles increases the contact surface area thereby having a positive influence on the heat transfer. It also comminutes the material and thus reduces the particle size in order to achieve better diffusion of the devulcanization system into the ground tire crumb. The dispersion ring in front of each module increases the backlog of the material and thereby increases the dwell time causing them to receive as many over-rolling motions of the planetary spindles as possible. This increases the filling level in the module and ensures that specific energy is applied for a better homogeneity of the material.

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Screening of Rubber Additives for the Design of the Devulcanization Process of Truck Tire Rubber

From a performance and environmental perspective

1. Introduction:

ASTM D 1566 currently defines vulcanization as ‘an irreversible process during which a rubber compound, through a change in its chemical structure (e.g., crosslinking), becomes less plastic while the elastic properties are improved and extended over a greater temperature range’. In ASTM 184A, devulcanization is defined as ‘a combination of de-polymerization, oxidation, and increased plasticity’. However, devulcanization of a sulfur-cured rubber is the process of cleaving, either totally or partially, of the sulfur crosslinks formed during the vulcanization process (Warner, 1994). It is preferable that de-polymerization (main chain cleavage) and main chain modifications are minimized during the process.

To recycle the rubber, the ideal design would be to selectively break carbon-sulfur and sulfur-sulfur linkages; considering their bond energy and stiffness they break by preference. Besides, chemical agents need to be employed (e.g. disulfide compounds) that react with the free radicals formed during the network breakdown to stop them from recombination. This operation restores the thermoplastic behavior of the material, allowing it to be processed again.

Conventional devulcanization aids (DA) are generally disulfide or mercaptan based, e.g. diphenyldisulfide (DPDS), dibutyldisulfide (DBDS), or diaryldisulfide (DADS). These type of compounds are expensive and have a repellant smell, thus making it difficult to use them on industrial scale. The need to design an environmentally sound and cost-effective devulcanization process requires the use of an environmentally safe process and devulcanization aids.

Besides, a shortcoming of the existing reclaiming processes is that these processes are mainly developed in view of producing a processable rubber material, and less on keeping the functionality of the material intact.

Within this study, different commercial rubber additives such as accelerators (Acc), antioxidants (A/Ox), coupling agents (CA) and modifiers are compared to the traditional devulcanization aids (DA) and screened according to the following aspects:

- Effectiveness for breakdown of the network
- Odor
- Processability

2. Experimental Part

2.1 Materials:

The whole truck tires were ground at room temperature (ambient grinding) to 2.5-8 mm in particle size with a bulk density of 1.4 g/cm^3 by Rumal bv, The Netherlands. The different commercial rubber additives such as accelerators, antioxidants, coupling agents and modifiers were choosen on the basis of a moeity being able to initiate scission of di- and polysulfidic bonds, to react with radicals or to donate hydrogen. Common rubber additives containing a disulfide group were screened for effective devulcanization of truck tire rubber. Table 1 shows a list of the different devulcanization aids.

Table 1: List of different devulcanization aids

Type	No.	Devulcanization Aid	Composition	Supplier
Traditional devulcanization aids	1	DPDS	Diphenyl disulphide	Sigma Aldrich
	2	DADS	Diaryl disulfide	Sigma Aldrich
	3	DBDS	Dibutyl disulphide	Sigma Aldrich
Accelerators	4	Rheno DTDM	80 % Dithiodimorpholine 20 % elastomer binder (EPDM/EVA) & dispersing agents	Rhein Chemie
	5	Rheno CLD	80 % Caprolactam disulfide, 20 % elastomer binder & dispersants	Rhein Chemie
	6	Rheno TBzTD	70 % Tetrabenzylthiuram disulfide (TBzTD), 30 % elastomer binder & dispersing agents	Rhein Chemie

	7	DTDM	*Dithiodimorpholine	DOG
	8	TBzTD	*Tetrabenzylthiuram disulfide	Performance additives
	9	CBS	Pure N-cyclohexyl-2-benzothiazole sulphenamide	Flexsys
	10	MBT	Pure 2-Mercaptobenzthiazole	Flexsys
	11	MBTS	Pure mercaptobenzothiazole disulphide	Flexsys
	12	Vultac-2	Phenol, 4-(1,1-dimethylpropyl)-, polymer with sulfur chloride (S_2Cl_2)	Arkema
Silanes	13	Si-69	Pure bis [3-(triethoxysilyl) propyl] tetrasulfide	Evonik
	14	Si-266	Pure bis [3-(triethoxysilyl) propyl] disulfide	Evonik
	15	Silquest A-1891	Pure gamma-Mercaptopropyltriethoxysilane	Evonik
Antioxidants	16	6PPD	Pure N-(1,3-Dimethylbutyl)-N'-phenyl-phenylene diamine	Lanxess
Peptiser	17	Renacit-10	Pure 2,2’-Dibenzamido diphenyldisulphide (DBD)	Lanxess

* Pure as well as on a polymeric binder

Zinc oxide (ZnO), stearic acid and sulfur were commercial grade as used in the rubber industry. All chemicals were used as received.

2.2 Preparation of Devulcanizates

The DA’s were added on an equimolar basis of active fragments (30 mmol/100g rubber compound), they were blended with TDAE oil (5%) and then swollen into the rubber at 65^{0}C for 30 mins in an oven. Devulcanization was carried out in an internal mixer (Brabender Plasticorder PL-2000) having a chamber volume of 50 ml and a cam type rotor, for 10 minutes at a mixer temperature of 170°C. A fill factor of 0.7 and a constant rotor speed of 50 rpm were used.

2.3 Mixing and Revulcanization of Devulcanized Rubber Compound (DRC):

The TGA analysis of the devulcanized rubber gives the polymer content, which is required for compounding on the basis of phr. The concentration of the following constituents present in devulcanized rubber are shown in Table 2:

Table 2: Composition of the devulcanized rubber crumb

Different Components	**%**
Oil	11.6
Polymer	54.0
Carbon Black	30.4
Ash	4.0

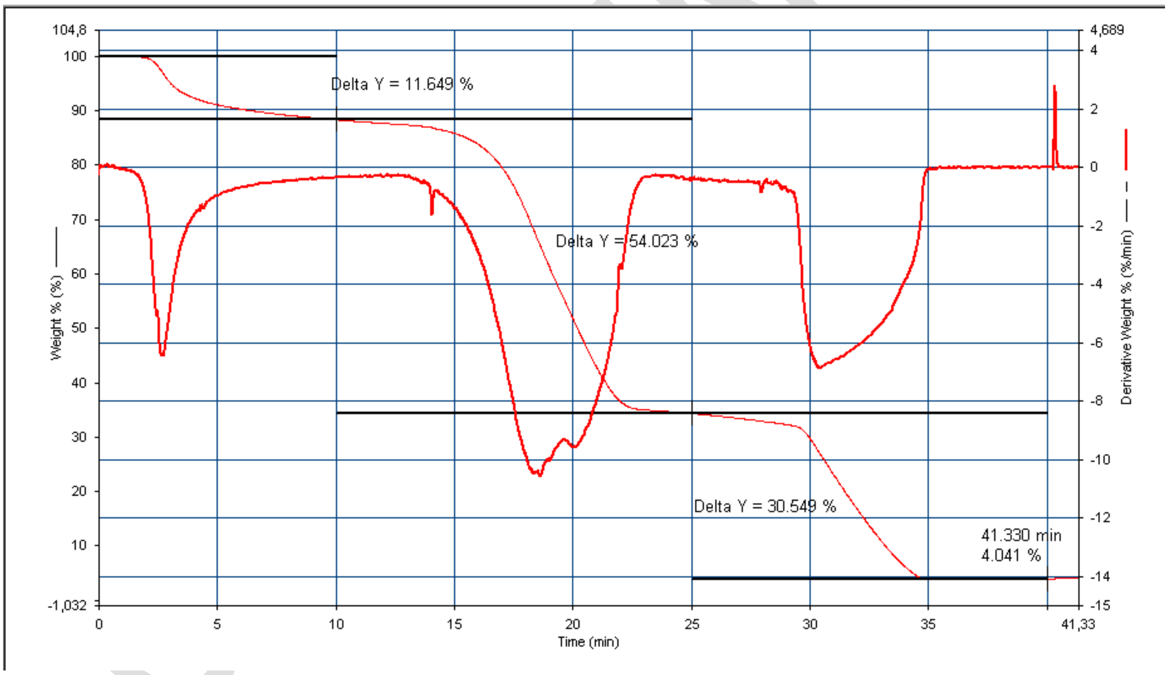


Figure 1: TGA analysis of devulcanized rubber crumb (Perkin Elmer TGA-7: heating rate: 20^{0}C per minute and switched to oxygen at 620^{0}C)

Compounding formulation

The Devulcanized Rubber Compound (DRC) was mixed with the curing system as shown in Table 3. The TGA analysis of the devulcanizates showed a polymer content of 54%, so for 100 g of rubber hydrocarbon content, 182 g of DRC had to be taken. The amount of curatives was based on the total polymer content of the devulcanized rubber.

Table 3: Formulation for devulcanized rubber compound

	phr
DRC	182
ZnO	5
Stearic acid	3
CBS	1.6
Sulfur	1.2

Mixing procedure

Mixing of devulcanized rubber compound (DRC) and compounding ingredients was done in the internal mixer (Brabender Plasticorder PL- 2000) having a mixing chamber volume of 50 ml and a cam type rotor at 40^0C for 8 mins with a fill factor of 0.8 and constant rotor speed of 50 rpm as shown in Table 4.

Table 4: Mixing procedure

Time (mins)	**Action**
0	Add DRC
1	
2	Add (ZnO + St. Acid)
3	
4	Add (Sulfur + CBS)
5	
6	
7	
8	Batch off

2.4 Molding

The test specimens were cured in standard molds by compression molding on an electrically heated hydraulic press (Wickert press WLP 1600). The rubber samples were vulcanized up to their respective optimum cure time by taking into account the thickness of the specimens (i.e., optimum curing time + thickness: 1 min extra for every 1 mm increase in thickness) at 140 °C temperature and 100 bar pressure. Moldings were cooled at the end of the curing cycle and stored in a cool and dark place for 24 hours before they were used for subsequent physical tests.

2.4 Characterization of Devulcanizates and Re-Vulcanized rubber:

2.4.1 Complex viscosity:

Complex viscosity values were analyzed via dynamic viscoelastic measurements performed at 100^0C by the Rubber Process Analyzer (RPA 2000, Alpha Technologies). The oscillation frequency was set in the range of 0.01-33 Hz at a constant strain of 0.56%. This strain was chosen in order to assure linear viscoelastic behavior during the test. The frequency-sweeps of cured specimens were followed after vulcanization at 140^0C in the RPA for the same sample. The storage (G') and loss (G'') shear modulus were measured. The complex viscosities, η*, were then calculated by the following equations, where ω is the frequency in radians per second:

$$(\eta^*)^2 = (\eta')^2 + (\eta'')^2 \qquad \textit{(Equation 1)}$$

Where,

$\eta' = G''/\omega$ *(Equation 2)*

$\eta'' = G'/\omega$ *(Equation 3)*

(Saiwari, 2013)

2.4.2 Rubber-Soluble Fraction:

The soluble (Sol) and insoluble (Gel) fractions of the devulcanized materials were determined by extraction in a Soxhlet apparatus. The devulcanized and vulcanized samples were extracted initially for 48 hours in acetone to remove low-molecular polar substances such as remains of accelerators and curatives, followed by an extraction for 72 hours in THF to remove the apolar components: oil and non-crosslinked polymer residues or soluble polymer released from the network by the devulcanization process. The extraction was followed by drying the samples in a vacuum oven at 75^0C and determining the weight loss until constant weight. The sol fraction was defined as the sum of the soluble fractions in acetone and THF (Saiwari, 2013).

2.4.3 Crosslink density:

The extracted devulcanized samples were swollen in toluene for 72 hours at room temperature. The weight of the swollen devulcanizates was measured after removing the excess surface liquid with absorption paper by pat drying. The Flory-Rehner equation is used for calculation of the crosslink density (ASTM D 6814-02) as shown in Equations 4 and 5.

$$\nu_e = -[\ln(1-V_r) + V_r + \chi_1 V^2_R] / [V_1(V^{1/3}_r - V_r)/2]$$ *Equation 4*

where,

ν_e = effective number of chains in a real network per unit volume,

V_r = volume fraction of polymer in a swollen network in equilibrium with pure solvent and is calculated as

$$V_r = \frac{[\text{Weight of dry rubber/density of dry rubber}]}{\frac{\text{weight of dry rubber}}{\text{density of dry rubber}} + \frac{\text{weight of solvent absorbed by sample}}{\text{density of solvent}}}$$ *Equation 5*

Where,

χ_1 = polymer-solvent interaction parameter [0.39 for the system NR/toluene] (M. Kojima, 2004)

V_1 = molecular volume of solvent

2.4.4 Horikx Plot:

For the development of a devulcanization process, an analytical tool is needed to determine the ratio of crosslink scission to random scission. The Horikx plot is such a tool, which establishes a simple relation existing between the soluble fraction of a network that has undergone scission and the effective number of chains in the gel fraction (as determined by swelling measurements) (Horikx, 1956). When main chain scission takes place, the relative decrease in crosslink density is given by,

$$1-\nu_f/\nu_i = 1- [(1-s_f^{1/2})^2/(1-s_i^{1/2})^2]$$ *(Equation 6)*

Where,

s_i and s_f is the soluble fraction of the rubber network before devulcanization and of the devulcanizate respectively,

ν_i and ν_f are the corresponding crosslink densities.

For pure crosslink scission, the soluble fraction is related to the decrease in crosslink density by

$$1-\nu_f/\nu_i = 1- [\gamma_f(1-s_f^{1/2})^2/\gamma_i(1-s_i^{1/2})^2]$$ *(Equation 7)*

where the parameters γ_i and γ_f are the average number of crosslinks per chain in the insoluble network before and after devulcanization respectively. The values for γi and γf are determined by Verbruggen (M. A. L. Verbruggen, 1999). Figure 2 gives a graphical representation of Equations 6 and 7.

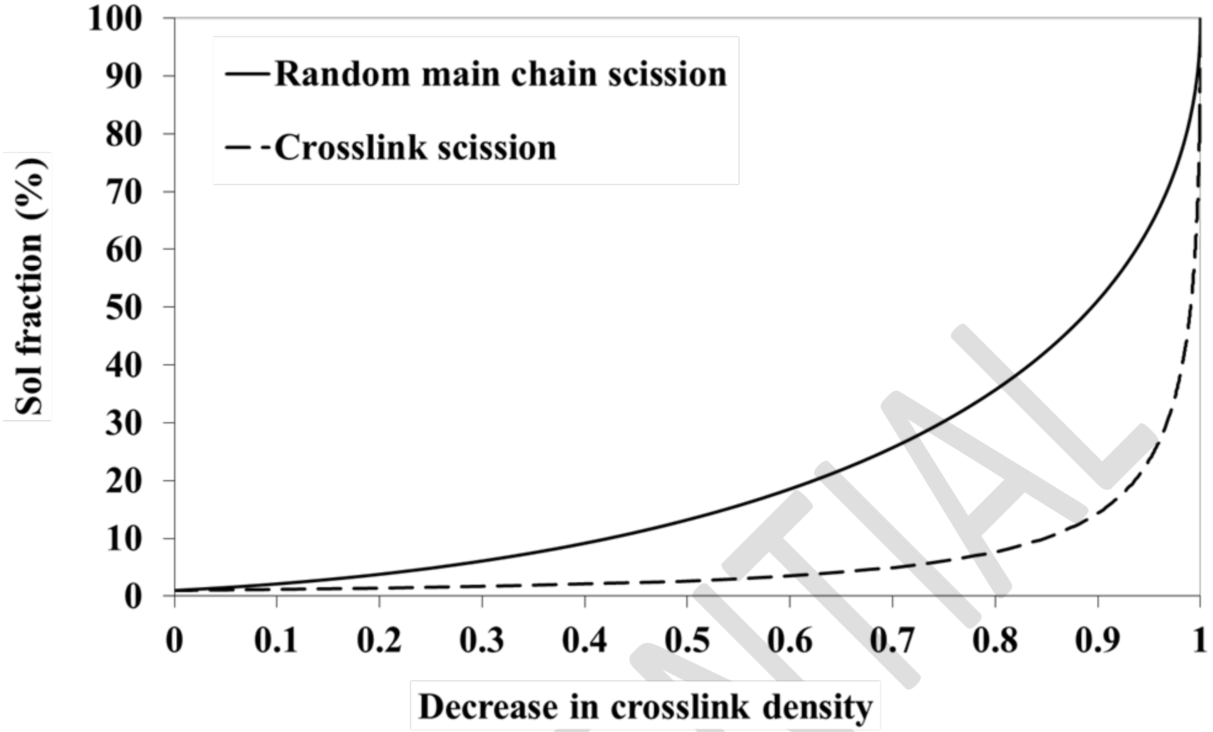


Figure 2: Random main chain scission and crosslink scission in a Horikx plot **(Saiwari, 2013)**

The fraction of soluble material in the degraded network is a measure of the number of scissions, and decrease in crosslink density is the decrease from the initial crosslink density of the rubber crumb. The curves in Figure 2 correspond to the situation where only main chains are broken (solid curve) and where only crosslinks are broken (dashed curve). In the case of crosslink scission only, almost no sol is generated until most of the crosslinks are broken; only then can the long chains be removed from the network. In the case of main-chain scission, sol is produced at a much earlier stage, because random scission of the polymers in the network results in small loose chains, which can easily be removed (Saiwari, 2013).

2.4.5 Cure Characteristics (ASTM D2064):

The cure characteristics were determined using a Rubber Process Analyzer (RPA 2000, Alpha Technologies). The change in torque was measured at a temperature of 140^0C, for a frequency of 0.833 Hz and 2.79 % strain. The optimal vulcanization time considering the thickness of the sample was determined and used for press-curing the samples.

2.4.6 Mechanical Properties:

Tensile tests were carried out on dumb-bell shaped specimens (type 2) according to ISO-37, using a Zwick Z1.0 tensile testing machine. The tests were performed at a constant crosshead speed of 500 mm/min, using a load cell of 500N.

3. Results & Discussion

3.1 Viscosity:

The plots of complex viscosity versus frequency of the devulcanizates with different devulcanization aids are shown in Figure 3. Apart from addition of 5 % oil for devulcanization process, the viscosity level decreases after devulcanization due to the cleavage of the three-dimensional rubber networks by both, main chain and crosslink scission. The requirement is such that devulcanized rubber needs to match the viscosity of the matrix compound to be blended with. Devulcanization with DPDS under the given process conditions results in a devulcanizate with a viscosity in the desired range; therefore the viscosities of the devulcanizates have to be evaluated relative to the viscosity of the DPDS devulcanizate. Generally the traditionally used devulcanization aids (i.e., DADS, DBDS, DPDS) give low viscosities, only superseded by the Renacit-10 devulcanizate having a viscosity lower than the DPDS devulcanizate.

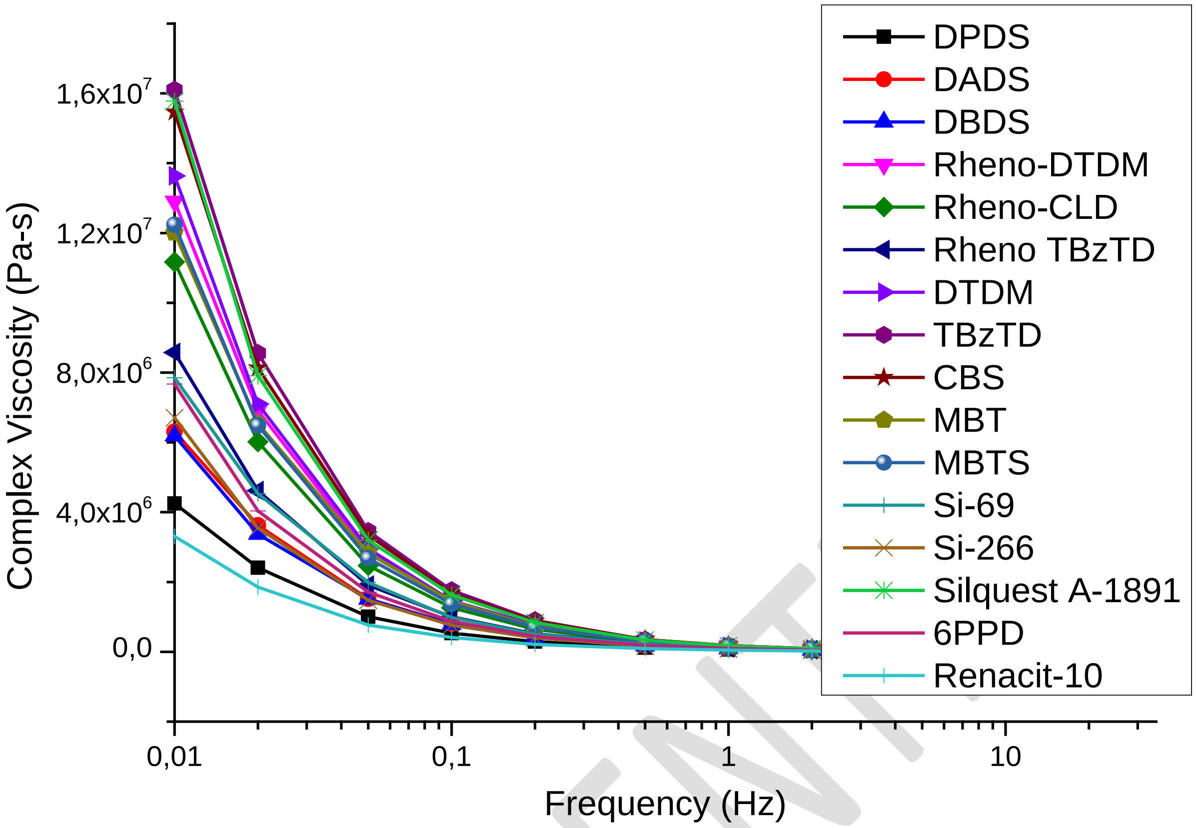


Figure 3: Complex Viscosity of the devulcanizates

In Figure 3, the devulcanizate with Vultac-2 is not shown since its complex viscosity is too high (x 10^{10}) compared to the other devulcanizates. An explanation for this might be that Vultac-2 is further crosslinking the tire crumb powder rather than devulcanizing it. However, this question is beyond the scope of this project.

3.2 Horikx plot:

The Horikx data were plotted for those devulcanizates with a high decrease in crosslink density and those falling in-between main chain scission and crosslink scission line, thus devulcanizing according to the mechanism assumed in the Horikx model: breaking of crosslinks throughout the whole particle, in contrast to an onion-peeling mecahnism where only outer layers are devulcanized.

The conventionally used devulcanization aids, DPDS, DADS and DBDS, showed a 60 % decrease in crosslink density superseded by only Renacit-10, which shows around 65% decrease in crosslink density (Figure 4). However, the high value of sol fraction of the Renacit-10 devulcanizate indicates a high level of polymer chain scission; this might be due to the devulcanization process temperature of 170^{0}C, a temperature at which natural rubber already degrades. As the melting temperature of Renacit-10 is around 136-150^{0}C, it gives the possibility to reduce the devulcanization temperature and also fine-tune the devulcanization process conditions in the extruder scale-up to subsequently reduce the degree of polymer scission.

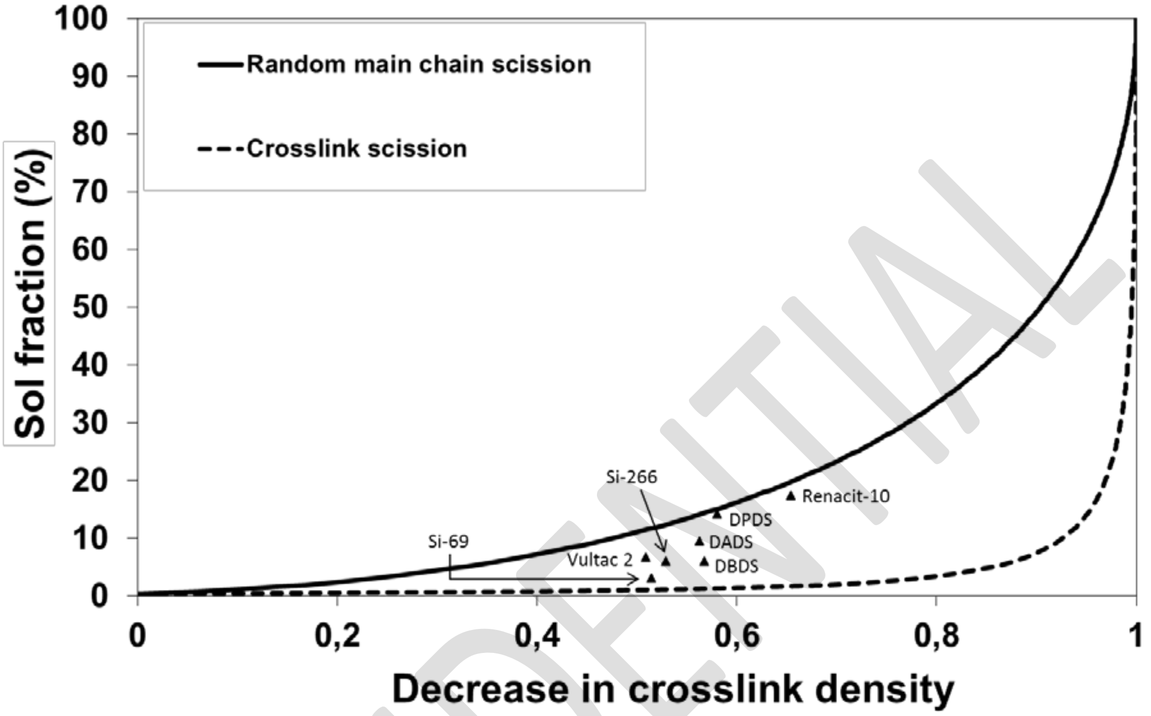


Figure 4: Horikx plot for promising devulcanizates

3.3 Curing after addition of curatives

The rheo curves were plotted after mixing the devulcanizates with the curing agents to study the curing activity. The curing recipe was kept constant; no adjustment of the sulfur or accelerator content was done. It is widely accepted that devulcanization happens at the β-carbon location (i.e., β carbon is the second carbon bond from the double bond) relative to the double bond (J. Dodds, 1983). This carbon atom also carries the hydrogen atoms which are split off for the formation of a sulfur crosslink. So after devulcanization, the curing tendency of the devulcanizate should decrease as the number of active crosslinking sites is reduced. It is also further obvious from Figure 5, that the Delta Torque (ΔT) is much lower for Renacit-10 devulcanizates compared to the other devulcanizates indicating that double bonds indeed reacted during the devulcanization process. It also indicates that the devulcanization aid concentration should be reduced to preserve the crosslinking activity of the polymer. Some of the devulcanization aids also interfere with the curing process giving rise to marching modulus, especially the silane based compounds. And moreover the minimum torque (MI) of the devulcanizates from the rheo curve, correlate very well with the complex viscosity data shown in Figure 3.

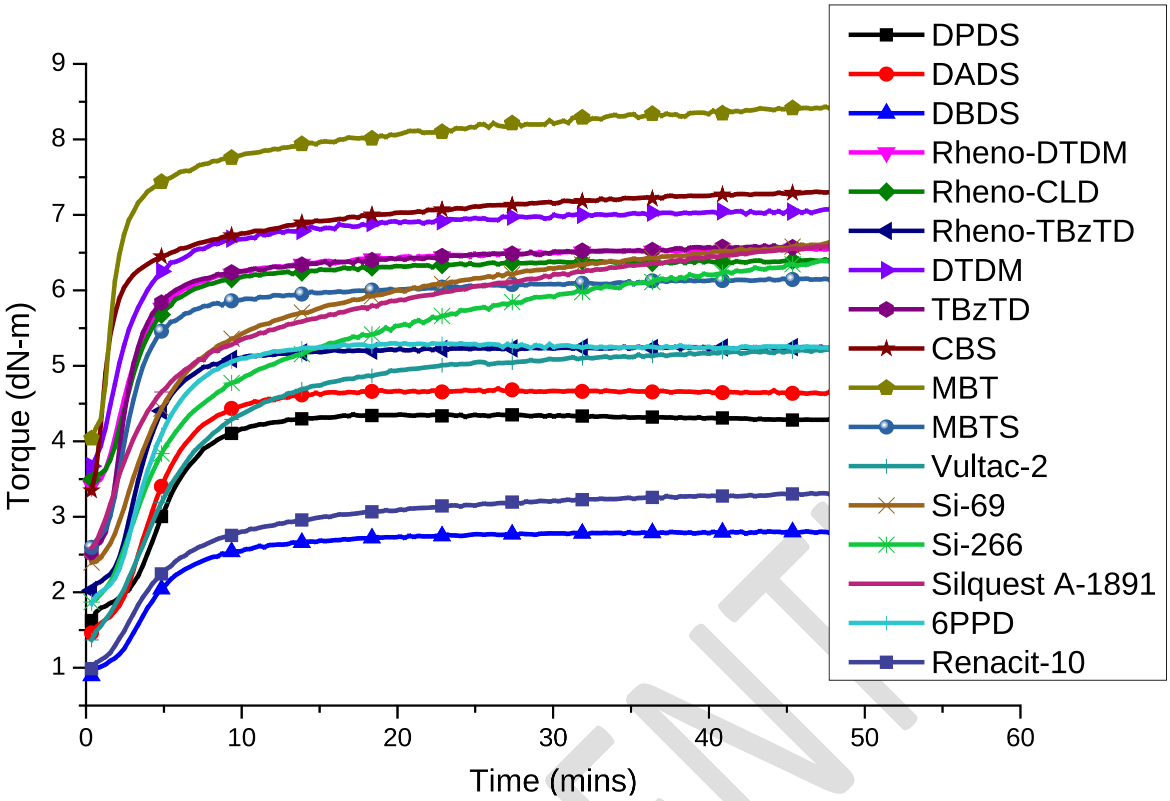


Figure 5: Rheo curve of devulcanizates after addition of curatives

Table 5: Δ Torque values of devulcanizates after addition of curatives

Type	**Devulcanization aid**	**Δ Torque (MH-Ml), dN.m**
Conventional DA's	DPDS	3.01
	DADS	3.41
	DBDS	2.12
Peptizer	Renacit-10 (DBD)	2.62
Antioxidants	6PPD	3.57
Rubber Accelerators	CBS	4.45
	MBT	5.24
	MBTS	3.85
	DTDM	3.81
	TBzTD	4.62
	Rheno-CLD	3.21
	Rheno-DTDM	3.43
	Rheno-TBzTD	3.39
	Vultac-2	4.04

Type	Devulcanization aid	Δ Torque (MH-Ml), dN.m
Silanes	Si-69	4.42
	Si-266	4.82
	Silquest A-1891	4.25

The Δ Torque values of the devulcanizates (Table 5) were graded on comparison with DPDS devulcanizate. The silanes are generally not much effective for devulcanization, due to higher sulfur content resulting in further crosslinking. The Δ Torque of rubber accelerators is generally higher than the DPDS devulcanizate, indicating that the crosslinking supersedes the devulcanization process. Only Renacit-10 has lower Torque than DPDS suggesting that it cleaves the crosslinks more than the DPDS.

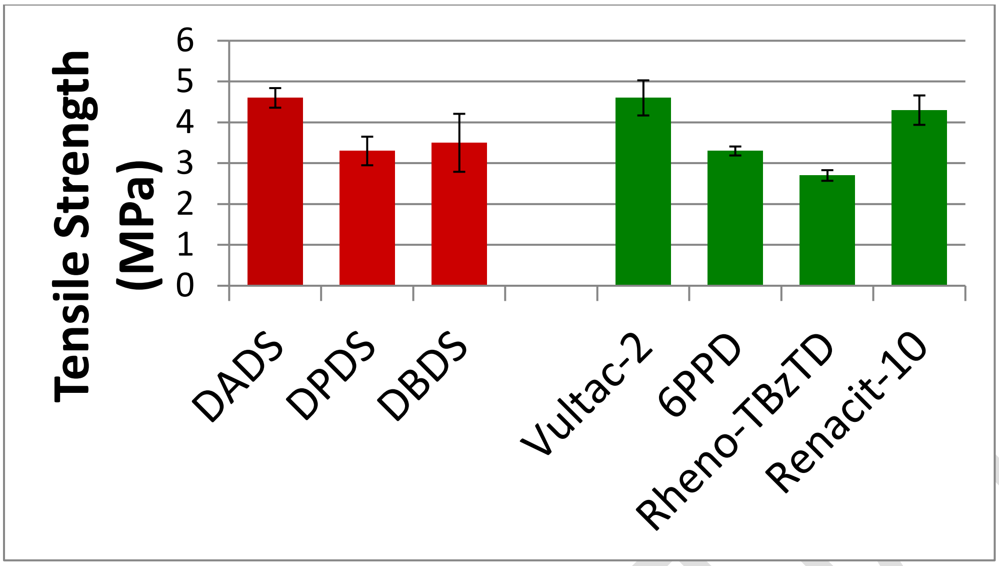
3.4 Tensile properties:

Four devulcanizates were choosen for further analysis on the basis of the following properties:

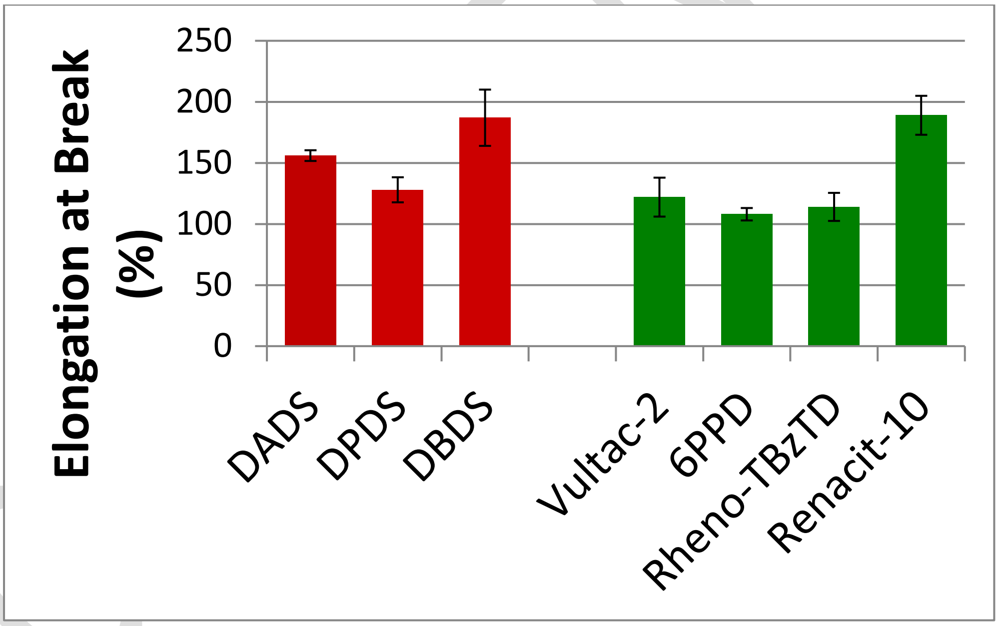
- Horikx plot: the data point of the devulcanizate needs to be as close as possible to the crosslink scission line
- Complex viscosity: low complex viscosity for easy processing
- Curing behaviour: high ΔTorque = MH - ML i.e., low initial viscosity with high curing tendency
- Sheetability: for easy batch off, judgded by sheeting out the devulcanizate in a two roll mill after the devulcanization process

These 4 devulcanizates were cured and the stress strain properties measured. In Figure 6, it is clearly seen that the Renacit-10 devulcanizate has comparable tensile properties to the conventional DPDS devulcanizate except for the modulus at 100% elongation. The low modulus of the Renacit-10 devulcanizate might be caused by excessive main chain scission, which was visible from the relatively high sol fraction in the Horikx plot as well (Figure 4).

a.)


Tensile Strength (MPa)
6
5
4
3
2
1
0
DADS
DPDS
DBDS
Vultac-2
6PPD
Rheno-TBzTD
Renacit-10

b.)


Elongation at Break (%)
250
200
150
100
50
0
DADS
DPDS
DBDS
Vultac-2
6PPD
Rheno-TBzTD
Renacit-10

c.)

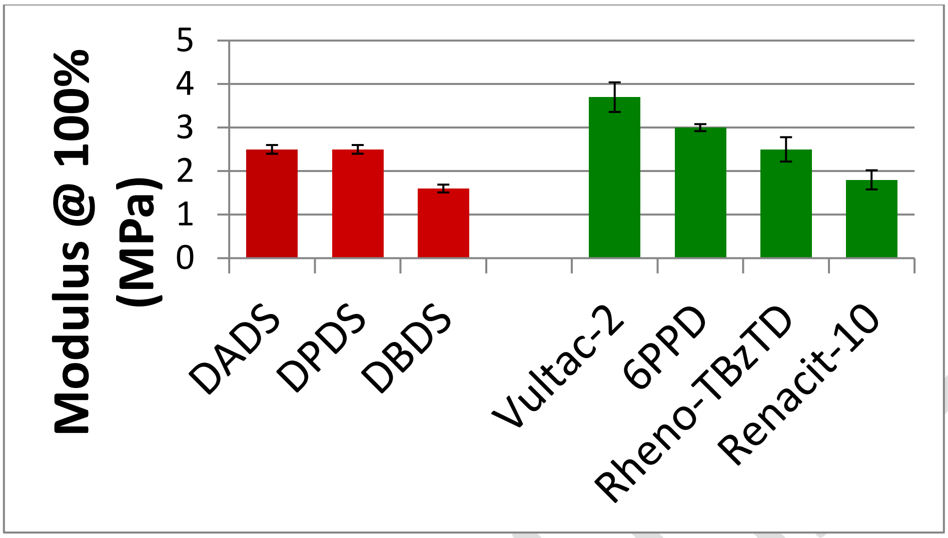


Figure 6: Tensile properties of the devulcanizates a.) Tensile Strength (MPa) b.) Elongation at Break (%) c.) Modulus at 100% Elongation (MPa)

3.5 Smell panel:

The devulcanizates after preparation were stored in zip lock covers. These devulcanizates were graded for smell with respect to the tradionally used DPDS devulcanizate as given in Table 6. The smell panel consisted of ETE group members with and without rubber experience. The outcome was, that silanes usually released ethanol fumes and had an intense odor, so these samples were placed on top for strong odor. From the smell panel results, it was clear that Renacit-10 devulcanizates was the least odor intensive devulcanizate compared to the conventionally used devulcanizates.

Table 5: Odor grading of the devulcanizates with respect to DPDS

Si-69
Si-266
Silquest
6PPD
Rheno- DTDM
DTDM
DBDS
MBT
CBS
DPDS
Vultac-2
MBTS
DADS
TBzTD
Rheno-CLD
Rheno-TBzTD
Renacit-10

4. Conclusion:

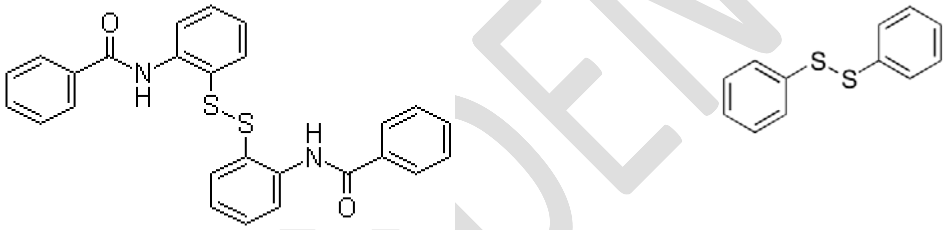
17 common rubber additives were compared concnerning their devulcanization effiiency, which was evaluated in terms of viscosity, sol content and decrease in crosslink density in a Horikx plot also giving the ratio of polymer to crosslink scission, and concerning the re-curing activity, tensile properties and odor. As reference, a DPDS devulcanizate was taken. For the design of the devucanization process, the overall best devulcanization aid from this screening turned out to be Reacit 10:

- The complex viscosity of the devulcanizate with Renacit 10 was comparable to the viscosity of the devulcanizate with DPDS.
- The sol content was comparable to the one of the devulcanizate with DPDS.
- The crosslink density decrease during devulcanization is even higher for the devulcanizate with Renacit 10 than for the one with DPDS.
- The rheo curve after addition of vulcanization agents was comparable to the curve of the devulcanizate with DPDS.

- The devulcanizate with Renacit 10 has comparable / better mechanical properties than the devulcanizate with DPDS.
- From the smell panel results, the devulcanizate with DPDS is in the medium range and the one with Renacit 10 gives a very low smell level level.

The results above show, that Renacit 10 is the best choice for an alternative to DPDS for the design of the mechano-chemical devulcanization process. Besides, Renacit 10 is generally used as a peptiser for the natural rubber mastication process, thereby eliminating the problem of incompatbility.

Renacit 10 has a core structure similar to DPDS as shown in Figure 6, with side groups on the benzene rings in ortho-position. The mechanism for both molecules is a scission of the disulfide bond, resulting in two equal radicals stabilized by the directly attached benzene ring. In the case of Renacit 10, the side group is an amide group attached to another benzene ring. In the resonance structure, the nitrogen of the amide carries a partly positive charge, but the benzene ring donates electrons. The net effect of this side is thus small, and the reactivity is comparable to the reactivity of DPDS.



Renacit 10 DPDS

2,2'-Dibenzamido diphenyl disulphide Diphenyl disulphide

Figure 6: Structure of the devulcanization aids; left: Renacit 10, right: DPDS

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Process Design
for Truck Tire Granulate Devulcanization in a Planetary Roller Extruder
Stage 1

1. Introduction

The thermal conductivity of rubber is rather low; therefore it is utilized for thermal insulation of e.g. cables etc. However, this insulating property can be a problem for rubber mixing and processing with regard to temperature distribution and control. Rubbers are generally mixed in internal batch mixers with a large volume, resulting in variations in cooling efficiency and thus large fluctuations in the quality of the material. A high surface area to volume ratio is necessary to improve the temperature control; this is achieved by using intermeshing instead of tangential mixers as shown in Figure 1. The next best equipment for good temperature control is the application of an extruder. A comparison of batch mixers and extruders is given in Table 1.

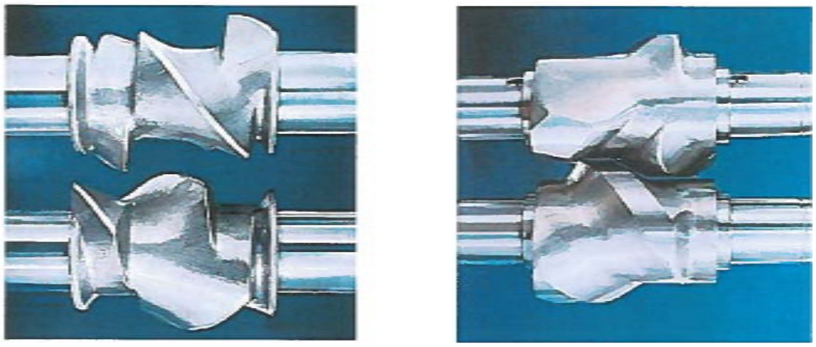


Figure 1: Different rotor geometries - Tangential (left image) & Intermeshing (right image) (Batton, 2006)

Table 1: Property differences between the Internal mixers and Extruders

	Internal Mixers	**Extruders**
Mixing process	Discontinuous as it includes feeding, mixing & emptying	Continuous single stage process
Energy & economic costs	High due to long intensive mixing time & capital cost	Low
Temperature distribution & control	Poor due to low surface contact area	High
Raw material feeding	Bale feeding	Pellets
After-treatment	Requires mill beneath the internal mixer for sheeting	Can be processed with gear pump or via flat film die
Self-cleaning	Material can stick to the ram or drop door	Material fed in always comes out, but with a certain residence time distribution due to dead zones

From Table 1, it is clear that extruders offer significant advantages in terms of process technique and economy for the devulcanization over internal mixers.

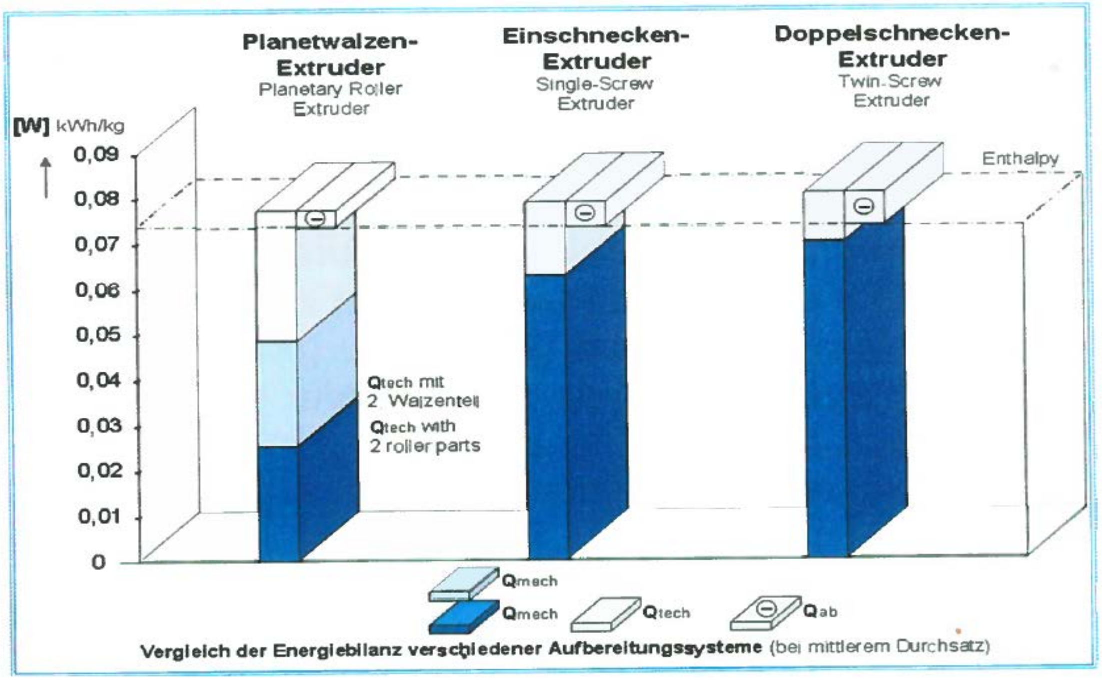


Figure 2: Energy balance for different extruders (Batton, 2006)

Figure 2 shows the energy balance of different extruders: the bottom parts in blue and dark grey show the mechanical energy input by the engine, the upper part shows the thermal energy input, and the outside part represents the radiation energy released by the machine surface. It is clear that the planetary roller extruder offers a higher heat exchange due to its larger available surface area by a factor of 5-10 (main spindle and planetary rollers) at less drive power compared to the other two types of extruder, namely Single and Twin Screw Extruder (Batton, 2006)

Characteristics of Planetary Roller Extruders

The Planetary Roller Extruder is a 'mixing heat exchanger' with a dynamic discharging effect, where at the rotation of the central spindle, the planetary spindles are rolling between the central spindle and the internally toothed cylinder assembly and rotate like planets. During this process, the material will be caught by the plunge of the spindle teeth and transferred into the corresponding tooth space where the material will be drawn-out into thin layers and brought forward by means of the helix. Due to helical gearing of the planetary system, a continuous rolling out of the material ensures the best self-cleaning effect.

Due to an extremely thin wall thickness (Figure 3) of the cylinder assembly, the central spindle and a larger contact area, the temperature control is excellent; this is strongly required for the exothermic devulcanization process. The introduction of pressurized water heating and an improved construction of the cooling channels allow a narrow product temperature control influencing the temperature profile of the material (Batton, 2006).

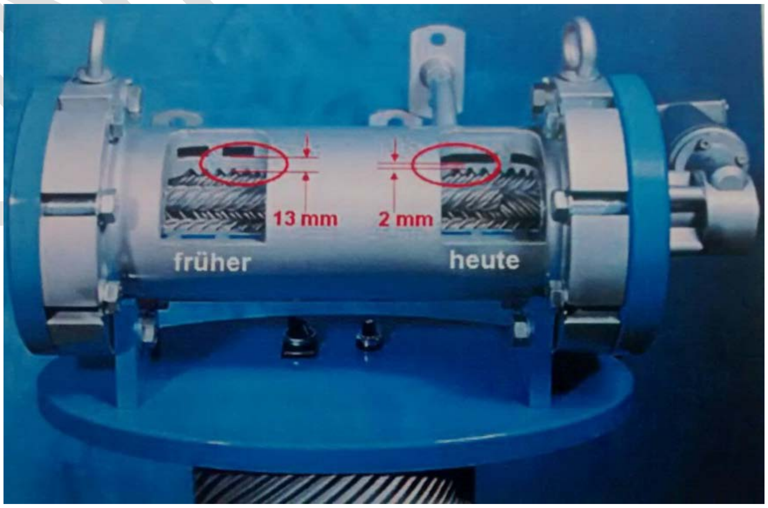


Figure 3: Roller model with new thermodynamics for excellent temperature control; left: old, right: new setup ((Batton, 2006)

Configuration Variety of Planetary Roller Extruders:

Planetary roller extruders are characterized by a great flexibility regarding their configuration. The central spindle of the planetary roller extruder can carry up to 6 separate modules. Depending on the capacity, the modules are available in the diameter range between 50 mm and 650 mm with lengths of 400 mm up to 1,400 mm which enables a capacity of 2 kg/h to 50 kg/h.

Depending on the diameter of the module, up to 24 planetary spindles per module can be positioned in the cylinder assembly. The planetary spindles are available in different designs, of which 4 are suitable for the devulcanization process (discussed in Chapter 2), namely

- Standard or conventional spindle
- Transversal mixing spindle
- Nap Spindle
- TT3 spindle

Besides, the length of the planets can be varied between module length and smaller planets being around 20 mm shorter.

Other assembly parts to be tailored for the devulcanization process are:

- Inlet units (feeding, injection, lateral feeding, feed valve)
- Processing units (degassing within or between modules, dispersion and intermediate stop rings)
- Outlet units (die shape)
- Special elements (online pressure and temperature control systems)

Process variables include:

- Central spindle screw speed and cooling
- Module temperature
- Feeding rate

2. Experimental

The process design described in this and the following chapter was done in a joint activity between the ENTEX, Rust & Mitschke GmbH, Bochum, Germany, Rumal BV and the Department of Elastomer Technology and Engineering, University of Twente (UT), The Netherlands. Entex is a supplier of planetary roller extruders.

2.1 Materials

The Ground Truck tire Rubber (GTR) used in this investigation was supplied by RUMAL BV, The Netherlands, with a particle size of 0.8-2.5 mm. The devulcanization aid (2,2'- dibenzamido diphenyldisulphide, DBD) was obtained from Thomas Swan & Co. Ltd., United Kingdom (Pepton-22). TDAE oil used as processing oil for the devulcanization was supplied by Hansen & Rosenthal, Germany.

2.2 Preparation of devulcanizates

2.2.1 Pre-treatment

GTR was pre-swollen in a mixture of DBD and TDAE oil for 30 minutes in a mixer at room temperature. It was stored in big bags at ambient temperature before delivering to Entex.

2.2.2 Devulcanization experiments

After devulcanization in the Planetary Roller Extruder, for each trial 2 samples were taken: one directly after the die and the other after passing through the cooling roll (Figure 4).

Figure 4: Die (left) & roll (right) samples from Planetary Roller Extruder

The samples were visually evaluated on consistency, tackiness, strang/sheet forming, dryness. Besides, the smell was taken as a material characteristic.

2.3 Mixing and Revulcanization of Devulcanized Rubber Compound (DRC)

Compound formulation

The devulcanized rubber compound (DRC) was mixed with the curing system as shown in Table 2. TGA analysis of devulcanizates showed that the rubber content is 54% (as discussed in Chapter 3), so for 100 g of rubber hydrocarbon content, 182 g of DRC had to be taken.The amount of curatives was based on the total polymer content of the devulcanized rubber.

Table 2: Formulation for re-vulcanization of the devulcanized rubber compound

	phr
DRC	182
ZnO	5
Stearic acid	3
CBS	1.6
Sulfur	1.2

Mixing procedure

Mixing of the devulcanized rubber compound (DRC) and the curing ingredients was done in an internal mixer (Brabender Plasticorder PL-2000) having a mixing chamber volume of 50 ml and a cam type rotor at 40^{0}C for 8 mins with a fill factor of 0.8 and constant rotor speed of 50 rpm as shown in Table 3.

Table 3: Mixing procedure

Time (mins)	**Action**
0	Add DRC
1	
2	Add (ZnO + Stearic acid)
3	
4	Add (Sulfur + CBS)
5	
6	
7	
8	Batch off

2.4 Preparation of devulcanizate blends with virgin natural rubber

Compound formulation

The devulcanized rubber compound (DRC) was blended with virgin natural rubber (NR) as shown in Table 4; further specification of the additives are given in Chapter 3. No adjustments were made for remaining curing additives and lower activity of the filler system. The formulation is representative of a truck tire tread compound, which is based on natural rubber.

Table 4: Formulation for Natural Rubber (NR)/ Devulcanized Rubber Compound (DRC) blends

	Virgin SMR-10 (phr)	**NR/DRC = 50/50 Blend (phr)**
NR (SMR-10)	100	50
DRC	-	91
ZnO	5	5
St. acid	3	3
Carbon Black (N330)	30	30
Silica (Ultrasil 7005)	8	8
TDAE oil	5	5
6PPD	3	3
Microcrystalline wax	1.5	1.5
CBS	1.6	1.6
Sulfur	1.2	1.2

Mixing procedure

The Devulcanized Rubber Compound (DRC) was blended with virgin natural rubber (NR) using a Brabender lab station internal mixer with 390 ml mixing chamber volume. The mixing procedure for the internal mixer is shown in Table 5 and further represented from the mixing curve in Figure 5. This masterbatch was mixed at a mixer temperature of 50^0C and at a constant rotor speed of 50 rpm for 12 minutes. The compound was stored in a fridge for a day before further processing.

Table 5: Mixing procedure for the NR/DRC Blends

Time (mins)	**Action**
0	Add NR /NR + DRC
1	
2	
3	Add ZnO
4	Half (CB + silica + ZnO + stearic acid + wax + oil)
5	
6	
7	Remaining (CB + silica + ZnO + stearic acid + wax + oil)
8	
9	
10	
11	
12	Batch off

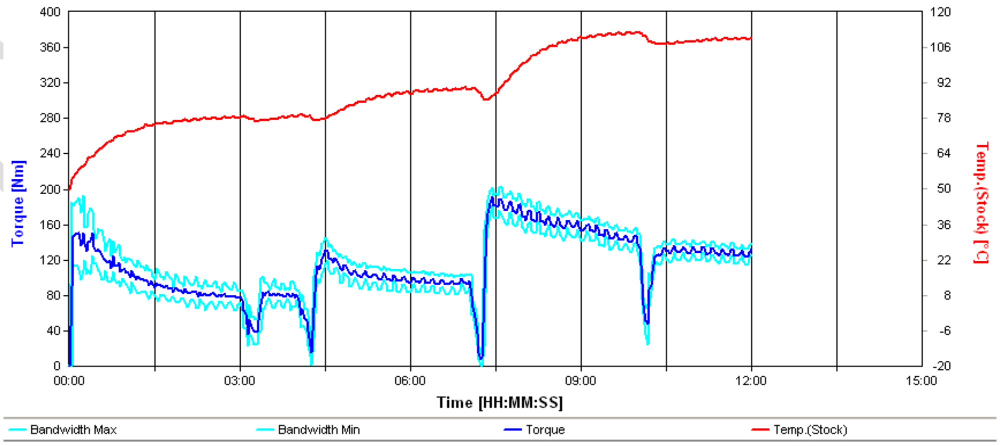


Figure 5: Example of a mixing curve (torque Vs time) for the Virgin Natural Rubber + Devulcanized Rubber Compound (DRC) blend masterbatch

The masterbatch was then mixed with the curatives (sulfur + CBS) in a 2-roll mill at room temperature for 5 mins at a small nip gap for better dispersion.

2.5 Moulding

The test specimens were cured in standard molds by compression molding in an electrically heated hydraulic press as explained in Chapter 3.

2.5 Characterization of the Devulcanizate, Re-Vulcanizate and Blends:

2.4.1 Mooney Viscosity (ASTM D1646)

Mooney viscosity measurements were made using a Mooney Viscometer (MV 2000VS, Alpha Technologies) with the rotor rotating at an angular velocity of 2 revolutions per minute. The principle of a Mooney viscometer is such that the rotor turns inside a closed cavity containing the test piece, where the shearing action takes place between the flat surfaces of the rotor and the walls of the chamber. The torque required to turn the rotor is monitored, with one Mooney unit corresponding to 0.083 Nm. The small rotor was used since viscosity of the devulcanized rubber compound (DRC) was high. Before the measurement, the devulcanizates passed a 2-roll mill for 3 times at room temperature for better compaction of the die samples.

The viscosity value is represented as MS(1+4) 100^0C, where

M → Mooney
S → Small rotor
1 → 1 minute pre-heating time
4 → 4 minute testing time
100^0C → Test temperature

2.4.2 Complex viscosity

Complex viscosity values were analyzed via dynamic viscoelastic measurements performed with the Rubber Process Analyzer (RPA 2000, Alpha Technologies) as described in Chapter 3.

2.4.3 Horikx plot

The Horikx plots were elaborated after the sol-gel analysis and crosslink density measurements as described in Chapter 3.

2.4.4 Cure characteristics (ASTM D2064):

The cure characteristics were determined using a Rubber Process Analyzer (RPA 2000, Alpha Technologies) as described in Chapter 3.

2.4.5 Mechanical properties:

Tensile tests were carried out on dumb-bell shaped specimens, using a Zwick Z1.0 tensile testing machine as described in Chapter 3.

3. Results & discussion

Design of the extruder setup and parameters and visual analysis of the devulcanizate

The process parameters are given in Appendix 1. The starting conditions for the design of the Planetary extruder setup-1 is as follows:

For this Trial-1 series, a 4 module setup with the temperature of the spindle being 190^0C, the module temperatures being 270/ 150/ 150/ 100^0C and a screw speed of 150 rpm was used. The spindles used in the modules were 5 long nap spindles in module 1 and 2, 6 long TT-3 spindles in module 3, and 3 long and 2 short igel spindles in module 4 as shown in Figure 6.

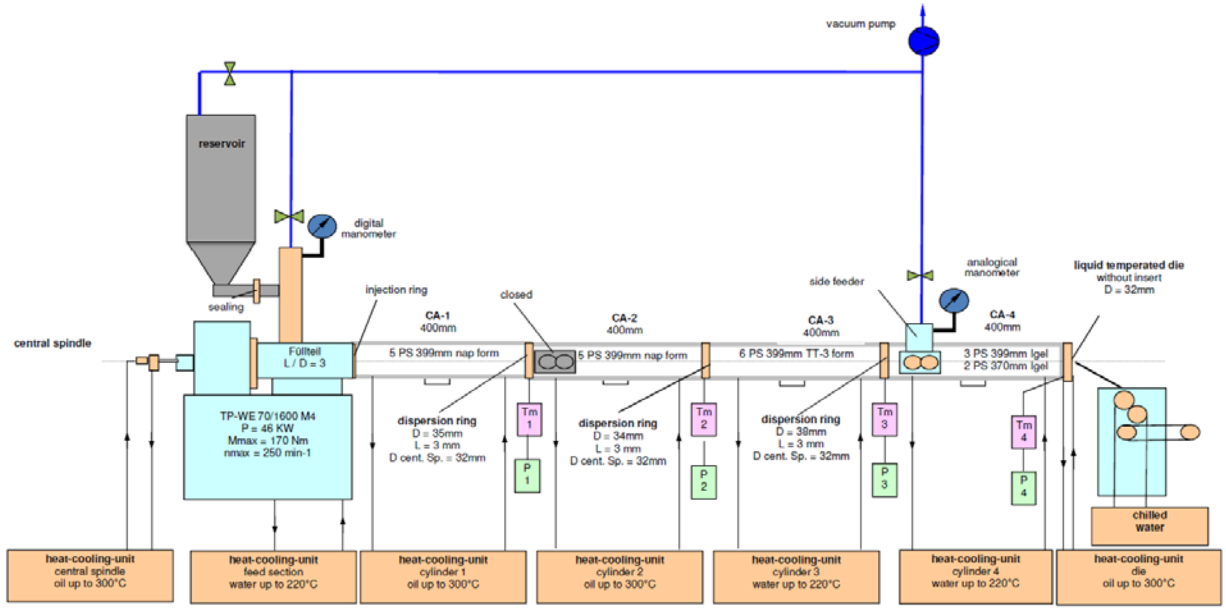


Figure 6: Design setup-1 for the planetary roller extruder

Trial-1 (setup-1): The 1st module was set at 270^{0}C, but this lead to overheating of the rubber and thus to degradation of the material.

Trial-2 (setup-1): The input material was pre-treated with the devulcanization system; however, it did not migrate into the rubber granules. There was a chance that the powdery surface coating of devulcanization aids would be sucked into the hopper by the vacuum. This was checked by switching off the vacuum. As a result, the temperature in the 1st module dropped and material at the outlet was not compact anymore. For this reason, and as there was finally no indication of major losses of devulcanization aid by the vacuum suction, the process should be performed under vacuum.

Trial-3 (setup-1): The vacuum was switched on again and the temperature of the 1st barrel was reduced to 210^{0}C. The material was not compact and was dry.

Trial-4 (setup-1): With reduced screw speed (70rpm) and lower 1st module temperature, there was no cohesion in the material.

Trial-5 (setup-1): The 2nd and 3rd module, the temperature was increased to keep the material on a higher temperature for a longer period.

To increase the dwell time, 2 more modules were added as shown in Figure 7.

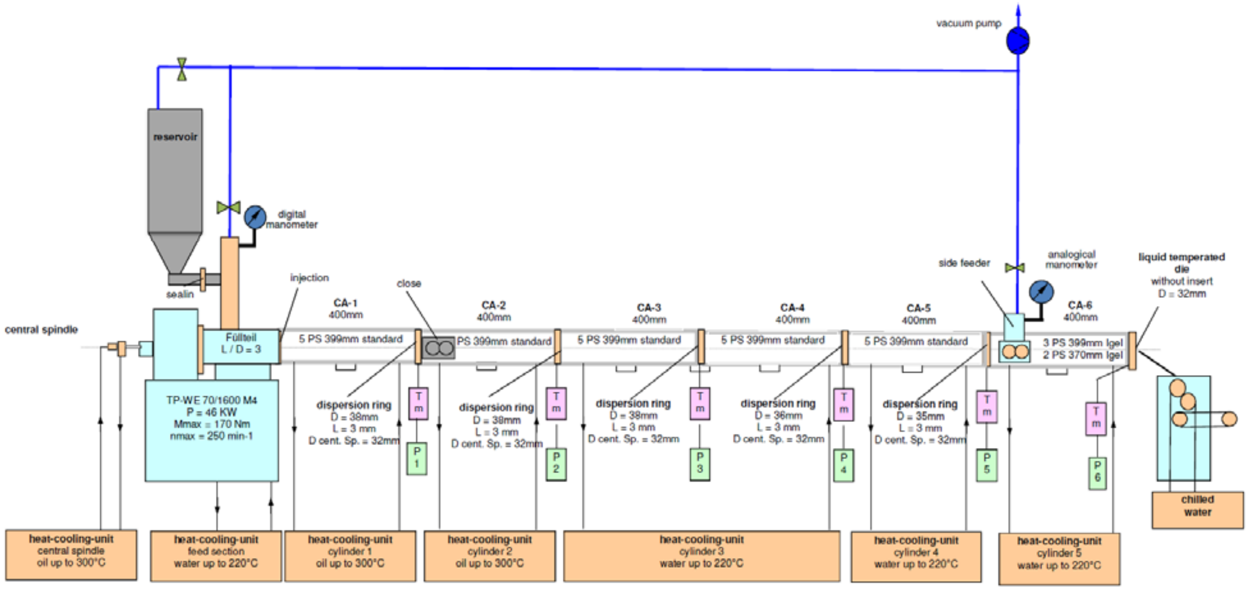


Figure 7: Design setup-2 for the planetary roller extruder

Trial-6 (setup-2): The cooling of the central spindle was switched off in this setting.

Trial-7 (setup-2): The cooling of the central spindle was switched on to reduce the temperature in all modules.

Trial-8 (setup-2): Increased screw speed (100 rpm) and reduced set temperature in all modules were applied to bring in more shear. The material is much more compact than in the settings before.

Trial-9 (setup-2): The shear was even more increased by using a higher screw speed (150 rpm) and decreasing the module temperature. The material outlet temperature was more than 200^{0}C and the material smelled badly.

Trial-10 (setup-2): The screw speed was reduced to decrease the material outlet temperature. The material was less consistent than before, and the outlet temperature was still 200^{0}C.

Trial-11 (setup-2): The temperature in the last barrel was increased to reduce the viscosity of the material and thus to reduce the shear stress in the last module, but still the material outlet temperature was much too high.

To reduce the material outlet temperature, TT-3 spindles were now used in the 5th and 6th modules as shown in Figure 8.

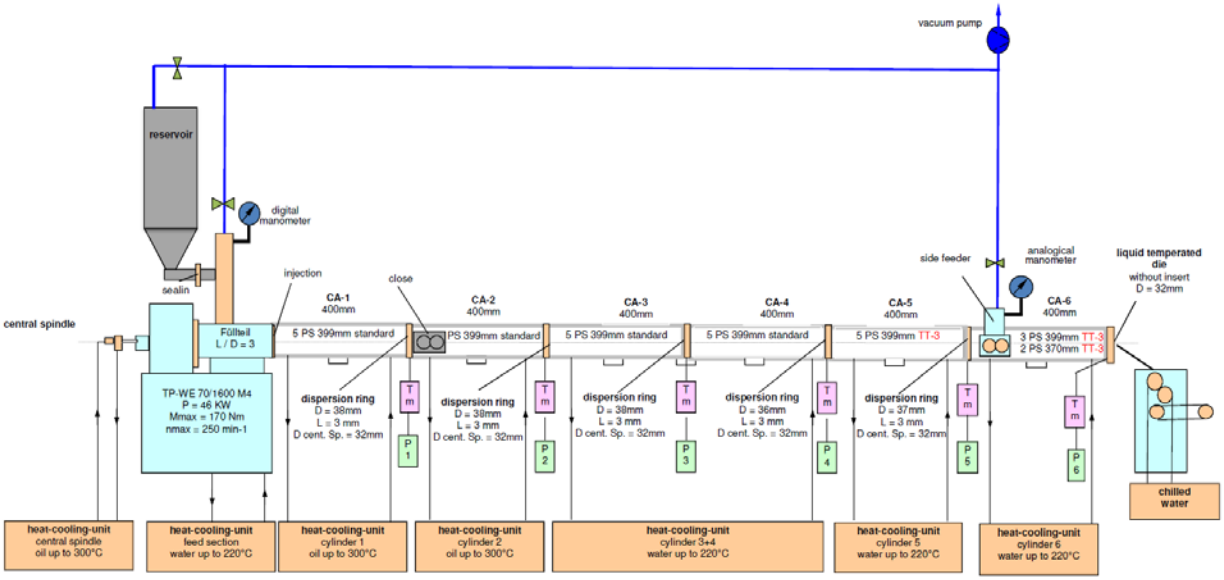


Figure 8: Design setup-3 for the planetary roller extruder

Trial-12 (setup-3): With a screw speed of 80 rpm, the throughput was too low (just 15 kg/h).

Trial-13 (setup-3): By switching off the heating of the central spindle, the outlet temperature decreased from 192^{0}C to 162^{0}C.

In the third module, one more spindle was added to make it 6 spindles as shown in Figure 9.

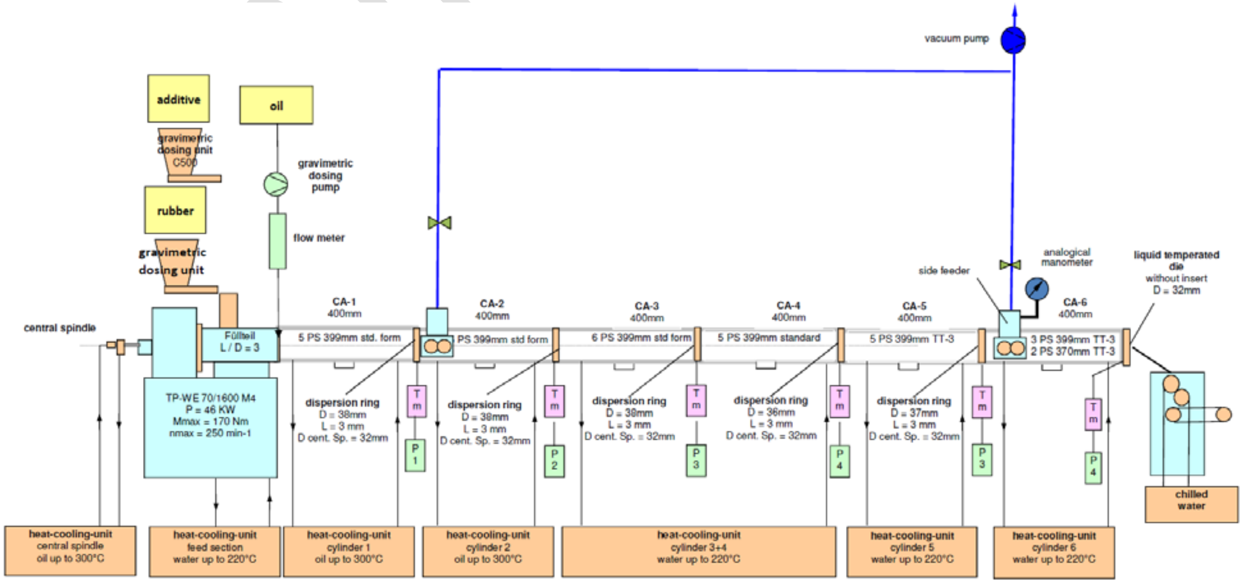


Figure 9: Design setup-4 for the planetary roller extruder

Trial-14 (setup-4): The material was extruded with this setup at 80rpm.

Trial-15 (setup-4): The temperature in the 1st barrel was reduced to prevent the material from overheating without vacuum. Vacuum is not possible in the 1st module, as the material is injected here.

Trial-16 (setup-4): The module temperatures were decreased to avoid overheating of the material. The effect was small, the material outlet temperature remained more or less similar to the previous trial (182^{0}C).

Trial-17 (setup-4): The devulcanization system (oil and DBD) were added separated in single components with the process conditions similar to the Trial-14.

Trial-18 (setup-4): The temperature in the 2nd module was increased to 170^{0}C: the material becomes more sticky.

To bring in more shear and for better mixing of oil and DBD in the first 2 modules, the standard spindles were replaced by nap spindles as shown in Figure 10.

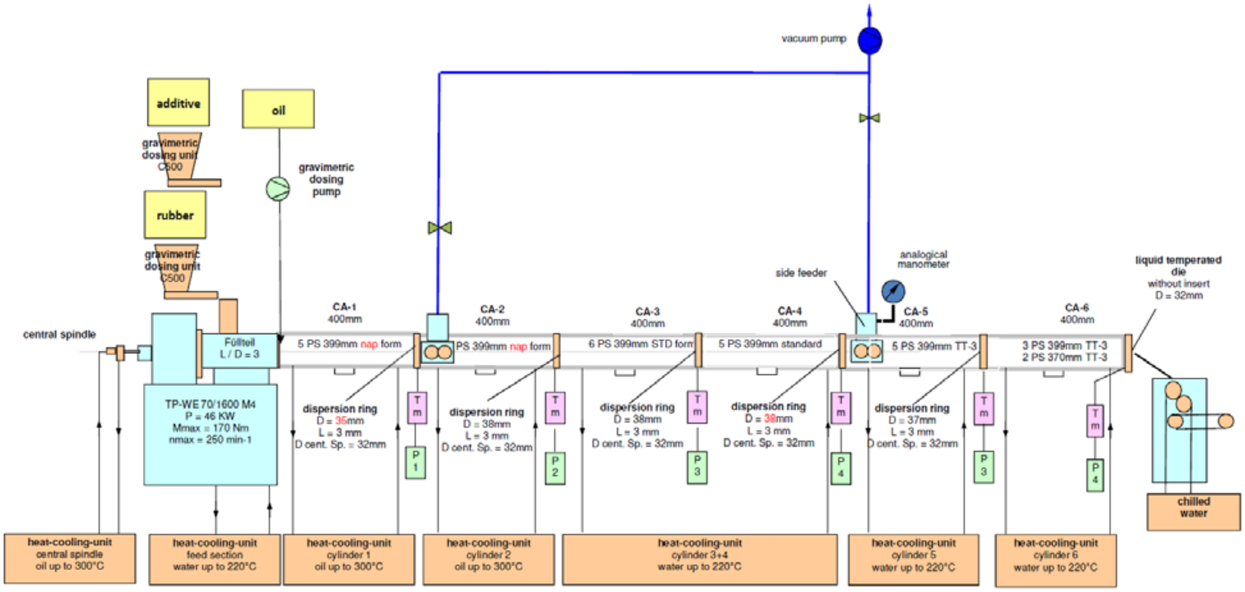


Figure 10: Design setup-5 for the planetary roller extruder

Trial-19 (setup-5): The torque was much higher with setup-5.

Trial-20 (setup-5): The module temperatures were reduced to decrease the material outlet temperature. However, this had no effect; the temperature remained 170^{0}C.

Trial-21 (setup-5): This trial was done only with tire granulate without the devulcanization system.

Trial-22 (setup-5): In this trial, tire granulate along with 5 phr TDAE oil only was used.

Trial-23 (setup-5): The pre-blended material was tested under the same conditions as in Trial-22 to study the difference: the torque was lower (124 instead of 148 Nm), and the outlet temperature of the devulcanizate was higher by 10^0C with the pre-blended material.

Some design rules for the extruder setup:

- Temperature settings of the first module are critical, especially when the devulcanization aids are added separately: the temperature must be high enough to melt the devulcanization aid, but if the temperature is too high it leads to degradation of the rubber.
- Higher screw speeds and lower temperatures lead to a better compaction of the devulcanizate.
- The temperature of the material is very sensitive to the heating of the central spindle. The module temperature has less influence.
- Standard spindles in the first modules are more effective in reducing the viscosity of the rubber than nap spindles.
- Pre-blended material instead of separate addition of oil and devulcanization aid results in a lower torque.

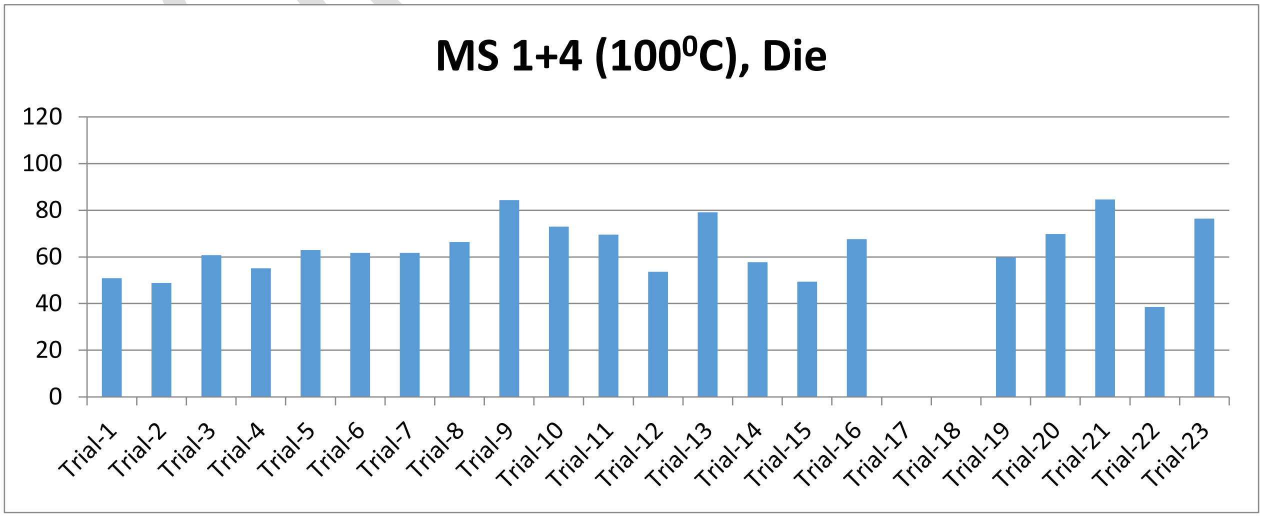
In-depth analysis of the devulcanizates

Pure devulcanizate

3.1 Mooney Viscosity

The Mooney viscosities of the devulcanizates are shown in Figure 11.

a.)



b.)

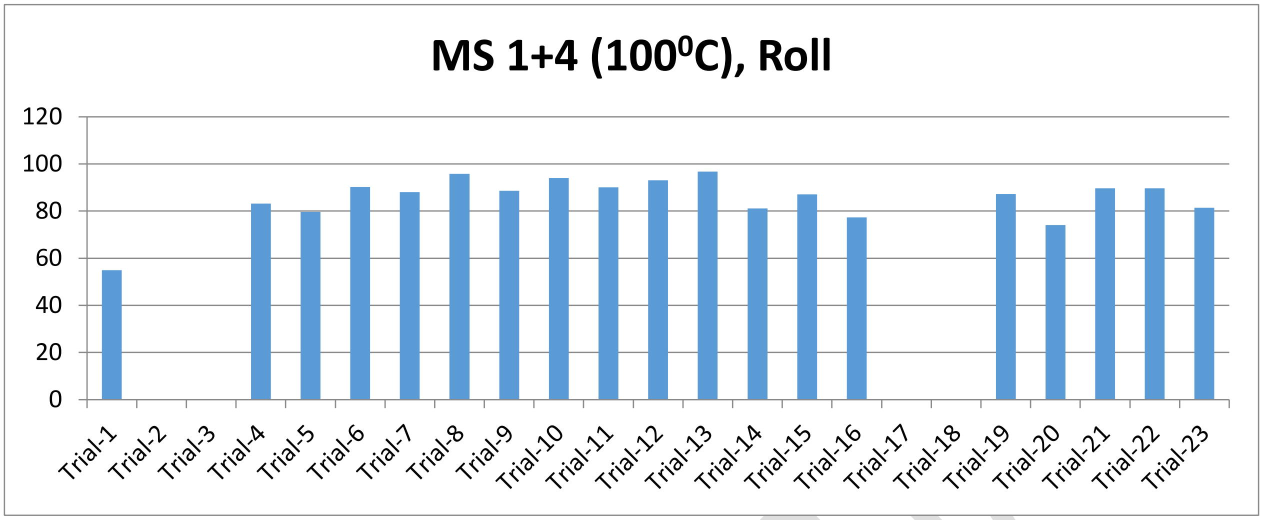


Figure 11: Mooney viscosity of the devulcanizates a.) Die samples b.) Roll samples

During Trial-17 and 18, the devulcanizates were degraded by the higher energy input during the devulcanization process due to a change in the starting material from pre-blended granulate to single components i.e., adding Ground Truck Tire Rubber (GTR), DBD and TDAE oil separately. Therefore, no measurements were done on these samples.

As a consequence of the separately dosing of the components, the material had a very high viscosity in the beginning, which required a higher energy input for the extra mixing step compared to the pre-blended starting material. The temperature was increasing, and the devulcanizates were degraded to a higher extent. The degradation was visible from fumes with the smell of burned rubber; the final product was rubber crumb instead of a coherent mass.

Trial-17: module temperature (135/150/150/150/100^0C) and screw speed (80 rpm)

Trial-18: module temperature (135/170/150/150/100^0C) and screw speed (80rpm)

In Trial-18, the temperature of module 2 was increased in order to boost the devulcanization reaction. As a consequence, the degree of devulcanization as well as the plasticity were higher, and less energy was brought into the material resulting in a lower outlet temperature.

The aim for viscosity is to be in the range of viscosities of tire compounds. This is important for an easy blending with virgin rubbers. From Figure 11, it can be seen that roll samples have higher Mooney viscosities than die samples due to better compaction of the sample and less thermal and oxidative degradation of the devulcanizates.

Table 6: Mooney viscosity of the 1 time and 3 times rolled devulcanizate

Batches	Mooney Viscosity (1 X Rolled)	Mooney Viscosity (3 X Rolled)
Trial-7	88	91
Trial-8	96	88
Trial-9	89	89
Trial-10	94	92
Trial-11	90	88
Trial-12	93	81
Trial-13	97	90
Trial-14	81	82
Trial-15	87	54

After exiting the extruder, the devulcanizates were rolled either once or 3 times for better cooling and to directly get a proper sheet. Table 3 shows the values of a choice of samples. The Mooney viscosity of 3 times rolled devulcanizates was generally lower, as more rolling leads to a softer compound and better compaction. The compaction also results in lower oxygen penetration preventing oxidation reaction, decreasing the degree of oxidative polymer scission which would finally decrease the viscosity. The influence of rolling on viscosity is therefore higher than the influence of oxidative degradation.

3.2 Complex viscosity

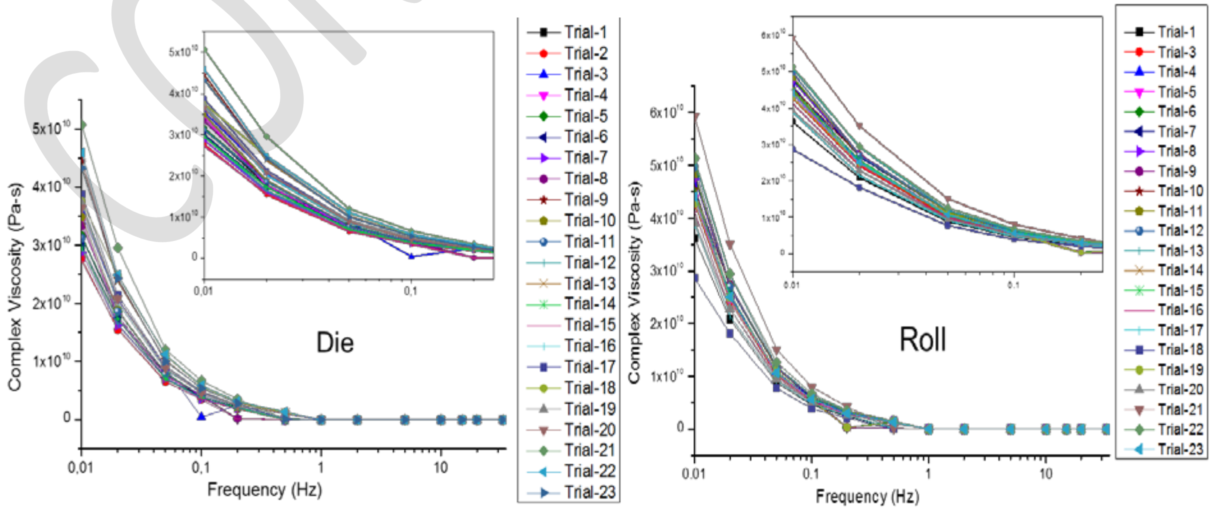


Figure 12: Frequency sweep for, left: Die and right: Roll devulcanizates

The plots of complex viscosity versus frequency of the different devulcanizates are shown in Figure 12. The viscosity level decreases after devulcanization due to the cleavage of the three-dimensional rubber network by both, main chain and crosslink scission. The requirement is such that the devulcanized rubber needs to match the viscosity of the virgin natural rubber or any other matrix compound to be blended with.

With respect to die samples, Trial-2 and 15 have the lowest viscosity. With Trial-2, a very high first module temperature of 270^{0}C led to a low viscosity of the devulcanizate, but for Trial-15, a low temperature in the 5 modules (150/150/150/150/100^{0}C) and a low screw speed (80 rpm), thus high residence time, decreases the viscosity to a greater extent due to higher shear. For roll samples, the decrease in complex viscosity was in the following order:

Trial-18< 1< 17 < 20

3.3 Horikx Plot

A Horikx plot was made for all roll devulcanizate samples as shown in the Figure 13.

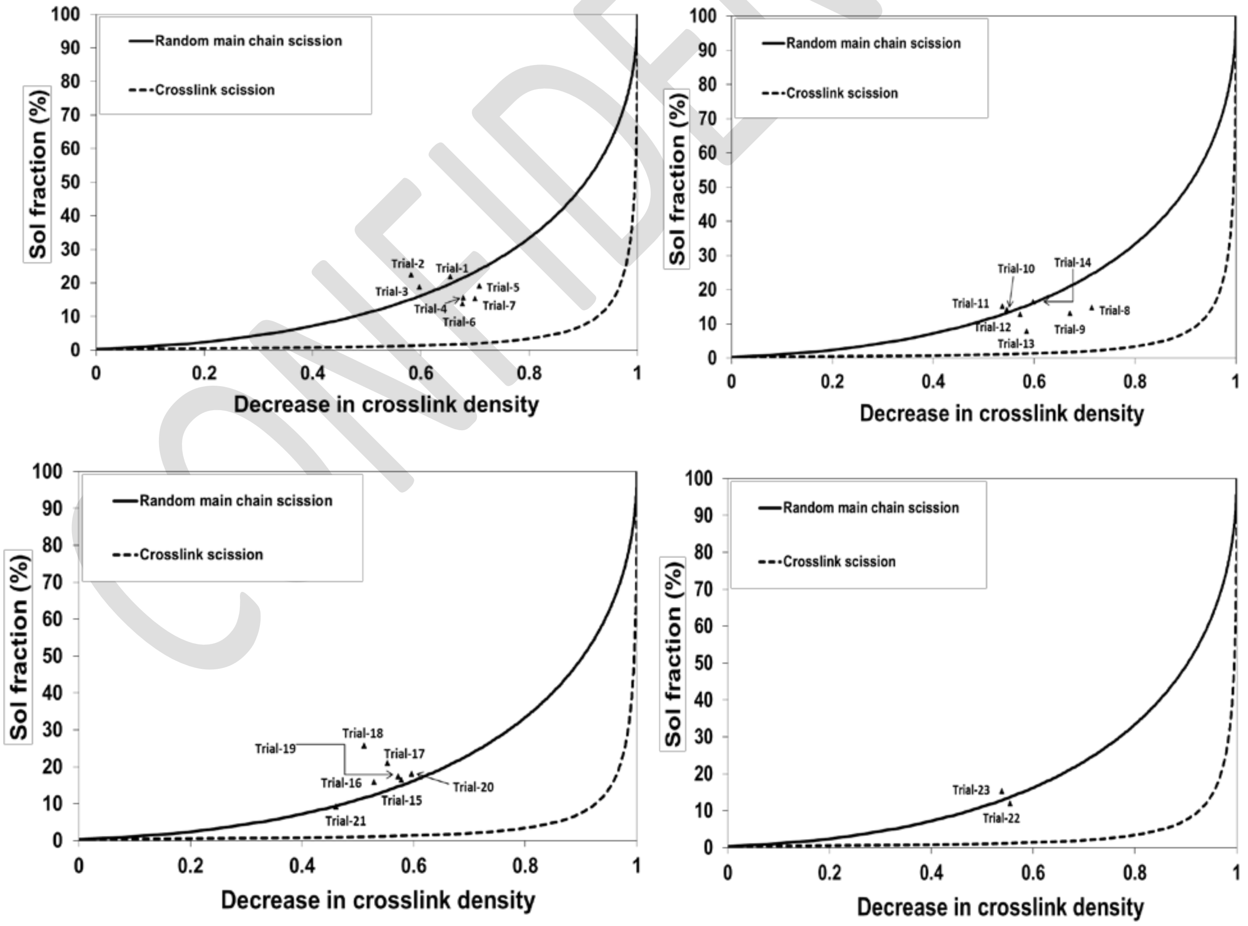


Figure 13: Horikx plots for roll devulcanizates

The sol content and the decrease in crosslink density are plotted in a Horikx plot; the ideal devulcanizate would have a low sol content and high decrease in crosslink density. However, 100% decrease in crosslink density is not possible due to bound rubber, monosulfidic crosslinks and onion peeling mechanism (Saiwari, 2013).

As explained in Chapter 3, the Horikx model is based on a homogenous devulcanization throughout the rubber granules; a change in this devulcanization mechanism under certain circumstances might be the reason for the off position of some data points. For these samples, the Horikx plot does not give the desired information. Therefore, for further analysis, only the samples fitting in the Horikx model will be taken into account.

Another problem is the sample homogeneity. For example, Table 7 shows the large difference between the crosslink density measurements of three samples from the same experiment: Trial-22 (cold roll) samples. The material coming out of the extruder is not homogenous, and there are still undevulcanized particles present in the devulcanized rubber. The samples from one run might thus have a lower or a higher content of devulcanized material, which is reflected in the variation of the analytical results.

Table 7: Crosslink density variations between different samples of one experiment

Batch	Crosslink Density, mol/cm-3	Average Crosslink Density, mol/cm-3	Standard deviation
Trial-22 (cold roll)	1.49E-04	1.92E-04	4.01E-05
	1.81E-04		
	2.46E-04		

Table 8: Sol content, %, and decrease in crosslink density, %, for the roll devulcanizate samples lying in-between the main chain and crosslink scission in the Horik plot (Figure 6)

Batches	**Sol content, %**	**Decrease in crosslink density, %**
Trial-4	22.9	68
Trial-5	25.2	71
Trial-6	21.8	68
Trial-7	22.8	70
Trial-8	22.4	71
Trial-9	21.3	67
Trial-12	21.1	57
Trial-13	17.9	59
Trial-21	18.8	46
Trial-22	20.6	55

The ideal characteritics for the devulcanizate are low sol content and high decrease in crosslink density. From Table 8, it is clear that Trial-5 has a high decrease in crosslink density, but on the other hand it has a rather high sol content. The high sol content can be explained by the higher module temperatures leading to a higher degree of main chain scission along with the crosslink scissions. The highest decrease in crosslink density is of the following order,

Trial-8 = 5 > 7 > 4 = 6 > 9

A low barrel temperature and moderate screw speed help in selective cleaving of crosslinks as for instance in Trial-8: the screw speed was 100 rpm and the barrel temperatures were (165/125/125/125/75^{0}C), and the decrease in crosslink density was 71% and the sol content was low with 22.4%.

The Horikx plot was made for die and roll samples of the same trials to see the effect of cooling on the devulcanizates as shown in Figure 14: The Horikx data points move to the right hand side for the roll samples compared to die samples. This can be explained by the cooling step, inhibiting the chain recombination reaction in the devulcanizate which results in an increase in crosslink density.

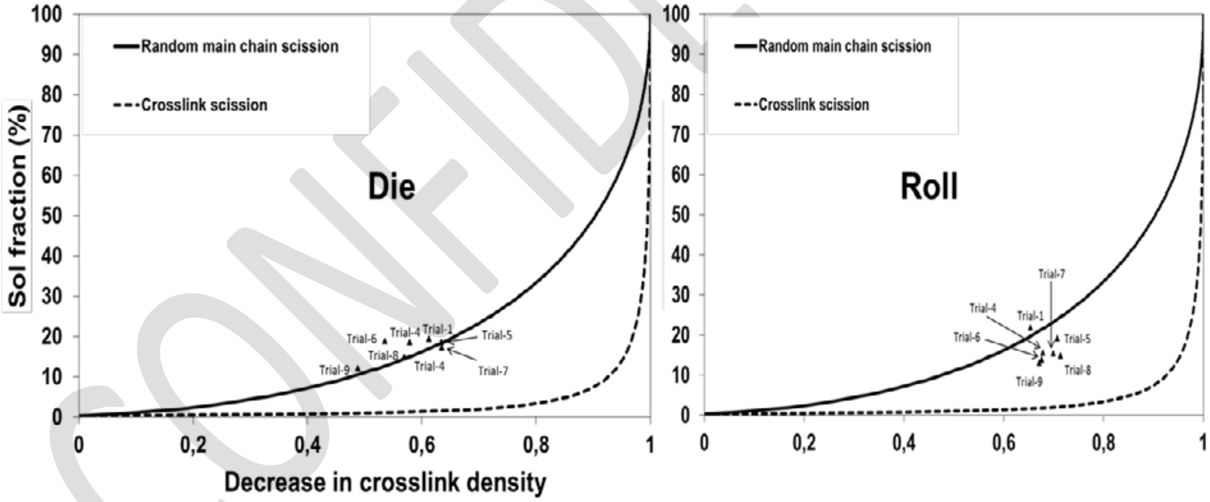


Figure 14: Horikx plot for Die (left) and b.) Roll devulcanizates (right)

However, for the trials without devulcanization aids, the Horikx data points behave oppositely: they move to the left hand side of the Horikx plot as shown in Figure 15 for roll samples. In this case, the active chain fragments are not scavenged by the devulcanization aid, but still existing in the devulcanizate. In the die samples, the oxygen can react with the fragments, avoiding recombination. The roll samples are more protected from oxygen, and therefore recombination occurs to a higher extent.

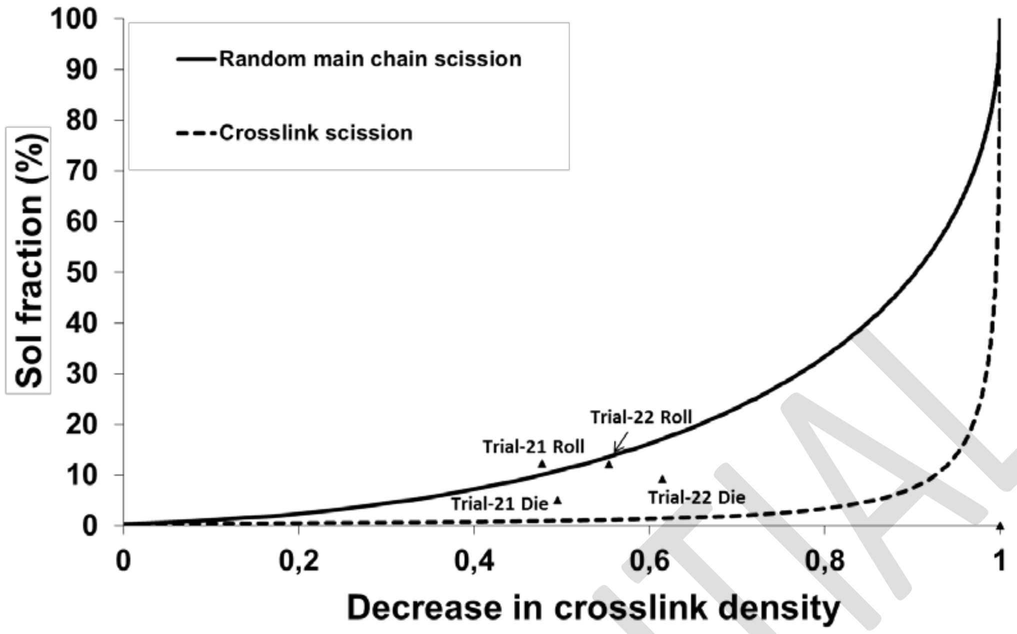


Figure 15: Horikx plot for Trial-21 and 22 of Die and Roll samples

3.4 Curing after addition of curatives

The rheo curves were plotted after mixing of the devulcanizates with the curing agents to study the curing kinetics as shown in Figure 16. Generally, the maximum torque of a vulcanizate is proportional to the crosslink density, if the compounds are similar. From Figure 17, it is seen that maximum delta torque values were observed for Trial-21 and 22, i.e., the devulcanizates without devulcanization aid. This supports the statement that the devulcanization aids react with allylic hydrogens in the polymeric chain and thus inactivate the polymer for re-crosslinking, as discussed in Chapter 3.

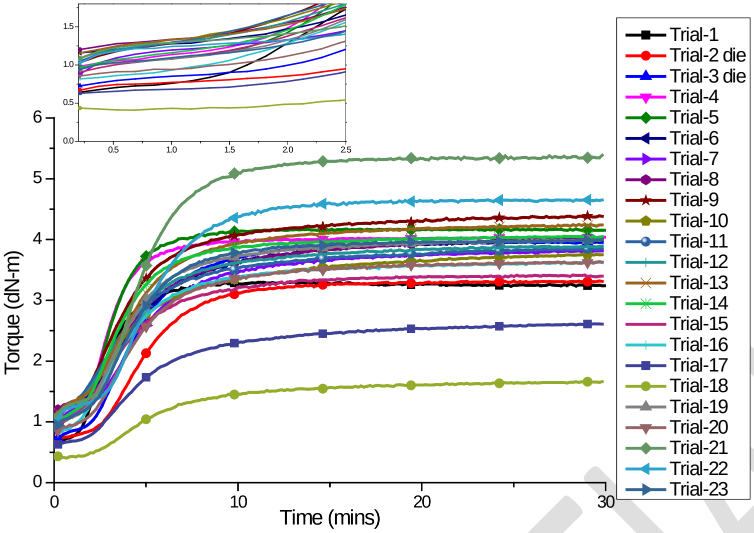


Figure 16: Rheo curves for the different devulcanizates after addition of curatives

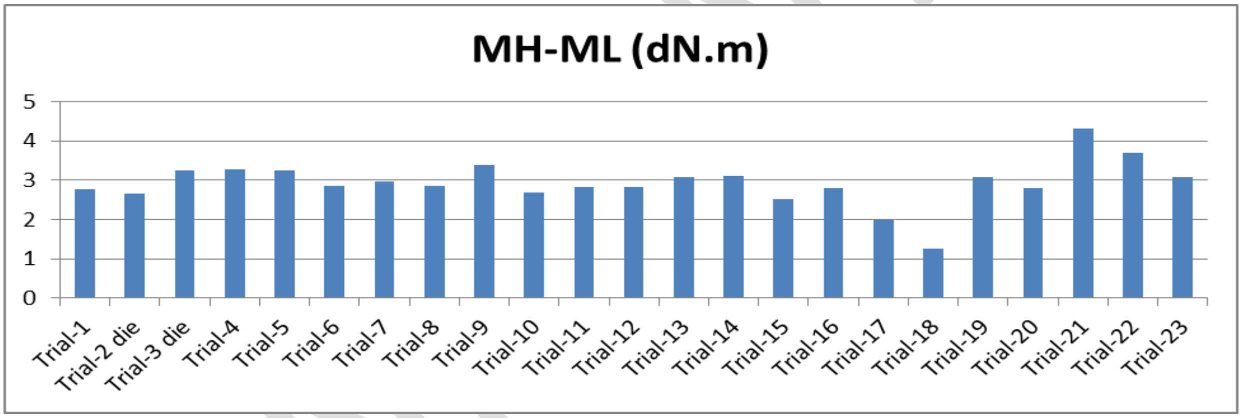


Figure 17: Delta torque (ΔT= MH-ML) for different devulcanizates

3.5 Tensile properties

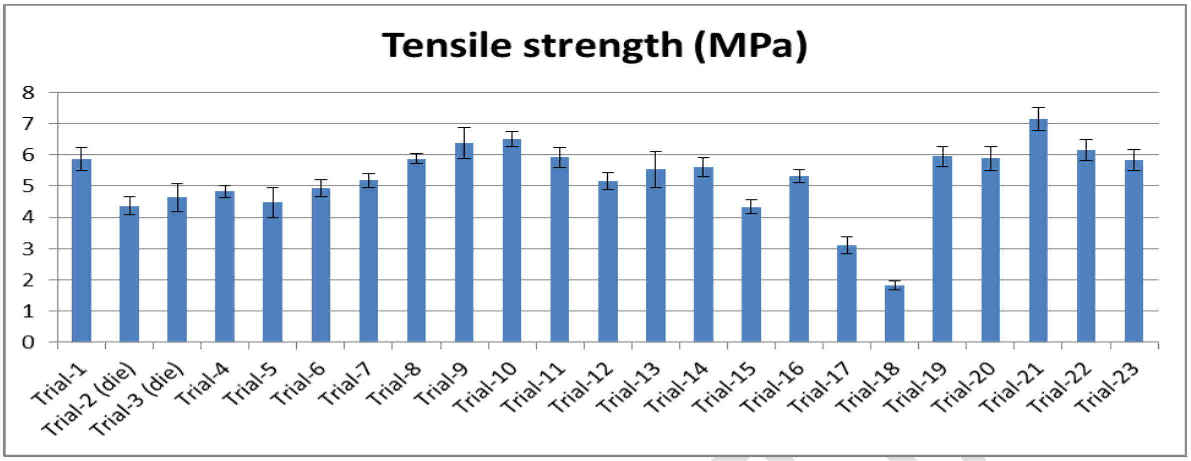


Figure 18: Tensile strength for rolled devulcanizates

From Figure 14, the roll samples can be ranked in terms of increasing tensile strength as follows:

Trial-21> 10> 9 >22

Generally, a higher delta torque value from the rheo curve corresponds with a higher tensile strength: a higher delta torque was observed for Trial-21 and 22 as seen from Figure 17. For Trial- 9 and 10, the barrel temperature was low (140/100/100/100/50^0C) and the screw speed was high (150 and 125 rpm respectively). This lowers the residence time in the barrel, and the polymer chains were sheared to a lower extent. This would result in higher delta torque values for this material.

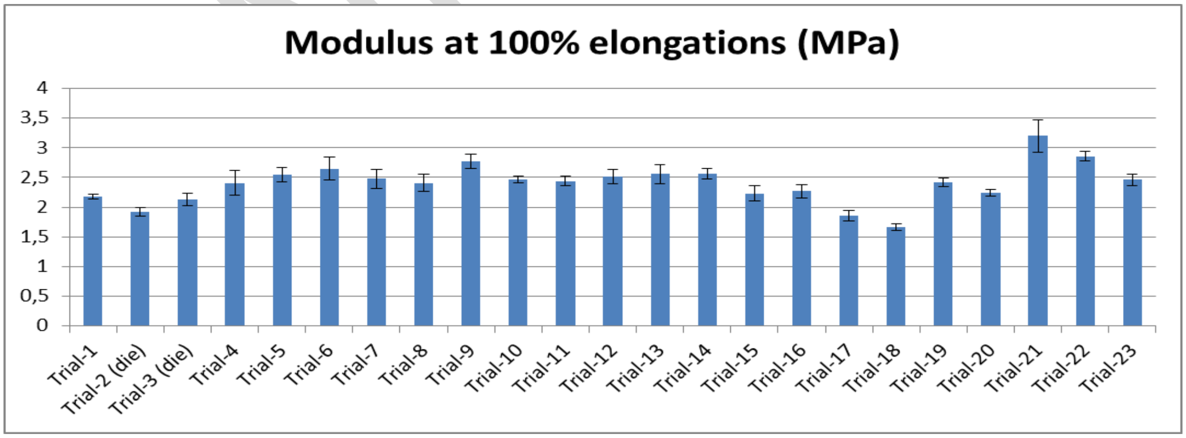


Figure 19: Modulus at 100% elongations (MPa) for the rolled devulcanizates

From Figure 19, it is clear that Trial-21 & 22 have the highest modulus values at 100% elongation; the samples with a delta torque and a high tensile strength.

Conclusions for the pure devulcanizates

Rolled samples result in compaction of the devulcanizate preventing oxygen entry; this material is also easier to transport and store. Moreover, roll samples also provide better properties by lowering the thermo-oxidative degradation seen by a decrease in sol content. Cooling the devulcanizate after exiting the extruder is therefore crucial in the process.

Requirements for an ideal devulcanizate:

- Horikx plot: Data points of the devulcanizate in-between the main chain and crosslink scission line, close to the crosslink scission line with high values of decrease in crosslink density
- (Complex) viscosity: Low viscosity for easy processing and blending with virgin polymers and matching the viscosity of virgin compounds
- Curing behaviour: High ∆Torque = MH - ML i.e., low initial viscosity with high curing tendency
- Tensile Properties: High tensile strength and medium modulus at 100% elongation

Selected pure devulcanizates based on these requirements:

- Horikx Plot: Trial- 4, 5, 6, 7, 8, 9
- Highest and lowest viscosity: Trial- 21 & 15 (Highest and lowest viscosity was chosen to study the difference in blending with respect to mixing and mechanical properties)
- High Tensile strength: Trial- 21, 10, 9, 22
  - ➔ Overall: Trial- 7, 8, 14

Trial-14 was one of the devulcanizates, where the devulcanization system was instantaneously mixed in and which showed good overall properties on the basis of the Horikx plot, low viscosity and high tensile strength.

From the pure devulcanizates, the 12 samples mentioned above were shortlisted and used for further blending trials with virgin natural rubber (SMR-10), and the properties were compared to the virgin natural rubber compound as given in Table 4.

Natural Rubber (NR) / Devulcanized Rubber Compound (DRC) Blends

Curing

The blends of DRC / virgin natural rubber have shorter scorch and cure times compared to the virgin NR compound, confirming the presence of active curing agents in the used tire rubber and thus in the DRC as seen in Figure 20.

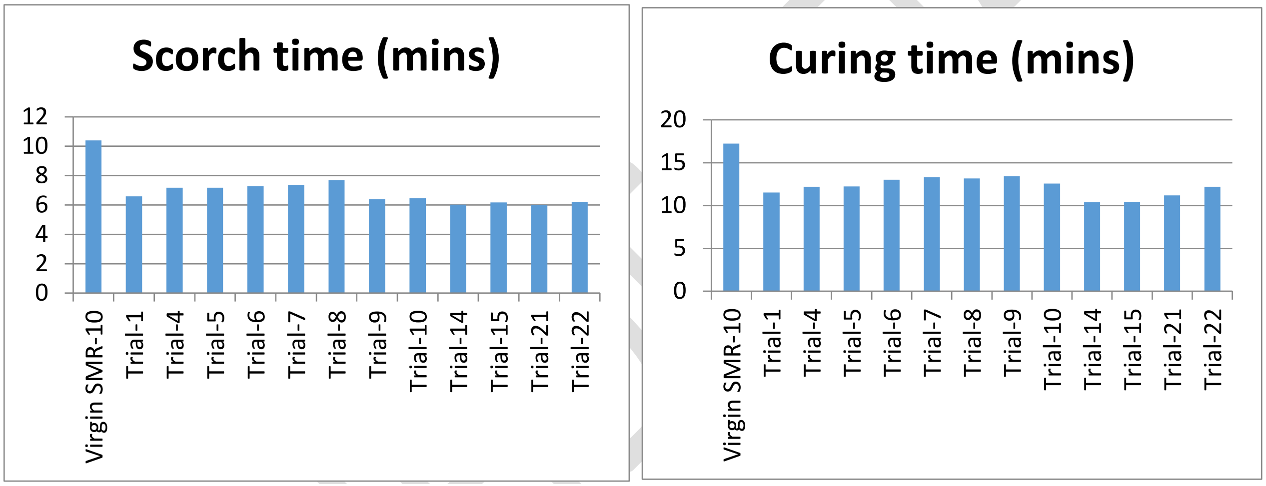


Figure 20: Scorch (left) and cure time (right) comparison between virgin SMR-10 and NR/ DRC Blends

The Δ torque values (Figure 21) are generally higher for devulcanized rubber blends, as the recycled rubber already contains fillers like carbon black and silica, which were not taken into account during compounding. Besides, devulcanized rubber contains some crosslinked gels, which will also increase the modulus to some extent. Devulcanizate Trial-21 and 22, without devulcanization aids, have maximum Δ torque values as also seen in Figure 17.

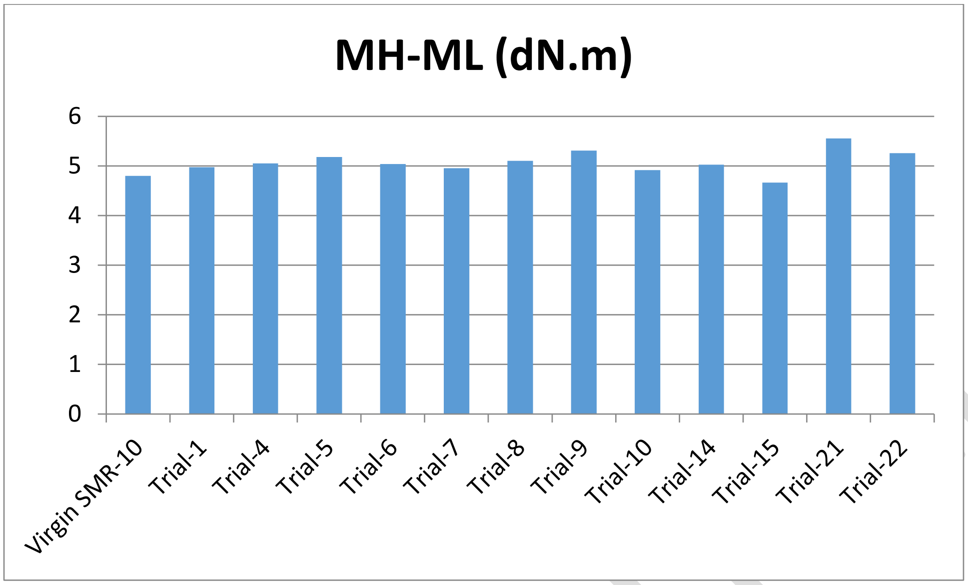


Figure 21: Delta Torque (ΔT) values for the virgin SMR-10 and NR/DRC Blends

Tensile properties

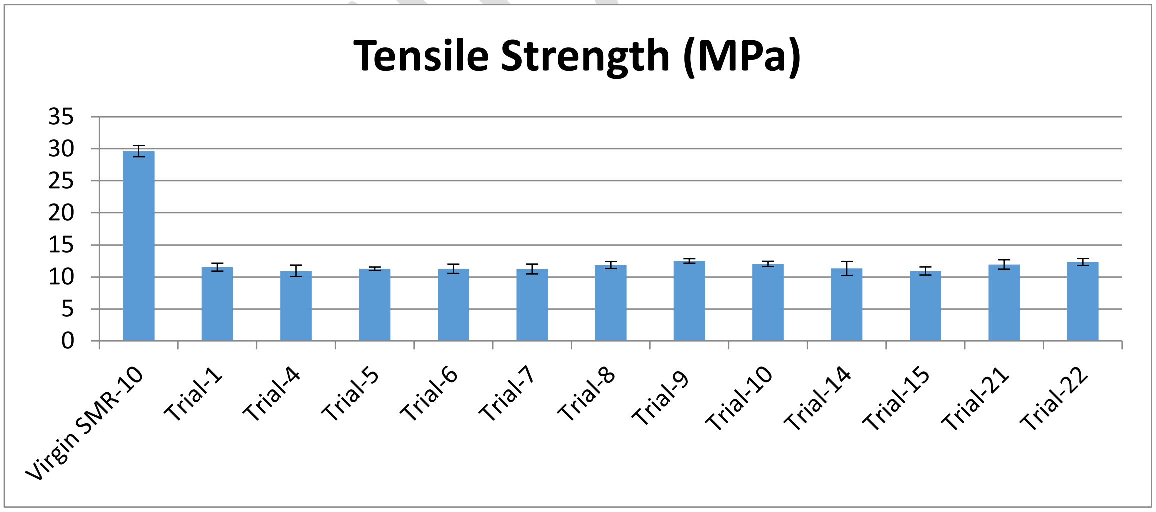


Figure 22: Tensile strength of virgin SMR-10 and NR/DRC blends

Higher delta torque values lead to better tensile strength properties, likewise, Trial-21, 22, 9 and 10 show better tensile strength compared to other NR/DRC blends (Figure 22). But the tensile strength and elongation of the devulcanizates are less than half of the tensile strength of the virgin SMR-10 as shown in Figure 23, indicating weak interfacial adhesion between the blend phases. According to Saiwari, this could also be the result of (Saiwari, 2013):

- Poor co-vulcanization between the blends,
- Incomplete re-vulcanization and a less developed network as the polymer of the devulcanizate might have severely been damaged during the devulcanization process
- Presence of remaining gel in the devulcanizate leading to stress accumulation

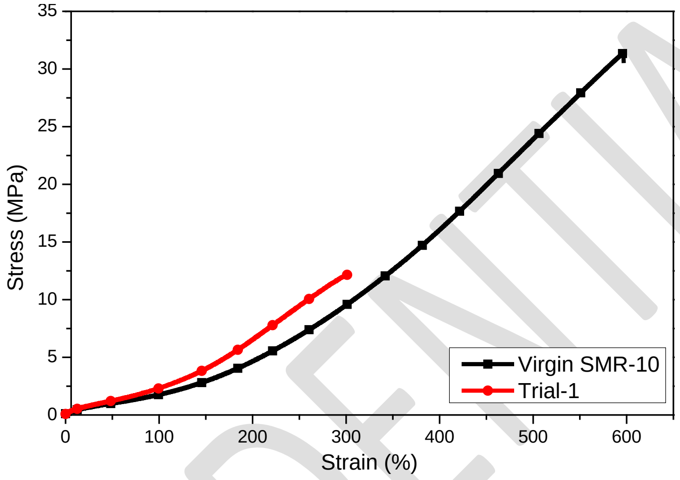


Figure 23: Stress strain curve of virgin SMR-10 and NR/DRC (Trial-1) blend

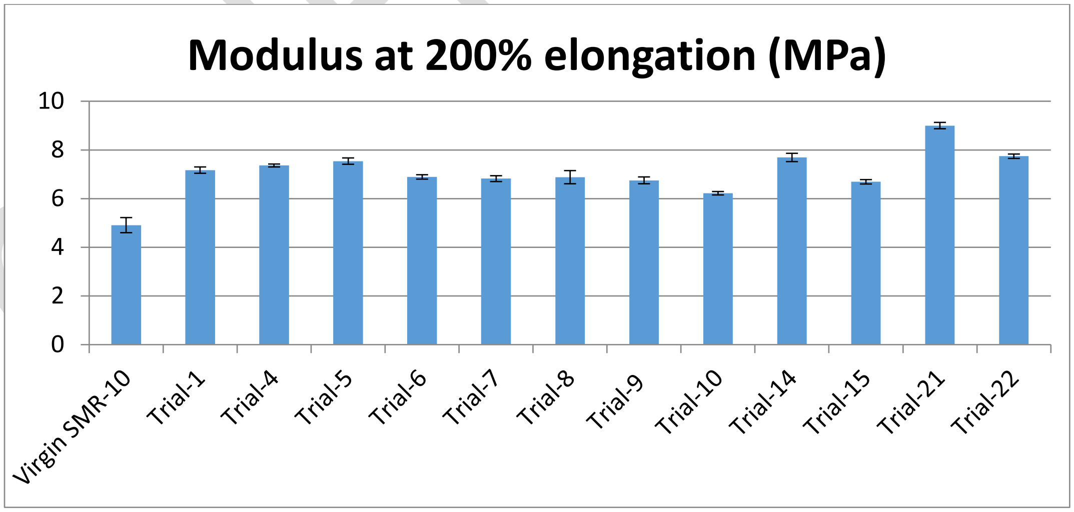


Figure 24: Modulus at 200% elongation of virgin SMR-10 and NR/DRC Blends

The devulcanizate rubber blends have higher modulus values at 200% elongation than the virgin SMR-10 compound (Figure 24) due to a higher crosslink density in the devulcanizate phase.

Hardness

Hardness of the devulcanized rubber is generally a bit higher compared to the virgin SMR-10 material (Figure 25), but the difference between the NR/DRC blends is too small to make any conclusions. The higher hardness will negatively influence the stress strain properties; therefore the conclusions based on stress strain data should only be based on trends and not on single values.

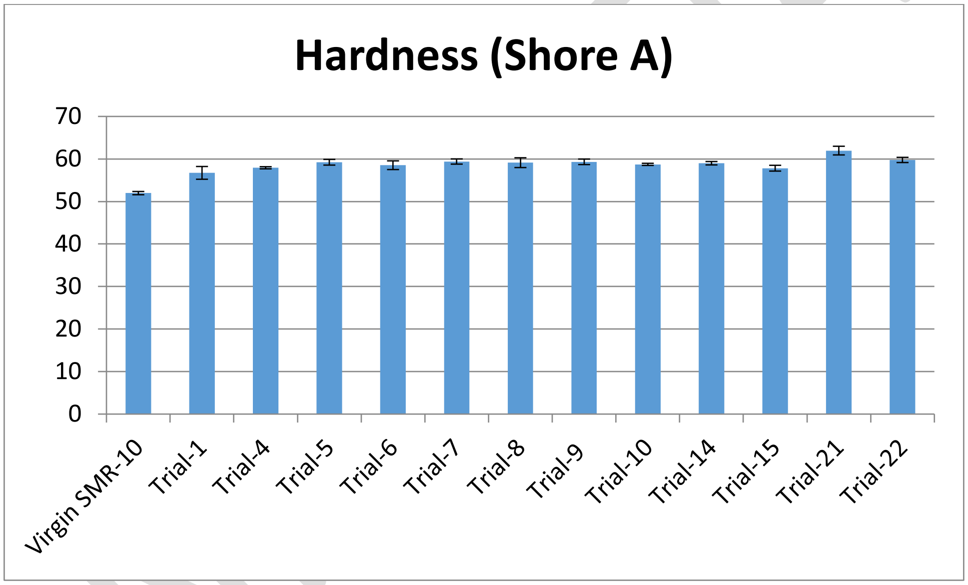


Figure 25: Hardness of the virgin SMR-10 and NR/DRC blends

Conclusions for the Natural rubber-devulcanized rubber blending trials

NR/DRC Blends have shorter scorch and curing time compared to the virgin SMR-10 compound confirming the presence of still active curing agents in the used tire rubber. The NR/ DRC blends have low tensile strength and elongation at break attributed to the presence of crosslinked gel in the matrix originating from the devulcanized rubber; this makes it difficult to disperse the devulcanizate in the virgin rubber matrix corroborated by higher viscosity during mixing. The main conclusion from the blending study is that a difference in properties between the devulcanizate blends of different process conditions was not distinguishable. Therefore, screening of the devulcanizates will further on be based on the pure devulcanizate properties alone.

Final Conclusion and process design

The temperature settings of the extruder are a major influencing parameter for the devulcanization, as it determines the efficiency of blending of separately added devulcanization chemicals with the rubber granulate, the degree of degradation of the rubber, and the onset of the devulcanization reaction. The screw speed should be moderate, and the temperature low for good compaction of the devulcanizate. Lower temperatures can best be achieved by the TCU settings of the central spindle. If torque is an issue, pre-blended material is a better choice than separate addition of oil and devulcanization aid.

From the pure devulcanizates, Trial- 7, 8, and 14 were chosen for the next trial session, as they show good overall properties considering the requirements on position in the Horikx plot, (complex) viscosity and tensile strength.

For the design of the process this implies:

- Low module temperatures: low degree of polymer scission
- Low screw speed: high residence time for better devulcanization reaction and good temperature control

Process Design for Truck Tire Granulate Devulcanization in a Planetary Roller Extruder

STAGE 2

1. Introduction

One of the outcomes of the first series of experiments to design the extruder setup for devulcanization of truck tire rubber (Chapter 4) was, that the process is difficult to fine-tune, to control and lacks robustness: the change of a single parameter within the process influences most other parameters as well, resulting in combined effects partly balancing each other out. Therefore, a new design approach was chosen: The setup of the planetary spindles was elaborated module by module to study the effect much more precisely and to better control the process. Included was also a study on instantaneously mixing the devulcanization system with the Ground Truck tire Rubber (GTR) in the extruder, avoiding the pre-blending step: Oil and devulcanization aid will be injected at a higher temperature in the first module. For the first 2 modules, the temperature of blending had to reach the melting point of the devulcanization aid (DBD), and for the remaining modules it was primarily important to lower the temperature to reduce main chain scission.

In the case of instantaneously mixing, the early oil addition can induce slip effects which need to be taken into consideration when evaluating the results. From the previous trials it was concluded that a higher shear in the first modules and a longer residence time is required for instantaneously mixed devulcanizates compared to the pre-blended material, so processing in this case would require

- Higher shear: The temperature of the central spindle as well as in the barrel of the first modules had to be low in order to cool down the rubber as much as possible to increase shear. In this case, the heating of the central spindle was switched off.

- Lower temperature of the barrel (but not below the melting point of DBD) for reducing the temperature to achieve higher shearing forces. Besides, polymer degradation is inhibited at low temperatures.
- Higher dwell time for good blending of the rubber and the devulcanization aids: This can be achieved by lowering the screw speed or adding extra modules. However, the module length cannot be increased beyond 6 modules, since the torque of the central spindle is fixed to 170 Nm.

For a better heat transfer, water was used starting from module 2 due to its higher specific heat capacity than oil.

The problems expected in increasing the number of modules are:

- Higher torque: The central spindle can withstand a maximum torque of 170 Nm; above this value there is a risk of breaking the central spindle.
- Synergistic effects of increasing the number of modules affect the process, as well as effects can balance each other out.
- Increase in residence time: In most cases, this decreases the throughput rate, ultimately reducing the efficiency of the production.

Configuration variation of Planetary Roller Extruders-2:

- TCU settings of the barrels: from melting point of DBD= 145^{0}C to lower temperatures
- Screw speed: for adjusting temperature and residence time, and for studying the effect of pre-blending versus instantaneously mixing
- Number and length of spindles: number of spindles between 3 and 7, full length (390 mm) or shorter spindles (370 mm) to increase the free volume in the extruder
- Dispersion rings between modules: to control the transition of the material to subsequent modules

The start of the process design was made with a single module for instantaneous mixing; if insufficient blending, a second module can be added. Basically, the process conditions of Trial-17 from test series 1 (Chapter 4) were selected, with the temperature of module 1 at 135^{0}C. The temperature of the first 2 modules had to be chosen in a way that the material temperature reached the melting point of the devulcanization aid (DBD). For the remaining modules, the TCU settings were primarily lower to inhibit the main chain scission.

Table 1 summarizes the setup of the three days of trials at the Entex pilot installation:

Table 1: Planetary Roller Extruder trials-2 at Entex

Day-1	Day-2	Day-3
Up to 2 modules were assembled	Up to 4 modules were set up	Other feedstock materials were used (i.e without DA & with/without oil)
1st module - nap spindle 2nd module - standard spindle	4 short & 3 long standard spindles in module 3 & 4	

2. Experimental

This test series was again performed in the pilot installation at Entex, in cooperation with Rumal.

2.1 Materials

The Ground Truck tire Rubber (GTR) used in this stage of the process design was supplied by RUMAL BV, The Netherlands, with a particle size of 0.8 - 2.5 mm. The devulcanization aid – DBD (2,2'- dibenzamido diphenyl disulphide, DBD) - was obtained from Thomas Swan & Co. Ltd., United Kingdom. TDAE oil used as processing oil for the devulcanization was supplied by Hansen & Rosenthal, Germany.

2.2 Preparation of devulcanizates

GTR was pre-swollen in a mixture of DBD and TDAE oil for 30 minutes at room temperature. From each trial, 2 samples were obtained: one directly from the die and the other one after passing through the cold roll.

The devulcanizate was evaluated during the tests by:

1. Visual Inspection concerning particle size, smoothness/remaining particles, consistency, tackiness
   After the first 2 modules, the particle size is controlled as the granulate is ground to a finer powder before the devulcanization starts. Once the reaction starts, it is checked whether the material forms a coherent mass, as is the case for a fully devulcanized rubber.
2. Material outlet temperature: The material outlet temperature from the extruder was measured by a temperature sensor in the extruder die as well as manually with a thermocouple.

2.3 Mixing and Revulcanization of Devulcanized Rubber Compound (DRC)

Compound formulation and mixing procedure

The compound recipe and mixing procedure are given in Chapter 4, Table 2 and 3.

2.5 Moulding

For moulding of the devulcanizate, the procedure as described in Chapter 4 was used.

2.5 Characterization of Devulcanizate, Re-Vulcanizate and Blends:

2.4.1 Mooney Viscosity (ASTM D1646)

Mooney viscosity measurements were made using a Mooney Viscometer (MV 2000VS, Alpha Technologies) with the rotor moving at an angular velocity of 2 revolutions per minute. The principle of a Mooney viscometer is such that rotor moves inside a closed cavity containing the test piece, where the shearing action takes place between the flat surfaces of the rotor and the walls of the chamber. The torque required to rotate the rotor is monitored, where one Mooney unit= 0.083 Nm.

The value is represented as ML(1+4) 100^0C, where

M $\rightarrow$ Mooney

L $\rightarrow$ Large rotor

1 $\rightarrow$ 1 minute pre-heat time

4 $\rightarrow$ 4 minute test time

100^0C $\rightarrow$ Test temperature

2.4.2 Rubber-Soluble Fraction:

The sol fraction of the devulcanizate was determined by extraction in Soxhlet apparatus, as described in chapter-3.

2.4.3 Crosslink density

The extracted samples were subsequently swollen in toluene for 72 hours at room temperature according to ASTM D 6814-02 as described in Chapter 3.

2.4.4 Cure Characteristics (ASTM D2064):

The cure characteristics were determined using a Rubber Process Analyzer (RPA 2000, Alpha Technologies) as described in Chapter 3.

2.4.5 Mechanical properties:

Tensile tests were carried out on dumb-bell shaped specimens, using a Zwick Z1.0 tensile testing machine as described in Chapter 3.

3. Results & discussion

Design of the extruder setup and parameters, and visual analysis of the devulcanizate

The starting conditions of the Planetary extruder setup-1 are given in Figure 1. All process parameters are given in Appendix 2.

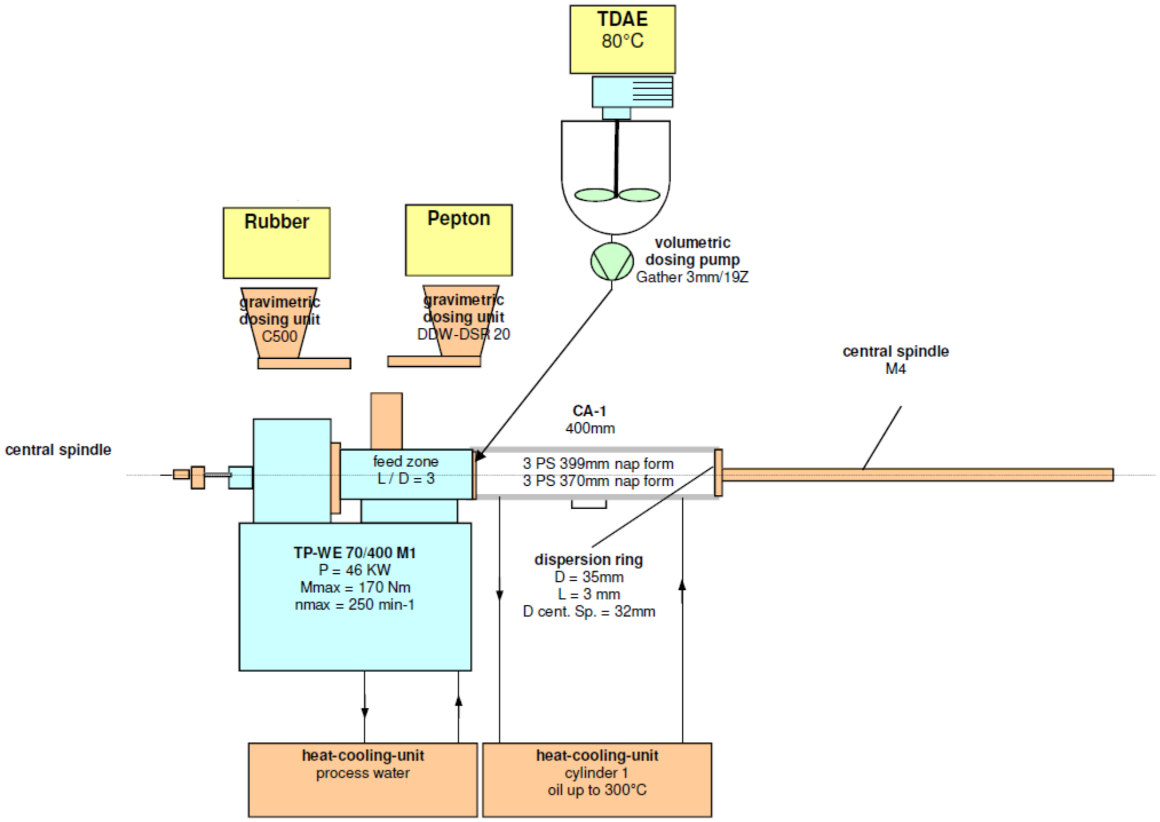


Figure 1: Design setup-1 for the planetary roller extruder

Trial -1 (setup-1): The devulcanization system (oil & devulcanization aid) and the ground tire rubber were mixed instantaneously in the extruder. Nap spindles were used for the first module to increase the shear and the dwell time. The material is very sticky due to higher module temperature and oil on the surface of the granulate, which could affect the free flowing nature of the material into the subsequent modules. As the devulcanization system was still visible on the surface of the granulate, the screw speed was reduced to increase the dwell time for oil and DBD.

Trial-2 (setup-1): After reducing the screw speed to 50rpm, the stickiness was reduced compared to Trial-1.

Trial-3 (setup-1): With a high screw speed of 80 rpm and low barrel temperature of 140^0C, the material temperature remained low and felt dry on touch.

Trial-4 (setup-1): Since the outlet temperature was rather low (136^0C) in Trial-3, the temperature of the barrel was increased to 160^0C in order to reach the melting temperature of DBD and to have a more efficient migration of the oil/DBD blend into the rubber particles. However, still the outlet temperature was 110^0C.

Trial-5 (setup-1): With 200^0C of barrel temperature, the outlet temperature of the material was around 120^0C only: still lower than the melting temperature of the DBD.

To further increase the material outlet temperature to the melting point of DBD, a stop ring with a lower diameter of 34mm was used. The adjusted design setup-2 is given in Figure 2:

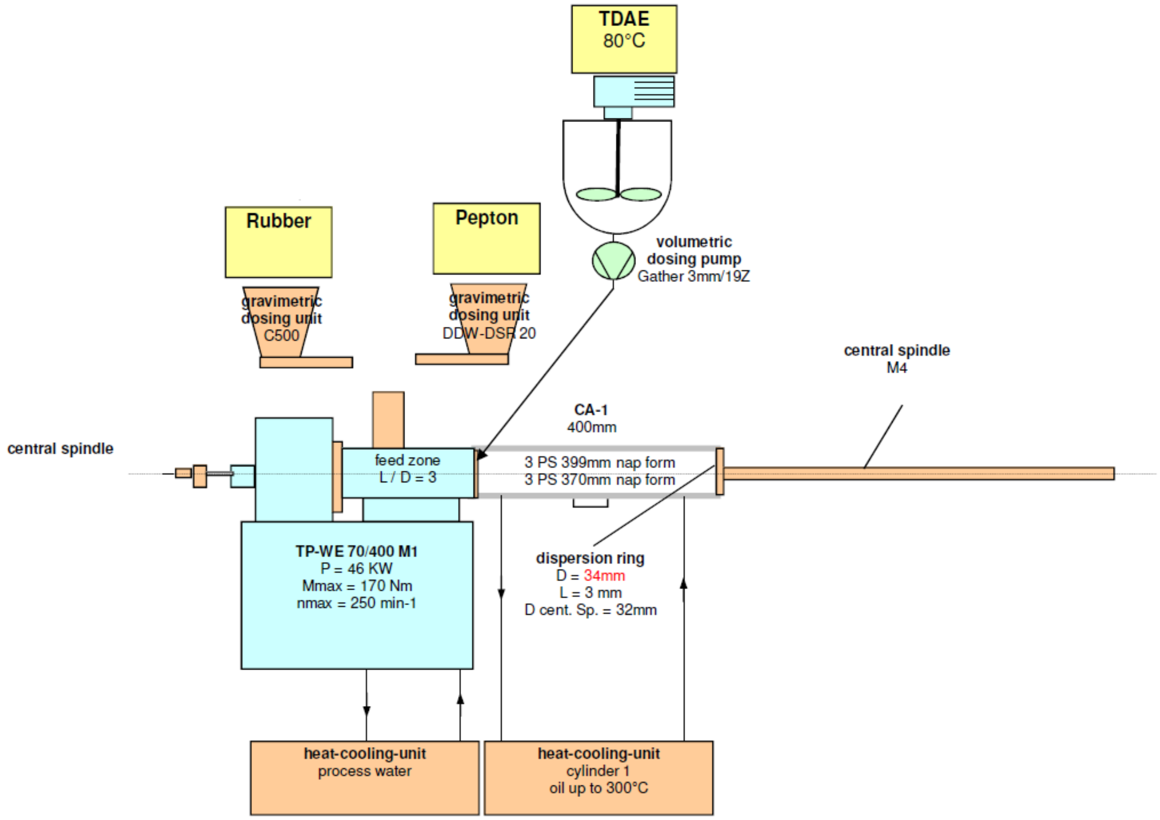


Figure 2: Design setup-2 for the planetary roller extruder

Trial-6 (setup-2): With a reduced diameter of the stop ring, the outlet temperature increased to 130^0C.

Trial-7 (setup-2): By increasing screw speed to 120rpm, the material outlet temperature was around 140^0C, just slightly below the melting point of DBD (T_m= 145^0C).

Trial-8 (setup-2): With a higher barrel temperature of 180^0C, the material outlet temperate was still around 140^0C, the same as in the previous trial due to lower dwell time which makes heat transfer difficult.

Trial-9 (setup-2): With a reduced screw speed, the outlet temperature was reduced to around 120^0C. The reason might be a lower energy input due to the reduced screw speed.

To increase the dwell time, a second module was constructed with 5 nap spindles for less transport of material, thus a higher dwell time, as shown in Figure 3.

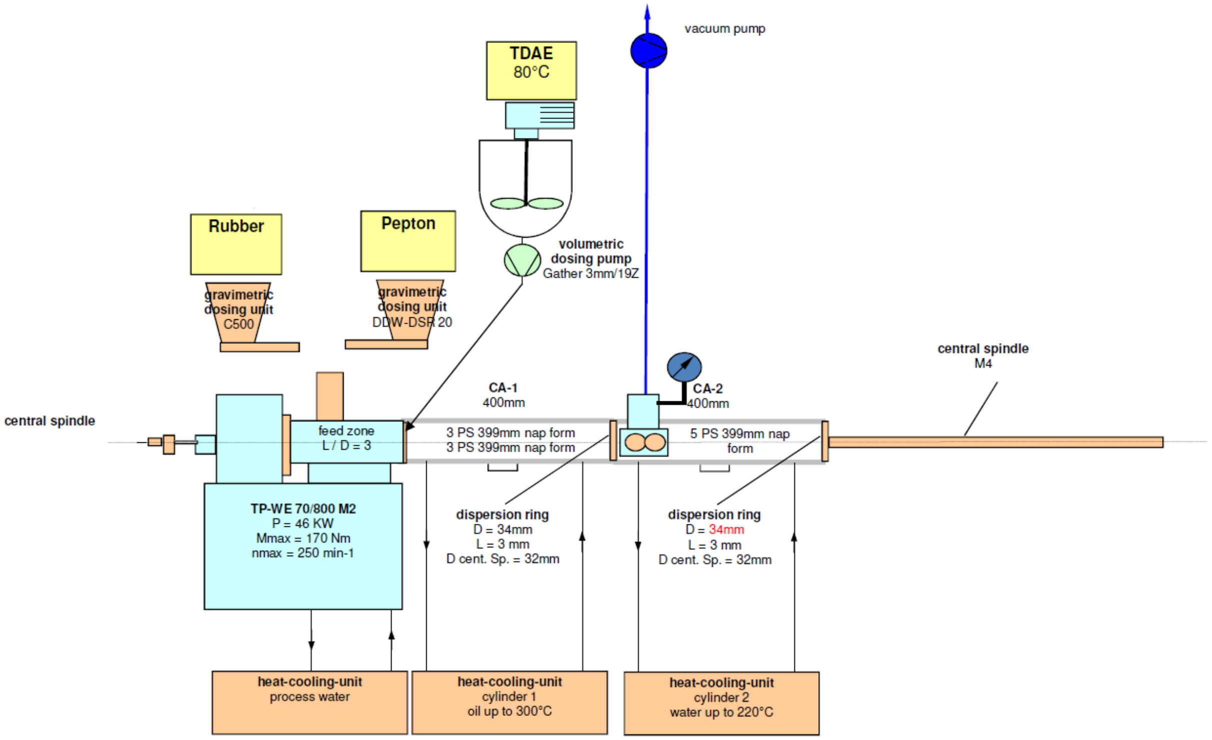


Figure 3: Design setup-3 for the planetary roller extruder

Trial-10 (setup-3): With a set temperature of the 1^{st} module of 180^0C and the 2^{nd} module of 170^0C, the mass outlet temperature was 225^0C: The addition of a second module had a drastic effect on the temperature. The sample exiting the extruder was degraded as indicated by the smell.

To reduce the shear, 5 standard spindles were now used for the second module (Figure 4).

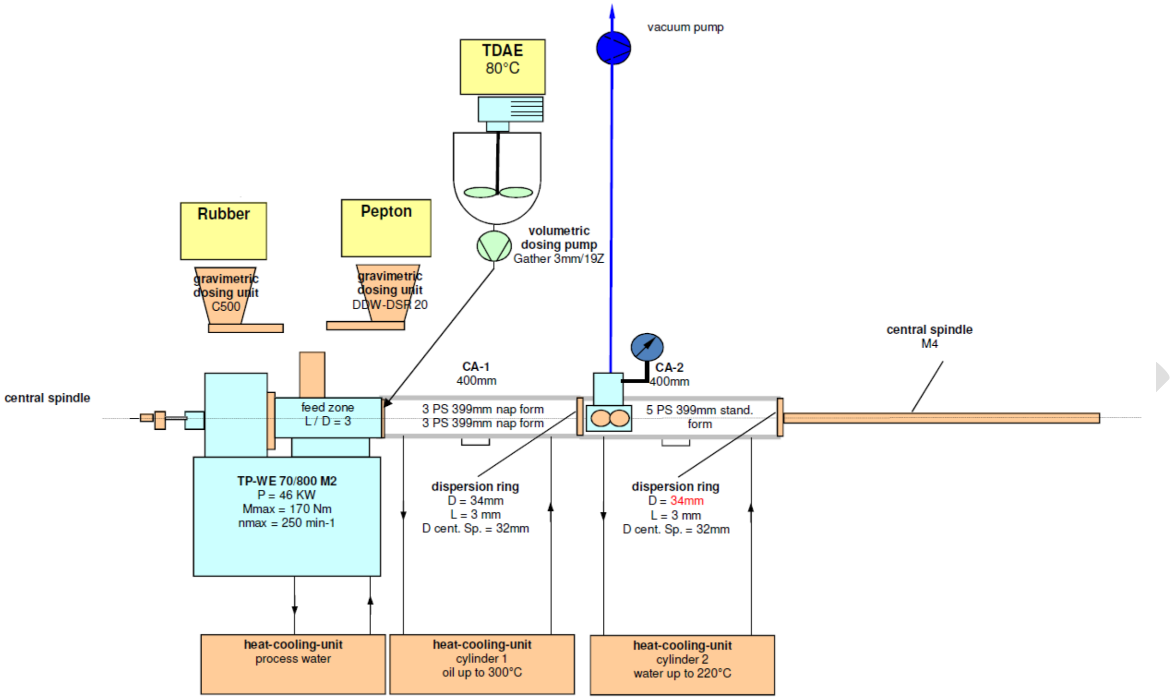


Figure 4: Design setup-4 for the planetary roller extruder

Trial-11 (setup-4): With the same process conditions of Trial-10, the material still degraded. Therefore, the stop ring diameter was increased from 34 mm to 38 mm to decrease the heat buildup when the material was pressed through the ring between module 1 and 2, as shown in Figure 5.

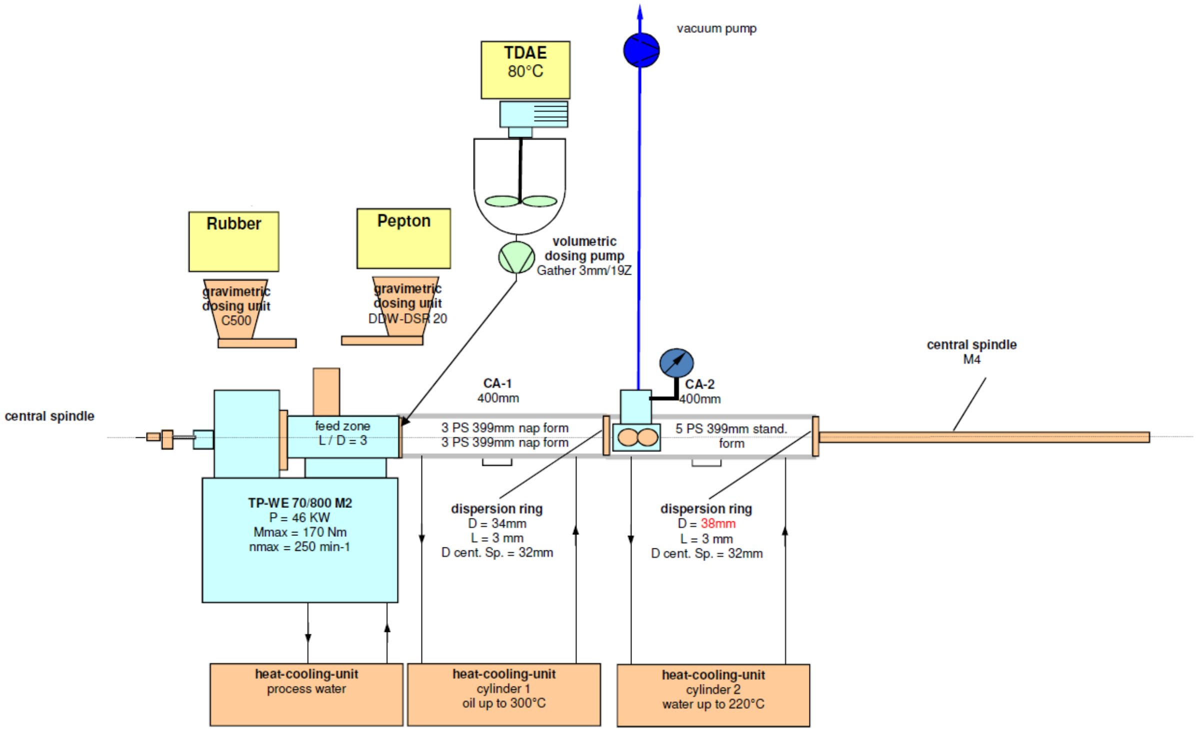


Figure 5: Design setup-5 for the planetary roller extruder

Trial-12 (setup-5): Even after increasing the stop ring diameter, the material outlet temperature was around 205^{0}C, in the same range as the previous trials.

For better temperature control and elimination of oxygen contact of the hot material leading to degradation, a 3rd module was built with 5 standard spindles (see Figure 6).

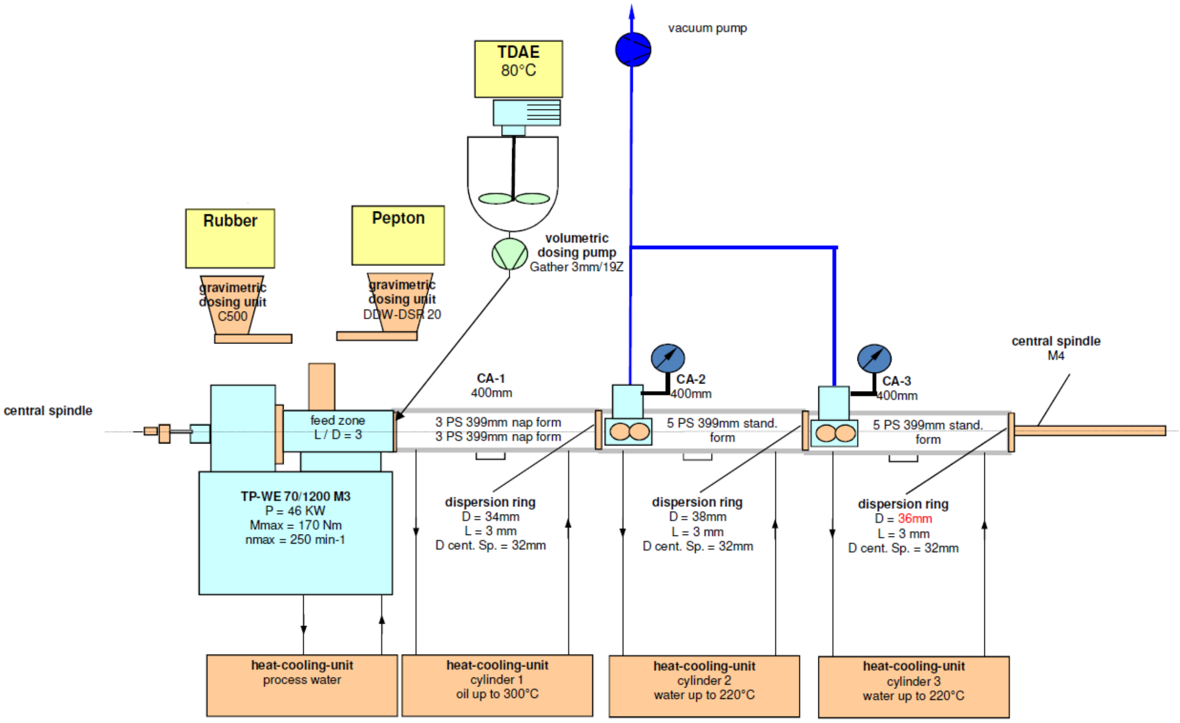


Figure 6: Design setup-6 for the planetary roller extruder

Trial-13 (setup-6): The outlet temperature after the 2nd module is still 10°C higher than in setup-5. The outlet temperature after the 3rd module is also high.

Again, the stop ring diameter was increased from 36mm to 38mm after module 3 to reduce the material outlet temperature as detailed in Figure 7.

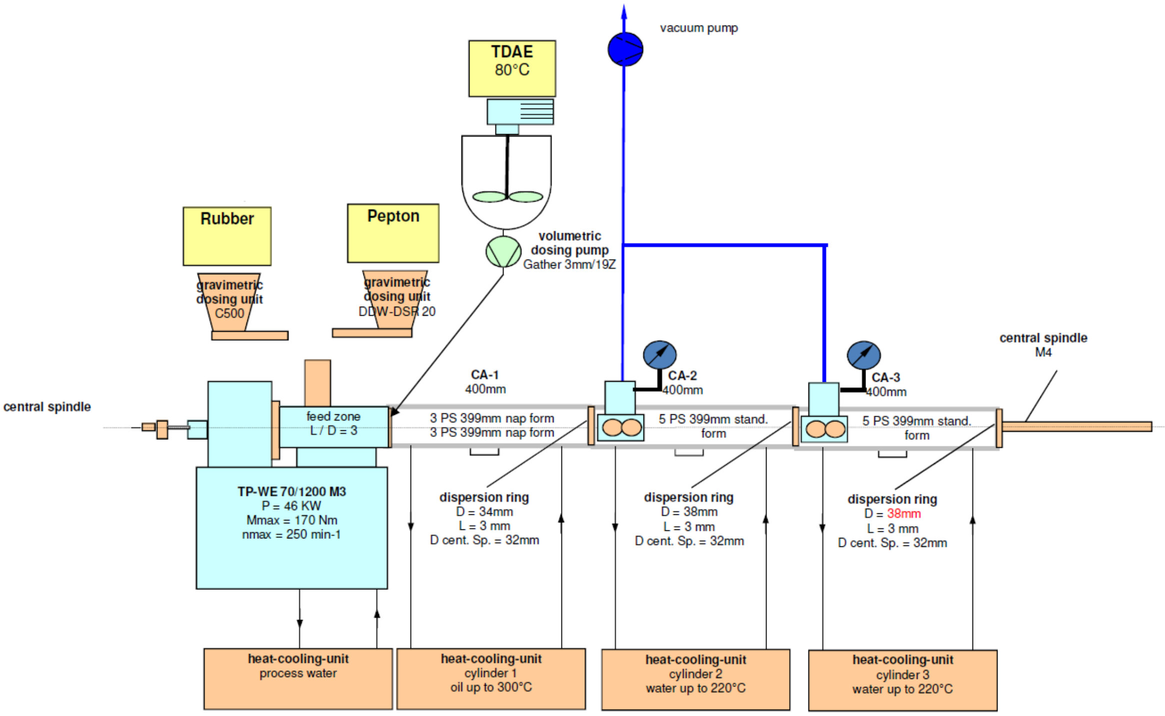


Figure 7: Design setup-7 for the planetary roller extruder

Trial-14 (setup-7): The effect of the larger dispersion ring on the outlet temperature was low.

As all the design changes to lower the material outlet temperate failed, redesign of the 2nd module with 7 standard spindles instead of 5 was proposed in order to decrease the dwell time. The design setup is shown in Figure 8.

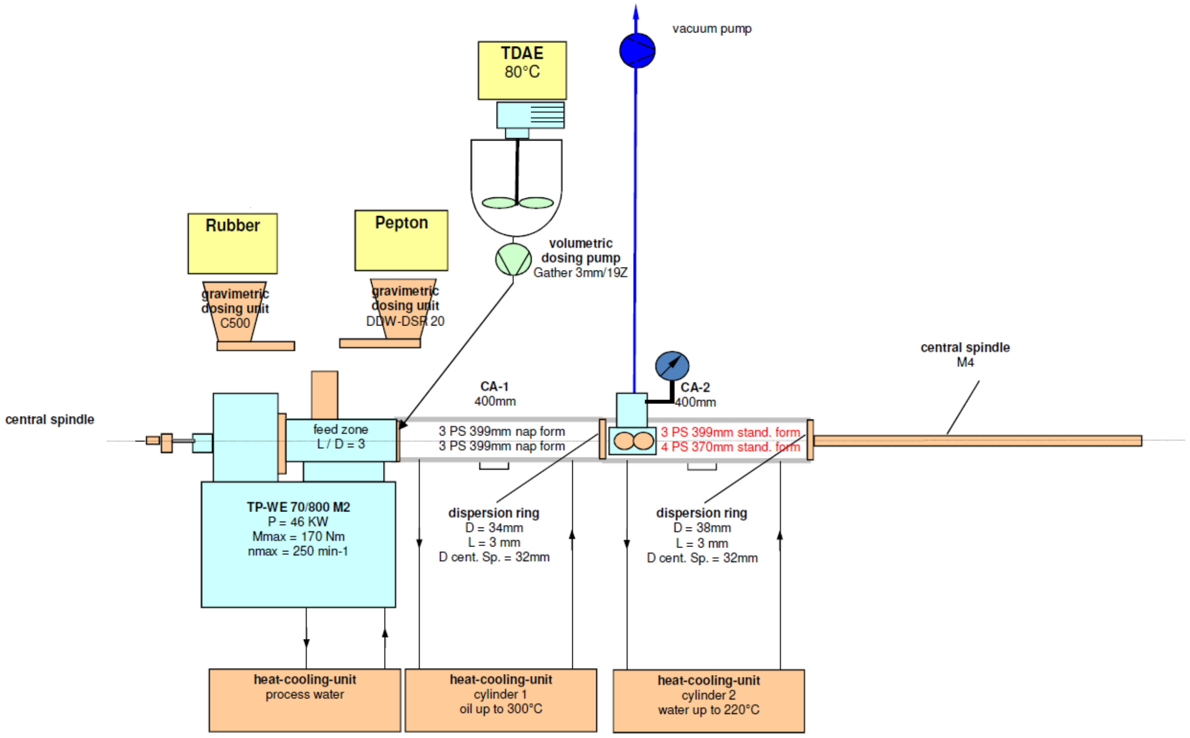


Figure 8: Design setup-8 for the planetary roller extruder

Trial-15 (setup-8): With the 7 standard spindles, the dwell time is so low that insufficient shear was applied to the tire crumb resulting in bigger particle sizes at the end compared to the earlier tests.

To increase the pressure on the material before exiting the extruder module 2, and thus to enhance the grinding effect, the diameter of the dispersion ring of the 2nd module was decreased from 38mm to 36mm (Figure 9).

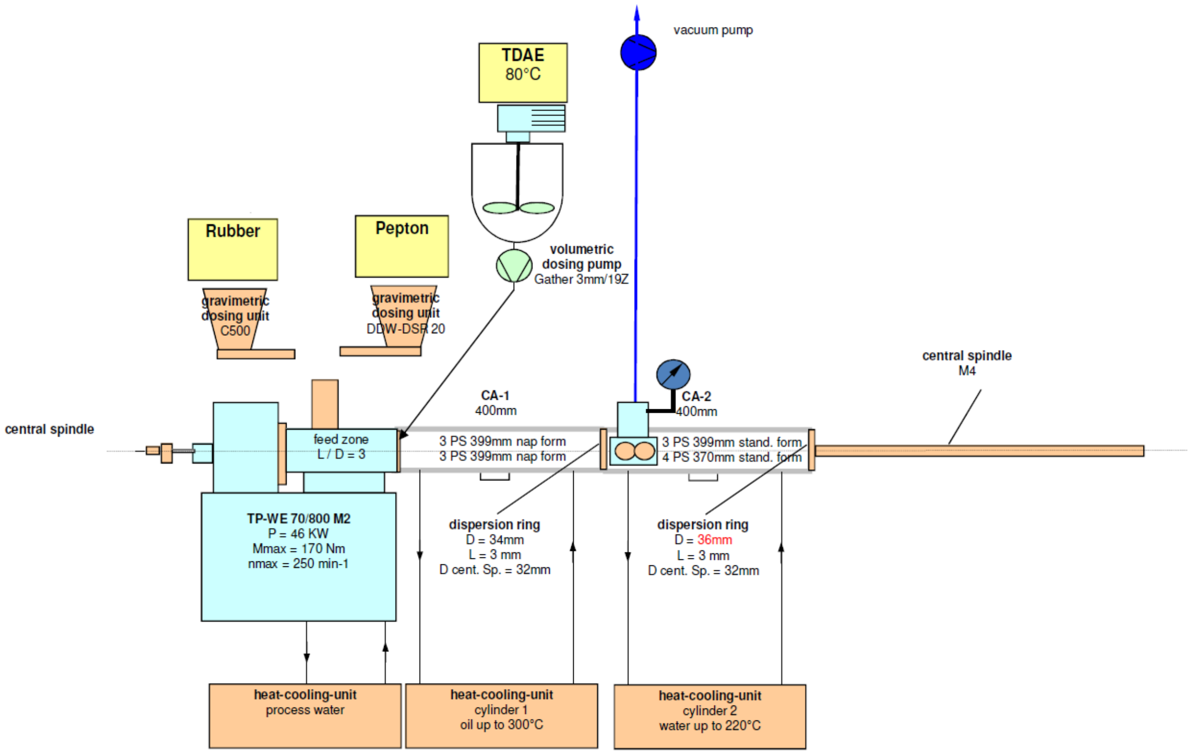


Figure 9: Design setup-9 for the planetary roller extruder

Trial-16 (setup-9): With the smaller dispersion ring, the material outlet temperature raises and the particle size is again large.

The 3rd module was designed as shown in Figure 10.

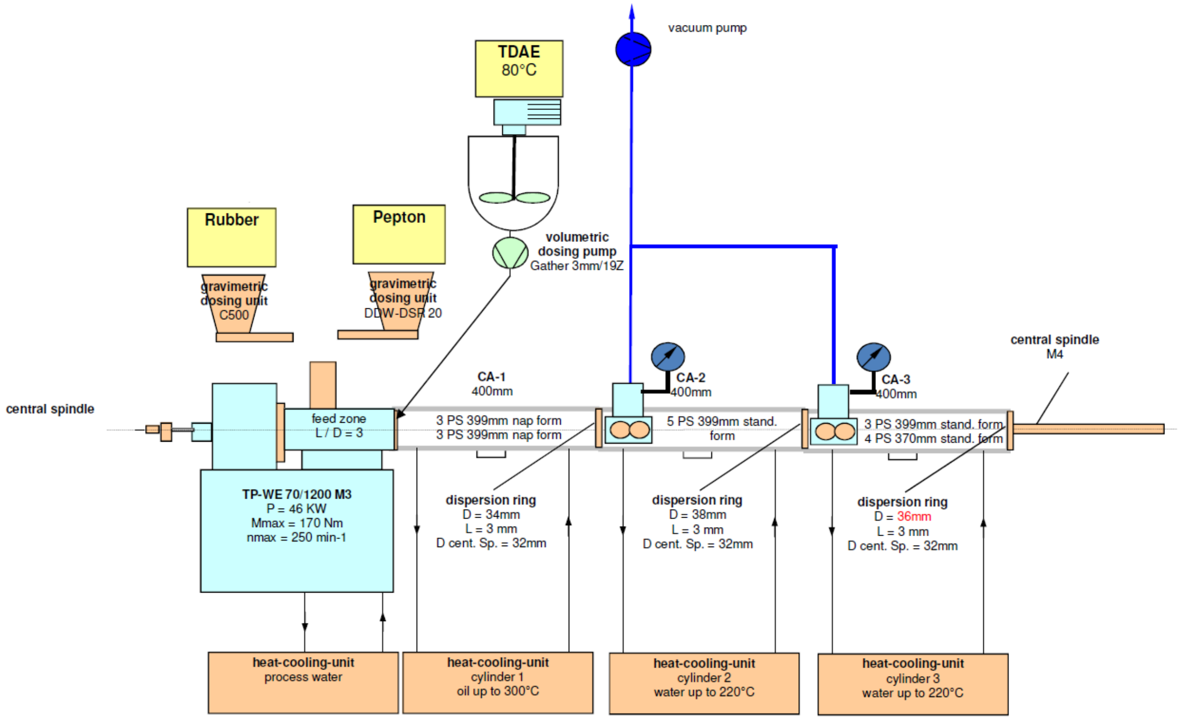


Figure 10: Design setup-10 for the planetary roller extruder

Trial-17 (setup-10): The material outlet temperature was in the same range as in the previous trial-16.

The 4th module was built by extrapolating setup-10. Additionally, a die was added with a diameter of 20mm and liquid temperation at the end of the 4th module. Details are given in Figure 11.

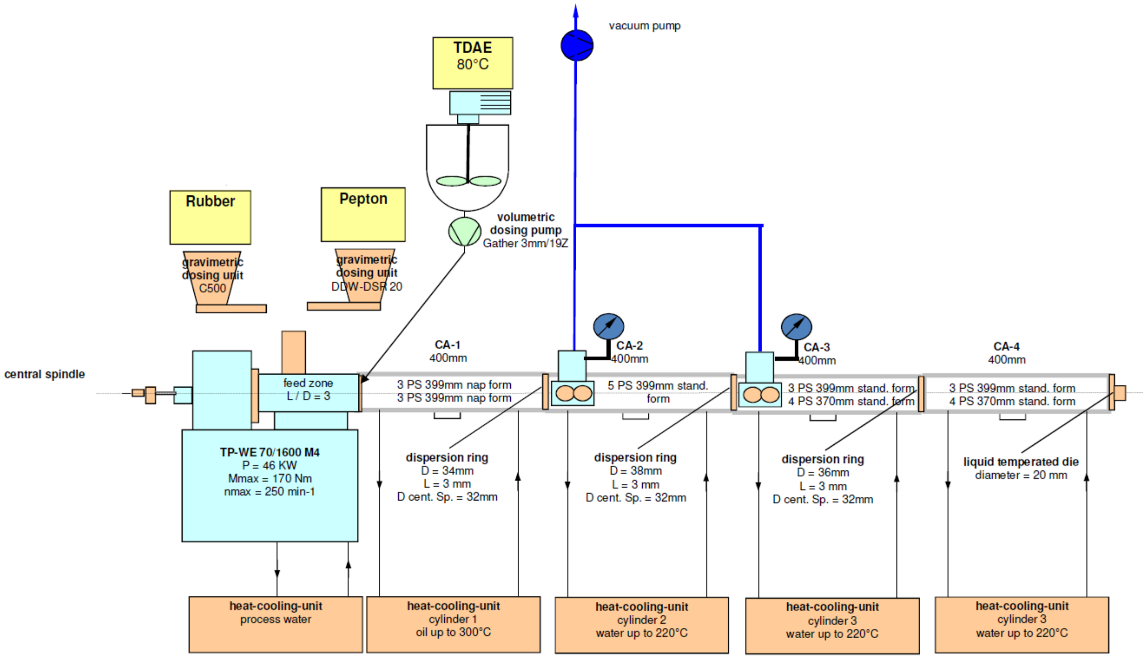


Figure 11: Design setup-11 for the planetary roller extruder

Trial-18 (setup-11): The material outlet temperature after module 4 is now around 180^{0}C. The particle size is smaller due to the higher pressure in front of the die, and the material looks very dry instead of sticky.

To increase the stickiness of the rubber when coming out of the extruder, the die opening diameter was even more reduced to 14mm as shown in Figure 12.

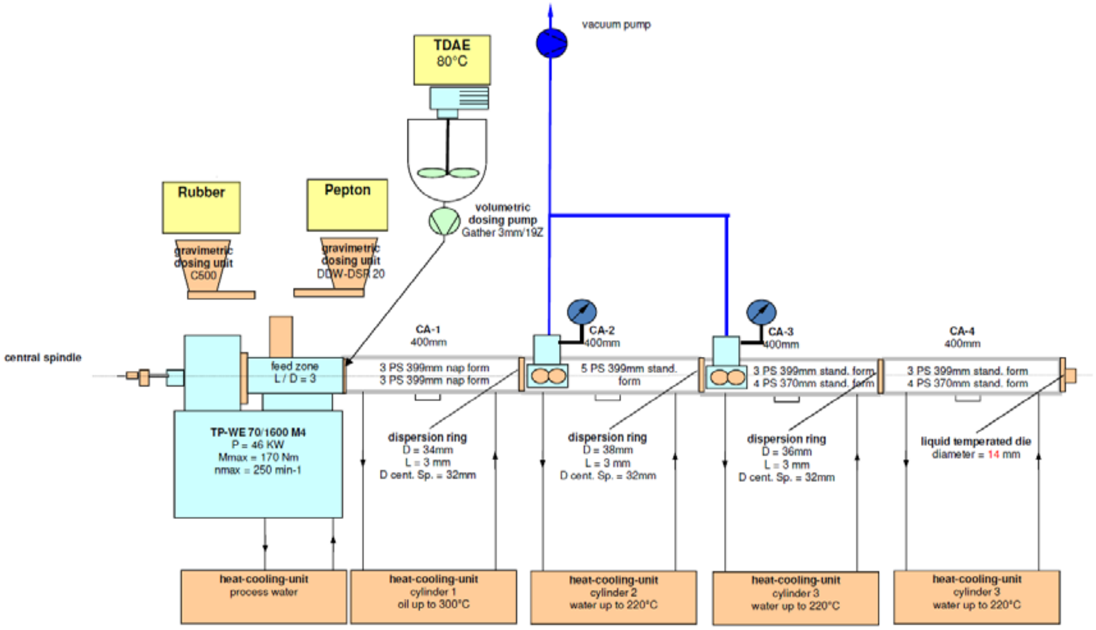


Figure 12: Design setup-12 for the planetary roller extruder

Trial-19 (setup-12): With the smaller die, the material is less consistent. The temperature of the 4th module was decreased to lower the outlet temperature, which was increased by the high pressure buildup. However, this was not effective; still the temperature raised.

Trial-20 (setup-11): Now again a larger temperated die was used to reduce the outlet temperature. Besides, a higher concentration of DBD was used for better devulcanization efficiency. The effect was that a more stable process was achieved.

Trial-21 (setup-11): Without any DBD, the pressure buildup in the 1st module was higher and also the material outlet temperature was higher.

Now the dosing point of DBD was changed from the main feed to the side feed in the 2nd module as shown in Figure 13. With this design, the oil can be incorporated first and the DBD is more effectively blended with the rubber.

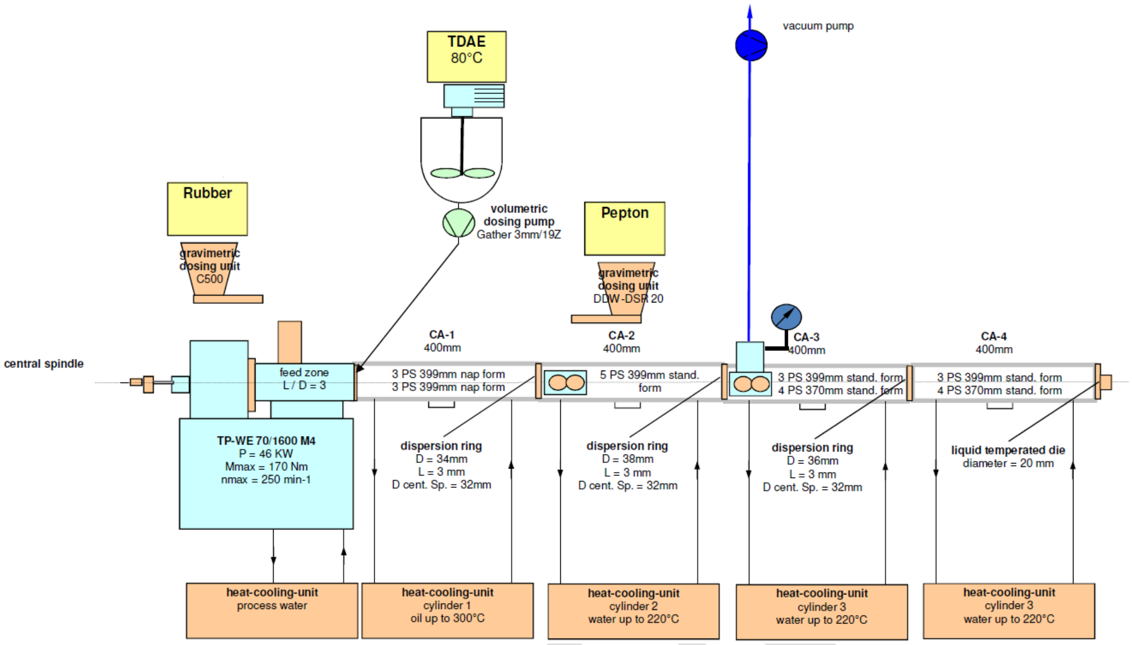


Figure 13: Design setup-13 for the planetary roller extruder

Trial-22 (setup-13): A very high torque was recorded for setup-13, and moreover the fluctuation of the pressure at the 2nd dispersion ring was so high that it was not possible to get a stable vacuum. Therefore the design setup was switched back to setup-11.

Trial-23 (setup-11): The raw material was changed to a finer rubber powder quality of 0.8-2.5mm tire crumbs. With this material, the pressure in the 1st dispersion ring was high. The set module temperature was therefore reduced from 180^0C to 150^0C to prevent overheating of the material.

Trial-24 (setup-11): Without DBD, the pressure and the temperature at the 1st ring are very high.

Trial-25 (setup-11): With premixed material, the temperature in the 1st module is still high like with the fine material, but the material at the extruder outlet is lot more compact.

Trial-26 (setup-11): The screw speed was increased to 100rpm to find the maximum output. However, with the higher screw speed, it was not possible control the mass temperature.

Trial-27 (setup-11): The screw speed was decreased again to 40 rpm for better control of the temperature and to increase the dwell time. As a consequence, the output was low and the pressure in the 1st ring was high.

Some design rules for the extruder setup:

- In the first module, the screw speed should be average and the barrel temperature low for a good grinding effect and low stickiness. Using just one module, the setup is rather insensitive to a change in extrusion parameters.
- Increasing the barrel temperature, smaller dispersion ring diameter, higher or lower screw speed (more shear, resp. higher residence time) only slightly influence the material temperature.
- Addition of extra modules result in a drastic increase in material temperature.
- The number of spindles has a significant influence on the residence time due to the variation of the free volume.
- Higher screw speeds for higher throughput goes at the expense of temperature control.
- Working with a die increases the pressure at the extruder outlet and results in a finer material. The diameter of the die has a strong influence on the material outlet temperature.
- Working without DBD increases pressure and temperature especially in the first modules.
- Later dosing of DBD resulted in high torque values and an unstable process in the first modules.
- Finer starting material results in torque increases and high temperatures.

It is important to note that the trends found here might be different if the setup of the extruder modules is basically different.

In-depth analysis of the devulcanizates

3.1 Mooney viscosity

The Mooney viscosity values of the devulcanizates from trial-10 on, for two or more modules, are depicted in Figure 14. Visual inspection and a high outlet temperature lead to the conclusion, that the devulcanizates from Trial-13 to Trial-16 are of lower quality.

A low Mooney viscosity in the range of the viscosity of virgin compounds is required for easy processing of the devulcanizates and also for better blending with virgin polymers. The values should be in the range of 60-70 MU.

The Mooney viscosities of the devulcanizates decrease in the order of

Trial- 20 < 19 < 25 < 22 < 23

Trial-10 and 11 have low Mooney viscosities as the material was heated to a greater extent by setting a higher module temperature for the 2 module set-up. To lower the output temperature, a larger stop ring was used with a diameter of 38mm for Trial-12, resulting in higher Mooney values indicating that the material was less effectively sheared. The 4 module setup starts from Trial-18, their Mooney viscosity values generally vary around 102-115 MU with not much differences. This indicates that insufficient devulcanization is happening, very probably due to low residence times.

Values here are higher than the values shown in Chapter 4, as the measurements here are done with a large rotor.

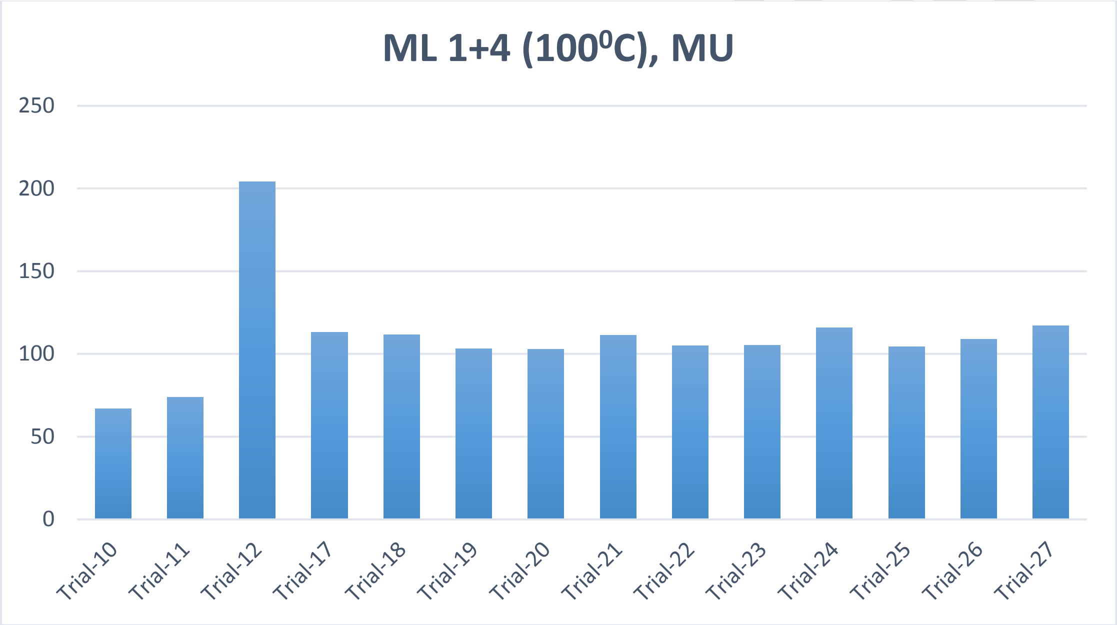


Figure 14: Mooney viscosity of the devulcanizates

3.2 Sol content and Crosslink density

The sol content and the crosslink density of the different devulcanizates are tabulated in Table 4. The ideal devulcanizate will have a low sol content and a high decrease in crosslink density. The trial-12 devulcanizate has very low sol content and low decrease in crosslink density as it was ineffectively devulcanized due to the large diameter stop ring. The decrease of the crosslink density is higher for an increased DBD dosage (trial-26) and also for devulcanizates with a high residence time caused by a low screw speed of 40 rpm (trial-27). The devulcanizates of trial-20 and 26 have high loadings of devulcanization aids of 7.5% of DBD, but trial-26 has a higher decrease in crosslink density compared to trial-20. This is caused by a high DBD dosage. In trial 20, a higher energy input by increasing the barrel temperature results in chain fragment recombination rather than breaking the crosslinks.

The process conditions for the devulcanizates of trial-20 and 21 were:

Trial-20: 180/200/150/130^{0}C (80 rpm)

Trial-26: 150/150/150/150^{0}C (100 rpm)

(Here all four module temperatures are indicated with slash marks and those in brackets indicate the screw speed.)

Usually, replasticizing without devulcanization aids (Trial-21, 24, and 27) requires a high energy input (i.e., shear and high temperature). The presence of process oil during devulcanization is to increase the plasticity of the matrix to effectively target the crosslink sites. The low particle size material (0.8-2.5mm) in the Trial-23 devulcanizate has a lower crosslink density decrease since the applied shear is significantly lower for the powder than for the granulate.

Table 2: Sol content and decrease in crosslink density of the devulcanizates

Batches	**Sol Content, %**	**Decrease in crosslink density, %**
Feedstock	5.7	0
Trial-10	29.6	28
Trial-11	24.4	37
Trial-12	18.9	29
Trial-17	20.4	34
Trial-18	23.9	36
Trial-19	22.0	39
Trial-20	25.1	17
Trial-21	23.1	40
Trial-22	23.9	39
Trial-23	25.2	35
Trial-24	23.6	35
Trial-25	24.3	39
Trial-26	24.6	42
Trial-27	22.2	43

The sol contents versus decrease of crosslink density of the devulcanizates are shown in Figure 15. As already mentioned, the ideal devulcanizate will have low sol content and high decrease in crosslink density. Only Trial- 19, 21 and 27 satisfy this condition.

Trial-19: 180/170/150/100^{0}C (80rpm) (with devulcanization aid-5% & oil-5%)

Trial-21: 180/200/150/130^{0}C (80rpm) (without devulcanization aid, only oil 5%)

Trial-27: 150/150/150/150^{0}C (40rpm) (without devulcanization aid, only oil 5%)

It is conclusive that a reduced outlet temperature and low energy input by shearing play an important role in decreasing the sol content and maximizing the decrease in crosslink density. What is astonishing, is that the devulcanizate without devulcanization agent also shows these characteristics.

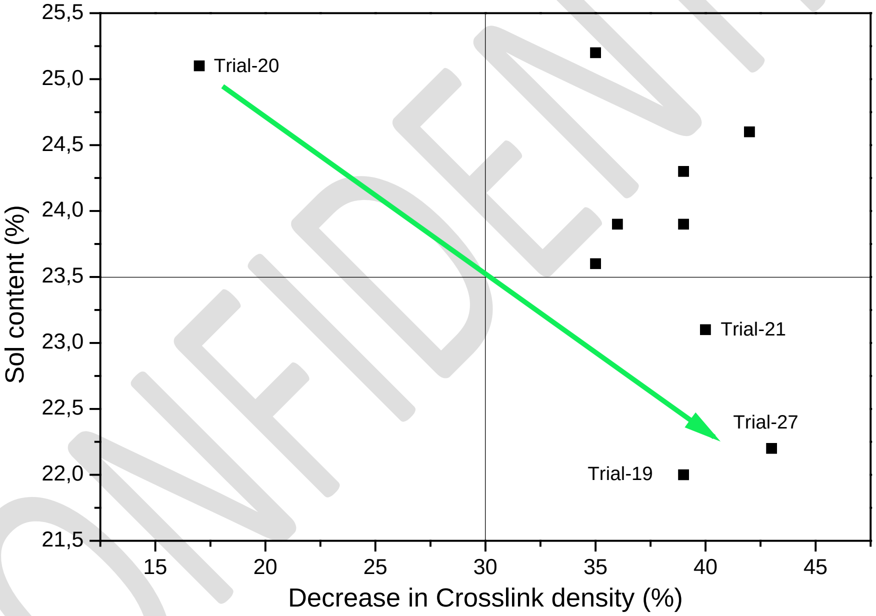


Figure 15: Sol content versus decrease in crosslink density of the devulcanizates

3.3 Curing curves

The rheo curves of the devulcanizates mixed with the curing system are plotted in Figure 16. The delta torque values obtained from the rheo curves (Figure 16) are shown in Figure 17. This property represents the re-vulcanization ability for the devulcanizates, and is higher for devulcanizates without devulcanization aids (Trial-21 and 27, only oil alone). This leads to the conclusion that the devulcanization aid consumes active sites, necessary for re-vulcanization. A higher amount of DBD added during the devulcanization process (Trial-20) further decreases the delta torque. The devulcanizate of Trial-26 has also a higher dosing of DBD, however it at the same time has a higher delta torque as it was extruded at higher screw speed, thus lower residence time, not giving enough time for the DBD to react completely.

Trial-21: 180/200/150/130^{0}C (80rpm) (without devulcanization aid, only oil 5%)

Trial-27: 150/150/150/150^{0}C (40rpm) (without devulcanization aid, only oil 5%)

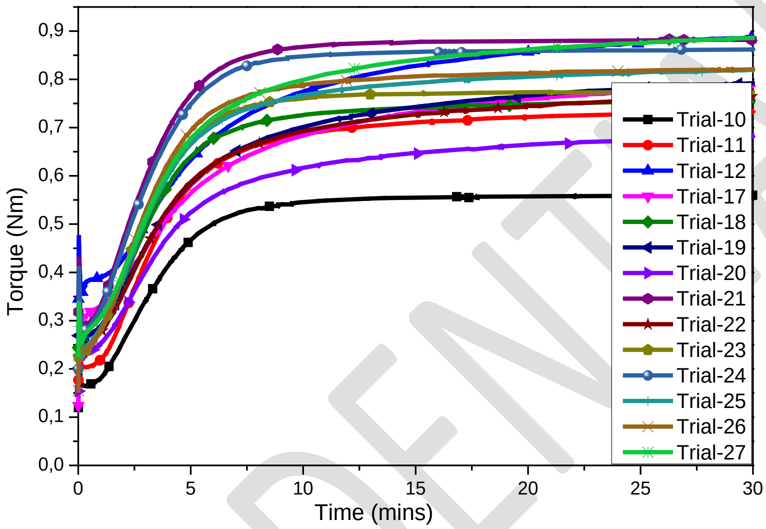


Figure 16: Rheo curves of the devulcanizates

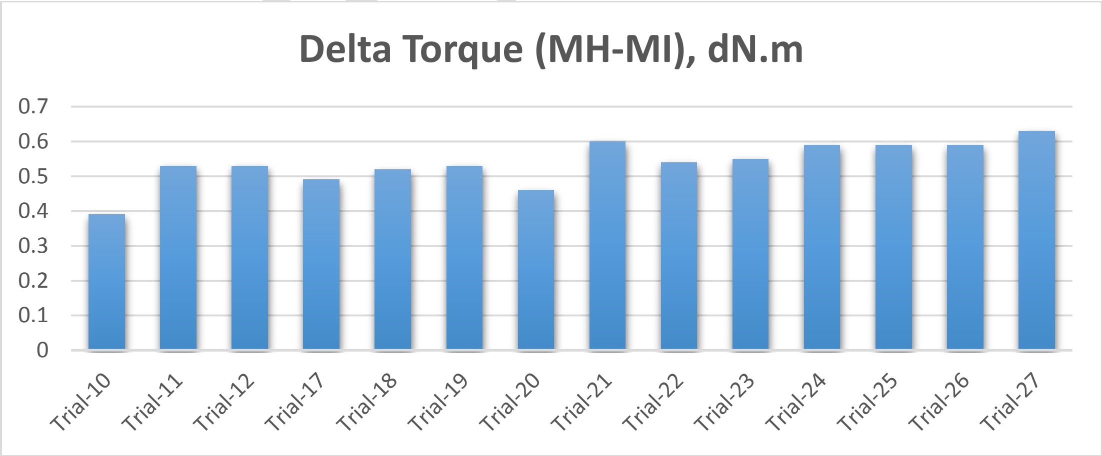


Figure 17: Delta torques of the devulcanizates from rheo curves in Figure 16

3.4 Tensile properties

The tensile strength values of the devulcanizates are plotted in Figure 18. The devulcanizates without DBD and with only oil (Trial- 21, 24, 27) showed a higher tensile strength, which can be explained from the higher delta torque values as already seen in Figure 17. Trial-26 (with a higher DBD loading of 7.5%) also shows higher tensile strength which is unusual when compared to the Trial-20 devulcanizate with same amount of DBD. This confirms the effect of the short residence time due to the higher screw speed used in Trial-26 as the polymer chain degradation is less.

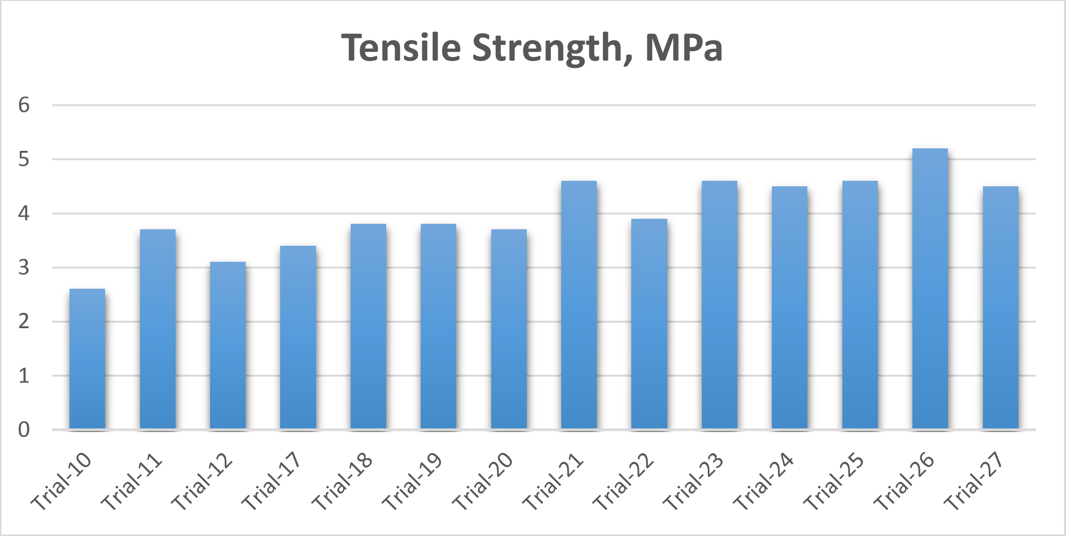


Figure 18: Tensile strength of the devulcanizates

3.5 Modulus and Hardness

Modulus at 100% elongation and hardness values of the devulcanizates are plotted in Figure 19 and 20 respectively. Modulus is correlated to the hardness measured at higher strains. Devulcanizates without DBD, only with oil (Trial-21 and 24) show higher hardness and modulus. The devulcanizate from Trial-27 does not follow this trend as it was sheared to a greater extent by using a low screw speed. Trial-20 (with a high DBD loading) initiates a high degree of chain cleavage resulting in lower hardness and modulus. Devulcanizates from Trial-23 with a low particle size of 0.8-2.5 mm as starting material have higher moduli and hardness values combined with low tensile strength. This materials was processed at the conditions the of larger particle size material, signaling that it was not effectively devulcanized.

Trial-21: 180/200/150/130^{0}C (80rpm) (without devulcanization aid, only oil 5%)

Trial-24: 150/150/150/150^{0}C (80rpm) (without devulcanization aid, only oil 5%)

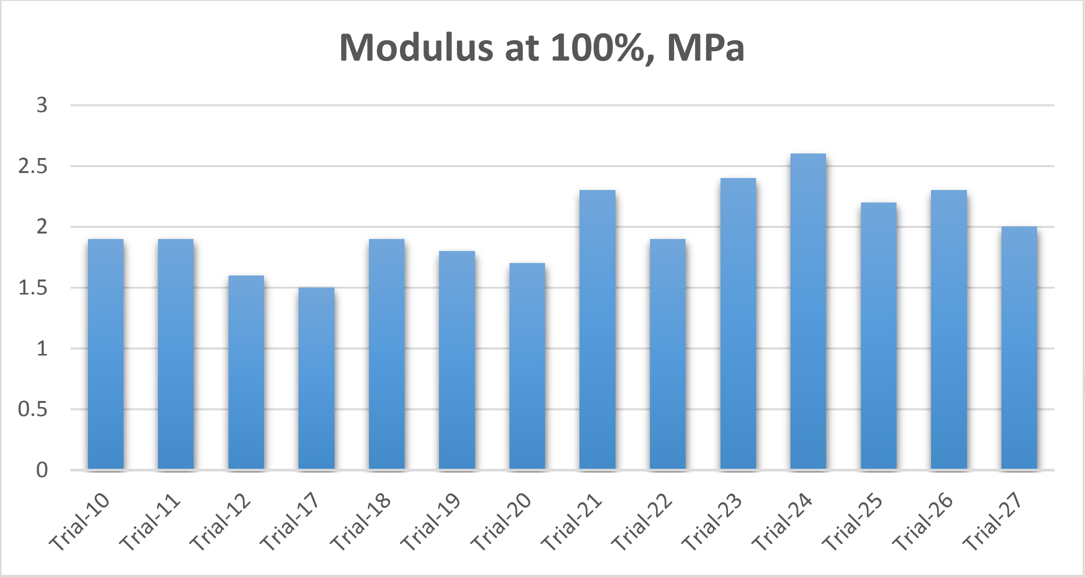


Figure 18: Modulus at 100% elongation of the devulcanizate

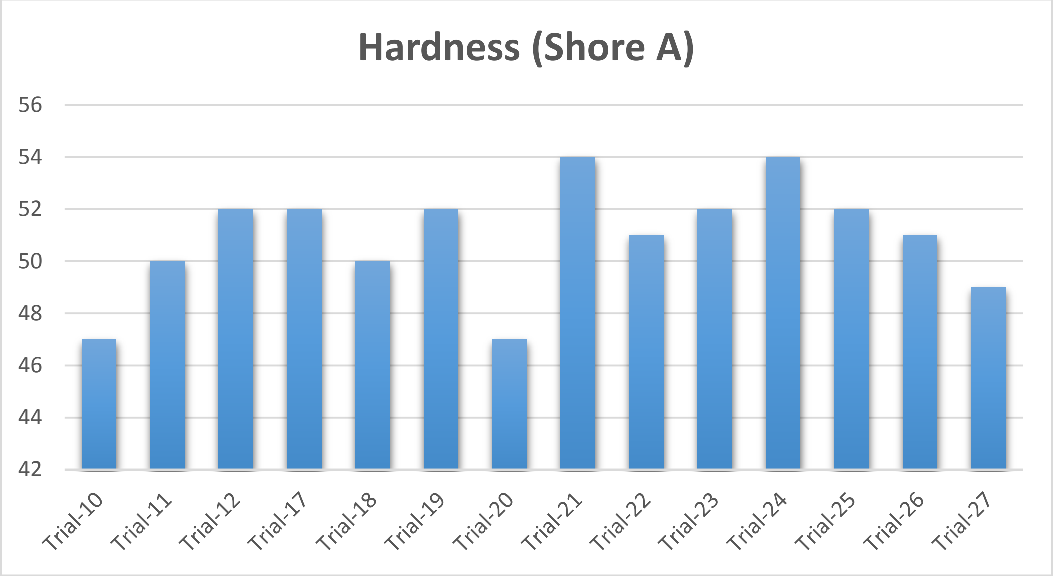


Figure 19: Hardness of the devulcanizates

4. Conclusions

When designing the extruder setup, the following rules have to be taken into consideration:

- For the devulcanization efficiency, the number of modules has the largest effect.
- Increasing barrel temperature, smaller dispersion ring diameter, higher or lower screw speed (more shear, resp. higher residence time) only slightly influence the material temperature.
- The number and length of the spindles is a way to adjust the residence time.
- The screw speed is effective in increasing the output, but critical for temperature control.
- A die at the extruder outlet increases the pressure and results in a finer material. The die diameter has a strong influence on the material outlet temperature.

For instantaneously mixing, when the devulcanization aids are fed into the planetary roller extruder together with the Ground Truck tire Rubber (GTR), 2 criteria need to be met:

- The material temperature in the first modules need at least to be equal to the melting point of the devulcanization aid.
- The blended material need to be transported easily to the subsequent modules.

Without the use of devulcanization agents, thus with the addition of only oil, a high energy input is needed to bring about effective plastification (reclaiming). Besides, the torque on the central spindle is very high.

A finer input material is not the solution to a better devulcanization.

Within the next trial session, the rubber granulate should be processed without devulcanization aid at low temperatures and low shear with the following module parameters: 150/150/150/1500C (40 rpm), similar to the process conditions of Trial-27 (5% TDAE oil). However, the high torque on the central spindle sets a limit to these process conditions.

Devulcanization aids not only increase the devulcanization efficiency but also lower the main chain modification by end capping the free radicals; therefore devulcanization aids should further be used at a moderate dosage of 5% or lower to retain a high curing activity.

Application study for the devulcanizate processed on the newly designed extruder line

Studying the properties of Devulcanized and Ground Rubber blends with virgin Natural Rubber

Introduction:

With the shortage of rubber materials in the aftermath of the world war II, Reclaim Rubber emerged as the third source of rubber hydrocarbon after natural rubber (NR) and synthetic rubber. But with the cheap crude oil prices in the 50's and 60's, and huge production of synthetic rubber initiated the demise of the reclaimed rubber industry in the Western World (Rubbermachineryworld, 2016).

By the late 70's, barring one or two reclaim rubber producers almost all manufacturers ceased to exist in the developed nations. After 2005, with the Chinese economy clocking at more than 10% GDP growth annually (GDP- Gross Domestic Product, which is the total market value of all final goods and services produced within the country annually), there was a concern worldwide about a possible shortage of natural and synthetic rubber (Historical GDP of China, 2016). The prices of natural and synthetic rubber along with the crude oil price began to rise rapidly. In addition, with the adverse effect of global warming, several countries became conscious about sustainability and environmental degradation. (Rubbermachineryworld, 2016)

Researchers around the world since then have been highlighting the role of reclaimed rubber from the point of view of sustainability and as an environmentally friendly raw material. However in recent times, the prices of natural and synthetic rubber crashed due to surplus availability. For instance, the current lower price of Natural Rubber is caused by two reasons: one due to stagnation of the Chinese economy, which is the largest consumer of Natural Rubber and thus causing significantly lower demand, and the other one being the larger plantations of Hevea trees in the tropical Asian countries. Especially Thailand, world’s largest producer of Natural Rubber latex, introduced governmental measures to improve the productivity in 2006-2007, and also the higher prices for Natural Rubber latex at that time made the people to follow the crowd (Chandrashekar, 2014). As for synthetic rubber, after the Western World removed the sanctions over the nuclear issue of oil rich countries, in 2014 Iran meant to recapture lost oil market by pumping in more oil; however, this led to cheaper oil prices cutting down the manufacturing cost of synthetic rubber production (Economic Times, 2016). Ultimately, there are currently fewer incentives for using more reclaim rubber despite of it being a more environmentally friendly raw material.

With reclaim rubber being eyed as a cheap filler, the extra edge offered by Devulcanized Rubber compounds with the improvement in mechanical and performance properties makes it stand out in the current scenario.

The current study tries to explore the potential of the devulcanized material processed in the newly designed extruder process. However, as the process design was not completed at the time when the application study was done, a preliminary, not fully optimized devulcanizate was used. The myth or the science behind the improvement of the properties offered by the devulcanized rubber against the ground or reclaimed rubber by blending with virgin rubber is analyzed. During this study, recycled truck tire rubber was blended with a compound based on Virgin Standard Malaysian Natural Rubber (SMR-10). The Ground Truck tire Rubber (GTR) is just size-reduced to 0.8-2.5 mm rubber crumb. This size-reduced Ground Truck tire Rubber (GTR) is then used as the starting material for the mechano-chemical devulcanization process in a planetary extruder to produce Devulcanized Rubber Compound (DRC).

2. Experimental

2.1 Materials

The Natural Rubber used in this project was Standard Malaysian Rubber with a dirt content of around 10% (SMR-10), and devulcanized rubber was prepared through mechano-chemical devulcanization in an Entex Planetary Extruder with the Ground Truck tire Rubber (GTR) mixed with 5 % devulcanization aid (2,2'- dibenzamido diphenyldisulphide- DBD, Thomas Swan & Co. Ltd., United Kingdom) and 5 % process oil (TDAE oil, Hansen & Rosenthal, Germany). The Ground Truck tire Rubber was supplied by RUMAL, with a particle size of 0.8-2.5 mm. The other compounding ingredients were carbon black (CB, N330, Vulcan 3, Cabot), highly dispersible silica (Ultrasil 7005, Evonik, Germany), N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD, Lanxess, Germany), TDAE oil (Hansen & Rosenthal, Germany), microcrystalline wax (MC Wax, Sasol, The Netherlands), zinc oxide (ZnO, Flexsys, The Netherlands), stearic acid (St. Acid, Flexsys, The Netherlands), N-cyclohexyl-2-benzothiazole sulfenamide (CBS, Flexsys, The Netherlands) and sulfur (Merck), all of industrial grade.

2.2 Compound composition for the DRC - virgin rubber blends:

The recycled tire rubber already contains constituents like carbon black, oil etc., their content in the blend with the virgin Natural Rubber batch needs to be made constant before comparing the properties between different blend batches with recycled rubber against the virgin rubber.

The results of a TGA analysis as shown in Figure 1 allows estimate the concentration of the following constituents from Table 1:

Table 1: Composition of the Devulcanized rubber crumb

Different Components	**%**
Oil	11.6
Polymer	54.0
Carbon Black	30.4
Ash	4.0

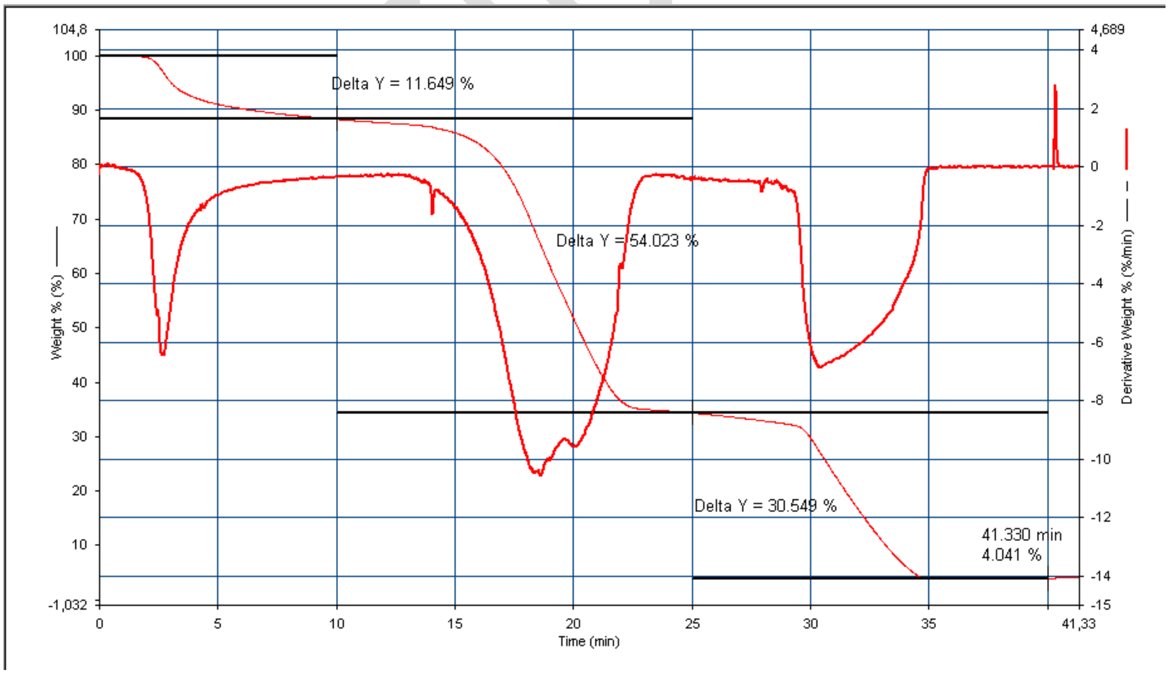


Figure 1: TGA analysis of devulcanized rubber compound (Perkin Elmer TGA-7: heating rate: 20^0C per minute and switched to oxygen at 620^0C)

The adjusted formulation is shown in Table 2. In the 80/20 Blend, 80 parts refers to the virgin Natural Rubber and the remaining 20 parts being the Devulcanized Rubber Compound (DRC) or Ground Truck tire Rubber (GTR) with the correction applied for the polymer content (TGA analysis of DRC and GTR were the same, with little variations in oil content of around 1 %; the added 5% of process oil is vaporized during the devulcanization process). In the case of the 50/50 blend, it is an equal ratio of both, virgin Natural Rubber and the polymer in the Devulcanized Rubber Compound (DRC) or in the Ground Truck tire Rubber (GTR) respectively. In truck tires, not much silica is used, generally it is less than 10 phr and no silane is used in the formulation.

Table 2: Formulations for the Virgin and blended rubber compounds.

	Virgin SMR-10 phr	**DRC/GTR Blend 8020 phr**	**DRC/GTR Blend 5050 Phr**
NR (SMR-10)	100	80	50
DRC/GTR		37	92.5
ZnO	5	5	5
St. Acid	3	3	3
Carbon Black (N330)	50	39	22
Silica (Ultrasil 7005)	8	6.5	4
TDAE Oil	10	5.7	-
6PPD	3	3	3
MC Wax	1.5	1.5	1.5
CBS	1.6	1.6	1.6
Sulfur	1.2	1.2	1.2

For instance for a 50/50 blend, 92.5 g DRC already contains 50 g elastomer, 28 carbon black, 11 g oil and 3.7 g silica.

The reported amounts of all the constituents such as carbon black, oil and silica have been deducted from the virgin batch to make the composition of the batches constant.

2.3 Preparation of Rubber compounds

2.3.1 Mixing:

Mixing of NR with devulcanized rubber was done using a Brabender internal mixer with 390 ml volume and a fill factor of 70% at 80 °C. For the blending of devulcanized rubber with the virgin natural rubber, the question arises how to prepare the blends of different rubbers to achieve a uniform viscosity at the end of the mastication stage. The mastication step is well pronounced for the Natural Rubber.

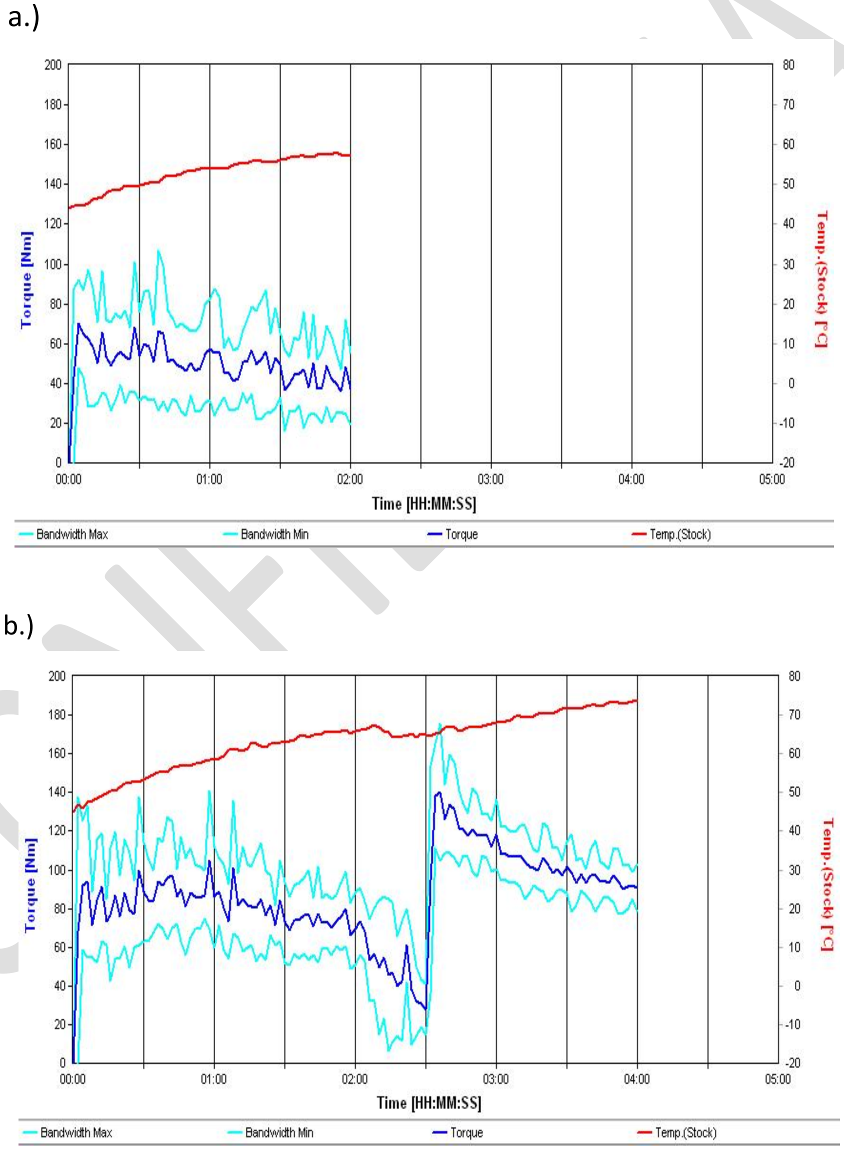


Figure 2: Mixing curves (Torque versus Time) for rubbers, a.) Virgin Natural Rubber at 100 phr, b.) 50 phr Natural rubber and 92.5 phr devulcanized rubber fed in 2 steps

The torque decrease and flattening of the torque is not seen when natural rubber was fed alone, since the chamber was only half filled; the material was not sheared enough as shown in Figure 2. So the Natural rubber along with the devulcanized rubber was fed together in a mixing process as described in Table 3, to completely fill the mixer and effectively shear the material inside the chamber, which is evident from Figure 3.

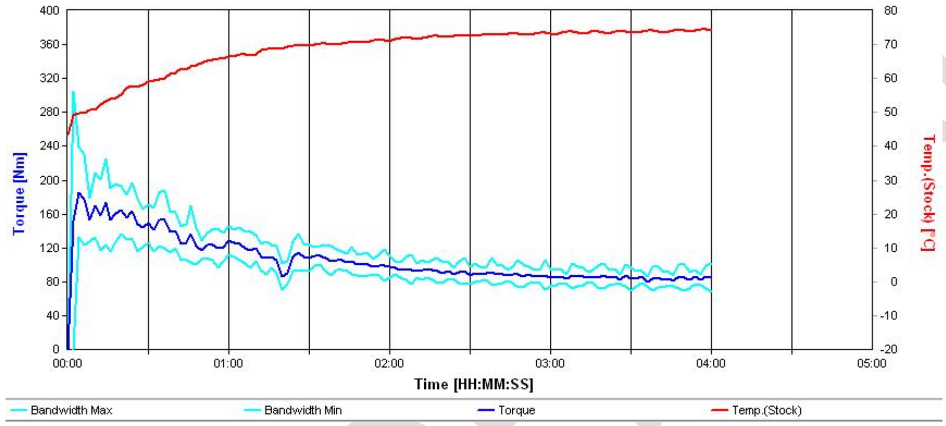


Figure 3: Mixing curve (Torque versus Time) for blending Virgin Natural and Devulcanized rubber together in a single step

Table 3: Mixing procedure

Time (mins)	**Action**
0	Add Virgin Rubber + DRC/GTR
1	
2	Add 6PPD
3	Half (CB + Silica + ZnO + St. Acid + wax + oil)
4	Remaining (CB + Silica + ZnO + St. Acid + wax + oil)
5	
6	Batch off

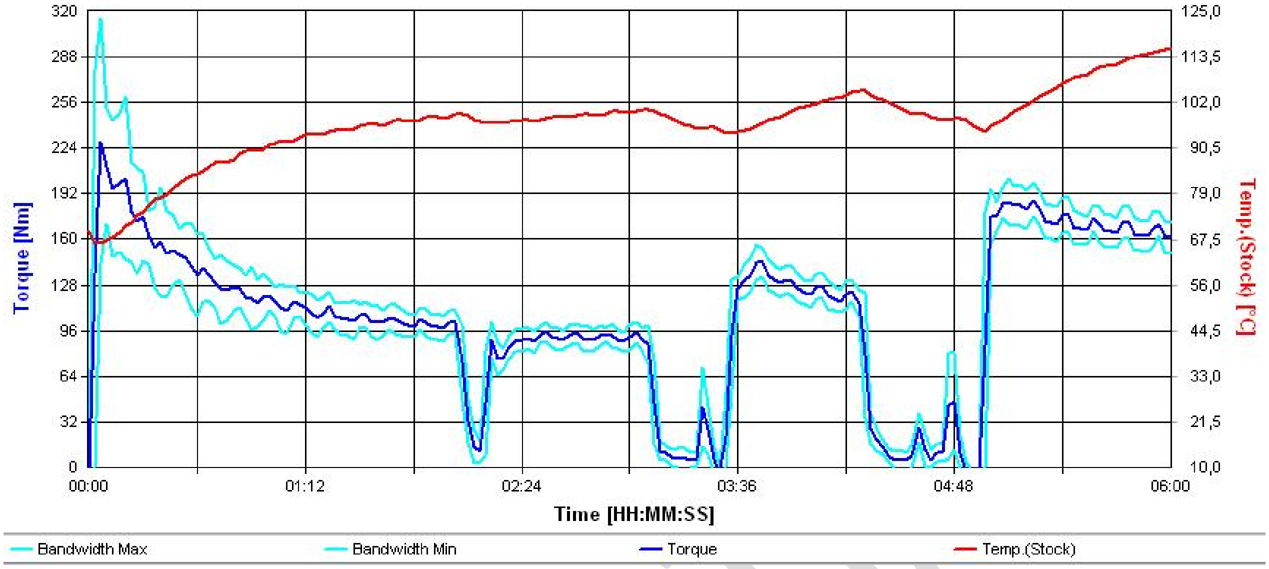


Figure 4: Mixing curve (Torque versus Time) for the Virgin Natural Rubber and Ground Truck tire Rubber (GTR) blend masterbatch

After mixing the compound at 80^0C for 6 mins (minutes) at 50 RPM (revolutions per minute), the compound was stored in the fridge for a day for maturation. The masterbatch was then mixed with the curatives (Sulphur + CBS) at a small nip gap for good dispersion in a 2-roll mill at room temperature for 5 mins.

2.3.2 Moulding:

The test specimens were cured in standard molds by compression molding in an electrically heated hydraulic press. The rubber samples were vulcanized up to their respective optimum cure time by taking into account the thickness of the specimens (i.e., optimum curing time + thickness like 1 min extra for 1 mm increase in thickness) at 140 °C temperature and 100 bar pressure. Moldings were cooled at the end of the curing cycle and stored in a cool and dark place for 24 hours and were used for subsequent physical tests.

2.4 Characterization:

2.4.1 Mooney Viscosity (ASTM D1646)

Mooney viscosity measurements were made using a Mooney Viscometer (MV 2000VS, Alpha Technologies) with the rotor rotating at an angular velocity of 2 revolutions per minute. The value is represented as ML(1+4) 100^0C, where

M → Mooney
L → Large rotor
1 → 1 minute pre-heat time
4 → 4 minute test time
100^0C → Test temperature

The Mooney viscosity measurement was followed by 2 mins stress relaxation at the end of the test by suddenly stopping the rotation of the rotor and measuring the power law decay of Mooney viscosity with respect to time.

The power law decay is given by Equation 1:

$$M = kt^{(-\alpha)} \qquad \textit{(Equation 1)}$$

where,

- M is the torque value in Mooney units
- k is the torque value at 1 second
- t is the time in seconds
- α is the rate of relaxation

In a log-log plot, this results in:

$$\log M = -\alpha \log t + \log k \qquad \textit{(Equation 2)}$$

The slope α generally gives an idea of elasticity and die swell based on the Mooney stress relaxation for the different rubber compounds.

A Mooney viscometer operates at constant strain and constant frequency. Since it is measured at just one shear rate, 1.6 s^{-1} (2 rpm), it's a so-called 1-point measurement.

2.4.2 Complex viscosity:

A frequency sweep was used to measure the viscoelastic properties of rubber with respect to time. Sinusoidal deformation is applied to the sample at constant temperature and amplitude of deformation. Complex viscosity values were analyzed via dynamic viscoelastic measurements performed at 100^0C by the Rubber Process Analyzer (RPA 2000, Alpha Technologies). The oscillation frequency was set in the range of 0.01-33 Hz at a constant strain of 0.56%. This strain was chosen in order to assure linear viscoelastic behavior during the test. The frequency-sweeps of cured specimens were followed by vulcanization at 140^0C in the RPA. The storage (G') and loss shear (G'') modulus were measured. The complex viscosities, η*, were then calculated by the following equations, when ω is the frequency in radians per second:

$$(\eta^*)^2 = (\eta')^2 + (\eta'')^2 \qquad \textit{(Equation 3)}$$

Where,

$\eta' = G''/\omega$ *(Equation 4)*

$\eta'' = G'/\omega$ *(Equation 5)*

2.4.3 Cure Characteristics (ASTM D2064):

The cure characteristics were determined using a Rubber Process Analyzer (RPA 2000, Alpha Technologies). The change in torque was measured at a temperature of 140^0C, for a frequency of 0.833 Hz and 2.79 % strain. The optimal vulcanization time considering the thickness of the sample as described in Chapter 3 was determined and used for press-curing the samples.

2.4.4 Payne Effect:

The Payne effect or filler-filler interaction of the carbon black reinforced masterbatch compounds was measured using an RPA 2000 at 100^0C, at a frequency of 0.5 Hz (Hertz) and varying strains in the range of 0.56 to 100%. The difference of storage moduli at low strain (i.e. 0.56%) and high strain (i.e. 100%) is reported.

2.4.5 Mechanical properties:

Tensile tests were carried out on dumb-bell shaped specimens (type 2) according to ISO-37, using a Zwick Z1.0 tensile testing machine. The tests were performed at a constant crosshead speed of 500 mm/min, using a load cell of 500N. The hardness of the samples was measured with a Zwick hardness tester, Shore A type, according to ASTM D2240.

2.4.6 Dynamic Mechanical Properties (DMA):

Dynamic mechanical analysis was performed on strips of 10 mm in width on a Metravib DMA+150 in tension mode. The isochronal frequency used was 10 Hz and the heating rate was 2°C/min with a dynamic load at 0.1% strain and a static load at 0.1% strain for a temperature sweep from -80^{0}C to +80^{0}C. At 0^{0}C, the loss angle correlates with the wet skid behaviour and traction of the tire, and at 60^{0}C, the loss angle correlates with the rolling resistance of a tire. For an ideal rubber compound, it should possess a high tan δ value at 0^{0}C, meaning that the viscous part is high compared to the elastic part, so the material can flow easily, make good contact with the wet road surface (wet grip) and can dissipate the energy input during braking. It should also possess a low tan δ value at 60^{0}C, so that the elastic content is higher than the viscous content, and thus the energy lost during deformation is low, decreasing the rolling resistance of the tire.

3. Results and Discussion

3.1 Mixing

The mixing curves for devulcanized and ground rubber blends with virgin rubber are shown in Figure 5. During the mastication stage, with the addition of devulcanized rubber and ground rubber, a torque increase is observed compared to virgin rubber, as the fill factor increases with the recycled rubber containing fillers and other rubber ingredients in addition to rubber alone. The loading of a higher percentage of ground rubber is a problem, as the rubber granulates are thrown off from the mixer as soon as the ram is opened since they are not a coherent mass. With the second stage loading of the filler and other additives, a step wise increase in torque is observed: with a higher carbon black loading, the compounds become stiff and the temperature increases requiring higher shearing action for better dispersion. At the end of the mixing stage, the viscosity is lower for the devulcanized rubber (50/50 blend) compared to ground rubber blends, as the devulcanized rubber was already exposed to high shearing conditions during the devulcanization process itself which turned it into a viscoelastic material. The low viscosity helps the carbon black to be easily incorporated in the matrix, the elastomer matrix can absorb the filler more easily, therefore the remaining mixing time can effectively be used for distribution and dispersion of the filler into the rubber matrix.

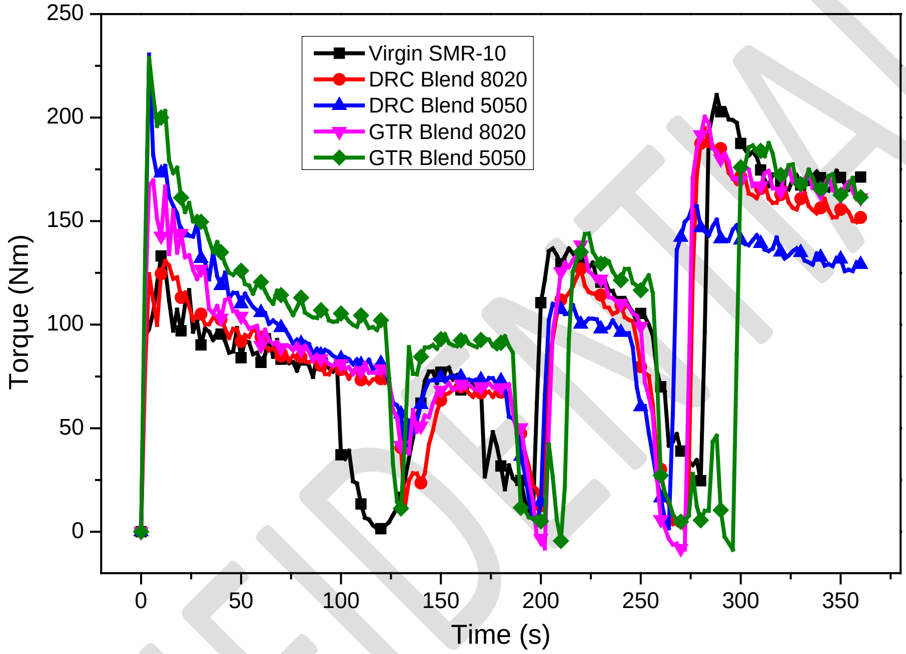


Figure 5: Mixing curve for Devulcanized and Ground rubber blends

3.2 Mooney viscosity

The initial Mooney viscosity of the devulcanized rubber is lower than that of the ground rubber blends: the devulcanized rubber has a higher content of low molecular weight chains acting as processing aid and also leading to a lower final Mooney viscosity. The Delta Mooney value quantifies the changes that occur in Mooney viscosity during the measurement and is used as a general indication of processability. The Mooney is higher for the ground rubber blends as these big size particles act as solid balls increasing the viscosity similar to the Einstein-Guth-Gold theories for viscosity or modulus increase with addition of particles (Einstein, 1911) (Guth, 1938).

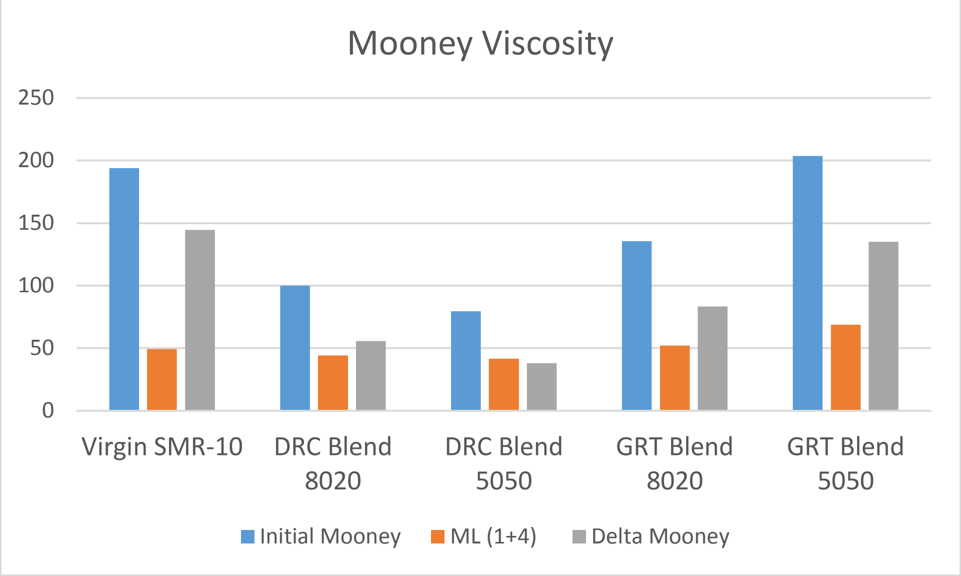


Figure 6: Mooney viscosity properties of the compounds

From the stress relaxation data in Figure 7, it is clearly visible that higher α values of blends with devulcanized rubber show a higher viscous content caused by the lower molecular weight polymeric chains: this fraction helps in plasticization. The lower α values for the ground rubber blends indicate a high elastic content.

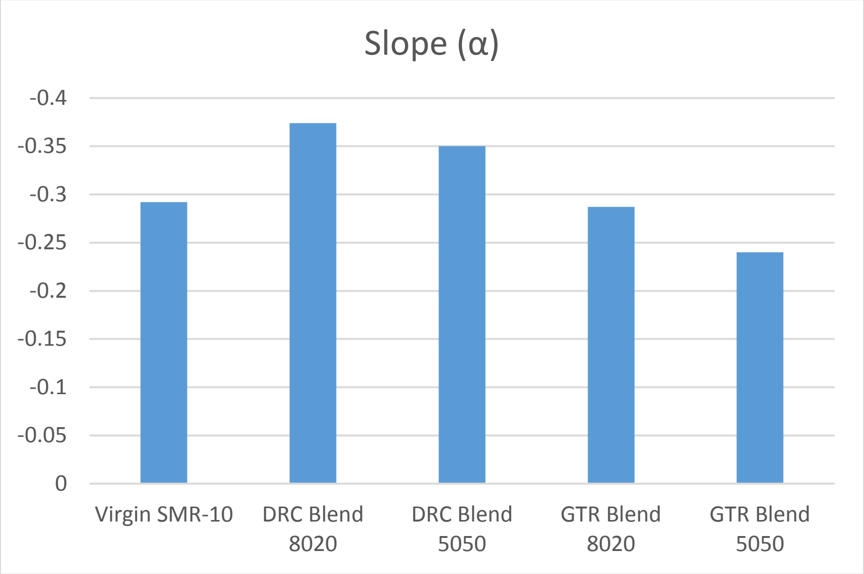


Figure 7: Relaxation rate constants (α) for the compounds

3.3 Complex viscosity

From the measurement of the complex viscosity in a frequency sweep as shown in Figure 8, it is clearly seen that Devulcanized rubber blends show a lower viscosity than the ground rubber blends: the former are much more sheared during the devulcanization process after the size reduction through the grinding process, verifying the Mooney viscosity data as shown in Figure 6. As for the ground rubber blends, the viscosity increases with increase in ground rubber content.

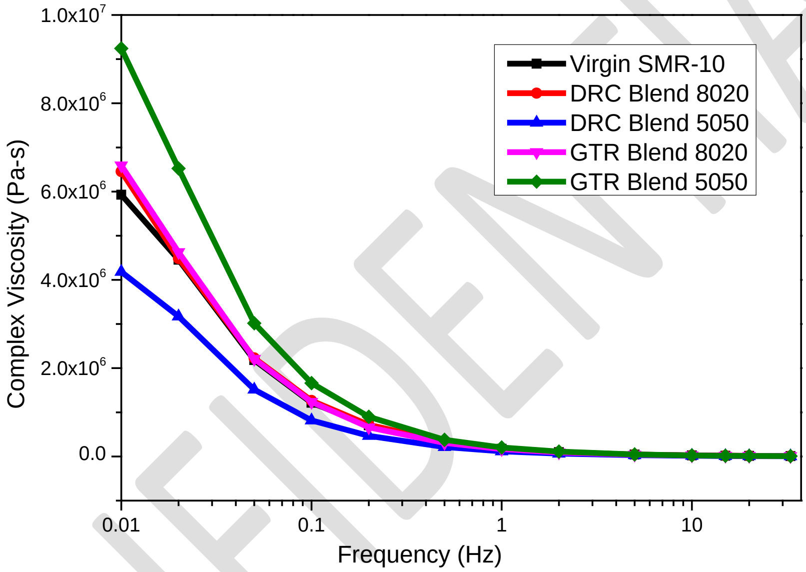


Figure 8: Frequency sweep of the compounds to measure complex viscosity

After the frequency sweep, the compounds were tested for their curing activity without addition of curatives in order to study if the remaining curing agents are still active in the devulcanized and ground tire rubber. A slight increase in torque was noticed (see Figure 9) after the curing reaction started, indicating that there is still a minor amount of active curatives.

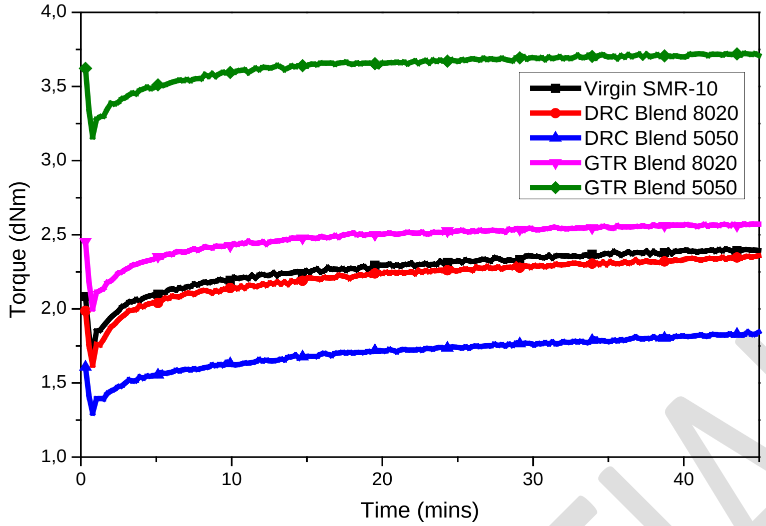


Figure 9: Rheo cure curves of the compounds before addition of curing agents

From the minimum torque values in the rheo graphs (Figure 9), which correlate with the complex viscosity data before addition of curatives, it is again indicated that the blend with devulcanized rubber has a lower viscosity than the one with ground rubber as the former is sheared, thus broken down, during the devulcanization process.

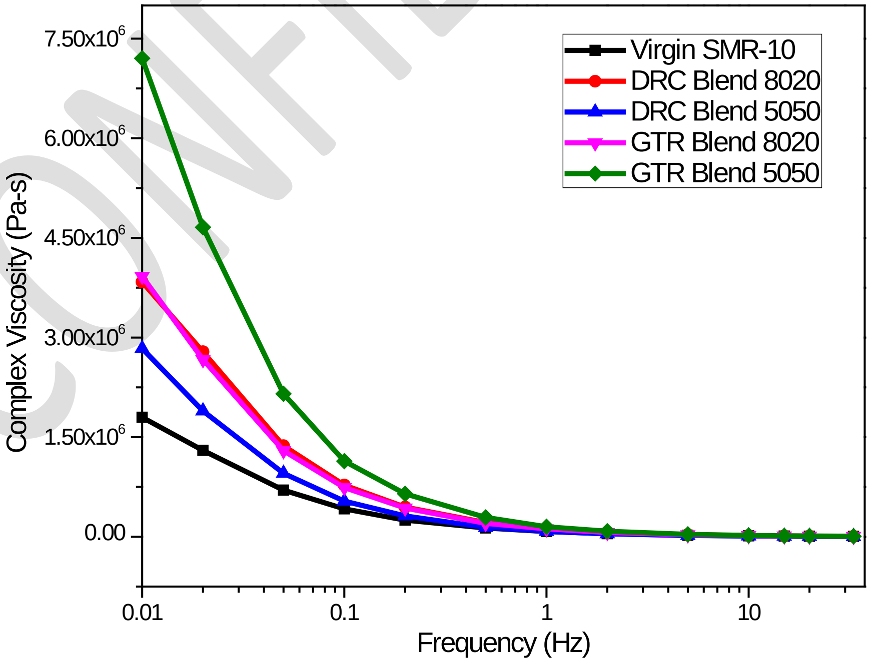


Figure 10: Frequency sweep of the compounds after addition of curatives

From Figure 10, the viscosity of DRC Blend 50/50 after 2 weeks is higher than that of the virgin Natural Rubber indicating that that the curatives present in the recycled rubber start to react slowly with the added curatives.

3.4 Payne effect

The Payne effect gives an idea about filler-filler interactions present in the filled rubber compounds. The Payne effect (Figure 11) was lowest for the devulcanized rubber blends with a higher blend ratio: the lower viscosity material i.e., lower molecular weight chains in the devulcanized rubber compared to the ground rubber blends, incorporates the filler particles easily. Therefore, the remaining mixing time is effectively used for uniform distribution and dispersion of the filler particles throughout the matrix. This can also be verified from the mixing curve of the compounds in Figure 5: the lower torque rise after carbon black addition is caused by easier incorporation of the filler by the devulcanized rubber, therefore the remaining mixing time is effectively used for distribution and dispersion of filler particles in the rubber matrix. This results in a lower Payne effect for devulcanized rubber mixed blends.

The shear modulus at higher strains is high for GTR blends as crosslinking is still present in the GTR leading to a higher modulus at higher strains.

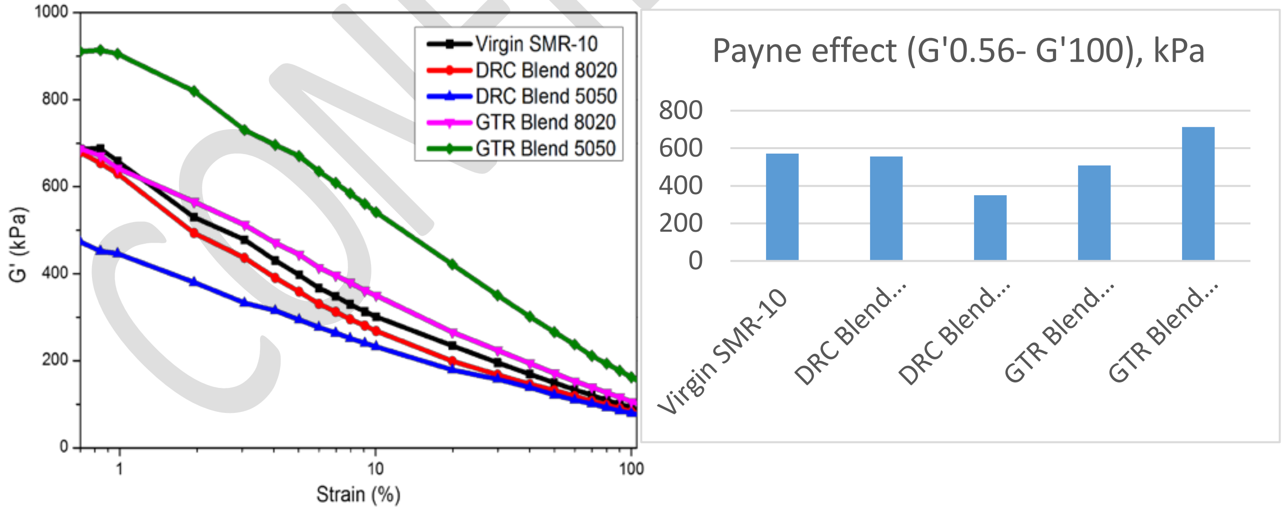


Figure 11: Payne effect for the compounds

3.5 Curing after addition of curatives

The devulcanized and ground rubber blends have a lower scorch and cure time compared to the virgin rubber compound (Figure 12). This is due to activation of remaining curing agents present in the recycled rubber by the addition of the extra curing system. In the post curing region for the devulcanized rubber blend, the slow increase of the torque signifies that the devulcanization agents also take part in the curing reaction leading to a marching modulus, as also inferred from the rheo curves in Figure 9, before the addition of the curing system.

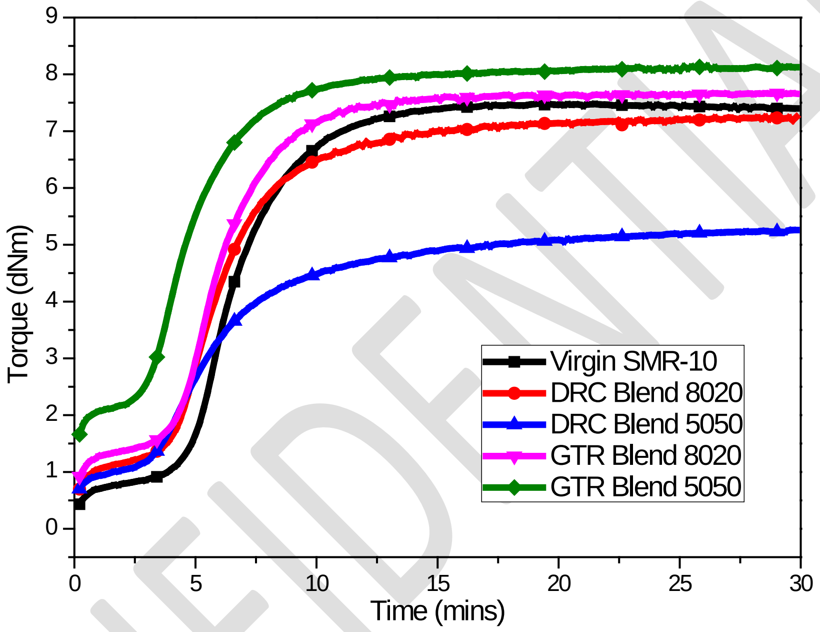


Figure 12: Rheo curves after addition of curatives

Devulcanized rubber reduces the crosslinking efficiency of the compound. This might be due to a consumption of active double bonds which are required for re-vulcanization (J. Dodds, 1983), as the devulcanization process attacks the double bonds as well. An indication of this effect is the lower Delta Torque in Figure 13, an indication of the curability of the rubber compound.

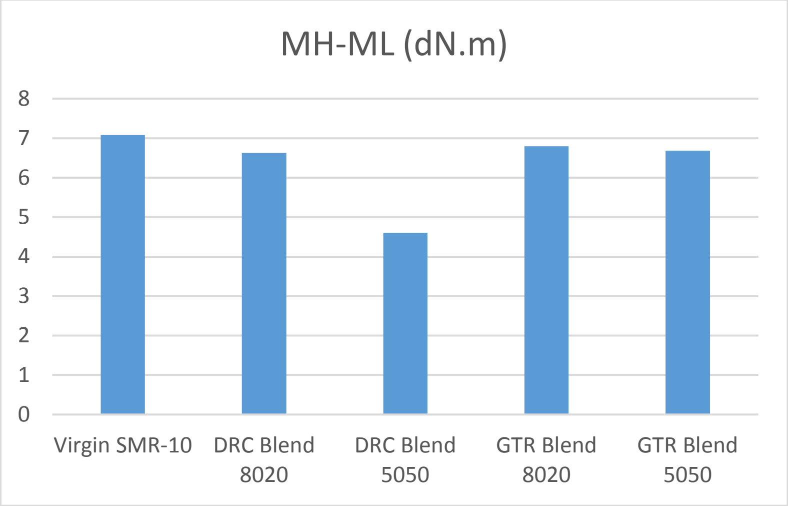


Figure 13: Delta Torque values for the compounds

The rheo curve was measured again after 2 weeks (Figure 14) to study the changes in curing activity with time. This gives information on the shelf life of the recycled rubber blends. Within this period, the scorch time was reduced and the minimum viscosity (Ml) increased compared to the virgin Natural Rubber compound, signaling the effect of active curing agents in the recycled rubber blends slowly getting activated, and another effect being the recombination of active chain fragments. Figure 15 shows a comparison of the curing activity of a DRC blend and the effect of time.

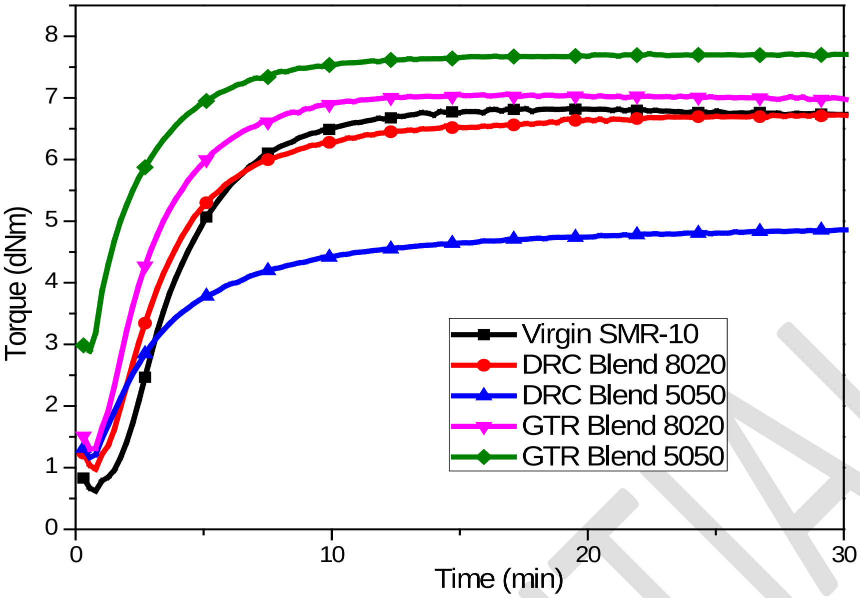


Figure 14: Rheo curves for the compounds after 2 weeks

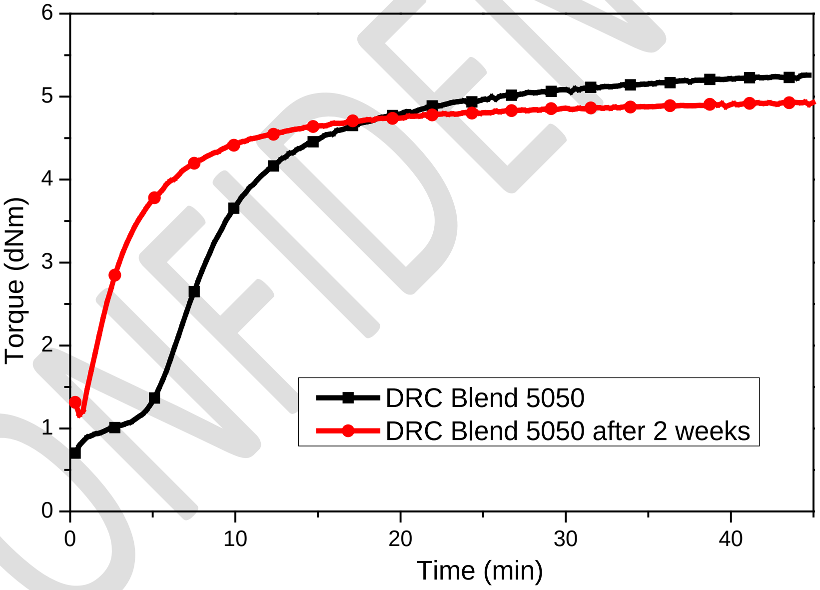


Figure 15: Rheo curves of a DRC Blend 5050 measured at different time intervals

3.6 Tensile properties

The tensile strength values of the devulcanized or ground rubber blends are lower compared to the virgin rubber compound as seen from Figure 16. The decrease in tensile strength is due to a weak interfacial adhesion between the recycled rubber particles and the matrix forming polymer. This is caused by the (still partly) crosslinked structure of the recycled rubber, as polymer chains are hindered for entangling with the molecules of the polymer matrix. The ground rubber as well as the devulcanized rubber contain crosslinked gel. When blended with virgin rubber, the gel remains as such without dispersing into the matrix of virgin rubber. This forms weak sites for stress dissipation into its surroundings (the continuous matrix), resulting in lower tensile stress (Adhikari. B, 2000). Elongation at break decreases with a higher percentage of devulcanized / ground rubber.

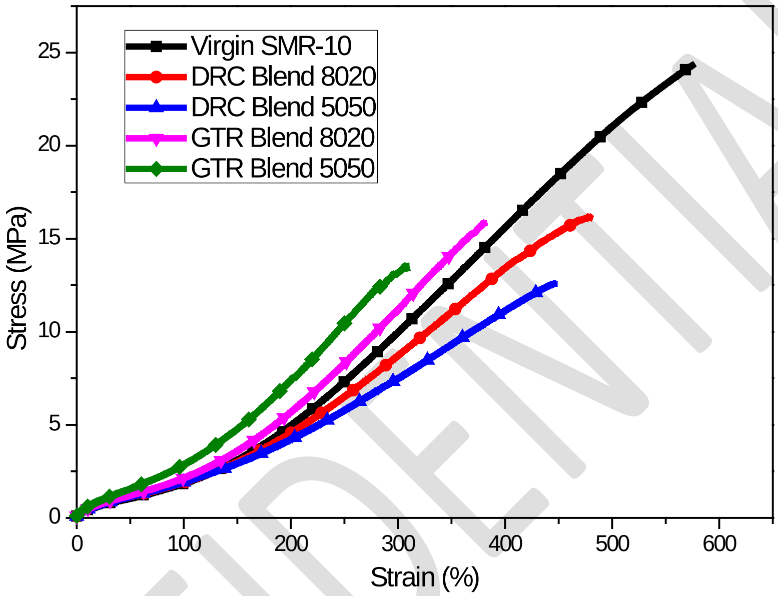


Figure 16: Stress strain properties of the cured materials

In the case of the virgin Natural Rubber vulcanizate, the rubber chains orient themselves in the direction of stretching and this creates crystallites (Strain Induced Crystallization). This contributes to high tensile strength and elongation by the crystallites tying together network chains. For revulcanized natural rubber with presence of a certain amount of main chain degradation and crosslinked gel, the formation of crystallites is inhibited. This lowers the elongation and tensile strength (Das, 2007).

From Figure 17, it is obvious that the modulus after vulcanization of blends with devulcanized rubber is lower compared to the virgin rubber compound due to generation of low molecular weight chains during the devulcanization process acting as a softener. The modulus of the ground rubber blends is higher than the modulus of the virgin rubber compounds. This is similar to the effect of non-reinforcing filler addition to a rubber compound.

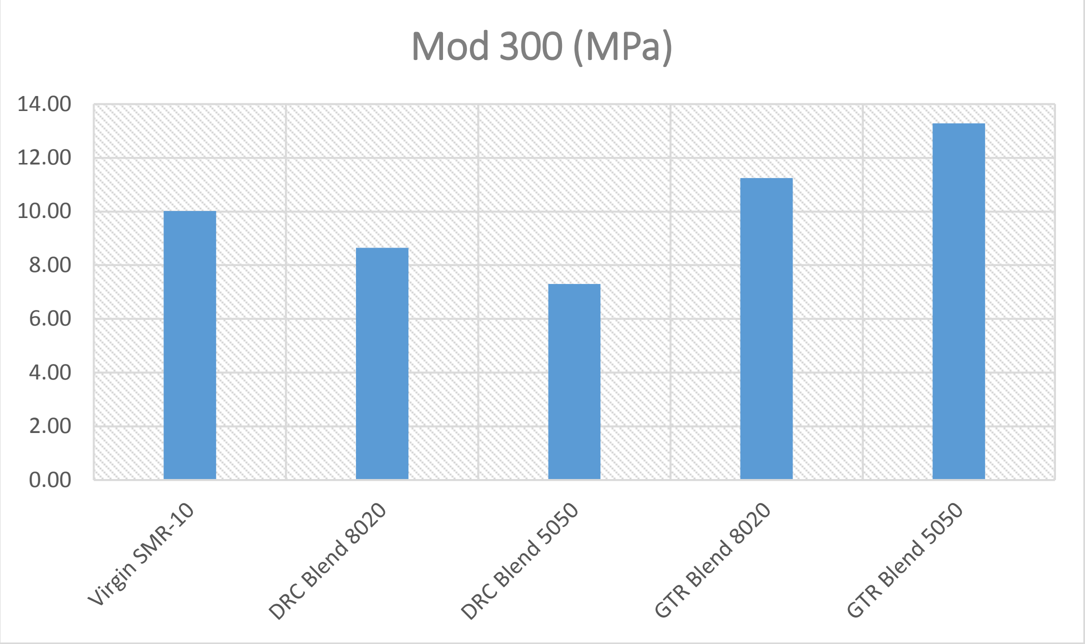


Figure 17: Modulus at 300% strain for the compounds

3.7 Dynamic mechanical properties

From Figure 18, it is clear that the tan δ peak shifts to slightly higher temperatures for higher recycled rubber loadings (i.e., for 50 / 50 blends), as the recycled rubber still contained some crosslinks and fillers which restrict the free chain movement of the virgin natural rubber molecules. The tan δ peak height decreases with increase in recycled rubber loading, as the recycled rubber reduces the elasticity due to its stiff network formation. The tan δ peak height decrease is higher for DRC compared to GRT blends at same blend ratio indicating the good dispersion of the carbon black caused by the DRC as seen from the Payne effect as well (Figure 11). The blend with devulcanized rubber has a high plasticity indicated by a high tan δ value at 60^0C. This is primarily due to high number of free chain ends being produced during the devulcanization process, which finally increases the rolling resistance. Both 50 / 50 blends show a high tan δ value at 0^0C which indicates better wet grip, thus better grip on a wet road. The blend with GRT also shows a low tan δ value at 60^0C, which is correlated to decreasing fuel consumption due to lower rolling resistance.

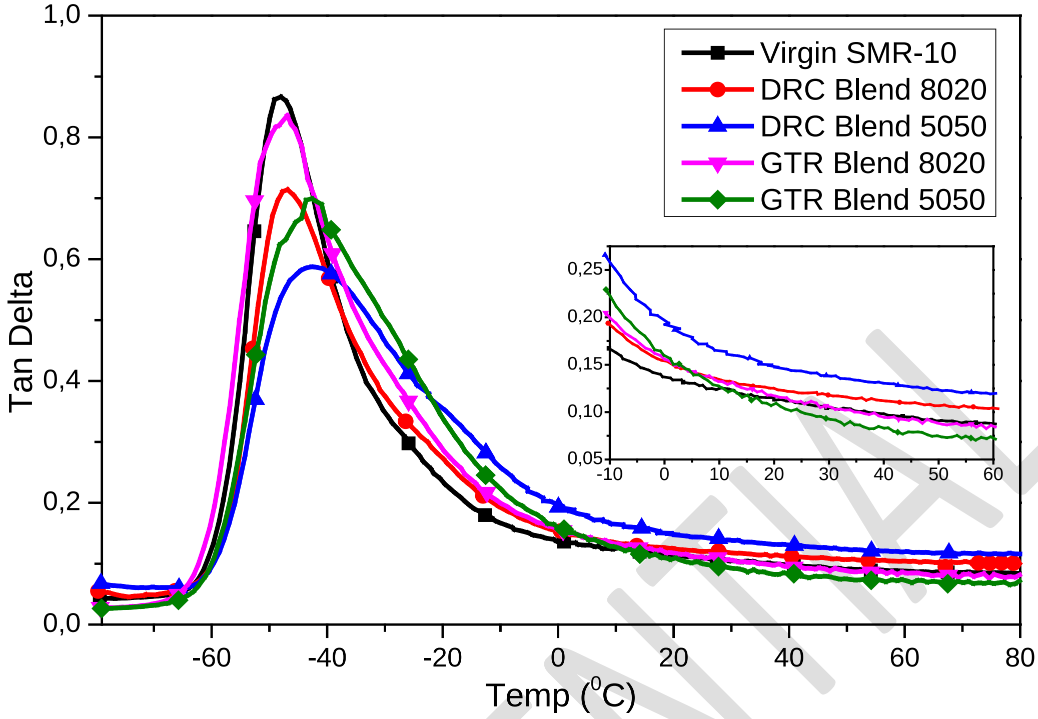


Figure 18: Temperature sweep - tan δ measurements for the different compounds

4. Conclusions

The use of devulcanized and ground rubber in blends with virgin Natural Rubber was studied. Neither devulcanized nor ground rubber in a blend with virgin natural rubber do bring a significant change in properties when the blend ratio is equal or below 20 %. Differences come to the fore when higher concentrations are used. This is partly caused by phase separation in the blend, and the only way for a better compatibility to reduce this phase separation is by reducing the particle size of the recycled rubber, both for the Ground Rubber Crumb and the Devulcanized Rubber Compound, for better homogeneity of the blend. Besides, the curing behavior is influenced by the presence of active remnants from the original curing system. In terms of stress strain properties, the devulcanizate has lower modulus values at higher strains, while the moduli at low strains are similar to the ones of the virgin natural rubber compound. Besides, the strain crystallization of the virgin natural rubber is disturbed for both materials, leading to a considerable decrease in strength properties compared to the natural rubber compound. The tensile strength reduction is caused by this effect rather than the properties of the recycled rubber. Dynamic properties are influenced in a way that the tan δ value at 0^0C is increasing when recycled rubber is added, indicating improvement in wet grip when this material is used in a tire tread compound.

The advantage of using the devulcanized rubber is the easier incorporation and dispersion of the fillers due to a higher amount of lower molecular weight polymeric material, as was seen in the Horikx plots in Chapter 3. Less energy is needed for the dispersion of the additives in the rubber matrix. However, the prime requirement of a viscosity match of the devulcanized rubber with the virgin natural rubber to make it easily blendable requires longer devulcanization times and/or higher temperatures. However, this bears the risk of polymer scission leading to poor mechanical properties in the current study.

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Summary

The amount of double bonds participating in the crosslinking process for vulcanizing rubber is around 5-10%. The major challenge for chemical devulcanization is the travel of the free radicals from the devulcanization aids to this 5-10% crosslinks present (for instance, in ebonite 32- 35% of crosslink sites are cured, higher curing inhibits elasticity) in the highly filled vulcanized rubber.

Another challenge in devulcanization process is the selective cleaving of the sulfur crosslinks. Due to desulfurization or network maturation of the semi-efficiently vulcanized rubber samples with a considerable amount of polysulfidic crosslinks , the latter get converted into mono- or disulfidic bonds during the service life of a tire. For these bonds, the process of selective cleaving by a mechano-chemical devulcanization process becomes ineffective. Figure 1 illustrates that extended heating of a vulcanizate has an effect on the sulfur rank and confirms that aging also severely effects the sulfur rank. This is a general problem related to devulcanization.

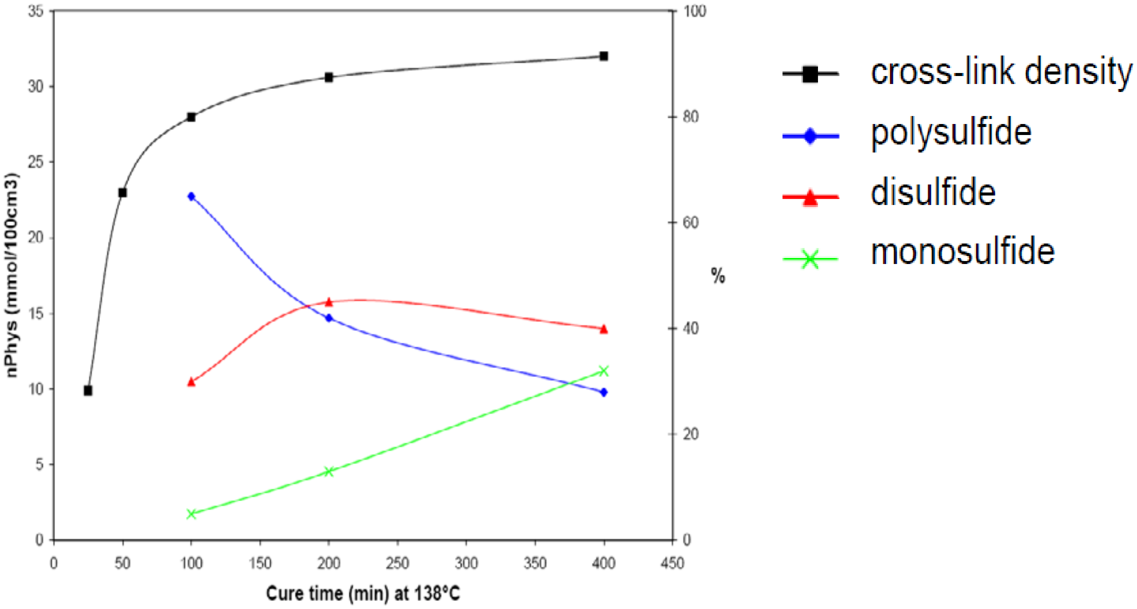

Figure 1: Duration of vulcanization; effect on sulfur rank (David R. Bauer, 2005)

For the devulcanization aids, the process of selective cleaving is a problem as it attacks both, the sulfidic crosslinks (decreases the crosslink density) as well as the double bonds (lowers re-curability). This was repeatedly noticed during re-curing of the devulcanizates.

The conclusion from Chapter 2, the literature study, was that the best practice for recycling of rubber is devulcanization, as it enables the rubber manufacturer to use a high-quality recycled material in larger quantities that commonly used. This chapter also highlights the various devulcanization aids for the design of an efficient and environmentally sound devulcanization processes for tire granulate.

Chapter 3 gives an overview of selected chemical compounds concerning their suitability as devulcanization aids. Dibenzamidophenyl disulfide (DBD), which is used as peptizing agent for the natural rubber mastication process, is the best choice for an alternative to DPDS for a mechano-chemical devulcanization process. However, the sol content of DBD devulcanizates is higher when applying the same process parameters as used for DPDS devulcanization, indicating a higher degree of polymer scission and resulting in a lower modulus. The degree of main chain breakdown can be lowered by decreasing the devulcanization process temperature in tune with the melting point of DBD.

Chapter 4 discusses the planetary roller extruder setup for the devulcanization process, in which the temperature settings of the extruder play a major influencing parameter for the devulcanization: It determines the efficiency of blending of separately added devulcanization chemicals with the rubber granulate, the degree of degradation of the material, and the onset and kinetics of the devulcanization reaction. For a good temperature control, the central spindle is more effective than the barrel. Other general design rules for the extruder setup deducted in this chapter:

- A moderate screw speed results in a sufficient residence time and a good temperature control.
- The higher the screw speed and the lower the temperatures, the more compact the devulcanizate is.
- For reducing the viscosity, standard spindles are more effective than nap spindles.

In a blend with a virgin compound, the addition of DRC results in a shorter scorch and curing time compared to the virgin compound, as it activates the remains of the curing agents still present in the rubber. The blends contain crosslinked gel originating from the devulcanized rubber; this makes it difficult to be dispersed in the virgin rubber matrix corroborated by higher viscosity during mixing. In terms of mechanical properties, testing the blends with virgin rubber is not discriminating.

In Chapter 5, the extruder setup of the planetary spindles was elaborated module by module to study the effect much more precisely and to better control the process. The residence time can be improved by lowering the screw speed, less spindles and short spindles in the module. Instantaneously mixing, when the devulcanization aids are fed into the planetary roller extruder together with the Ground Truck tire Rubber, two main criteria are required: The first one being the material temperature in the second module, which at least needs to be equal to the melting point of the devulcanization aid. The second requirement is that the rubber blended with the devulcanization aids needs to be transported easily to the subsequent modules.

Other design rules for the extruder are:

- Residence time, thus number of modules, has the most effect on devulcanization efficiency.
- Screw speed increases output, but inhibits temperature control.
- Presence of a die results in a finer material, and the die diameter has a strong influence on the material outlet temperature.
- A finer input material does not result in a more efficient devulcanization.

From the application study on blending the recycled rubber with the virgin rubber (Chapter 6), it became obvious that the presence of particles played a major role in crack propagation of the tensile samples. The mixing process is easier with devulcanized rubber and addition of carbon black, as seen from the lower mixing torque. Devulcanized rubber blends gives rise to lower tan δ at low temperatures, an indication of better wet grip. This is due to an increase in the number of free chain ends during the devulcanization process.

For further research

- The mechanistic role of disulfide compounds and thiols used in the reclaiming/devulcanization process is not established till date. So a model compound study needs to be performed to for better analysis of the devulcanization reaction.
- The synergistic action of a combination of different devulcanization aids and oil needs to be studied for increasing the efficiency of radical scavenging. Besides, diffusion studies of the devulcanizing system into the ground tire crumb could help in improvement of the devulcanization process.

- And finally, the question rises how many times the same rubber can be recycled and reused, as higher shear or energy input during the recycling process breaks the polymer main chain bonds reducing its strength.
- The devulcanizate has an expiry date, meaning that its properties change over time This mechanism need to be understood to predict future properties of the material.
- Variation of feedstock and influence on processing and end product properties need to be studied. For instance, the content of natural rubber in the tire compound increases when the price of natural rubber decreases.
- Interaction of fresh carbon black or any other filler with devulcanized rubber.
- To further carry out application study of recycled rubber blends by lowering the amount of curatives, for instance with lower amount of accelerators could be an option.

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Appendix-1

Rumal

06820t0000

TP-WE 70/1600 M4
Devulkanisation of Rubber

2015-03-03-06

☒ Auftragstammblatt	☒ Termin	
	☐ Stempelkarte	
☒ Materialeingang	☒ Anlieferung	EB 4075
☒ Aufgabenstellung	☐ Fragenkatalog	
	☒ Versuchsplanung	
☒ Vorbereitung	☐ Sonderanfertigung	
	☒ Extruder	
	☐ Nachfolge	
	☒ Halle/Besucherraum	
	☐ Versuchsunterlagen	
☒ Dokumentation	☒ Versuchsprotokoll	
	☐ Nachbesprechung	
	☐ Versuchsbericht	
	☒ Auswertung	Mooney-Messung
	☐ Ablage Muster	
	☐ Gesamtprotokoll	
☒ Materialausgang	☐ Entsorgt (Kunststoffmüll)	
	☒ Rücklieferung	komplett
	☐ Einlagerung	
☒ Abbau/Reinigung	☒ Extruder	
	☒ Dosierwerk	
	☒ Nachfolge	
☒ Kosten der Versuche	☒ trägt der Kunde	☐ werden intern verrechnet
☒	☒ Extruder TP-WE 70	2400 / M6
	☐ Zusätzliche Dosierwerke	
	☐ Wasserbad	
	☐ Entgasung	
	☒ sonstiges	KB 70
	☐ Zus. Wasseranschluß	
	☐ Radialgranulierung	
	☐ reinigungsintensive Materialien	
☒ Versuchsabmeldung	☒ Verteiler	Kunde; BKF; Fr.: Pietrek

test report **TP-WE 70/1600 M4**

company:	**Rumal**	**commission no.:**	**06820t0000**
present:	**Mr. Migchels; Mr. Van den Brand**	**(Rumal)**	ENTEX
	Mrs. Dr. Ir. Dierkes; Mr. Rajendran	**(Universit of Twente)**	
	Mr. Dr.Ir. Reuvenkamp	**(apollo)**	leading: M.Gerdon
	Mr. Wallis	**(BKF)**	date: 2015-03-03-06
	Mr. Gerdon	**(ENTEX**	

			Trial no 1					
setting no:			**1**	**2**	**3**	**4**	**5**	
setup			**1**					
date			**03.03.**	**03.03.**	**03.03.**	**03.03.**	**03.03.**	
time			11:45	12:05	13:50	13.25	13:45	
Extruder								
power Extruder (P-max = 46 KW)		KW	7	6,6	7,3	5,8	5,2	
torque Extruder min.		Nm	37	36	40	62	56	
torque Extruder max. (M-max motor = 170 Nm)		Nm	38	36	40	63	57	
speed Extruder (n-max = 250 min-1)		min-1	150	150	150	75	75	
dosing units								
dosing of rubber premix		%	100	100	100	100	100	
dosing of rubber premix		kg/h	25,00	25,00	25,00	25,00	25,00	
speed of the feeder		rpm	32,26	32,26	32,26	32,26	32,26	
capacity set		kg/h	25	25	25	25	25	
temperature control								
temp. cooling water		°C	9	9	9	9	9	
temp. feed section		°C	9	9	9	9	9	
setting temperature central spindle		°C	190	190	190	190	190	
temp. central spindle oil flow		°C	190	187	193	186	187	
temp. central spindle oil return		°C	179	174	177	173	174	
mass flow central spindle oil		m³/min	0,007	0,007	0,007	0,007	0,007	
heat flow central spindle		kW	2,4	2,8	3,5	2,8	2,8	0,0
setting temperature cylinder 1		°C	270	270	210	190	190	
temp. cylinder 1 oil flow		°C	271	271	211	191	191	
temp. cylinder 1 oil return		°C	267	267	209	189	189	
mass flow cylinder 1 oil		m³/min	0,047	0,048	0,05	0,05	0,05	
heat flow cylinder 1		kW	6,1	6,3	3,2	3,1	3,1	0,0
setting temperature cylinder 2		°C	150	150	150	150	190	
temp. cylinder 2 oil flow		°C	151	151	150	150	190	
temp. cylinder 2 oil return		°C	151	151	151	150	189	
mass flow cylinder 2 oil		m³/min	0,05	0,05	0,05	0,05	0,046	
heat flow cylinder 2		kW	0,0	0,0	-1,5	0,0	1,4	0,0
setting temperature cylinder 3		°C	150	150	150	150	175	
temp. cylinder 3 oil flow		°C	149,6	149,6	149,6	149,6	174,6	
temp. cylinder 3 oil return		°C	149,3	149,2	149,1	149,1	173,8	
mass flow cylinder 3 oil		m³/min	0,054	0,054	0,054	0,054	0,054	
heat flow cylinder 3		kW	0,6	0,7	0,8	0,8	1,3	0,0
setting temperature cylinder 4		°C	100	100	100	100	100	
temp. cylinder 4 water flow		°C	100,8	100,8	100,8	100,8	100,8	
temp. cylinder 4 water return		°C	101	101	101	101	101	
mass flow cylinder 4 water		m³/min	0,054	0,054	0,054	0,054	0,054	
heat flow cylinder 4		kW	-0,6	-0,6	-0,6	-0,6	-0,6	0,0
total heat flow		kW	8,6	9,2	5,4	6,2	8,2	0,0
temp. Extruder die oil		°C	-	-	-	-	-	
mass temperature/pressure								
T-1 melt temp. between cylinder 1 & 2		°C	263	245	236	221	229	
T-2 melt temp. between cylinder 2 & 3		°C	190	182	193	194	207	
T-3 melt temp. between cylinder 3 & 4		°C	167	165	170	160	175	
T-4 melt temp. at the die		°C	117	117	120	118	116	
T-5 melt temp. Outlet manuel		°C	200	193	210	180/190	183	
P-1 melt pressure cylinder 1 & 2		bar	4,5	6	9	14	15	
P-2 melt pressure cylinder 2 & 3		bar	6	6	5	14	8	
P-3 melt pressure cylinder 3 & 4		bar	0	0	0	0	0	
P-4 melt pressure at the die		bar	3	3	0,7	0,3	0	
Vacuum								
Vacuum		mbar	21	20	19	19	19	
Mooney - Viscosity								
die	ML 1+4 (100°C) initial	ML1	140	135	140	185	175	
	ML 1+4 (100°C) end	ML1+4	95,06	94,45	115,13	100,92	114,09	
sheet	ML 1+4 (100°C) initial	ML1	135	-	150	180	180	
	ML 1+4 (100°C) end	ML1+4	94,8	-	127,92	150,03	144,87	
output								
specific capacity		KWh/kg	0,28	0,264	0,292	0,232	0,208	

remark

Target: nisation of rubber

setting 1

set the temperature of the 1st module up to 270°C to start the process.
The temperatures are much too high. It looks like that we degredate the material to much.

setting 2

switch of the vaccum at the hopper too see if ther is an differenz in the material quality.
The temperature at the first ring drops down to 245 °C.
The qulity of the amterial becomes worse, it is no compakt strand anymore

setting 3

switch on the vaccum at the hopper again and reduce the temperatur in the first barrel.
At 210°C set temperature the pressure in front of the die drops under 1 bar and the material is verry try.

setting 4

reduce the speed of the central spindle and the temperature in the fist barrel ther is no more cohesion in the material.

setting 5

increase the temperatur in barrel 2+3 too keep the material longer on high temperature.

			Trial no 2						remark
setting no:			**6**	**7**	**8**	**9**	**10**	**11**	**Target:** devulkanisation of rubber
setup			**2**						
date			**04.03.**	**04.03.**	**04.03.**	**04.03.**	**04.03.**	**04.03.**	
time			09:35	10:03	10:30	11:00	11:25	11:50	**setting 6**
Extruder									increase the number of barrel to increase the dwell time
power Extruder (P-max = 46 KW)		KW	11,6	10,7	13,5	15,3	16,5	15,4	change the diameter of the dispergen rings and the kind of
torque Extruder min.		Nm	116	157	109	82	107	99	planetary spindels for a better temperature controle.
torque Extruder max. (M-max motor = 170 Nm)		Nm	118	158	110	83	108	102	the centrel spindel do not heat at this setting.
speed Extruder (n-max = 250 min-1)		min-1	80	56	100	150	125	125	
dosing units									**setting 7**
dosing of rubber premix		%	100	100	100	100	100	100	switch on the TCU of the central spindel. The temperatures
dosing of rubber premix		kg/h	25,00	25,00	25,00	25,00	25,00	25,00	in all modules decreases.
speed of the feeder		rpm	32,26	32,26	32,26	32,26	32,26	32,26	
capacity set		kg/h	25	25	25	25	25	25	**setting 8**
temperature control									increase the speed of the centrale spindle to create
temp. cooling water		°C	9	9	9	9	9	9	more sheer and reduce the set temperature too keep
temp. feed section		°C	9	9	9	9	9	9	the mass temperature low.
setting temperature central spindle		°C	off	120	100	80	80	80	The material is much more sticky than in the settings
temp. central spindle oil flow		°C	-	120	100	77	80	81	before.
temp. central spindle oil return		°C	-	122	104	62	88	88	
mass flow central spindle oil		m³/min	-	0,005	0,005	0,005	0,003	0,003	**setting 9**
heat flow central spindle		kW	-	-0,3	-0,6	2,2	-0,7	-0,6	increase the speed too 150 rpm and reduce the set
setting temperature cylinder 1		°C	190	190	165	140	140	140	temperature in the barrels again.
temp. cylinder 1 oil flow		°C	191	191	166	139	139	139	The temperature in the PRE looks okay, but at the outlet
temp. cylinder 1 oil return		°C	188	188	164	141	141	141	it is more than 200°C and the material smells bad.
mass flow cylinder 1 oil		m³/min	0,051	0,051	0,051	0,054	0,051	0,051	
heat flow cylinder 1		kW	4,8	4,8	3,2	-3,3	-3,1	-3,1	**setting 10**
setting temperature cylinder 2		°C	150	150	125	100	100	100	decreasing the speed to reduce the outlet temperautre.
temp. cylinder 2 oil flow		°C	150	150	126	100	101	102	the strand is more brittle than before.
temp. cylinder 2 oil return		°C	150	150	126	100	101	102	When we decrease the speed, the mass temperature in M1
mass flow cylinder 2 oil		m³/min	0,051	0,051	0,052	0,053	0,053	0,053	decreases to 183°C but the temperatures in M2, M3 and
heat flow cylinder 2		kW	0,0	0,0	0,0	0,0	0,0	0,0	M4 raises.
setting temperature cylinder 3		°C	150	150	125	100	100	100	The outlet temperature is still 200°C
temp. cylinder 4 water flow		°C	150,6	149,3	125	100,5	99,1	99,5	
temp. cylinder 3 water return		°C	150	148,8	125,1	101	99,8	99,9	**setting 11**
mass flow cylinder 3 + 4 water		m³/min	0,04	0,04	0,04	0,04	0,04	0,04	increase the temperature in the last barrel
heat flow cylinder 3		kW	1,0	0,6	-0,1	-0,6	-0,8	-0,5	to reduce the sheer stress in there and so the
setting temperature cylinder 5		°C	150	150	125	100	100	100	temperature.
temp. cylinder 5 water flow		°C	150	150	125,2	100,6	100,5	100,6	The outlet temperature is much too high.
temp. cylinder 5 water return		°C	149,6	149,5	125,1	100,8	100,7	100,7	
mass flow cylinder 5 water		m³/min	0,054	0,054	0,054	0,054	0,054	0,04	
heat flow cylinder 5		kW	0,9	1,1	0,3	-0,6	-0,6	-0,2	
setting temperature cylinder 6		°C	100	100	75	50	50	100	
temp. cylinder 6 water flow		°C	100	100	75,9	46,4	50,5	99,4	
temp. cylinder 6 water return		°C	99,8	99,8	76	46,1	50,9	99	
mass flow cylinder 6 water		m³/min	0,054	0,054	0,054	0,054	0,054	0,054	
heat flow cylinder 6		kW	0,6	0,6	-0,3	1,0	-1,4	1,2	
total heat flow		kW	7,2	6,8	2,4	-1,3	-6,6	-3,2	
temp. Extruder die oil		°C	-	-	-	-	-	-	
mass temperature/pressure									
T-1 melt temp. between cylinder 1 & 2		°C	203	195,4	194,2	201	183	191	
T-2 melt temp. between cylinder 2 & 3		°C	195	190	178,8	168	165	163	
T-3 melt temp. between cylinder 3 & 4		°C	188	185	175	164	160	159	
T-4 melt temp. between cylinder 4 & 5		°C	189	186	175	161	165	160	
T-5 melt temp. between cylinder 5 & 6		°C	178	181	170	157	164	166	
T-6 melt temp. in front of die		°C	85	101	106	104	100	106	
T-7 melt temp. Outlet manuel		°C	165	174	178	200	200	220	
P-1 melt pressure cylinder 1 & 2		bar	12	15	9	6	5	6	
P-2 melt pressure cylinder 2 & 3		bar	12	16	7	4	5,5	5	
P-3 melt pressure cylinder 3 & 4		bar	-	2	-	-	-	0	
P-4 melt pressure cylinder 4 & 5		bar	12	18	12	9	11	10	
P-5 melt pressure cylinder 5 & 6		bar	9	15	8	8	12	10	
P-6 melt pressure in front die		bar	0,6	0,7	1,2	1,8	2	1,8	
Vacuum									
Vacuum		mbar	18	16	17	18	17	18	
Mooney - Viscosity									
die	ML 1+4 (100°C) initial	ML1	80	115	120	185	125	110	
	ML 1+4 (100°C) end	ML1+4	73,42	89,99	96,8	151,77	110,97	103,49	
sheet	ML 1+4 (100°C) initial	ML1	130	50	198	190	190	150	
	ML 1+4 (100°C) end	ML1+4	128,7	23,02	178,93	149,64	169,39	139,92	
output									
specific capacity		KWh/kg	0,464	0,428	0,54	0,612	0,66	0,616	

			Trial no 2						**remark**
setting no:			**12**	**13**	**14**	**15**	**16**	**17**	**Target:** devulkanisation of rubber
setup			**3**		**4**				
date			**04.03.**	**04.03.**	**05.03.**	**05.03.**	**05.03.**	**05.03.**	
time			15:05	15:55	10:00	10:30	11:45	13:25	
Extruder									
power Extruder (P-max = 46 KW)		KW	9,4	13,5	12	11,5	14,6	9,1	**setting 12**
torque Extruder min.		Nm	98	134	122	117	152	92	throughput is too low, only 15 kg/h
torque Extruder max. (M-max motor = 170 Nm)		Nm	100	137	123	118	150	93	
speed Extruder (n-max = 250 min-1)		min-1	80	80	80	80	80	80	**setting 13**
dosing units									switch off the central spindel and increase the throughput
dosing of rubber premix		%	100	100	100	100	100	91,266	too see if ther is an impact. The outlet temperature
dosing of rubber premix		kg/h	15,00	25,00	25,00	25,00	25,00	22,82	decreases to 162°C.
speed of the feeder		rpm	32,30	51,00	-	-	-	-	
dosing of TDAE		%	-	-	0	0	0	4,563	setting 14
dosing of TDAE		kg/h	-	-	0,00	0,00	0,00	1,14	start the trials with this setup and the premixed material
dosing of Peption		%	-	-	0	0	0	4,171	
dosing of Peption		kg/h	-	-	0,00	0,00	0,00	1,04	**setting 15**
capacity set		kg/h	15	25	25	25	25	25	reduce the temperatre in the fisrt modul to prevent the
temperature control									material from overheating without vacuum.
temp. cooling water		°C	9	9	9	9	9	9	no differnez in the torque.
temp. feed section		°C	9	9	9	9	9	9	
setting temperature central spindle		°C	120	off	off	off	off	120	**setting 15**
temp. central spindle oil flow		°C	120	-	-	-	-	118	reduce the temperatures more till the masimum torque is
temp. central spindle oil return		°C	121	-	-	-	-	117	reached.
mass flow central spindle oil		m³/min	0,005	-	-	-	-	0,004	
heat flow central spindle		kW	-0,2	-	-	-	-	0,1	**setting 17**
setting temperature cylinder 1		°C	190	190	190	150	135	135	start with single components
temp. cylinder 1 oil flow		°C	191	191	188	150	136	135	the temperature in the first and second modul is much
temp. cylinder 1 oil return		°C	188	190	190	149	134	134	lower than bevore. This could be an effect of the oil
mass flow cylinder 1 oil		m³/min	0,051	0,051	0,05	0,051	0,051	0,051	what is injectet now and increase the lubrication
heat flow cylinder 1		kW	4,8	1,6	-3,1	1,6	3,1	1,5	in the machine.
setting temperature cylinder 2		°C	150	150	150	150	135	150	
temp. cylinder 2 oil flow		°C	150	151	150	150	136	150	
temp. cylinder 2 oil return		°C	150	151	150	150	136	150	
mass flow cylinder 2 oil		m³/min	0,051	0,051	0,051	0,052	0,052	0,052	
heat flow cylinder 2		kW	0,0	0,0	0,0	0,0	0,0	0,0	
setting temperature cylinder 3		°C	150	130	150	150	120	150	
temp. cylinder 4 water flow		°C	150,3	128,8	150,3	150,3	120,8	149,7	
temp. cylinder 3 water return		°C	149,6	129,2	150,5	150,2	121,7	148,8	
mass flow cylinder 3 + 4 water		m³/min	0,04	0,04	0,04	0,04	0,04	0,04	
heat flow cylinder 3		kW	1,1	-0,5	-0,3	0,1	-1,1	1,1	
setting temperature cylinder 5		°C	150	130	150	150	120	150	
temp. cylinder 5 water flow		°C	150,1	130,3	150	150,2	120,5	150,3	
temp. cylinder 5 water return		°C	149,4	130,3	150	149,9	120,6	149,8	
mass flow cylinder 5 water		m³/min	0,054	0,054	0,054	0,054	0,054	0,054	
heat flow cylinder 5		kW	1,5	0,0	0,0	0,6	-0,3	1,1	
setting temperature cylinder 6		°C	100	50	100	100	70	100	
temp. cylinder 6 water flow		°C	100	48,5	100,4	100	69,6	100	
temp. cylinder 6 water return		°C	99,8	49	100,3	100	70,4	100	
mass flow cylinder 6 water		m³/min	0,054	0,054	0,054	0,054	0,054	0,054	
heat flow cylinder 6		kW	0,6	-1,7	0,3	0,0	-2,6	0,0	
total heat flow		kW	7,9	-0,6	-3,2	2,3	-0,8	3,9	
temp. Extruder die oil		°C	-	-	-	-	-	-	
mass temperature/pressure									
T-1 melt temp. between cylinder 1 & 2		°C	200	208	196	153	173	134	
T-2 melt temp. between cylinder 2 & 3		°C	189	199	212	203	199	152	
T-3 melt temp. between cylinder 3 & 4		°C	184	178	199	201	183	182	
T-4 melt temp. between cylinder 4 & 5		°C	181	174	196	188	181	194	
T-5 melt temp. between cylinder 5 & 6		°C	175	176	182	187	168	188	
T-6 melt temp. in front of die		°C	87	100	94	116	117	99	
T-7 melt temp. Outlet manuel		°C	192	162	188	185	182	182	
P-1 melt pressure cylinder 1 & 2		bar	13	15	9	2	6	4	
P-2 melt pressure cylinder 2 & 3		bar	10	16	15	22	14	6	
P-3 melt pressure cylinder 3 & 4		bar	-	-	-	6	4	13	
P-4 melt pressure cylinder 4 & 5		bar	9	10	9	9	13	11	
P-5 melt pressure cylinder 5 & 6		bar	3	7	5	5	8	6	
P-6 melt pressure in front die		bar	1	0,7	1	1	1,5	0,5	
Vacuum									
Vacuum		mbar	18	19	18	15	15	15	
Mooney - Viscosity									
die	ML 1+4 (100°C) initial	ML1	90	172	-	-	-	85	
	ML 1+4 (100°C) end	ML1+4	69,2	127,66	-	-	-	61,33	
sheet	ML 1+4 (100°C) initial	ML1	145	200	195	83	135	-	
	ML 1+4 (100°C) end	ML1+4	147,08	173,06	152,72	73,26	110,14	-	
output									
specific capacity		KWh/kg	0,62667	0,54	0,48	0,46	0,584	0,364	

			Trial no 2					
setting no:			**18**	**19**	**20**	**21**	**22**	**23**
setup			**4**	**5**				
date			**05.03.**	**06.03.**	**06.03.**	**06.03.**	**06.03.**	**06.03.**
time			13:55	09:40	10:20	10:45	11:00	11:45
Extruder								
power Extruder (P-max = 46 KW)		KW	10,7	13	13,4	15,8	16,3	13,5
torque Extruder min.		Nm	108	134	135	144	146	121
torque Extruder max. (M-max motor = 170 Nm)		Nm	110	135	137	145	148	124
speed Extruder (n-max = 250 min-1)		min-1	80	80	80	90	90	90
dosing units								
dosing of rubber SCRAP		%	91,266	91,266	91,266	100	95,238	100
dosing of rubber SCRAP		kg/h	22,82	22,82	22,82	25,00	23,81	25,00
dosing of TDAE		%	4,563	4,563	4,563	0	4,762	0
dosing of TDAE		kg/h	1,14	1,14	1,14	0,00	1,19	0,00
dosing of Peption		%	4,171	4,171	4,171	0	0	0
dosing of Peption		kg/h	1,04	1,04	1,04	0,00	0,00	0,00
capacity set		kg/h	25	25	25	25	25	25
temperature control								
temp. cooling water		°C	9	11	11	11	11	11
temp. feed section		°C	9	105	105	105	105	105
setting temperature central spindle		°C	120	120	off	off	off	off
temp. central spindle oil flow		°C	119	120	-	-	-	-
temp. central spindle oil return		°C	120	122	-	-	-	-
mass flow central spindle oil		m³/min	0,005	0,005	-	-	-	-
heat flow central spindle		kW	-0,2	-0,3	-	-	-	-
setting temperature cylinder 1		°C	135	150	150	150	150	150
temp. cylinder 1 oil flow		°C	136	150	151	151	151	150
temp. cylinder 1 oil return		°C	134	149	149	150	150	149
mass flow cylinder 1 oil		m³/min	0,051	0,051	0,051	0,051	0,051	0,051
heat flow cylinder 1		kW	3,1	1,6	3,1	1,6	1,6	1,6
setting temperature cylinder 2		°C	170	150	130	130	130	130
temp. cylinder 2 oil flow		°C	171	150	131	131	131	131
temp. cylinder 2 oil return		°C	170	150	131	131	131	131
mass flow cylinder 2 oil		m³/min	0,051	0,052	0,052	0,052	0,052	0,052
heat flow cylinder 2		kW	1,6	0,0	0,0	0,0	0,0	0,0
setting temperature cylinder 3		°C	150	150	130	130	130	130
temp. cylinder 4 water flow		°C	149,6	150,3	128,6	130,2	129,7	129,3
temp. cylinder 3 water return		°C	149,5	149,8	128,8	130,5	130,2	129,5
mass flow cylinder 3 + 4 water		m³/min	0,04	0,04	0,04	0,04	0,04	0,04
heat flow cylinder 3		kW	0,1	0,8	-0,2	-0,4	-0,6	-0,2
setting temperature cylinder 5		°C	150	150	130	130	130	130
temp. cylinder 5 water flow		°C	150,1	150,2	130,3	130,2	130,3	130,3
temp. cylinder 5 water return		°C	149,7	149,8	130,1	130,1	130,1	130,2
mass flow cylinder 5 water		m³/min	0,054	0,054	0,054	0,054	0,054	0,054
heat flow cylinder 5		kW	0,9	0,9	0,5	0,2	0,5	0,2
setting temperature cylinder 6		°C	100	100	80	80	80	80
temp. cylinder 6 water flow		°C	100,3	100,1	80,6	81,1	80,7	81
temp. cylinder 6 water return		°C	100,1	100,3	80,9	81,2	81,2	81,2
mass flow cylinder 6 water		m³/min	0,054	0,054	0,054	0,054	0,054	0,054
heat flow cylinder 6		kW	0,6	-0,6	-0,9	-0,3	-1,6	-0,6
total heat flow		kW	6,1	2,3	2,4	1,1	-0,1	0,9
temp. Extruder die oil		°C	-	-	-	-	-	-
mass temperature/pressure								
T-1 melt temp. between cylinder 1 & 2		°C	137	202	199	244	226	215
T-2 melt temp. between cylinder 2 & 3		°C	181	202	195	195	204	189
T-3 melt temp. between cylinder 3 & 4		°C	193	191	180	181	187	179
T-4 melt temp. between cylinder 4 & 5		°C	191	187	177	179	187	175
T-5 melt temp. between cylinder 5 & 6		°C	187	193	184	179	189	176
T-6 melt temp. in front of die		°C	111	-	-	-	-	-
T-7 melt temp. Outlet manuel		°C	162	170	170	189	175	185
P-1 melt pressure cylinder 1 & 2		bar	2	25	25	20	26	22
P-2 melt pressure cylinder 2 & 3		bar	17	8	10	7	8	8
P-3 melt pressure cylinder 3 & 4		bar	2	0	0	0	0	0
P-4 melt pressure cylinder 4 & 5		bar	9	4	7	6	5	7
P-5 melt pressure cylinder 5 & 6		bar	8	9	10	9	8	9
P-6 melt pressure in front die		bar	2	-	-	-	-	-
Vacuum								
Vacuum		mbar	15	40	40	40	40	40
Mooney - Viscosity								
die	ML 1+4 (100°C) initial	ML1	80	-	-	-	-	-
	ML 1+4 (100°C) end	ML1+4	47,36	-	-	-	-	-
sheet	ML 1+4 (100°C) initial	ML1	-	172	145	200	200	187
	ML 1+4 (100°C) end	ML1+4	-	145,55	129,11	163,27	162,07	147,4
output								
specific capacity		KWh/kg	0,428	0,52	0,536	0,632	0,652	0,54

remark

Target: devulkanisation of rubber

setting 18
while we increase the temperature in M2 the torque
rise to, because the material becomes more sticky.
reduce the oil to 2,5 phr made no differenz. With 2,5phr was
no sample possible.

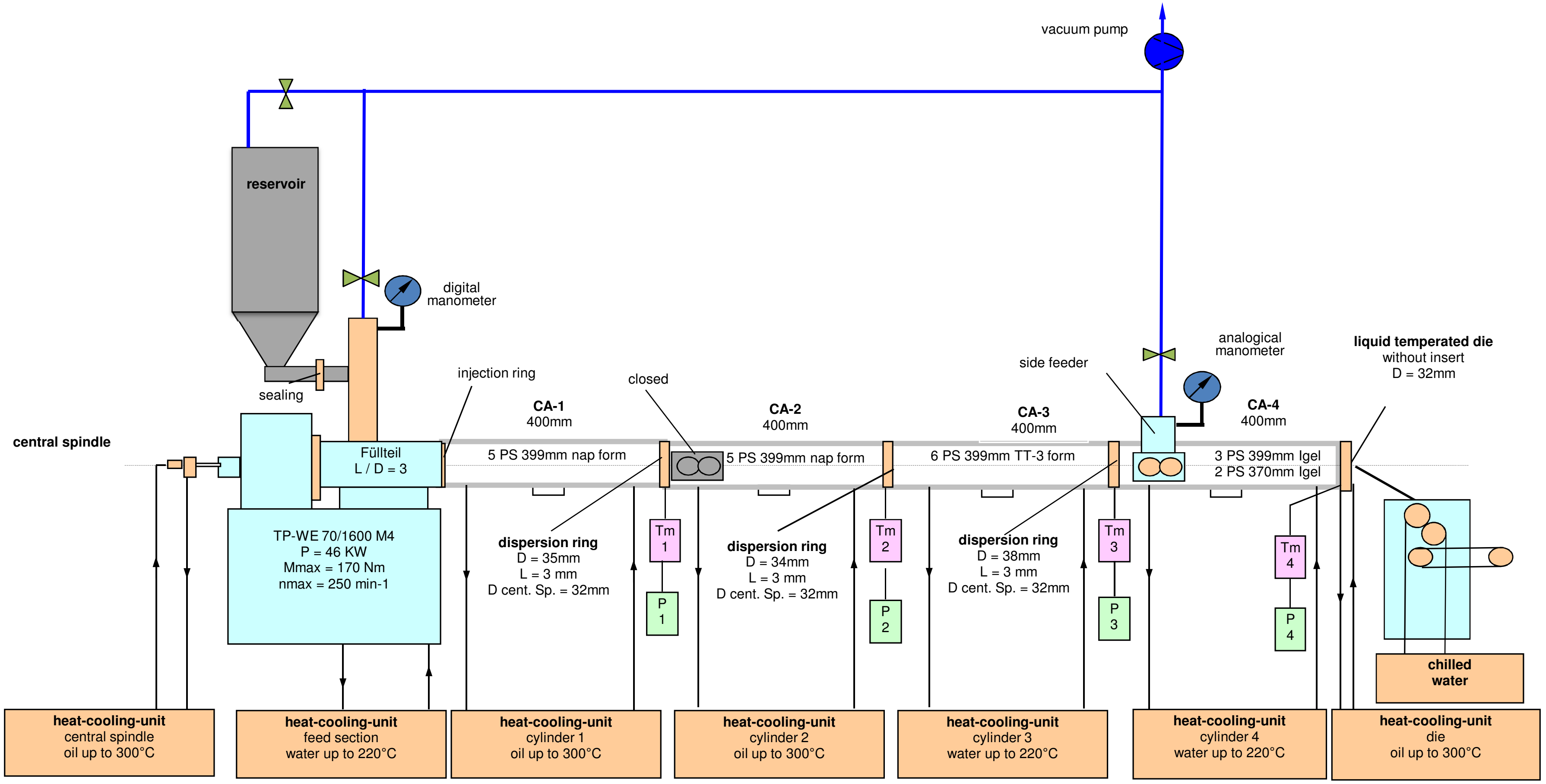
setting 19
changing too setup 5 for a better mixing of the oil
and Peption in the first moduls.
the torque is much higer then with the setup before.

setting 21
only pure rubber without additves

setting 22
only rubber with 5phr TDAE

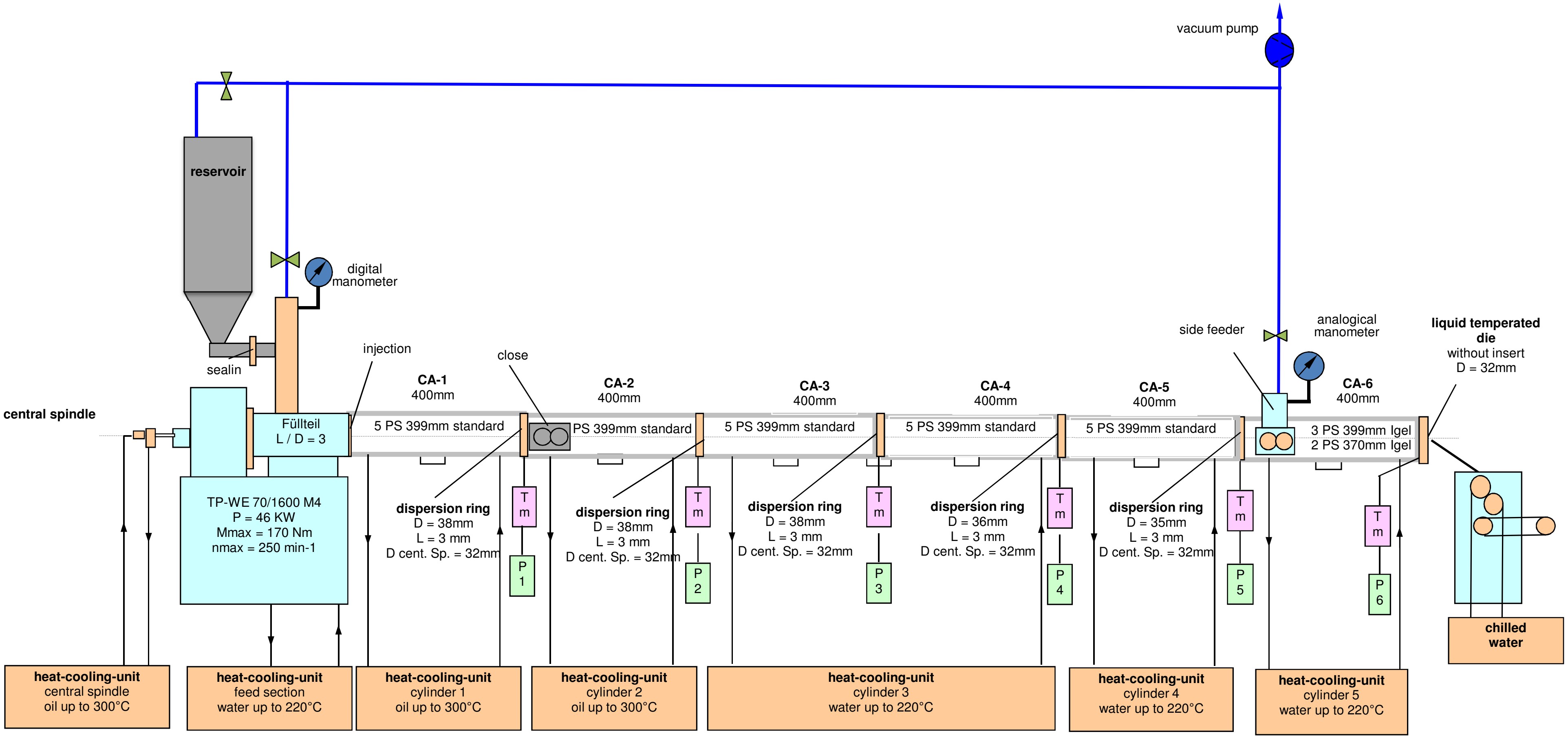
setting 23
changing back too the preblended material too see the
differenz too this setup.

setup 1



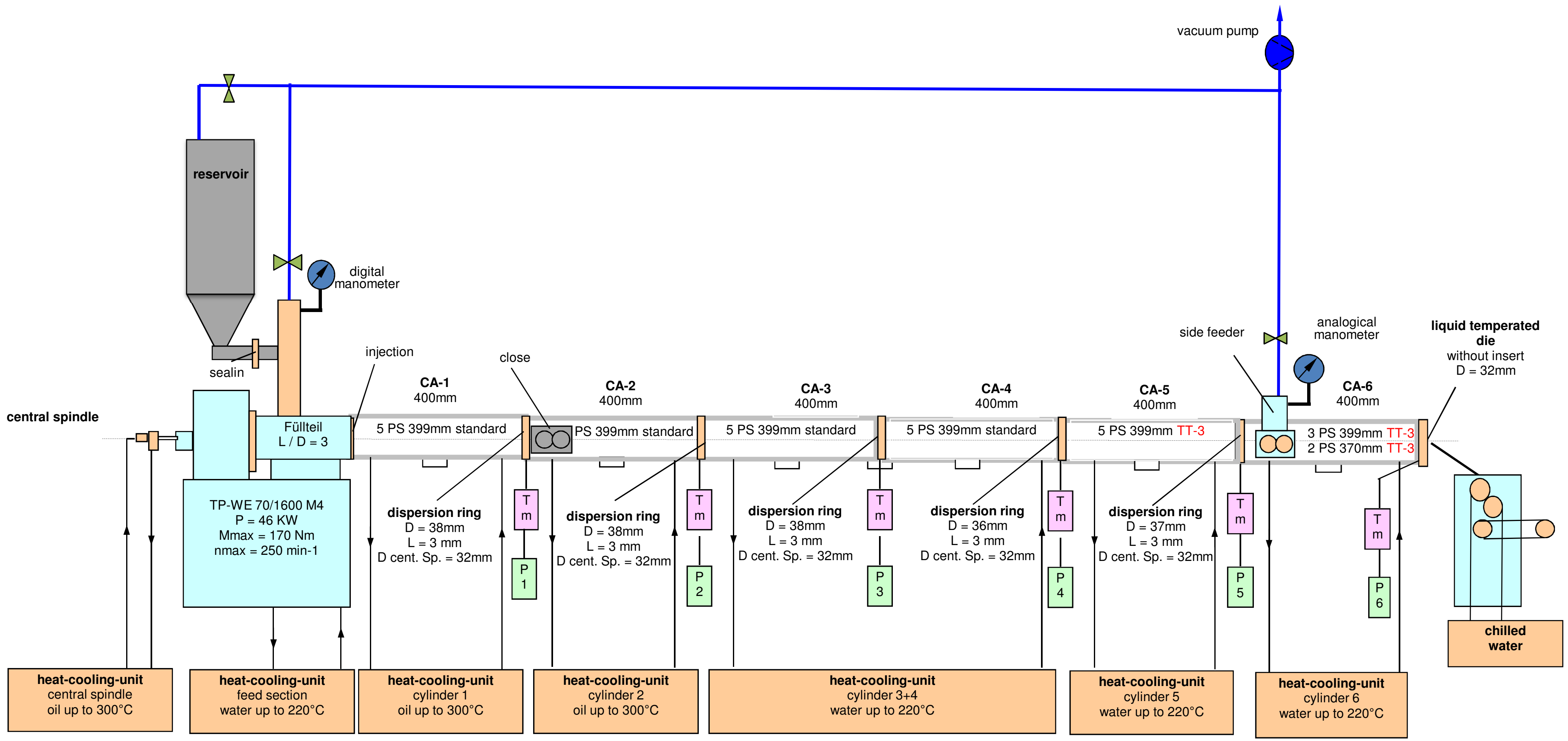
Firma:	Rumal	
Kom.-Nr.:	06820t0000	ENTEX
Datum:	2015-03-03-06	
Stand:	2015-03-09	Erstellt durch: M. Gerdon

setup 2



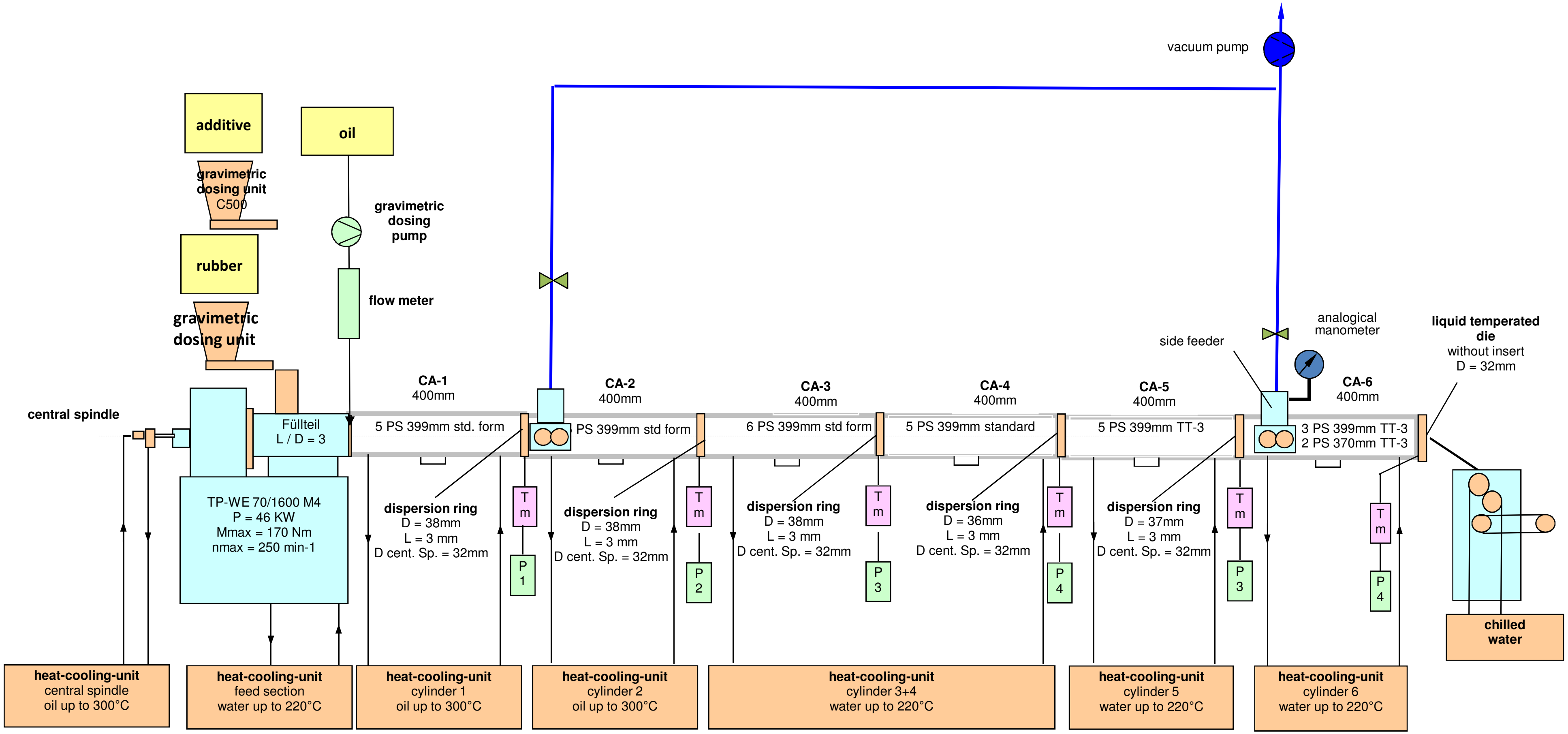
Firma:	**Rumal**	
Kom.-Nr.:	06820t0000	
Datum:	2015-03-03-06	
Stand:	2015-03-09	Erstellt durch: M. Gerdon

setup 3



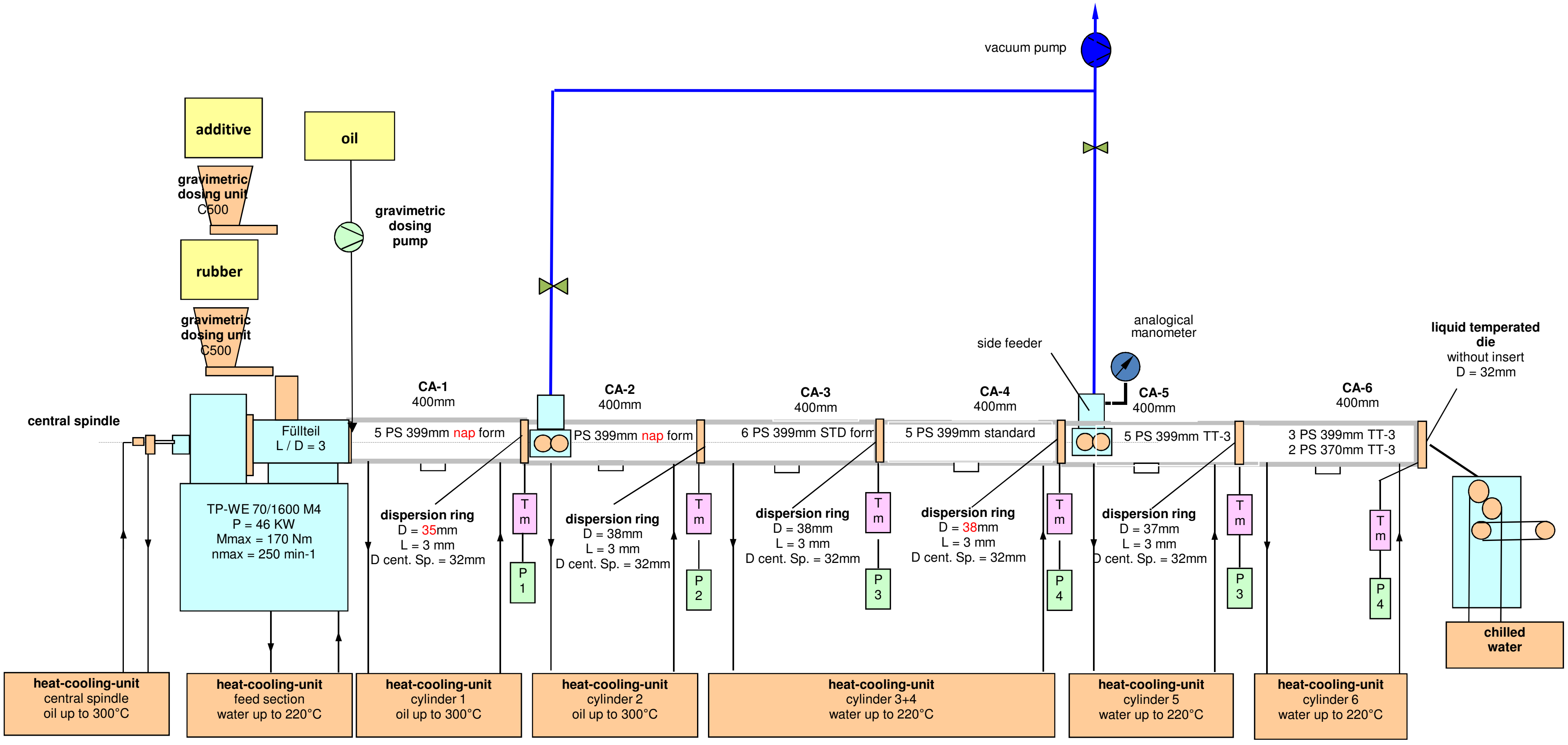
Firma:	**Rumal**	
Kom.-Nr.:	06820t0000	
Datum:	2015-03-03-06	
Stand:	2015-03-09	Erstellt durch: M. Gerdon

setup 4



Firma:	**Rumal**	
Kom.-Nr.:	06820t0000	
Datum:	2015-03-03-06	
Stand:	2015-03-09	Erstellt durch: M. Gerdon

setup 5



Firma:	**Rumal**	
Kom.-Nr.:	06820t0000	
Datum:	2015-03-03-06	
Stand:	2015-03-09	Erstellt durch: M. Gerdon

Appendix- 2

Rumal
06820t0001

TP-WE 70/1600 M4
Devulkanisation of Rubber

2015-12-02-04

☒ Auftragstammblatt	☒ Termin	
	☐ Stempelkarte	
☒ Materialeingang	☒ Anlieferung	EB 4314; 4316
☒ Aufgabenstellung	☐ Fragenkatalog	
	☒ Versuchsplanung	
☒ Vorbereitung	☐ Sonderanfertigung	
	☒ Extruder	
	☐ Nachfolge	
	☒ Halle/Besucherraum	
	☐ Versuchsunterlagen	
☒ Dokumentation	☒ Versuchsprotokoll	
	☐ Nachbesprechung	
	☐ Versuchsbericht	
	☐ Auswertung	
	☐ Ablage Muster	
	☐ Gesamtprotokoll	
☒ Materialausgang	☐ Entsorgt (Kunststoffmüll)	
	☒ Rücklieferung	nur Abfall
	☒ Einlagerung	
☒ Abbau/Reinigung	☒ Extruder	
	☒ Dosierwerk	
	☒ Nachfolge	
☒ Kosten der Versuche	☒ trägt der Kunde	☐ werden intern verrechnet
☒	☒ Extruder TP-WE 70	1600/M4
	☐ Zusätzliche Dosierwerke	
	☐ Wasserbad	
	☐ Entgasung	
	☒ sonstiges	KB 70
	☐ Zus. Wasseranschluß	
	☐ Radialgranulierung	
	☐ reinigungsintensive Materialien	
☒ Versuchsabmeldung	☒ Verteiler	Kunde; BKF; Fr.: Pietrek

test report **TP-WE 70/1600 M4**

company:	**Rumal**	commission no.:	**06820t0001**
present:	**Mr. Migchels; Mr. Van den Brand**	**(Rumal)**	
	Mrs. Dr. Ir. Dierkes; Mr. Dr. Ir. Noordermeer; Mr. Rajendran	**(Universit of Twente)**	
	Mr. Wallis	**(BKF)**	leading: M.Gerdon
	Mr. Gerdon	**(ENTEX**	date: 2015-12-02-04

		Trial no 1						remark
setting no:		**1**	**2**	**3**	**4**	**5**	**6**	**Target:** devulkanisation of rubber
setup		1					2	
date		**02.12.**	**2.12.**	**2.12.**	**2.12.**	**2.12.**	**2.12.**	
time		10:30	10:45	11:40	12:00	12:15	13:30	**setting 1**
Extruder								the material is very sticky. So it looks
power Extruder (P-max = 46 KW)	KW	2,8	2,3	2	1,6	1,5	2	like that the TDAE is only on the surface of the Granulate
torque Extruder min.	Nm	29	37	19	17	15	21	reduce the speed for more dwell time.
torque Extruder max. (M-max motor = 170 Nm)	Nm	29	37	19	17	15	21	The flow of the TCU is to low.
speed Extruder (n-max = 250 min-1)	min-1	80	50	80	80	80	80	
dosing units								
dosing of rubber granulat	%	90	90	90	90	90	90	**setting 2**
dosing of rubber granulat	kg/h	22,50	22,50	22,50	22,50	22,50	22,50	with a lower speed the material is not so sticky anymore.
dosing of pepton	%	5	5	5	5	5	6	the outlet temp. is lower.
dosing of pepton	kg/h	1,25	1,25	1,25	1,25	1,25	1,50	
dosing of TDAE	%	5	5	5	5	5	6	
dosing of TDAE	kg/h	1,25	1,25	1,25	1,25	1,25	1,50	**setting 3**
speed of the TDAE pump	rpm	141,98	141,98	141,98	141,98	141,98	172,84	higer speed but lower temp. at the first barrel.
capacity set	kg/h	25	25	25	25	25	25	cleaning the filter of the TCU to get more
temperature control								flow. The temperature of the material is pretty low
temp. cooling water	°C	15	15	15	15	15	15	and the material is very dry.
temp. feed section	°C	15	15	15	15	15	15	
setting temperature cylinder 1	°C	160	161	140	160	200	160	
temp. cylinder 1 oil flow	°C	161	162	141	161	201	161	**setting 4**
temp. cylinder 1 oil return	°C	149	149	138	157	195	157	by increasing the setting temp. the mass temp. Comes
mass flow cylinder 1 oil	m³/min	0,007	0,007	0,034	0,034	0,033	0,033	down. That can be effect of less shear by higher temp.
heat flow cylinder 1	kW	2,6	2,8	3,1	4,2	6,3	4,1	and so a better control of it.
setting temperature cylinder 2	°C	-	-	-	-	-	-	
temp. cylinder 2 oil flow	°C	-	-	-	-	-	-	
temp. cylinder 2 oil return	°C	-	-	-	-	-	-	**setting 5**
mass flow cylinder 2 oil	m³/min	-	-	-	-	-	-	also at a set temp. of 200°C the outlet temp, is okay.
heat flow cylinder 2	kW	-	-	-	-	-	-	The material becomes more sticky.
setting temperature cylinder 3	°C	-	-	-	-	-	-	reduce the diameter of the ring to get more temp.
temp. cylinder 3 oil flow	°C	-	-	-	-	-	-	by shear because the results of the last test shows that
temp. cylinder 3 oil return	°C	-	-	-	-	-	-	more shear gives a better quality.
mass flow cylinder 3 oil	m³/min	-	-	-	-	-	-	
heat flow cylinder 3	kW	-	-	-	-	-	-	
setting temperature cylinder 4	°C	-	-	-	-	-	-	**setting 6**
temp. cylinder 4 water flow	°C	-	-	-	-	-	-	chang the diameter of the dispergenring to 34mm
temp. cylinder 4 water return	°C	-	-	-	-	-	-	the outlet temp. is much higher than before.
mass flow cylinder 4 water	m³/min	-	-	-	-	-	-	Also the pressure at the ring.
heat flow cylinder 4	kW	-	-	-	-	-	-	The material is not sticky.
total heat flow	kW	2,6	2,8	3,1	4,2	6,3	4,1	
temp. Extruder die oil	°C	-	-	-	-	-	-	
mass temperature/pressure								
T-1 melt temp. between cylinder 1 & 2	°C	185	179	136	132	144	128	
T-2 melt temp. between cylinder 2 & 3	°C	-	-	-	-	-	-	
T-3 melt temp. between cylinder 3 & 4	°C	-	-	-	-	-	-	
T-4 melt temp. at the die	°C	-	-	-	-	-	-	
T-5 melt temp. Outlet manuel IR	°C	170	165	113	110	120	130	
P-1 melt pressure cylinder 1 & 2	bar	20	27	8	9	10	16	
P-2 melt pressure cylinder 2 & 3	bar	-	-	-	-	-	-	
P-3 melt pressure cylinder 3 & 4	bar	-	-	-	-	-	-	
P-4 melt pressure at the die	bar	-	-	-	-	-	-	
Vacuum								
Vacuum	mbar	-	-	-	-	-	-	
output								
specific energy	KWh/kg	0,112	0,092	0,08	0,064	0,06	0,08	

test report **TP-WE 70/1600 M4**

company:	**Rumal**	**commission no.:** **06820t0001**
present:	**Mr. Migchels; Mr. Van den Brand**	**(Rumal)**
	Mrs. Dr. Ir. Dierkes; Mr. Dr. Ir. Noordermeer; Mr. Rajendran	**(Universit of Twente)**
	Mr. Wallis	**(BKF)**
	Mr. Gerdon	**(ENTEX**

leading: M.Gerdon
date: 2015-12-02-04

		Trial no 1					
setting no:		**7**	**8**	**9**	**10**	**11**	**12**
setup		**2**			**3**	**4**	**5**
date		**2.12.**	**2.12.**	**2.12.**	**2.12.**	**2.12.**	**2.12.**
time		13:40	13:50	14:00	16:00	16:45	18:20
Extruder							
power Extruder (P-max = 46 KW)	KW	2,7	2,5	1,5	4,3	4	2,7
torque Extruder min.	Nm	18	16	16	44	40	27
torque Extruder max. (M-max motor = 170 Nm)	Nm	18	16	16	44	40	27
speed Extruder (n-max = 250 min-1)	min-1	120	120	80	80	80	80
dosing units							
dosing of rubber granulat	%	90	90	90	90	90	90
dosing of rubber granulat	kg/h	22,50	22,50	22,50	22,50	22,50	22,50
dosing of pepton	%	5	5	5	5	5	5
dosing of pepton	kg/h	1,25	1,25	1,25	1,25	1,25	1,25
dosing of TDAE	%	5	5	5	5	5	5
dosing of TDAE	kg/h	1,25	1,25	1,25	1,25	1,25	1,25
speed of the TDAE pump	rpm	141,98	141,98	141,98	141,98	141,98	141,98
capacity set	kg/h	25	25	25	25	25	25
temperature control							
temp. cooling water	°C	15	15	15	15	15	15
temp. feed section	°C	15	15	15	15	15	15
setting temperature cylinder 1	°C	160	180	180	180	180	180
temp. cylinder 1 oil flow	°C	161	181	181	181	180	181
temp. cylinder 1 oil return	°C	157	176	176	176	175	175
mass flow cylinder 1 oil	m³/min	0,034	0,034	0,034	0,034	0,034	0,034
heat flow cylinder 1	kW	4,2	5,3	5,3	5,3	5,3	6,4
setting temperature cylinder 2	°C	-	-	-	170	170	170
temp. cylinder 2 oil flow	°C	-	-	-	169,3	169,5	169,5
temp. cylinder 2 oil return	°C	-	-	-	168,9	169	168,4
mass flow cylinder 2 oil	m³/min	-	-	-	0,04	0,04	0,04
heat flow cylinder 2	kW	-	-	-	0,5	0,7	1,5
setting temperature cylinder 3	°C	-	-	-	-	-	-
temp. cylinder 3 oil flow	°C	-	-	-	-	-	-
temp. cylinder 3 oil return	°C	-	-	-	-	-	-
mass flow cylinder 3 oil	m³/min	-	-	-	-	-	-
heat flow cylinder 3	kW	-	-	-	-	-	-
setting temperature cylinder 4	°C	-	-	-	-	-	-
temp. cylinder 4 water flow	°C	-	-	-	-	-	-
temp. cylinder 4 water return	°C	-	-	-	-	-	-
mass flow cylinder 4 water	m³/min	-	-	-	-	-	-
heat flow cylinder 4	kW	-	-	-	-	-	-
total heat flow	kW	4,2	5,3	5,3	5,9	6,0	7,9
temp. Extruder die oil	°C	-	-	-	-	-	-
mass temperature/pressure							
T-1 melt temp. between cylinder 1 & 2	°C	130	135	136	150	145	142
T-2 melt temp. between cylinder 2 & 3	°C	-	-	-	220	202	182
T-3 melt temp. between cylinder 3 & 4	°C	-	-	-	-	-	-
T-4 melt temp. at the die	°C	-	-	-	-	-	-
T-5 melt temp. Outlet manuel IR	°C	130	115	117	230	207	175
P-1 melt pressure cylinder 1 & 2	bar	16	16	13	11	11	13
P-2 melt pressure cylinder 2 & 3	bar	-	-	-	17	26	8
P-3 melt pressure cylinder 3 & 4	bar	-	-	-	-	-	-
P-4 melt pressure at the die	bar	-	-	-	-	-	-
Vacuum							
Vacuum at M2	mbar	-	-	-	10	10	10
Vacuum at M3	mbar	-	-	-	-	-	-
output							
specific energy	KWh/kg	0,108	0,1	0,06	0,172	0,16	0,108

remark

Target: devulkanisation of rubber

setting 7
higher speed to see if the dwell time is high enough
the outlet temp. rais a littel bit, but is still under the 140 °C

setting 8
higher temperature in the barrel makes no differenz
in the other process parameter.

setting 9
with the lower speed the material becomes more sticky.
That could be an effect of the pepton wich is now molten.
it is the same effect that the customer can see when he
reached an temperature of 140°C in the internal mixer.

setting 10
assembeling the 2nd modul. At an set temp. of 200°C
the outlet temp is much too high.
Reduce the temp. in the 2nd module too 170°C and
the pressure in front of the 1st ring drops after a few
minutes from 21 bar to 11 bar. After that the temp. in the
first zone drops straight from 204 °C to 151°C.
But the outlet temp. after the 2nd module is the same.
It is still to high.

setting 11
change to Standard spindles because of the high
outlet temp.
The outlet temp. now is 20K lower but almost high.

setting 12
increase the diameter of the dispergion ring after the 2nd
module to get a better posibility to control the temperatur.
The outlet temp is okay now.

test report **TP-WE 70/1600 M4**

company: **Rumal**
commission no.: **06820t0001**

present: **Mr. Migchels; Mr. Van den Brand** **(Rumal)**
Mrs. Dr. Ir. Dierkes; Mr. Dr. Ir. Noordermeer; Mr. Rajendran **(Universit of Twente)**
Mr. Wallis **(BKF)**
Mr. Gerdon **(ENTEX**

leading: M.Gerdon
date: 2015-12-02-04

		Trial no 1						**remark**
setting no:		**13**	**14**	**15**	**16**	**17**	**18**	**Target:** devulkanisation of rubber
setup		**6**	**7**	**8**	**9**	**10**	**11**	
date		**03.12.**	**03.12.**	**03.12.**	**03.12.**	**03.12.**	**03.12.**	
time		09:30	10:10	11:40	12:05	14:00	16:45	
Extruder								**setting 13**
power Extruder (P-max = 46 KW)	KW	5	4,5	1,8	2,5	4,3	5,3	Assemble the 3rd modul.
torque Extruder min.	Nm	50	46	17	25	47	54	The temperatur after the 2nd barrel is 10K higer than in
torque Extruder max. (M-max motor = 170 Nm)	Nm	50	46	17	25	47	55	setup 5.
speed Extruder (n-max = 250 min-1)	min-1	80	80	80	80	80	80	The outlet temp. is to high.
dosing units								
dosing of rubber granulat	%	90	90	90	90	90	90	
dosing of rubber granulat	kg/h	22,50	22,50	22,50	22,50	22,50	22,50	**setting 14**
dosing of pepton	%	5	5	5	5	5	5	changing to a bigger dispergion ring to reduce the outlet
dosing of pepton	kg/h	1,25	1,25	1,25	1,25	1,25	1,25	temp. The effect is pretty low.
dosing of TDAE	%	5	5	5	5	5	5	Also lower set temp. in the 3rd Modul maks no differenz
dosing of TDAE	kg/h	1,25	1,25	1,25	1,25	1,25	1,25	
speed of the TDAE pump	rpm	141,98	141,98	141,98	141,98	141,98	141,98	
capacity set	kg/h	25	25	25	25	25	25	**setting 15**
temperature control								with 7 standard spindels the dwell time in the barrel is so
temp. cooling water	°C	15	15	15	15	15	15	low that the process dosen't start.
temp. feed section	°C	15	15	15	15	15	15	the partiel size becomes bigger.
setting temperature cylinder 1	°C	180	180	180	180	180	180	
temp. cylinder 1 oil flow	°C	181	181	180	180	-	181	
temp. cylinder 1 oil return	°C	176	176	175	175	-	176	**setting 16**
mass flow cylinder 1 oil	m³/min	0,034	0,034	0,034	0,034	-	0,034	with a smaler dispergen ring the outlet temp. rais and the
heat flow cylinder 1	kW	5,3	5,3	5,3	5,3	-	5,3	process starts, but the particels are still to big.
setting temperature cylinder 2	°C	170	170	170	170	170	170	
temp. cylinder 2 oil flow	°C	169,6	169,5	169,5	169,6	169,5	169,5	
temp. cylinder 2 oil return	°C	169	168,8	168,7	169	168,9	169	**setting 18**
mass flow cylinder 2 oil	m³/min	0,04	0,04	0,04	0,04	0,04	0,04	with a high pressure in front of the die the particle
heat flow cylinder 2	kW	0,8	0,9	1,1	0,8	0,8	0,7	size becoms smaler. The material looks very dry but
setting temperature cylinder 3	°C	170	170	-	-	150	150	is as sticky it should be.
temp. cylinder 3 oil flow	°C	171,8	171,3	-	-	151,5	151,4	
temp. cylinder 3 oil return	°C	170,3	169,8	-	-	150,4	150,5	
mass flow cylinder 3 oil	m³/min	0,04	0,04	-	-	0,04	0,04	
heat flow cylinder 3	kW	2,0	2,0	-	-	1,7	1,4	
setting temperature cylinder 4	°C	-	-	-	-	-	150	
temp. cylinder 4 water flow	°C	-	-	-	-	-	150	
temp. cylinder 4 water return	°C	-	-	-	-	-	149,3	
mass flow cylinder 4 water	m³/min	-	-	-	-	-	0,054	
heat flow cylinder 4	kW	-	-	-	-	-	1,2	
total heat flow	kW	8,1	8,2	6,4	6,1	2,6	8,6	
temp. Extruder die oil	°C	-	-	-	-	-	160	
mass temperature/pressure								
T-1 melt temp. between cylinder 1 & 2	°C	146	145	142,8	147	147	153	
T-2 melt temp. between cylinder 2 & 3	°C	192	187	173	178	191	185	
T-3 melt temp. between cylinder 3 & 4	°C	205	201	-	-	173	195	
T-4 melt temp. at the die	°C	-	-	-	-	-	195	
T-5 melt temp. Outlet manuel IR	°C	215	210	160	175	170	180	
P-1 melt pressure cylinder 1 & 2	bar	13	13	14	12	13	12	
P-2 melt pressure cylinder 2 & 3	bar	5	6	5	12	5	4	
P-3 melt pressure cylinder 3 & 4	bar	15	10	-	-	18	18	
P-4 melt pressure at the die	bar	-	-	-	-	-	17	
Vacuum								
Vacuum at M2	mbar	10	10	10	10	60	10	
Vacuum at M3	mbar	10	10	-	-	80	20	
output								
specific energy	KWh/kg	0,2	0,18	0,072	0,1	0,172	0,212	

test report **TP-WE 70/1600 M4**

company:	**Rumal**	**commission no.:**	**06820t0001**
present:	**Mr. Migchels; Mr. Van den Brand**	**(Rumal)**	
	Mrs. Dr. Ir. Dierkes; Mr. Dr. Ir. Noordermeer; Mr. Rajendran	**(Universit of Twente)**	
	Mr. Wallis	**(BKF)**	leading: M.Gerdon
	Mr. Gerdon	**(ENTEX**	date: 2015-12-02-04

		Trial no 1					
setting no:		**19**	**20**	**21**	**22**	**23**	**24**
setup		**12**	**11**		**13**	**11**	
date		**03.12.**	**04.12.**	**4.12.**	**04.12.**	**04.12.**	**04.12.**
time		17:30	08:40	09:05	11:00	13:10	13:33
Extruder							
power Extruder (P-max = 46 KW)	KW	7,4	5,8	9	9,6	8,2	10,5
torque Extruder min.	Nm	75	59	89	98	83	106
torque Extruder max. (M-max motor = 170 Nm)	Nm	76	58	89	99	83	106
speed Extruder (n-max = 250 min-1)	min-1	80	80	80	80	80	80
dosing units							
dosing of rubber granulat	%	90	87,5	95	90	90	90
dosing of rubber granulat	kg/h	22,50	21,88	23,75	22,50	22,50	22,50
dosing of pepton	%	5	7,5	0	5	5	0
dosing of pepton	kg/h	1,25	1,88	0,00	1,25	1,25	0,00
dosing of TDAE	%	5	5	5	5	5	5
dosing of TDAE	kg/h	1,25	1,25	1,25	1,25	1,25	1,25
speed of the TDAE pump	rpm	141,98	141,98	141,98	141,98	141,98	141,98
capacity set	kg/h	25	25	25	25	25	25
temperature control							
temp. cooling water	°C	15	15	15	15	15	15
temp. feed section	°C	15	15	15	15	15	15
setting temperature cylinder 1	°C	180	180	180	150	150	150
temp. cylinder 1 oil flow	°C	181	181	181	151	151	-
temp. cylinder 1 oil return	°C	176	176	176	147	147	-
mass flow cylinder 1 oil	m^3/min	0,034	0,034	0,034	0,034	0,034	-
heat flow cylinder 1	kW	5,3	5,3	5,3	4,2	4,2	-
setting temperature cylinder 2	°C	170	200	200	150	170	150
temp. cylinder 2 oil flow	°C	169,3	199,5	199,5	147,9	169,6	148,8
temp. cylinder 2 oil return	°C	168,7	198,6	198,8	147	169,2	148,8
mass flow cylinder 2 oil	m^3/min	0,04	0,04	0,04	0,04	0,04	0,04
heat flow cylinder 2	kW	0,8	0,8	0,6	1,5	0,5	0,0
setting temperature cylinder 3	°C	150	150	150	150	150	150
temp. cylinder 3 water flow	°C	151,5	151,8	152,1	151,8	151,8	152
temp. cylinder 3 water return	°C	150,3	150,9	151,1	150,6	150,6	151
mass flow cylinder 3 oil	m^3/min	0,04	0,04	0,04	0,04	0,04	0,04
heat flow cylinder 3	kW	1,9	1,4	1,6	1,9	1,9	1,6
setting temperature cylinder 4	°C	100	130	130	130	150	150
temp. cylinder 4 water flow	°C	100,9	130,3	129,8	130	150	150,2
temp. cylinder 4 water return	°C	101,2	129,8	129,4	129,5	149,1	149,3
mass flow cylinder 4 water	m^3/min	0,054	0,054	0,054	0,054	0,054	0,054
heat flow cylinder 4	kW	-0,5	0,8	0,7	0,8	1,5	1,5
total heat flow	kW	7,5	8,4	8,2	8,4	8,1	3,1
temp. Extruder die oil	°C	160	160	160	160	160	160
mass temperature/pressure							
T-1 melt temp. between cylinder 1 & 2	°C	146	165	210	188	207	240
T-2 melt temp. between cylinder 2 & 3	°C	184	201	228	188	212	198
T-3 melt temp. between cylinder 3 & 4	°C	177	187	193	183	180	189
T-4 melt temp. at the die	°C	189	188	200	189	189	202
T-5 melt temp. Outlet manuel IR	°C	195	210	250	185	180	
P-1 melt pressure cylinder 1 & 2	bar	13	9	35	39	28	30
P-2 melt pressure cylinder 2 & 3	bar	7	5	1	2	7	0
P-3 melt pressure cylinder 3 & 4	bar	16	14	12	13	8	11
P-4 melt pressure at the die	bar	38	21	27	23	18	27
Vacuum							
Vacuum at M2	mbar	200	5	5	-	10	150
Vacuum at M3	mbar	200	5	5	140	10	150
output							
specific energy	KWh/kg	0,296	0,232	0,36	0,384	0,328	0,42

remark

Target: devulkanisation of rubber

setting 19
with the smaler die the material is much more brittle.
reduce the temperature in the 4th module because
of a very high outlet temp.
The outlet temp. comes down as an effect of this.

setting 20
using more pepton for a better devulkanisation.
the process is stable. The material is as fin as yesterday.

setting 21
setting with out any pepton.
The pressure at the 1st ring is pretty high.
Also the temperaturat over all rings and the outlet temp.
The particles are very smal.

setting 22
change the dosing point of the pepton from main feed
to side feed in 2nd module.
degrease the temperature in 1st and 2nd module
to get not so much radikals by oxigen.
with this setup we get an verry high torque.
The fluctuation of the pressure at the 2nd dispergenring
is so high that it is not possible to suck a stable vaccum.
change back to setup 11

setting 23
changing to finer raw material 0,8-2,2mm diameter.
The pressure at the 1st ring is pretty high.
we have to reduce the set temp. in this barrel from 180°C
to 150°C to prevent the material to overheat.

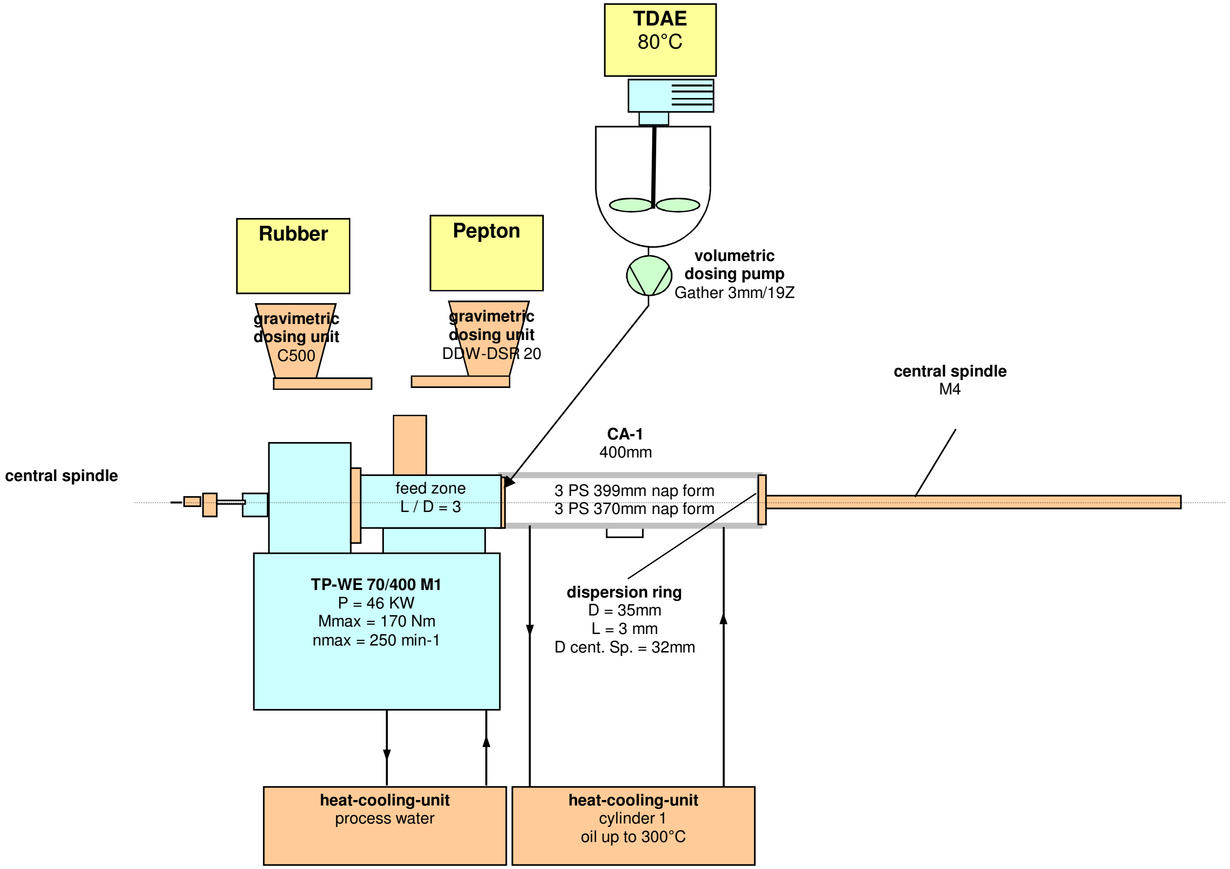
setting 24
setting without pepton
the pressure and the Temperature at the 1st ring is
much to high.

test report **TP-WE 70/1600 M4**

company:	**Rumal**	commission no.: **06820t0001**
present:	**Mr. Migchels; Mr. Van den Brand**	**(Rumal)**
	Mrs. Dr. Ir. Dierkes; Mr. Dr. Ir. Noordermeer; Mr. Rajendran	**(Universit of Twente)**
	Mr. Wallis	**(BKF)** leading: M.Gerdon
	Mr. Gerdon	**(ENTEX** date: 2015-12-02-04

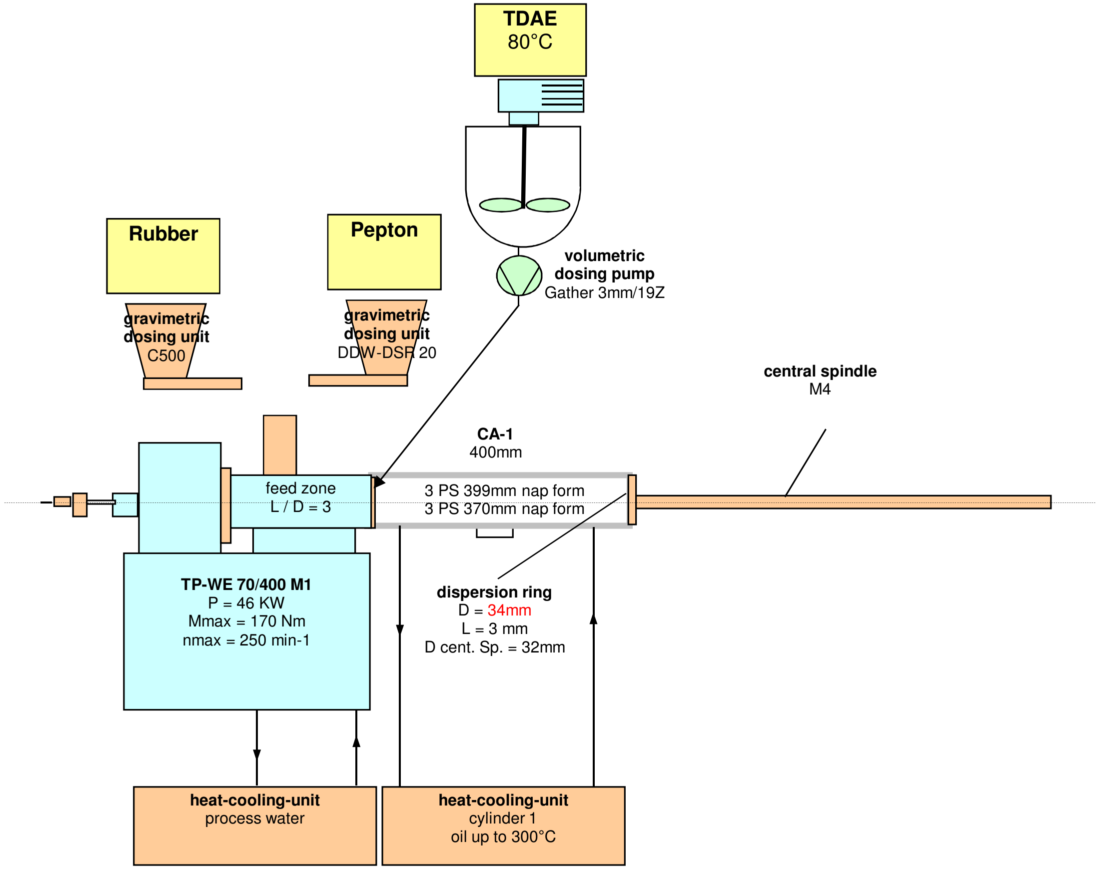
		Trial no 1						**remark**
setting no:		**25**	**26**	**27**				**Target:** devulkanisation of rubber
setup		**11**						
date		**04.12.**	**04.12.**	**04.12.**				
time		14:05	14:30	15:00				
Extruder								**setting 25**
power Extruder (P-max = 46 KW)	KW	9,8	18,6	7,6				chaning to premixed material
torque Extruder min.	Nm	98	150	155				The temperature in the 1st module is still to high like the
torque Extruder max. (M-max motor = 170 Nm)	Nm	98	151	158				setting with the fine material.
speed Extruder (n-max = 250 min-1)	min-1	80	100	40				The strand is much more compact than in the settings
dosing units								before.
dosing of rubber granulat	%	100	87,5	95				
dosing of rubber granulat	kg/h	25,00	21,88	23,75				
dosing of pepton	%	0	7,5	0				**setting 26**
dosing of pepton	kg/h	0,00	1,88	0,00				try to find the max. output.
dosing of TDAE	%	0	5	5				At this settings the output is maximum. With an higer
dosing of TDAE	kg/h	0,00	1,25	1,25				output we need more speed and it is not possible to
speed of the TDAE pump	rpm	-	141,98	141,98				controle the mass temperature anymore.
capacity set	kg/h	25	25	25				
temperature control								
temp. cooling water	°C	15	15	15				**setting 27**
temp. feed section	°C	15	15	15				reduce the speed to increase the dwell time.
setting temperature cylinder 1	°C	150	150	150				At 40 rpm the max. torque is reached.
temp. cylinder 1 oil flow	°C	151	151	151				The outlet temp. is pretty low, but the pressure at the 1st
temp. cylinder 1 oil return	°C	147	147	147				ring is very high.
mass flow cylinder 1 oil	m^3/min	0,034	0,034	0,034				
heat flow cylinder 1	kW	4,2	4,2	4,2				
setting temperature cylinder 2	°C	150	150	150				
temp. cylinder 2 oil flow	°C	150,1	150,2	150				
temp. cylinder 2 oil return	°C	150,1	150,6	149,9				
mass flow cylinder 2 oil	m^3/min	0,04	0,034	0,034				
heat flow cylinder 2	kW	0,0	-0,5	0,1				
setting temperature cylinder 3	°C	150	150	150				
temp. cylinder 3 oil flow	°C	152	152,1	151,9				
temp. cylinder 3 oil return	°C	151,1	152	150,8				
mass flow cylinder 3 oil	m^3/min	0,04	0,04	0,04				
heat flow cylinder 3	kW	1,4	0,2	1,7				
setting temperature cylinder 4	°C	150	150	150				
temp. cylinder 4 water flow	°C	150	148,7	149,6				
temp. cylinder 4 water return	°C	149,3	148,3	148,6				
mass flow cylinder 4 water	m^3/min	0,054	0,04	0,04				
heat flow cylinder 4	kW	1,2	0,5	1,2				
total heat flow	kW	6,8	4,3	7,3				
temp. Extruder die oil	°C	160	160	160				
mass temperature/pressure								
T-1 melt temp. between cylinder 1 & 2	°C	220	232	207				
T-2 melt temp. between cylinder 2 & 3	°C	203	224	194				
T-3 melt temp. between cylinder 3 & 4	°C	171	190	168				
T-4 melt temp. at the die	°C	180	194	173				
T-5 melt temp. Outlet manuel IR	°C	160	181	155				
P-1 melt pressure cylinder 1 & 2	bar	28	38	41				
P-2 melt pressure cylinder 2 & 3	bar	6	9	12				
P-3 melt pressure cylinder 3 & 4	bar	5	10	8				
P-4 melt pressure at the die	bar	11	17	14				
Vacuum								
Vacuum at M2	mbar	300	300	300				
Vacuum at M3	mbar	100	100	100				
output								
specific energy	KWh/kg	0,392	0,744	0,304				

setup 1



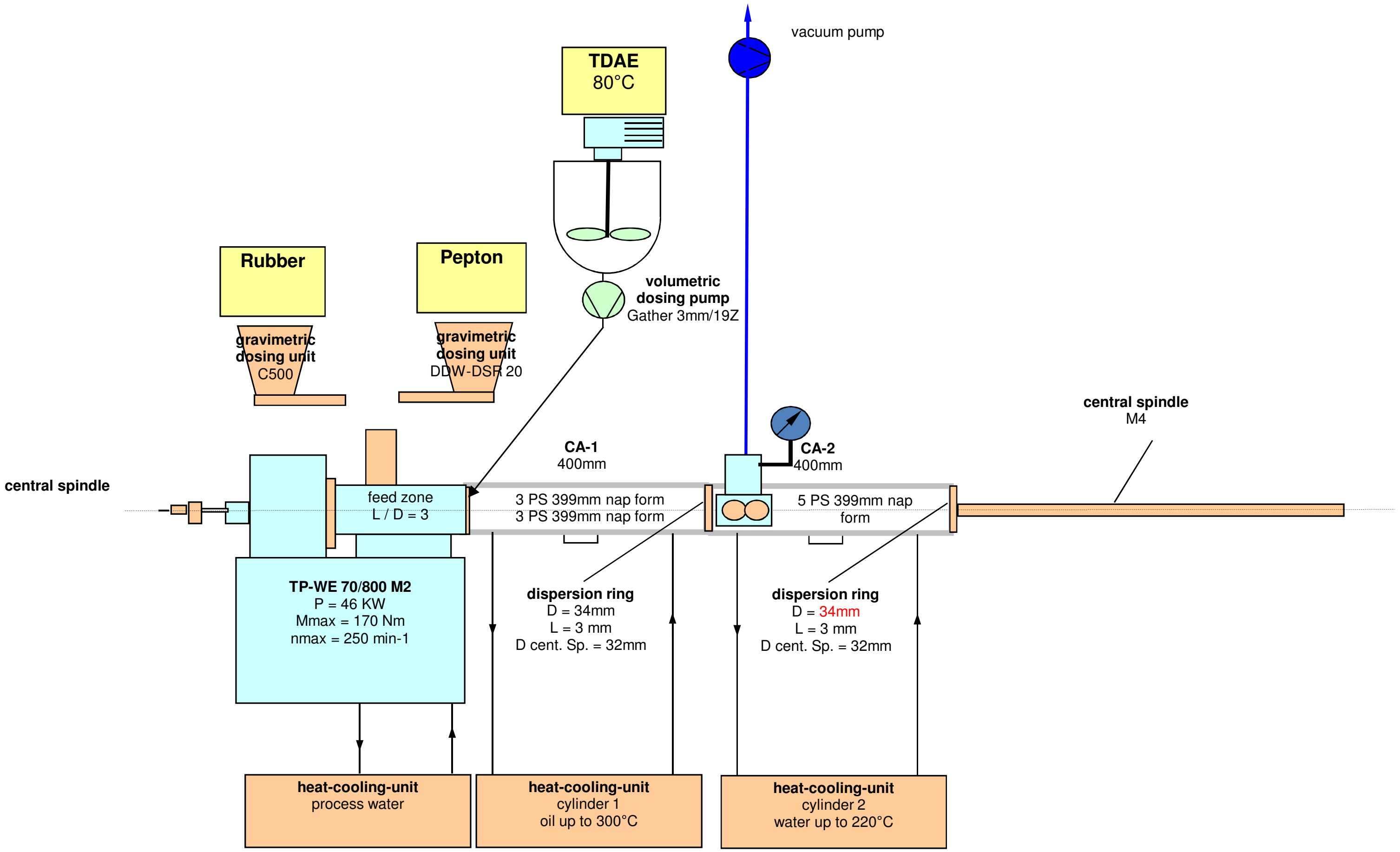
Firma:	**Rumal**	
Kom.-Nr.:	06820t0001	
Datum:	2015-12-02-04	ENTEX
Stand:	2015-12-07	Erstellt durch: M. Gerdon

setup 2



Firma:	**Rumal**	
Kom.-Nr.:	06820t0001	ENTEX
Datum:	2015-12-02-04	
Stand:	2015-12-07	Erstellt durch: M. Gerdon

setup 3



Firma:	**Rumal**	
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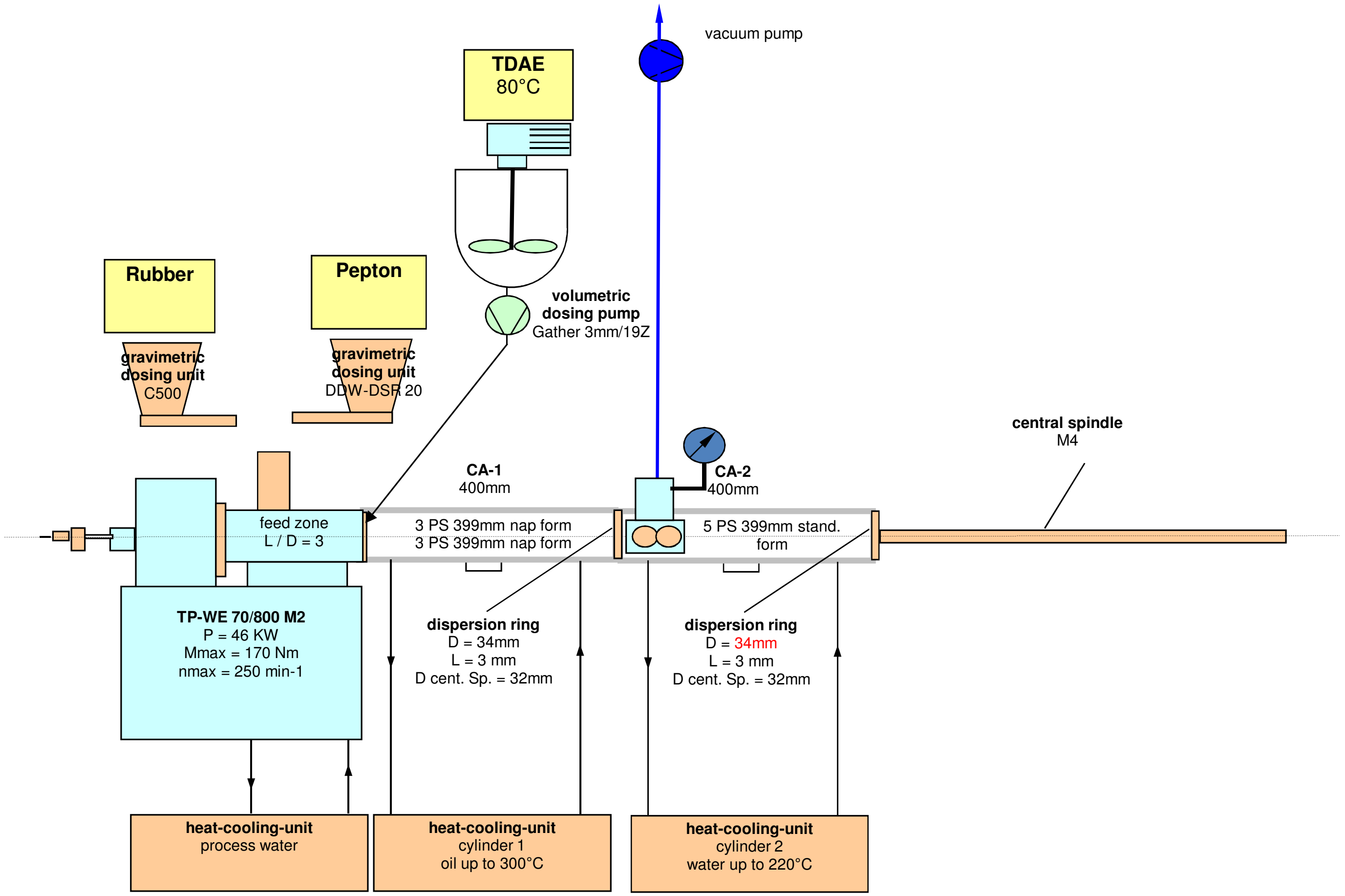
Datum:	2015-12-02-04	
Stand:	2015-12-07	Erstellt durch: M. Gerdon

setup 4



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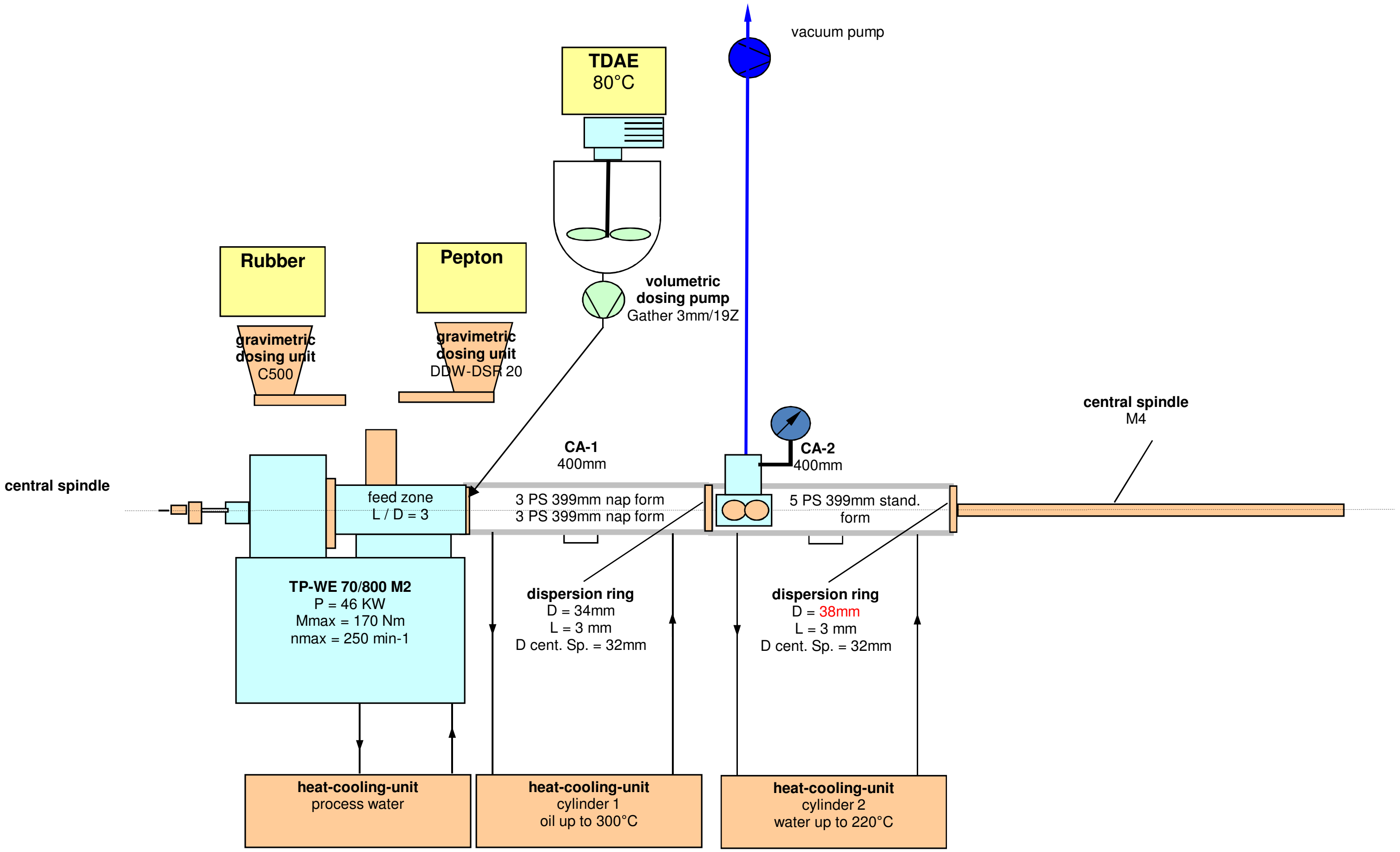
Kom.-Nr.:	06820t0001	ENTEX
Datum:	2015-12-02-04	
Stand:	2015-12-07	Erstellt durch: M. Gerdon

setup 5



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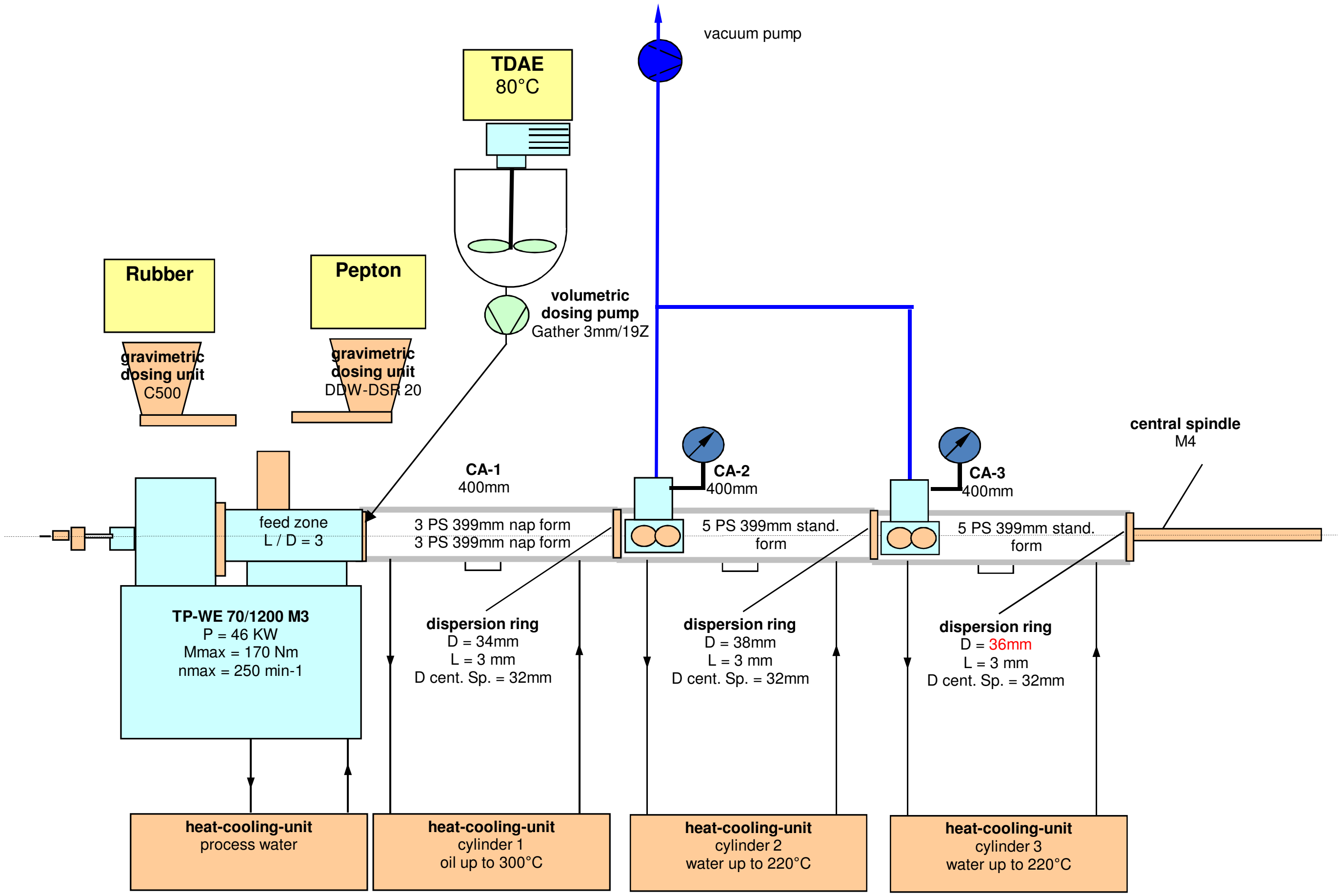
setup 6



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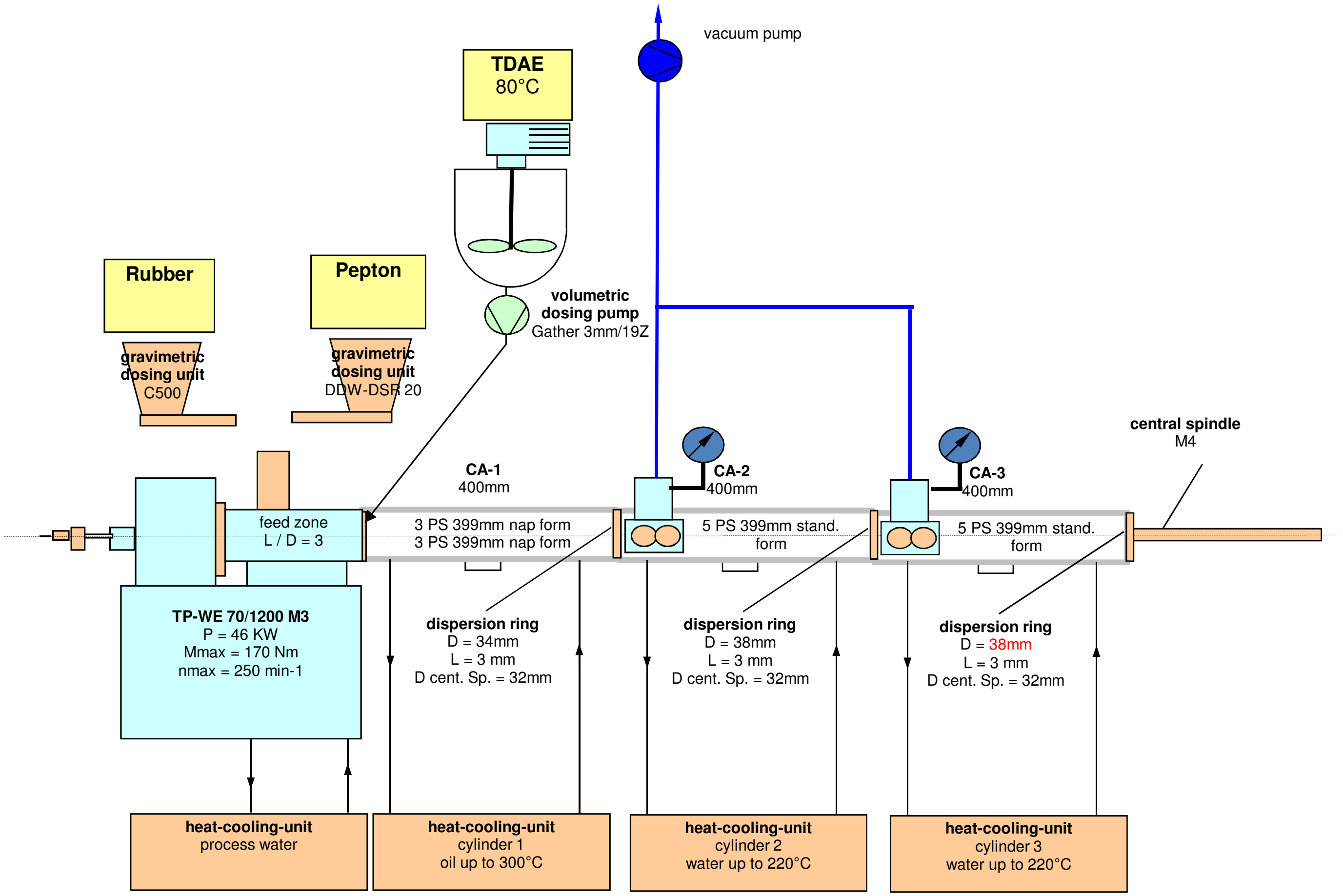
Datum:	2015-12-02-04	
Stand:	2015-12-07	Erstellt durch: M. Gerdon

setup 7



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Kom.-Nr.:	06820t0001	
Datum:	2015-12-02-04	
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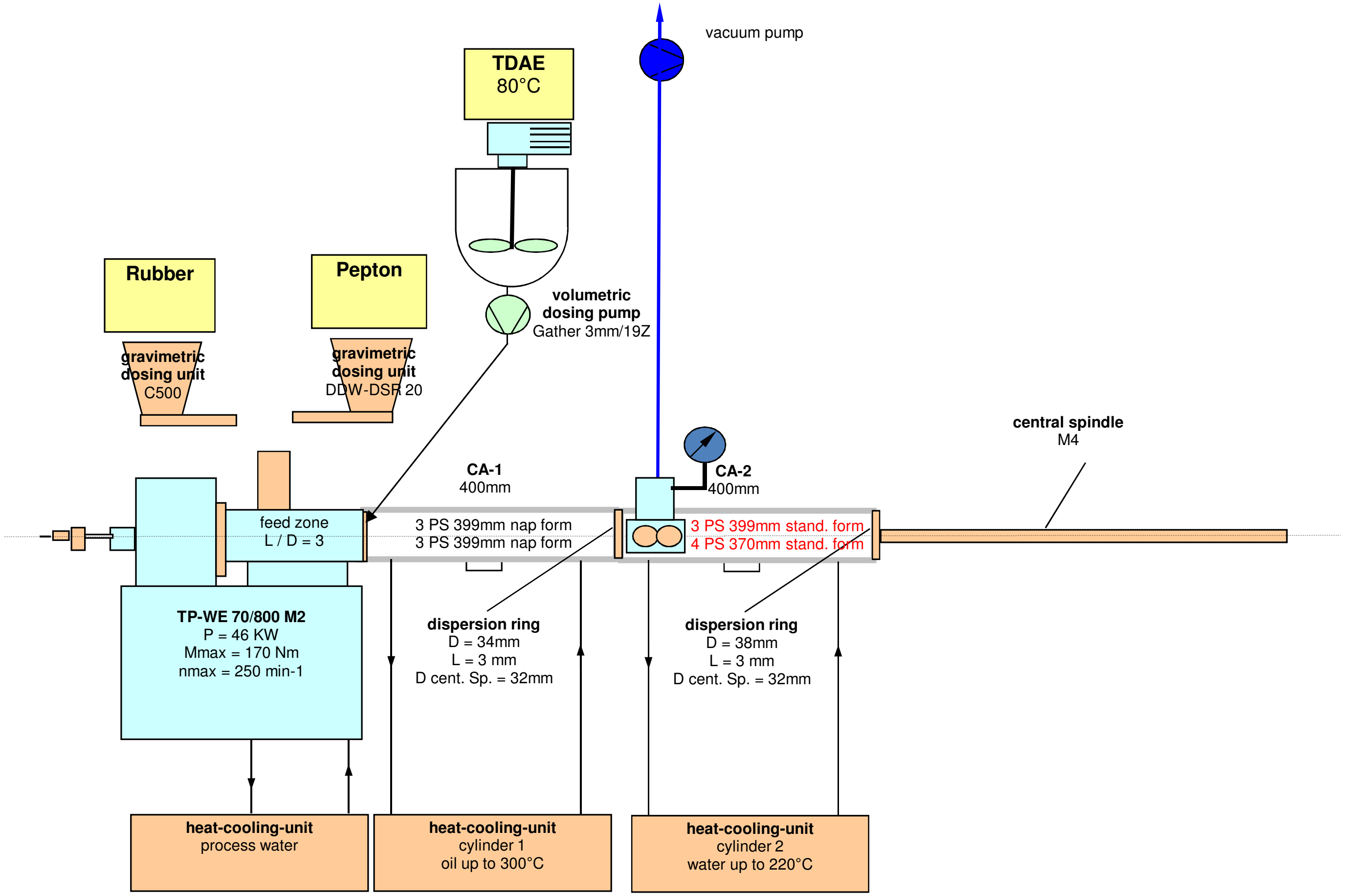
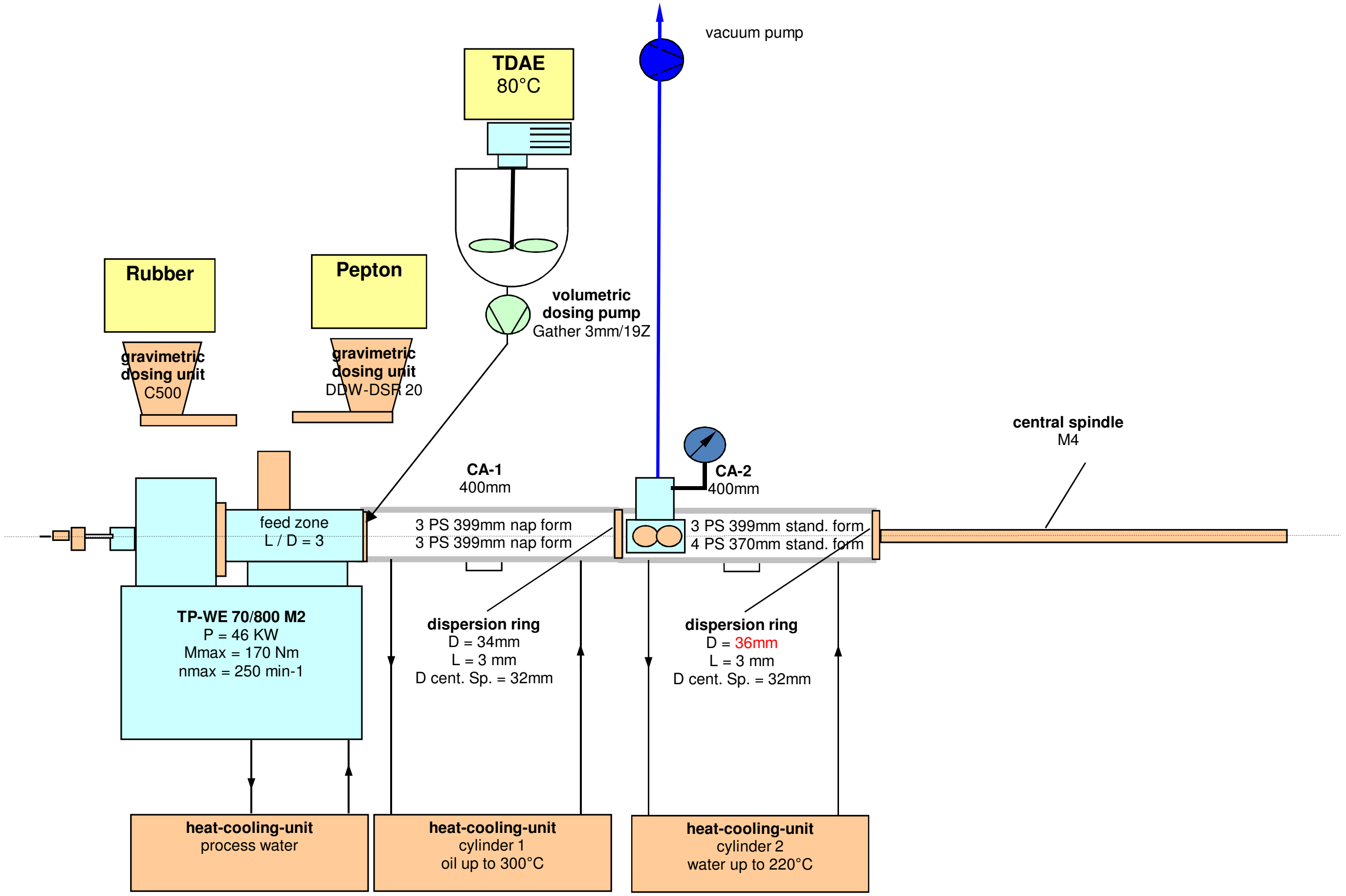
setup 8



Firma:	**Rumal**	
Kom.-Nr.:	06820t0001	
Datum:	2015-12-02-04	
Stand:	2015-12-07	Erstellt durch: M. Gerdon

setup 9



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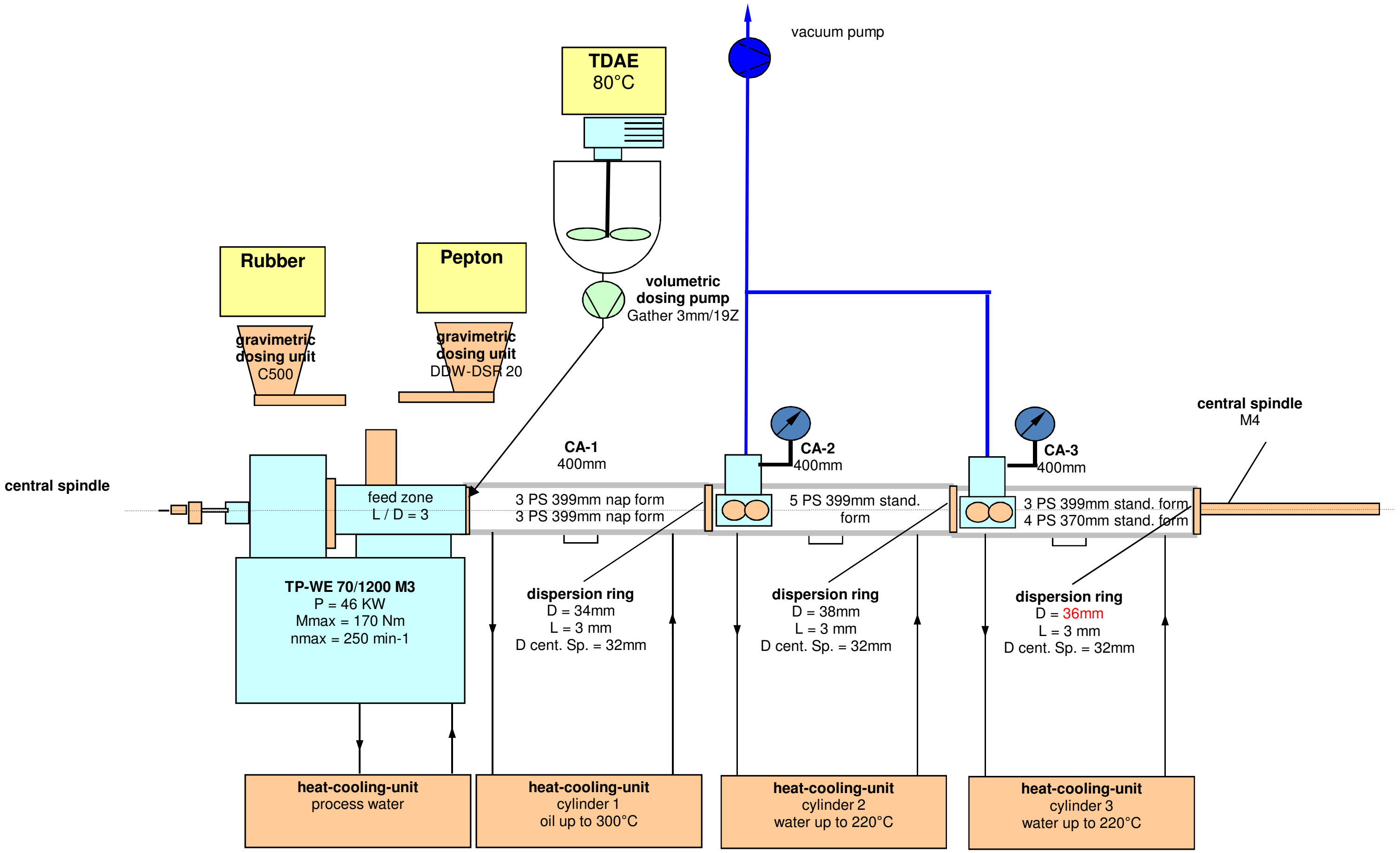
Kom.-Nr.:	06820t0001	ENTEX
Datum:	2015-12-02-04	
Stand:	2015-12-07	Erstellt durch: M. Gerdon

setup 10



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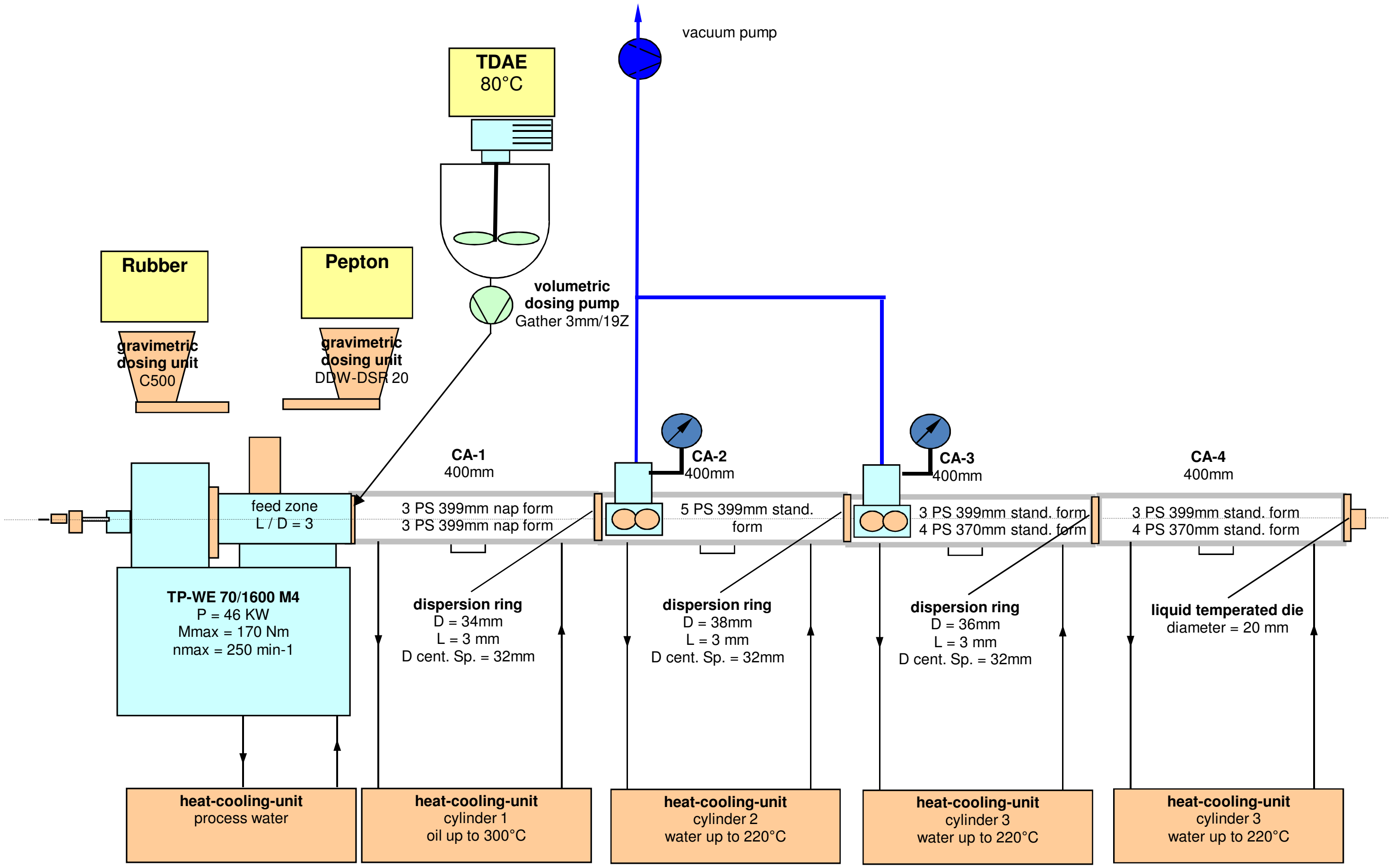
Kom.-Nr.:	06820t0001	
Datum:	2015-12-02-04	
Stand:	2015-12-07	Erstellt durch: M. Gerdon

setup 11



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Datum:	2015-12-02-04	
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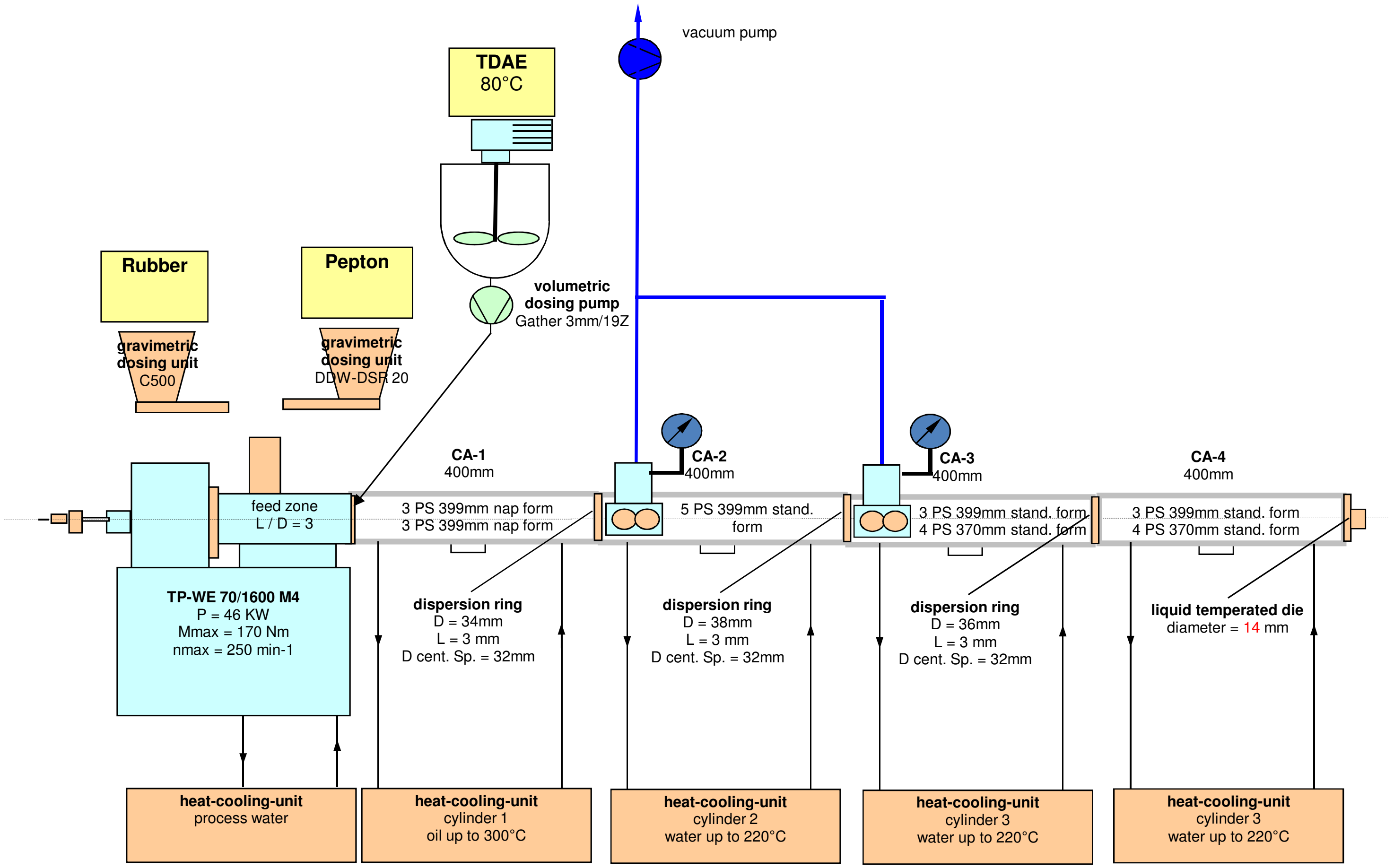
setup 12



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Kom.-Nr.:	06820t0001	
Datum:	2015-12-02-04	
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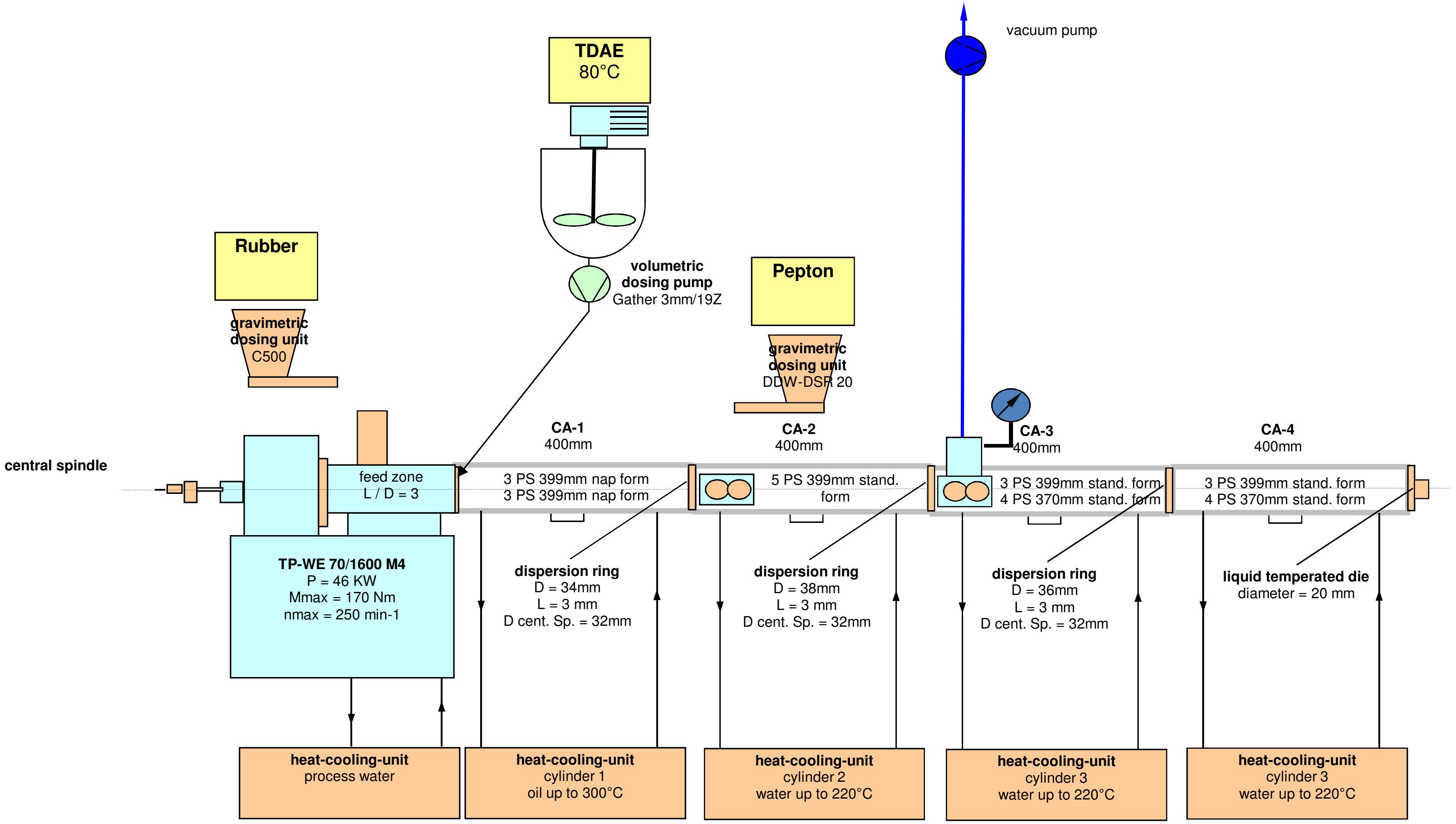
setup 13



Firma:	**Rumal**	
Kom.-Nr.:	06820t0001	ENTEX
Datum:	2015-12-02-04	
Stand:	2015-12-07	Erstellt durch: M. Gerdon

Appendix-3

Process Design
for Truck Tire Granulate Devulcanization
in a Planetary Roller Extruder

STAGE 3

1. Introduction

Stage-3 is the continuation of the stage 2 trials after its 4 module setup with the rubber granulate to be processed with and without devulcanization aid at low temperatures and low shear. The following module parameters were used: 150/150/150/150^{0}C (40 rpm), similar to the process conditions of Trial-27.

2. Experimental

This test series was again performed in the pilot installation at Entex, in cooperation with Rumal.

2.1 Materials

The Ground Truck tire Rubber (GTR) used in this stage of the process design was supplied by RUMAL BV, The Netherlands, with a particle size of 0.8 - 2.5 mm. The devulcanization aid – DBD (2,2'- dibenzamido diphenyldisulphide, DBD) - was obtained from Thomas Swan & Co. Ltd., United

Kingdom. TDAE oil used as processing oil for the devulcanization was supplied by Hansen & Rosenthal, Germany.

2.2 Preparation of devulcanizates

GTR was pre-swollen in a mixture of DBD and TDAE oil for 30 minutes at room temperature. From each trial, 2 samples were obtained: one after passing it through the cold roll (CR) and the other by cooling with dry ice containing CO_2 gas (DIC).

The devulcanizate was evaluated during the tests by:

1. Visual Inspection concerning particle size, smoothness/remaining particles, consistency, tackiness.
2. The material outlet temperature from the extruder was measured by a temperature sensor in the extruder die as well as manually with a thermocouple.

2.3 Mixing and Revulcanization of Devulcanized Rubber Compound (DRC)

2.3.1 Compound formulation and mixing procedure:

The compound recipe and mixing procedure are given in Chapter 4, Table 2 and 3.

2.4 Moulding

For moulding of the devulcanizate, the procedure as described in Chapter 4 was used.

2.5 Characterization of Devulcanizate, Re-Vulcanizate and Blends

2.5.1 Complex viscosity:

Complex viscosity values were analyzed via dynamic viscoelastic measurements performed with the Rubber Process Analyzer (RPA 2000, Alpha Technologies) as described in Chapter 3.

2.5.2 Rubber-Soluble Fraction:

The sol fraction of the devulcanizate was determined by extraction in a Soxhlet apparatus, as described in chapter-3.

2.5.3 Cure Characteristics (ASTM D2064):

The cure characteristics were determined using a Rubber Process Analyzer (RPA 2000, Alpha Technologies) as described in Chapter 3.

2.5.4 Mechanical properties:

Tensile tests were carried out on dumb-bell shaped specimens, using a Zwick Z1.0 tensile testing machine as described in Chapter 3.

3. Results & discussion

Design of the extruder setup and parameters and visual analysis of the devulcanizate

The process parameters are given in Appendix 3. The starting conditions for the design of the Planetary extruder setup-3 as shown in Figure 1, is as follows:

The setup-1 series of 4 spindles was similar to the Trial-27 settings from stage 2 trials. The module temperatures are 120/150/150/150^{0}C and a screw speed of 70 rpm was used. The spindles used in the modules were 6 long nap spindles in module 1, 5 standard spindles in module 2, and 3 long standard spindles (399mm) and 4 short standard spindles (370mm) in module 3 and 4 to increase the free volume as shown in Figure 1.

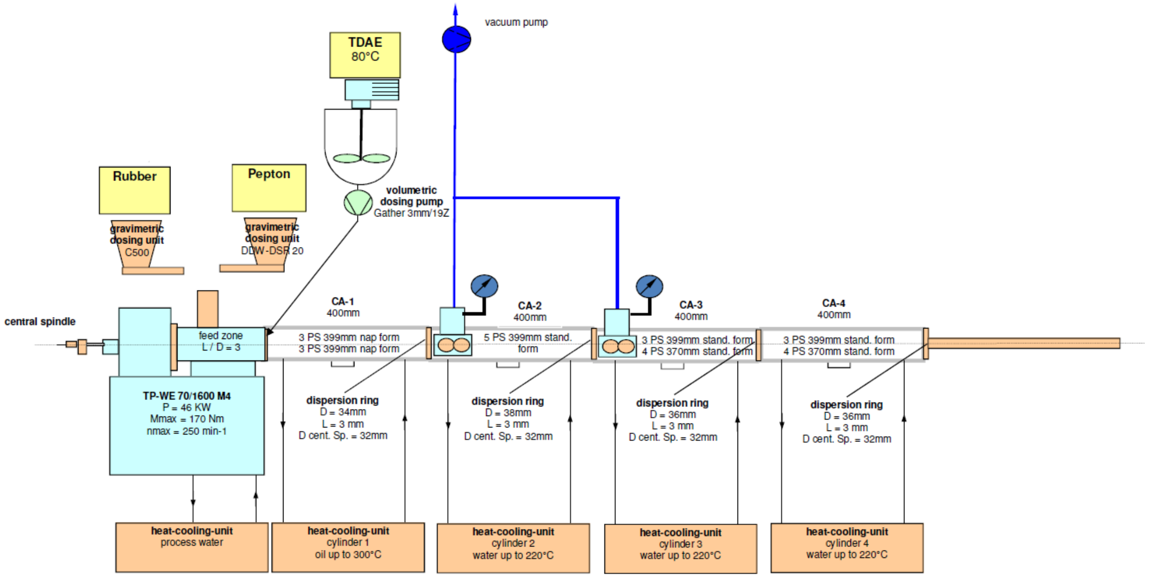


Figure 1: Design setup-1 for the planetary roller extruder

Trial-1 (setup-1): The first module was set at a low temperature of 120^{0}C, since the mass temperature was higher than during the trials in stage 2. As this observation was made more often during the extruder trials at all stages, this indicates that repeatability of the extruder conditions is a critical factor. For this trial, pre-swollen granulate was used.

Trial-2 (setup-1): The screw speed of the central spindle was increased to 100 rpm using pre-blended material, but the material outlet temperature was still high (215^{0}C).

Trial-3 (setup-1): With same screw speed but at low module temperatures of 90/100/100/100^{0}C, the material outlet temperature was still around 200^{0}C. Probably the shear increases the material temperature.

Trial-4 (setup-1): With same module temperature, the screw speed was lowered to 60 rpm, but still the material outlet temperature was around 200^{0}C.

Trial-5 (setup-1): With same settings, the feed rate was halved to 12 Kg/hr. But still the material outlet temperature was around 200^{0}C, as the low feed rate increases the residence time in the extruder.

Trial-6 (setup-1): With same feed rate, the screw speed was lowered to 40 rpm. But again the material outlet temperature was still around 200^{0}C, as the residence time was further prolonged.

Trial-7 (setup-1): With settings similar to Trial-4 and a screw speed of 60 rpm, the devulcanization system was added separately. The temperature and pressure of the 3rd and 4th module were higher compared to the 1st and 2nd module, indicating that the devulcanization reaction is happening in the 3rd and 4th module.

Trial-8 (setup-1): To start the devulcanization reaction earlier, the temperature in module 1 was increased to 150^{0}C.

Trial-9 (setup-1): By switching off the DBD supply, the pressure at the 1st ring between module 1 and 2 was increased from 10 to approximately 40 bar, and also the temperature raised very fast.

Trial-10 (setup-1): The oil loading was increased to 10% to reduce the pressure. However, the pressure was still the same as in Trial-9, but the particle size of the material was smaller than in Trial-9.

Trial-11 (setup-1): The settings were similar to Trial-8 with a screw speed of 70 rpm. With the introduction of DBD again, the viscosity and the pressure dropped to a greater extent: The devulcanization aid is crucial in controlling the pressure in the modules.

Trial-12 (setup-1): With the same settings, the screw speed was increased to 100 rpm. The particle size becomes larger than in Trial-11, and the torque decreases compared to Trial-11.

Trial-13 (setup-1): The same settings as Trial-12, but at half feed rate (= 12 Kg/hr) and a screw speed of 60 rpm to get a longer residence time.

Trial-14 (setup-1): The same settings as trial-12 and half feed rate, and the screw speed was lowered to 30 rpm.

Trial-15 (setup-1): With otherwise the same settings as in Trial-12, the standard feed rate of 25 Kg/hr and a screw speed of 30 rpm was used. The particle size was bigger than in the previous trial.

Trial-16 (setup-1): With a lower temperature in the 1st module of 100^{0}C, the screw speed was increased to 100 rpm. Very fine material was obtained at the end of the process. This indicates that the starting temperature should be low for a good grinding effect.

In order to increase the pressure at the extruder exit, a longer and cone shaped stop ring was used at the end of 4th module as shown in Figure 2.

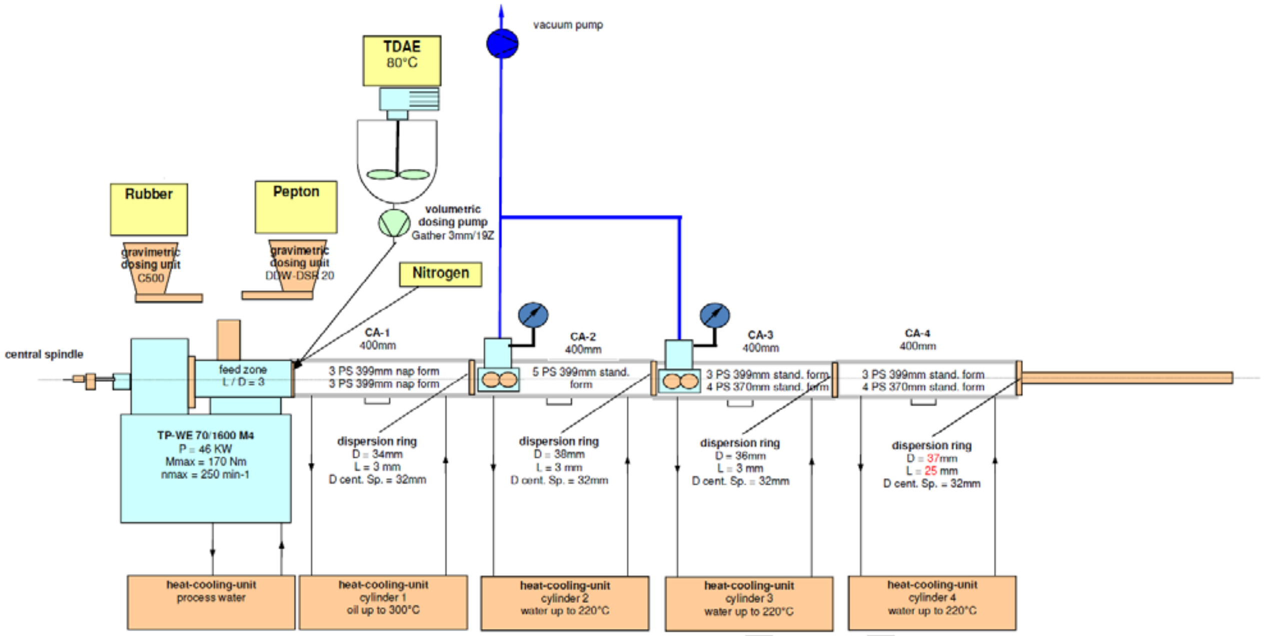


Figure 2: Design setup-2 for the planetary roller extruder

Trial-17 (setup-2): The outlet temperature was lower, around 180^0C, and fluffy material was obtained at the end of process. From visual inspection, this material looks rather good.

Trial-18 (setup-2): N_2 gas was introduced only at the end of the 1st module to study the effect of a reduction of oxygen on the devulcanization reaction. The material outlet temperature (170^0C) was lower than for Trial-17, but the material looked the same as in Trial-17. This leads to the conclusion, that from visual inspection the presence of nitrogen, or in other words the absence of oxygen, had no effect on the devulcanization.

The starting conditions on the second day were similar the ones of Trial-17, but with a reduced stop ring diameter of 35 mm.

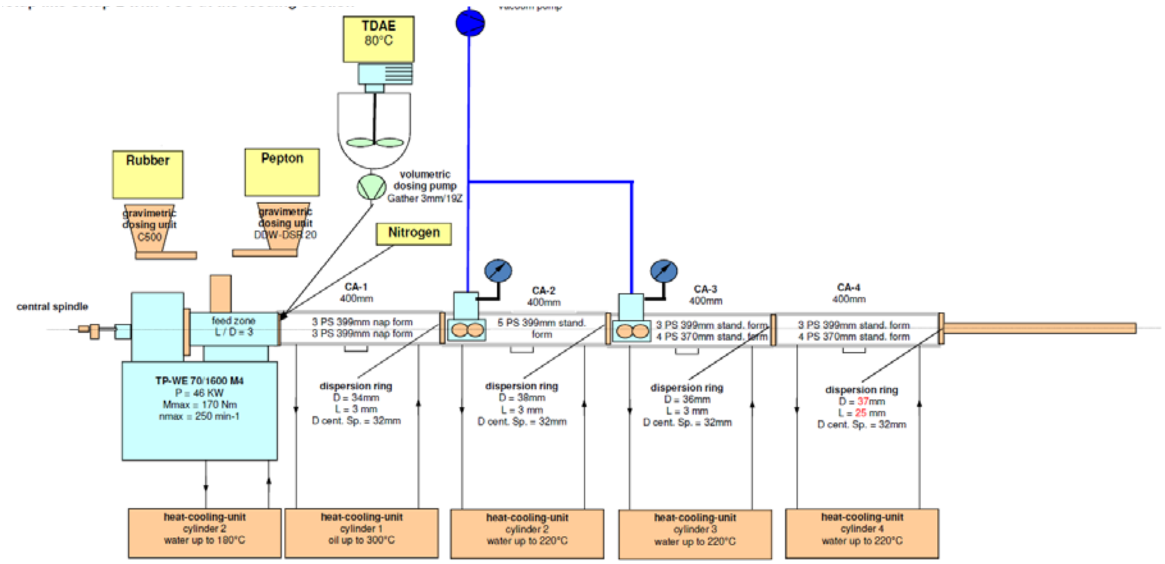


*Figure 4: Design setup-4 for the planetary roller extruder**

** There was no setup-3*

Trial-19 (setup-4): The material looks the same as in Trial-17.

The cone shaped ring diameter was reduced to 35 mm as shown in Figure 5.

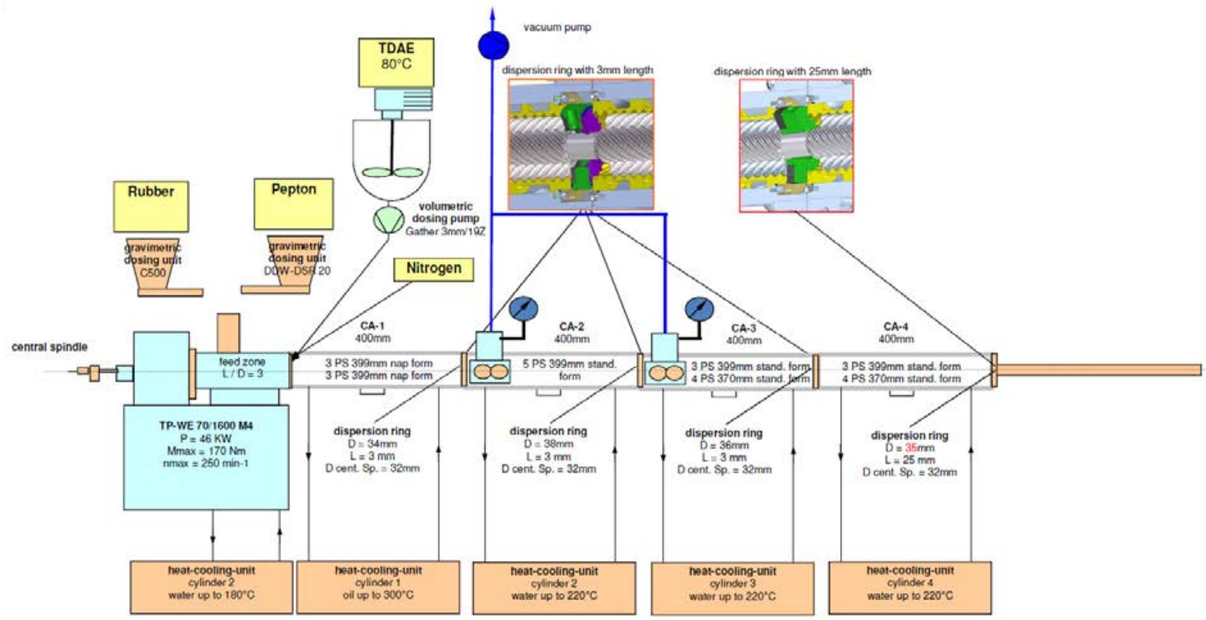


Figure 5: Design setup-5 for the planetary roller extruder

Trial-20 (setup-5): The torque and the outlet temperature are much higher than with the new dispersion ring.

The cone shaped ring diameter was increased to 37 mm in module 4 and 5, with 6 standard spindles, of which 3 short ones (370 mm) and 3 long ones (399 mm) in module 5, to increase the dwell time as shown in Figure 6.

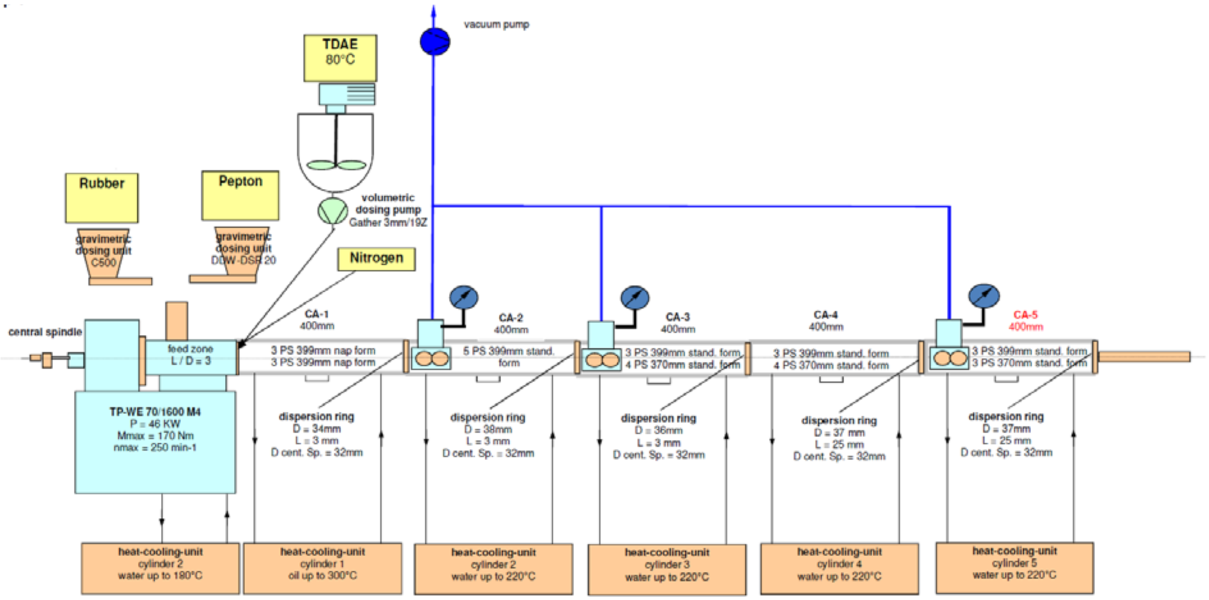


Figure 6: Design setup-6 for the planetary roller extruder

Trial-21 (setup-6): With a screw speed of 100 rpm, the temperature buildup was high, approximately 200^{0}C.

Trial-22 (setup-6): The screw speed was reduced to 70 rpm to increase the dwell time and reduce shearing forces. The dwell time was approximately 170 seconds.

Trial-23 (setup-6): The temperature of the 5th barrel was reduced to 70^{0}C to further reduce the temperature buildup. However, the maximum torque was reached at such a low temperature in the last module.

4 Igel spindles, 2 short ones (370 mm) and 2 long ones (399 mm), were now used for a more efficient cooling as shown in Figure 7.

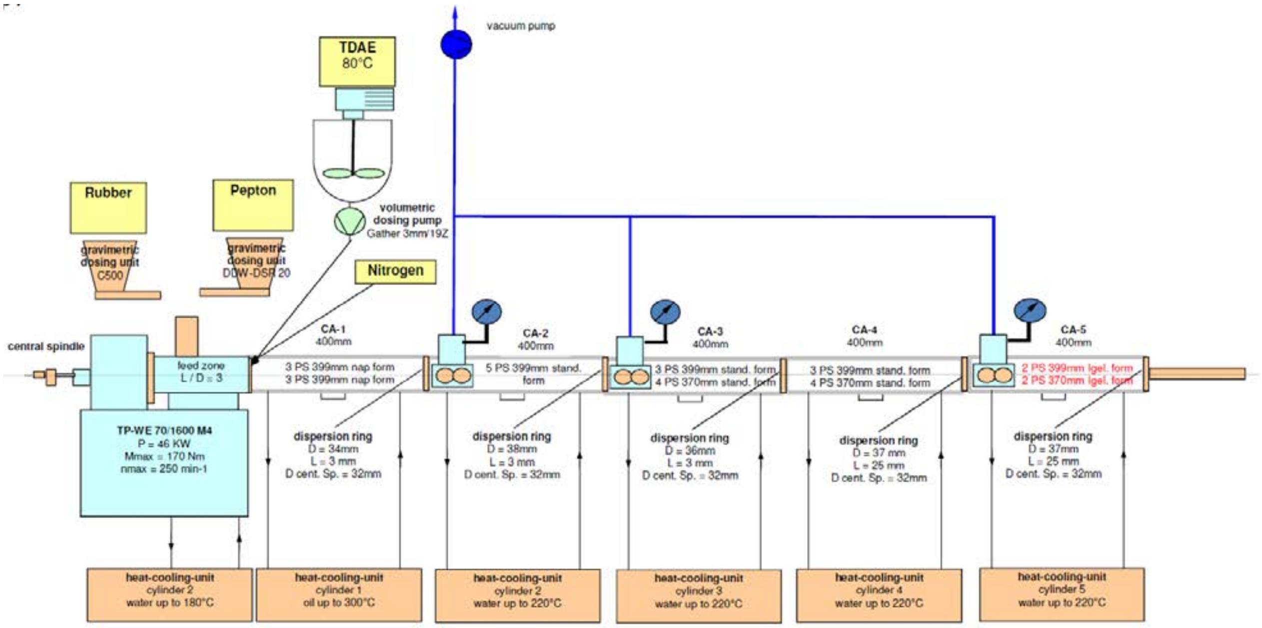


Figure 7: Design setup-7 for the planetary roller extruder

Trial-24 (setup-7): No difference in outlet temperature and torque with this setup compared to the earlier trial.

Trial-25 (setup-7): Module 2 temperature was increased to start the devulcanization reaction earlier. The mass outlet temperature was the same, but the torque was lower.

The cone shaped dispersion ring diameter was further increased to 40 mm as shown in Figure 8.

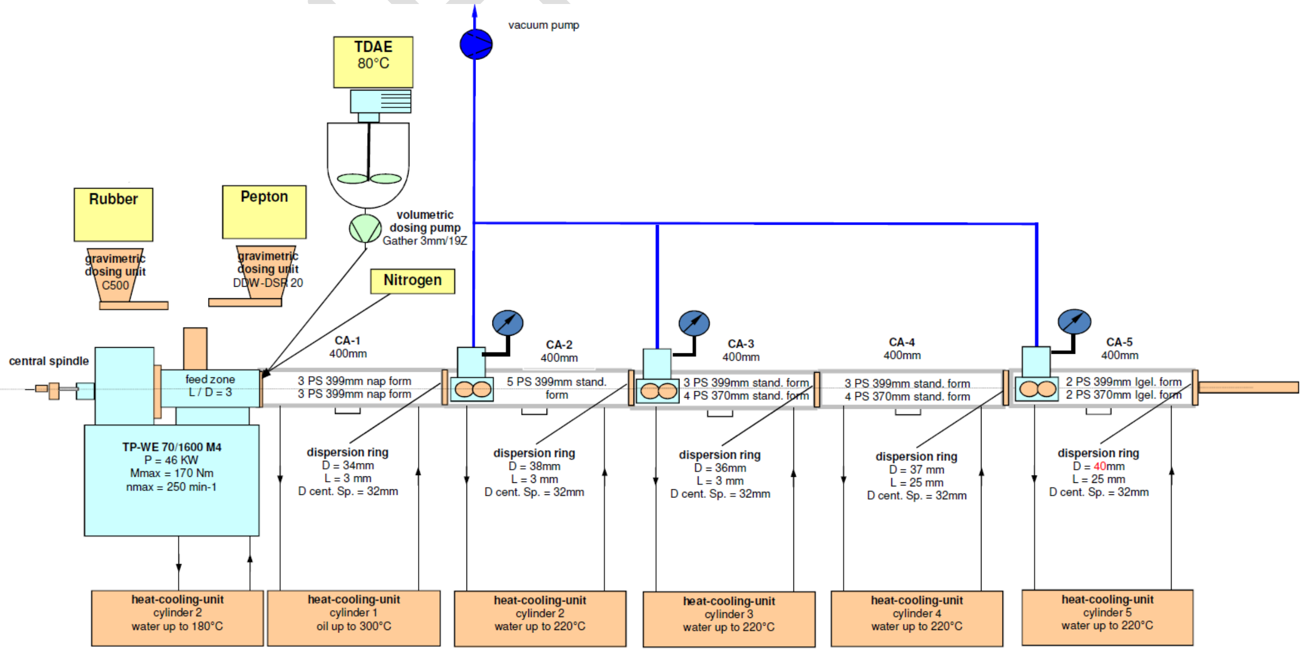


Figure 8: Design setup-8 for the planetary roller extruder

Trial-26 (setup-8): The material outlet temperature was much lower, but the material was not so sticky anymore.

In module 5, 4 igel spindles were replaced by 5 TT-3 spindles, again to get a more efficient cooling, as shown in Figure 9.

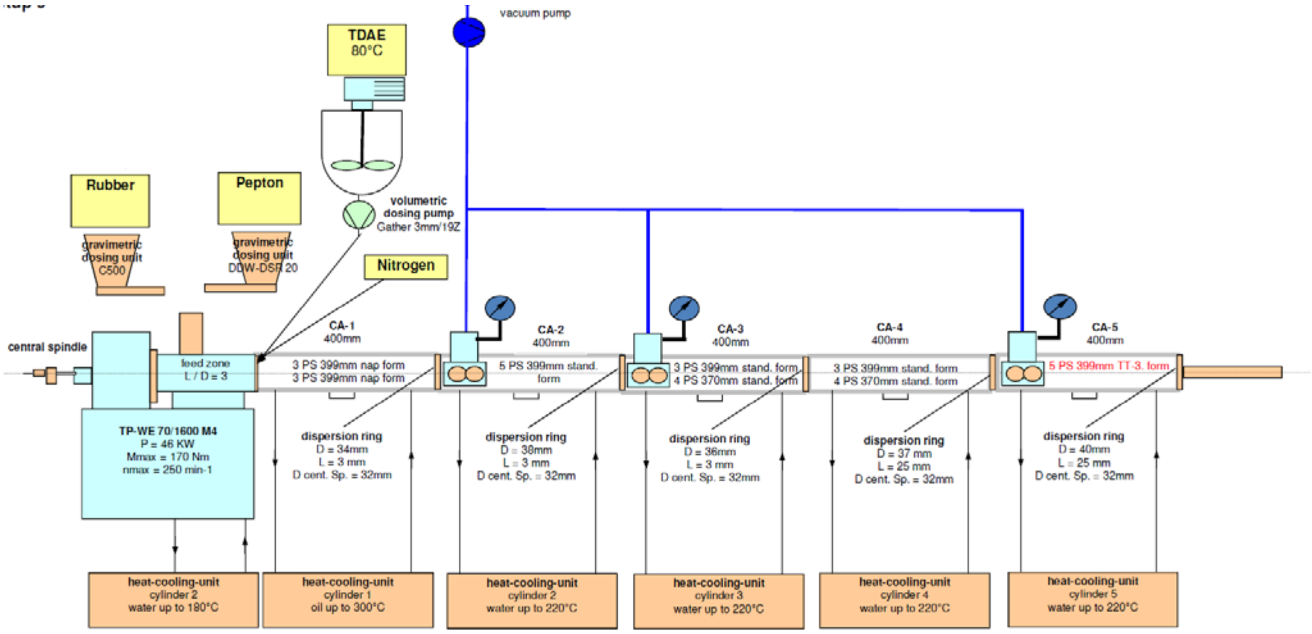


Figure 9: Design setup-9 for the planetary roller extruder

Trial-27 (setup-9): With the same settings as for Trial-26, the material outlet temperature was very low (145^{0}C).

The 6th module was built with the same setup as the 5th module with TT-3 spindles as shown in Figure 10.

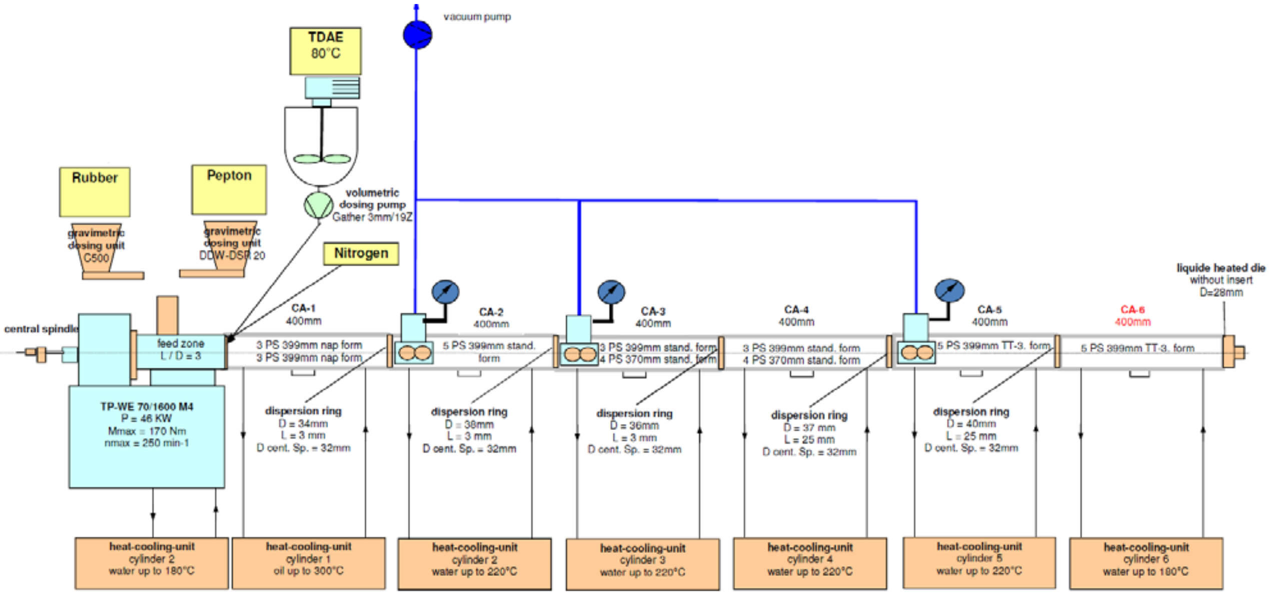


Figure 10: Design setup-10 for the planetary roller extruder

Trial-28 (setup-10): The material was very brittle, but after cooling it down on the cold roll, it formed a sheet.

Trial-29 (setup-10): The screw speed was increased for higher shear, but the output was too low. The reason was a strong vacuum suction: the material ended up in the trap of the vacuum pump. Therefore the vacuum was reduced to 200mbar.

Trial-30 (setup-10): With the same setting as Trial-29, the DBD amount was lowered. The material did not form a uniform sheet on cold rolling anymore; this led to the conclusion that a decrease in DBD content reduces the sheet forming ability.

Trial-31 (setup-10): The starting material was changed to a finer particle size tire rubber crumb and separate dosing of DBD and oil. The particle size was 0.8-2 mm.

Trial-32 (setup-10): The starting material was changed to a pre-blended finer particle size tire rubber crumb with a particle size of 0.8-2 mm.

In-depth analysis of the devulcanizates

The comparison between the devulcanizates was done the basis of the same number of modules.

3.1 Mooney Viscosity

Mooney viscosity measurements require a compact mass to be tested. The problem with most of the devulcanizates was that they were not compact, and there are air entrapments. To eliminate these, the samples were rolled on the 2-roll mill for a definite time; however, the 2-roll milling softens the polymer and affects the properties. In order to make the material more compact, the compression molding press was used. It turned out that room temperature pressing was of no use, since the material did not flow to form a sheet. Therefore higher temperatures were used, but little compaction did take place at 100^{0}C. However, this temperature was already too high, since a curing reaction did take place. For this practical reason, only the complex viscosity was used.

3.2. 4 Modules

3.2.1. Complex viscosity

The plots of complex viscosity versus frequency of the different devulcanizates are shown in Figure 11. For roll samples, the decrease in complex viscosity was in the following order:

Trial- 4 << 16 < 13 <1 << 20 = 17 < 5 = 2

The process conditions for the lowest viscosity cold roll devulcanizates are:

Trial-4: 120/150/150/150^{0}C (60rpm)

Trial-16: 90/100/100/100^{0}C (100rpm)

Trial-13: 150/150/150/150^{0}C (60rpm)

Generally a lower screw speed, which also increases the residence time, and a lower module temperature decrease the viscosity.

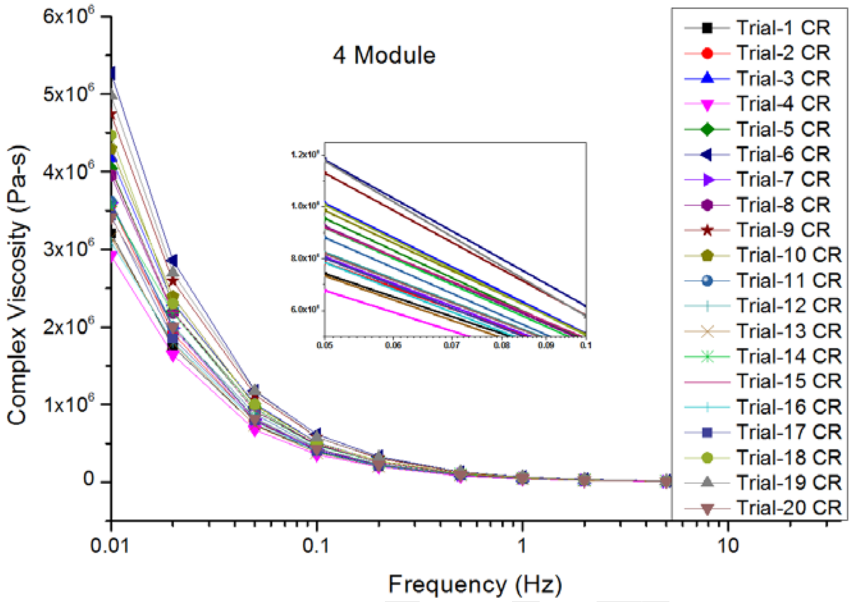


Figure 11: Complex viscosity measurements in a frequency sweep of 4 module cold rolled (CR) devulcanizates

3.2.2. Curing after addition of curatives

The maximum delta torque values obtained from rheometer curves were plotted after mixing of the devulcanizates with the curing agents to study the curing kinetics as shown in Figure 12. The delta torque values are increasing in the following order:

Trial-6> 3> 9> 10> 19

Trial-6 was half fed, increasing the residence time. Therefore the rubber should be more effectively be devulcanized. Trial-3 was processed at lower barrel temperatures (temperature lower than the melting point of DBD). Trial-9 and 10 had no DBD, only oil present for 5 and 10 % respectively. All the process conditions confirmed that a higher delta torque is seen for samples that are not effectively devulcanized or devulcanized without DBD signaling that DBD reacts with the double bonds of the elastomers affecting the re-curability of the devulcanizates.

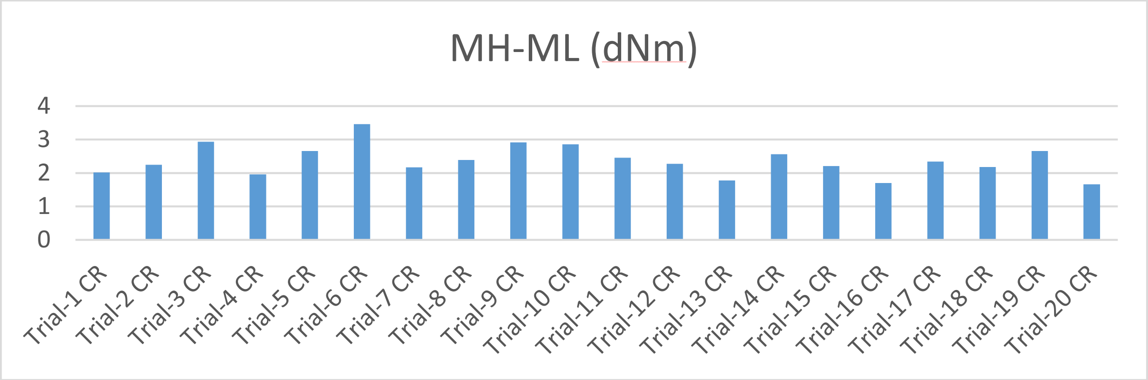


Figure 12: Delta torque (ΔT= MH-ML) for 4 module devulcanizates

3.2.3. Tensile Strength

The tensile strength values of the cold rolled devulcanizates are shown in Figure 13. The roll samples can be ranked in terms of increasing tensile strength as follows:

Trial-3> 6> 17> 18> 19

Generally, a higher delta torque value from the rheometer curve corresponds to a higher tensile strength. The high delta torque values were correlated to a samples with a low degree of polymer degradation by the disulfide, in particular at double bonds. So the less degraded samples also show high tensile strength values . Trial-17 and 18, which have a low outlet temperature due to a large diameter of the cone shaped stop ring, also have a higher tensile strength due to the lower degree of thermal degradation.

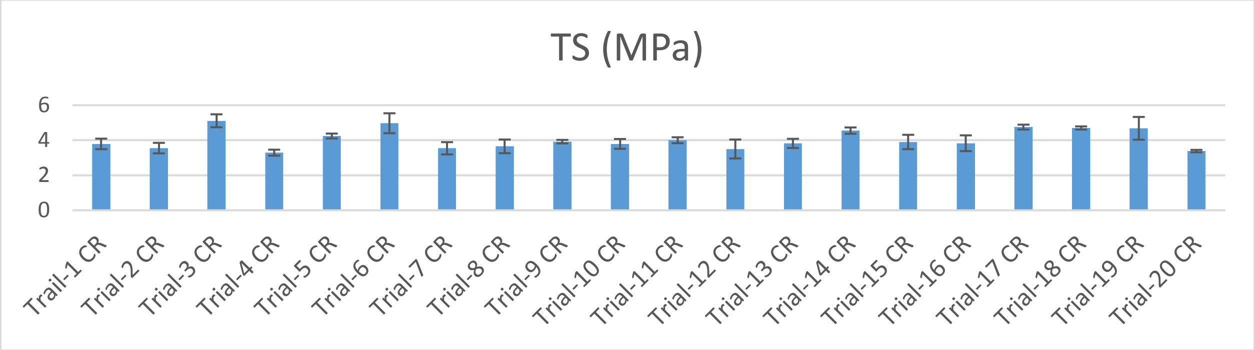


Figure 13: Tensile strength for 4 module devulcanizates

3.2.3. Sol Content

The sol content values of the 4 module setup are depicted in Figure 14. The sol content of the devulcanizates increases in the order of:

Trial- 19 < 9 < 5 < 3 < 18

The process conditions for the low sol content devulcanizates are:

Trial-19: 90/100/100/100^{0}C (100rpm)

Trial-9: 150/150/150/150^{0}C (60rpm)

Trial-5: 120/150/150/150^{0}C (60rpm)

Trial-3: 90/100/100/100^{0}C (100rpm)

Trial-18: 90/100/100/100^{0}C (100rpm)

From the process conditions of the devulcanizates, it is clear that low temperatures and low screw speeds leads to low sol contents, confirming earlier results.

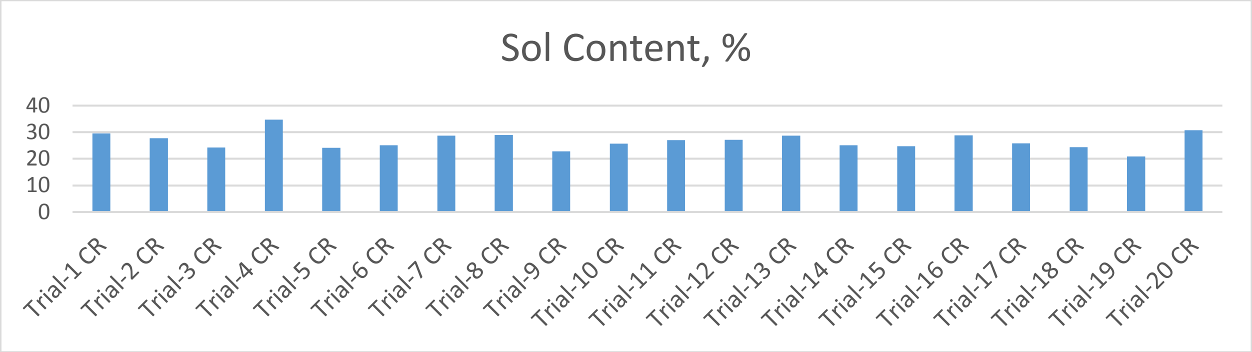


Figure 14: Sol contents of the 4 module devulcanizates

3.2.4. Conclusions for 4 modules

- **Low sol content**: Trial- 19 < 9 < 5 < 3 < 18
- **Lowest viscosity**: Trial- 4 < 16 < 13 < 1 < 20
- **High TS**: Trial- 3> 6> 17> 18> 19

On the basis of low sol content and mechanical properties, trial-3 and 19 possess overall good devulcanizate properties. However, in terms processability these samples do not perform best: the viscosity is rather high due to a low DBD concentration or a low devulcanization temperature.

This indicates once again that a balance has to be found between degree of devulcanization and degradation of the polymer.

3.3. 5 Modules

3.3.1. Complex viscosity

The plots of complex viscosity versus frequency of the different devulcanizates are shown in Figure 15. The complex viscosity of the devulcanizates in increasing order is:

Trial- 24 < 23 = 25 < 21 = 22

The process conditions of the lowest complex viscosity devulcanizates are:

Trial-24: 90/100/100/100/70 (70rpm)

Trial-23: 90/100/100/100/70 (70rpm)

Trial-25: 90/150/100/100/70 (70rpm)

The difference between Trial-23 and 24 are the spindles in module 5: 3 short and 3 long standard spindles in Trial-23 versus 2 short and 2 long igel spindles in Trial-24. The low module temperatures and screw speeds, which also increase the residence time, decrease the viscosity. This again emphasizes the importance of a sufficient long residence time.

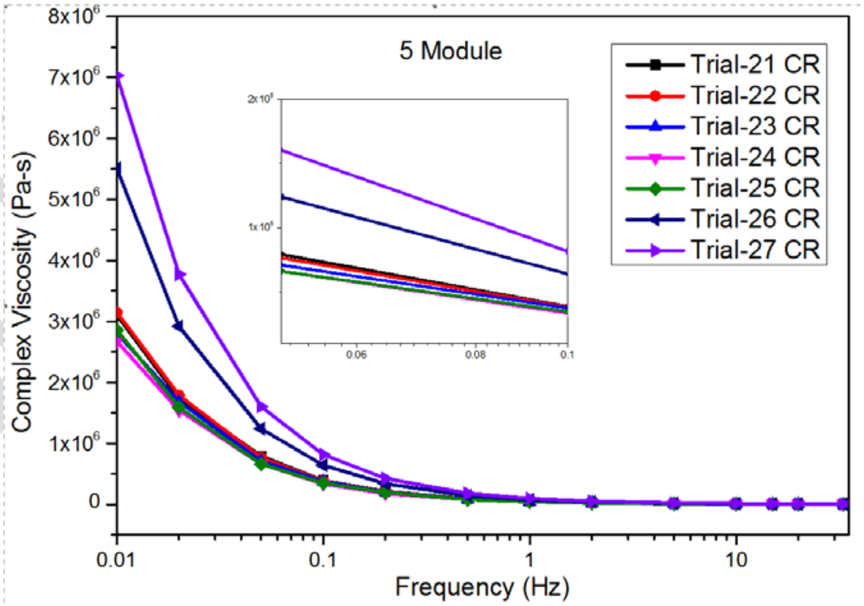


Figure 15: Complex viscosity measurements in a frequency sweep of 5 module devulcanizates

3.3.2. Curing after addition of curatives

The maximum delta torque values obtained from rheometer curves were plotted after mixing of the devulcanizates with the curing agents to study the curing kinetics as shown in Figure 16. The delta torque values in a decreasing order are ranked as:

Trial- 26 > 27 > 23 > 25 > 22

Trial-26 has the same process conditions as Trial-25, except that the last module dispersion ring diameter was increased from 37 mm to 40 mm, which decreases the shear resulting in a lower sol content. Trial-27 offered better cooling with 5 TT-3 spindles in the last module: these spindles are the most effective ones for cooling purposes. Trial-23 has the lowest module temperature at 70^0C.

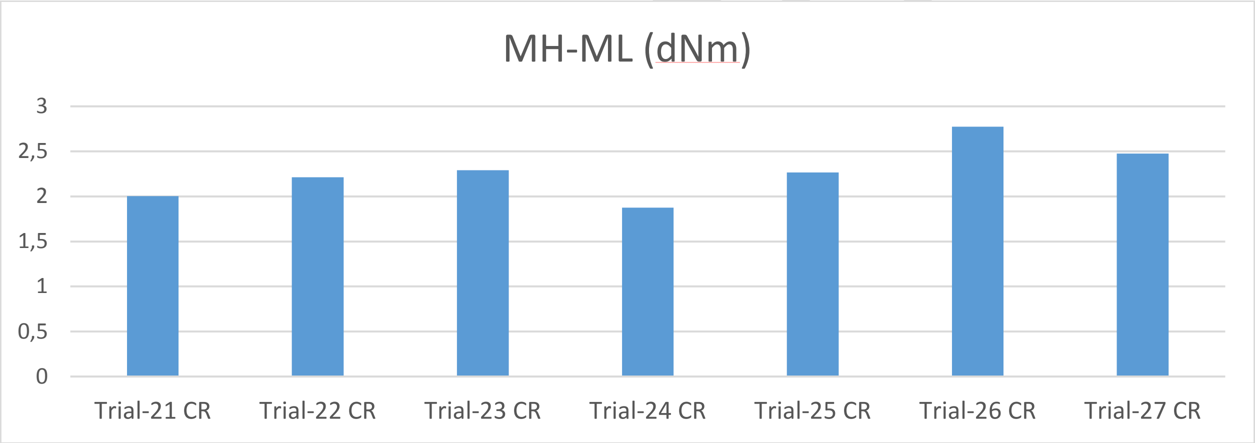


Figure 16: Sol content of 5 module devulcanizates

3.3.3. Tensile strength

The tensile strength values of the cold rolled devulcanizates for 5 modules are shown in Figure 17. The samples with the highest tensile strength values in decreasing order are:

Trial- 26 > 23 > 27 > 25 = 21 > 22,

Which, again, is more or less in the same order as the delta torque values shown in Figure 17.

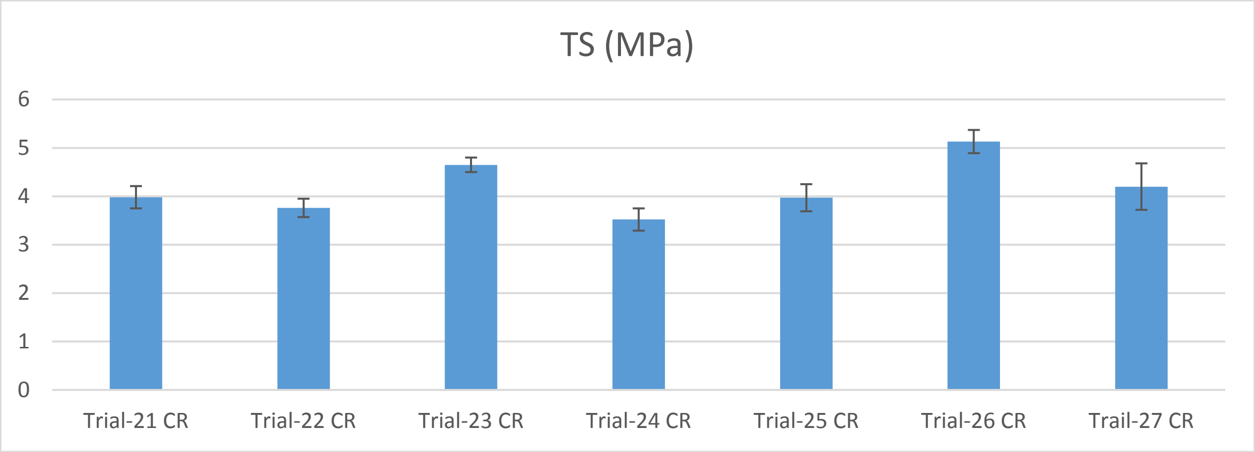


Figure 17: Tensile strength of 5 module devulcanizates

3.3.4. Sol content

The sol content of the 5 module devulcanizates are visualized in Figure 18. In an increasing order, the sol content values are ranked as follows:

Trial- 27 < 26 < 23 < 21 < 25

These values has very good correlation with the delta torque values.

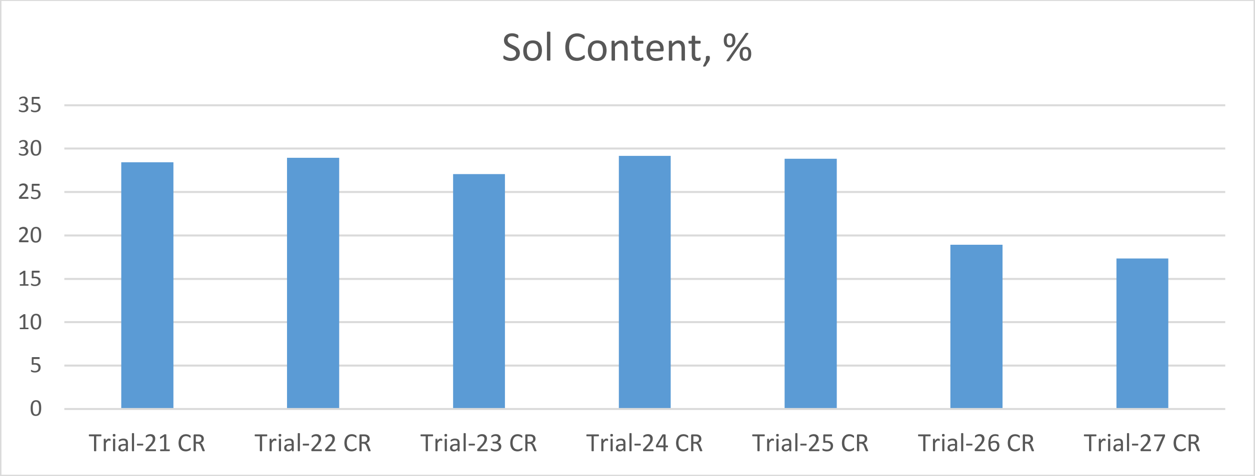


Figure 18: Sol content of the 5 module devulcanizates

3.3.5. Conclusion for 5 modules

- **Low sol content**: Trial- 27 < 26 < 23 < 21 < 25
- **Lowest viscosity**: Trial- 24 < 23 = 25 < 21 = 22
- **High TS**: Trial- 26 > 23 > 27 > 25 = 21 > 22

Trial-23 possesses overall good devulcanizate properties considering low sol content, lowest viscosity and high tensile strength. The process parameters of Trial-23 are 90/100/100/100/70^0C (70rpm) and its measured outlet temperature is 188^0C. It is clear that the lower energy input provided by a low temperature and a low screw speed leads to better devulcanizate properties.

3.4. 6 modules

3.4.1. Complex viscosity

The complex viscosity was plotted versus frequency in Figure 19. The viscosities in increasing order are as follows:

Trial-29< 31< 30= 28

Generally, there is not much change in viscosity. The viscosity of the Trial-32 sample could not be plotted into the same graph, since it was very high.

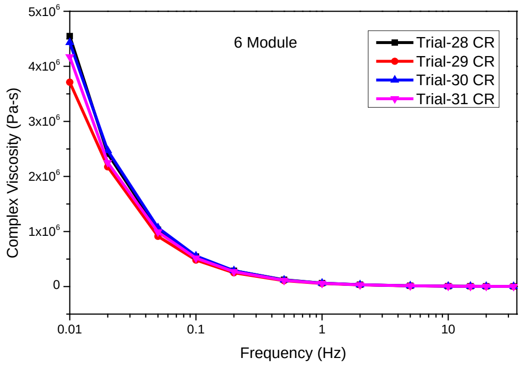


Figure 19: Complex viscosity measurements in a frequency sweep of 6 module devulcanizates

3.4.2. Curing after addition of curatives

The maximum delta torque values obtained from rheometer curves were plotted after mixing of the devulcanizates with the curing agents as shown in Figure 20.

The delta torque values in decreasing order are:

Trial-32 > 30 > 31 > 28 > 29

Trial-32, in which the preblended devulcanization system of oil and DBD was used with the finer material of 0.8-2.5 mm particle size, used the same devulcanization temperature as was used for the larger particle size crumb. Due to the finer granulametry, this material was less sheared. Trial-30, in which only half the loading of DBD (2.5%) was used, resulted in higher delta torque values as there was less DBD to react with double bonds and thus deactivate the polymer. Trial-31, which uses plain rubber granulate as starting material without DBD and oil, has a higher delta torque since there is no DBD at all to react with double bonds.

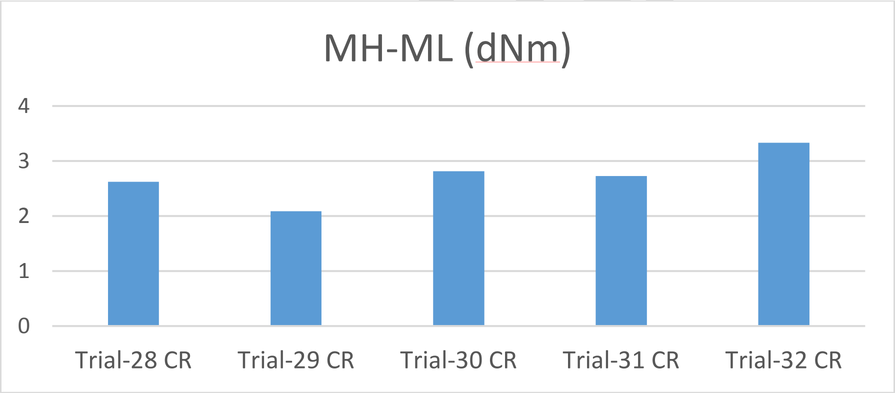


Figure 10: Delta torque values of the 6 module devulcanizates

3.4.3. Tensile strength

The tensile strength values of the 6 module devulcanizates are shown in Figure 21. The tensile strength values in increasing order are as follows:

Trial- 31 < 30 < 32 < 28 < 29

Again, here is a very good correlation with the delta torque values.

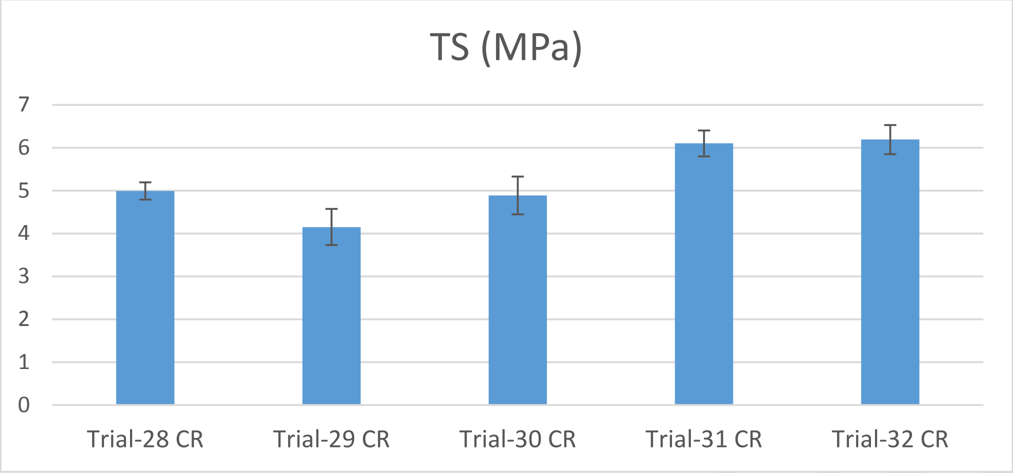


Figure 11: Tensile properties of the 6 module devulcanizates

3.4.4. Sol content

The sol content of 6 module devulcanizates are visualized in Figure 22. The sol content values are increasing in the following order:

Trial- 31 < 30 < 32 < 28 < 29

In this case, the sol values are inverse proportional to the delta torque values: a low sol content correlates with high delta torque values. This is another indication, that high delta torque values are caused by a low degree of polymer degradation.

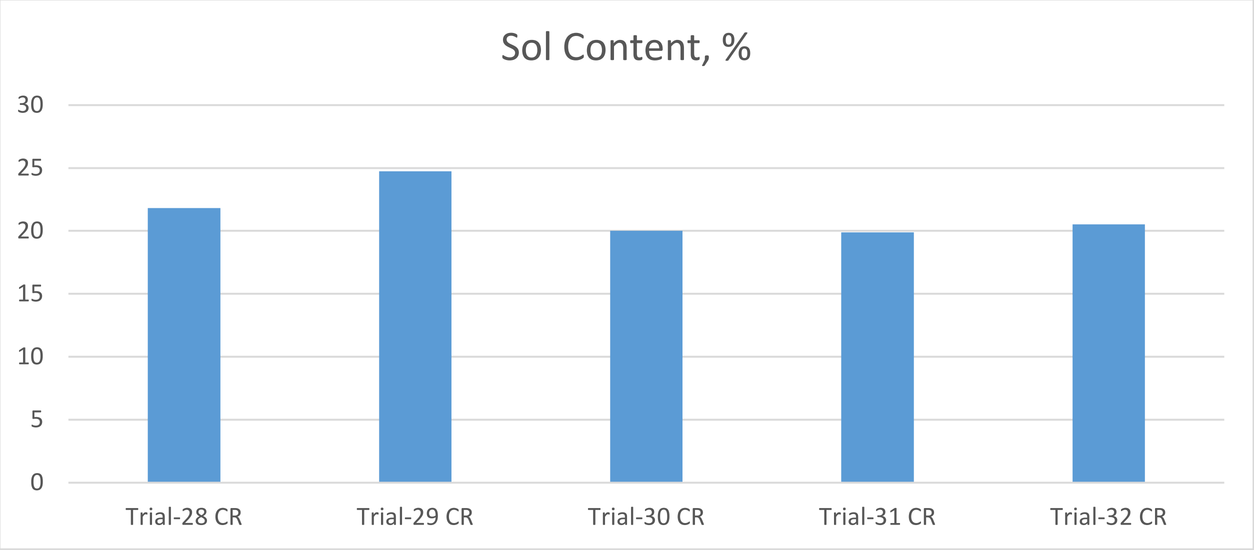


Figure 12: Sol content of 6 module devulcanizate

3.4.5. Conclusion for 6 modules

- **Low sol content:** Trial- 31 < 30 < 32 < 28 < 29
- **Lowest viscosity**: Trial- 29 < 31 < 30 = 28
- **High TS**: Trial- 32 > 31 > 28 > 30 > 29

Considering sol content, viscosity and tensile strength, Trial-31 possesses overall good devulcanizate properties. Trial-31 uses plain rubber granulate with a particle size of 0.8-2 mm as a starting material without oil and DBD.

The experiences and correlations from these trials lead to the following setup for the next test series:

Table 1: Further trial setup

	4 modules (Trial-3)	5 modules (Trial-23)
Barrel temperature (^{0}C)	90/100/100/100	90/100/100/100/70
Screw speed (rpm)	100	70
Measured outlet temperature (^{0}C)	197	188
Torque (Nm)	134	160
Starting material	Pre-blend	Separate dosing- 90/5/5

As there were only 3 trials done with the standard granulate with the 6th module, the optimal module setup conditions for this material cannot be deducted. Further tests with the standard input material are necessary.

3.5. Difference between cold rolled and dry ice cooled samples

3.5.1. Complex viscosity

The complex viscosity versus frequency sweep was plotted for 5 modules and 6 modules in Figure 23 and 24 respectively. There is not much difference in viscosity caused by cold rolling or dry ice cooling as the viscosity differs in the order of only 0.5 X 10^6 Pa.s.

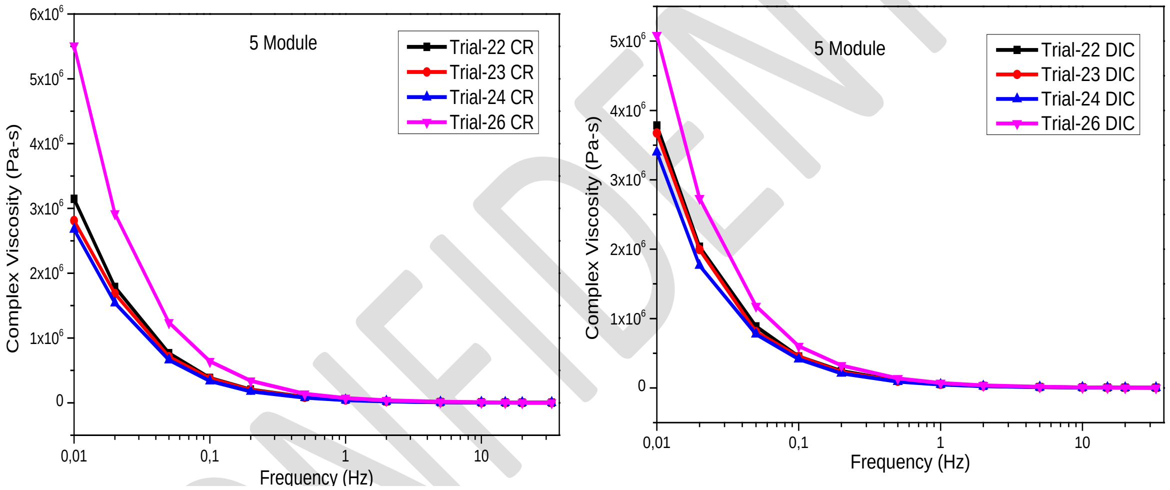


Figure 13: Complex viscosity measurements in a frequency sweep of the 5 module devulcanizates, left: cold rolled, right: dry ice cooled

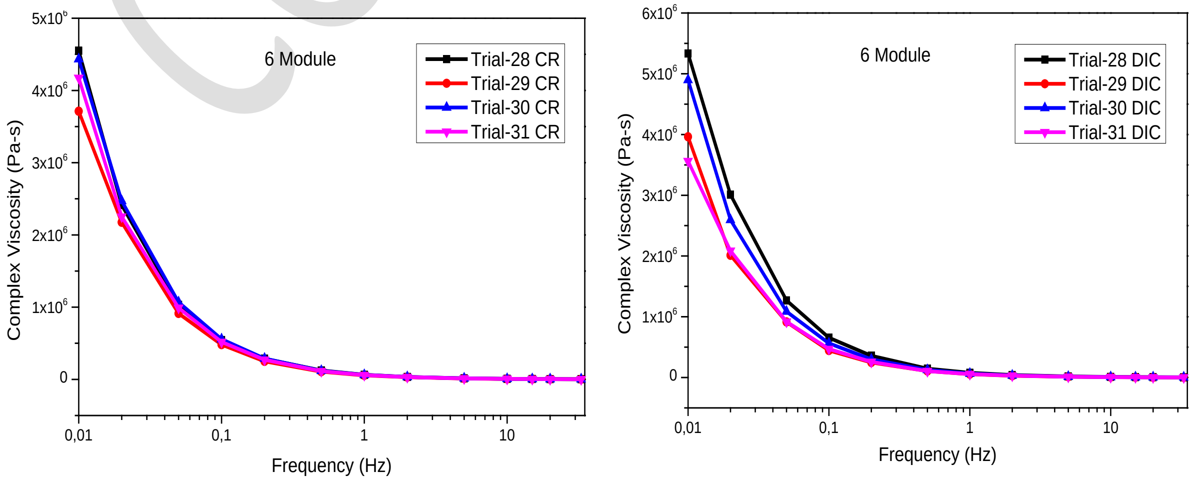


Figure 24: Complex viscosity measurements in a frequency sweep of 6 module devulcanizates, left: cold rolled, right: dry ice cooled

3.5.2. Tensile strength

The tensile strength values of the samples for 5 and 6 modules are tabulated in Table 2 and 3 respectively. From these tables, it is clear that there is no significant difference between the cold roll and dry ice cooled samples.

Table 2: Tensile strength of the 5 module devulcanizates

5 modules	Cold roll (CR), MPa	Dry ice cooled (DIC), MPa	Difference, MPa
Trial-22	3.8	4.2	-0.4
Trial-23	4.7	4.6	0.1
Trial-24	3.5	4.4	-0.9
Trial-25	4.0	4.8	-0.8
Trial-26	5.1	5.3	-0.2

Table 3: Tensile strength of the 6 module devulcanizates

6 modules	Cold roll (CR), MPa	Dry ice cooled (DIC), MPa	Difference, MPa
Trial-28	5.0	5.3	-0.3
Trial-29	4.2	4.8	-0.6
Trial-30	4.9	5.1	-0.2
Trial-31	6.1	5.9	0.2
Trial-32	6.2	5.8	0.4

3.5.3. Conclusions for cold roll versus dry ice cooling

There is not much difference between cold rolled and dry ice cooled devulcanizates in terms of

- Complex viscosity
- Tensile strength
- Modulus at 100% elongation

This is according to the expectations, as the cooling efficiency of dry ice is not very high due to the solid state of the ice. Liquid nitrogen cooling is more effective and a better alternative to dry ice.

3.6. Repeatability of experiments

Trial- 17 and 19 were done under the same circumstances on different days in order to control the reproducibility of the extruder process. The sol content values (Table 4), complex viscosities (Figure 25) and cure curves (Figure 26) of the devulcanizates show variations in these properties due to differences in

1. Process parameters in spite of same of settings
2. Input material properties

Table 4: Sol content of the devulcanizate of Trial 17 and 19

	Sol content,%
Trial-17 CR	25.9
Trial-19 CR	20.9

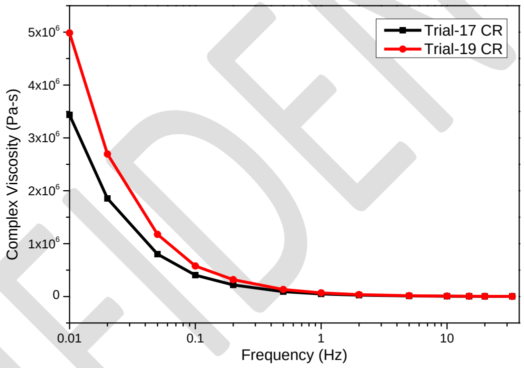


Figure 25: Complex viscosity measurements in a frequency sweep of Trial-17 and 19

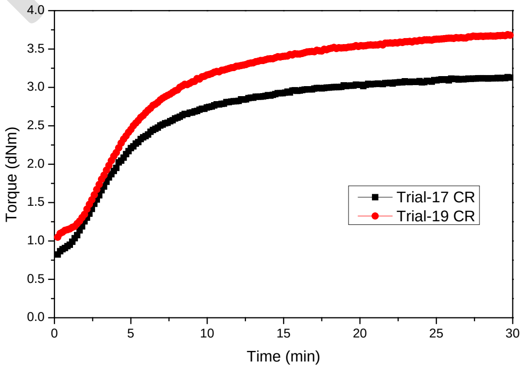


Figure 26: Rheometer curves for Trial-17 and 19

3.7. Difference between cooling spindles

All other process parameters were kept constant to study the effect of different cooling spindles. The igel and the TT-3 spindles are known for the best cooling effect; in this study these two spindels will directly be compared. Another difference is the diameter of the dispersion ring. The process parameters were as follows: 90/150/100/100/70^{0}C (70 rpm)

Table 5 shows the 5th module setup:

Table 5: 5th module setup

	5th module
Trial-25 CR	2L/ 2S Igel spindles
Trial-27 CR	5 TT-3 spindles

The complex viscosity, see Figure 27, increased in the following order:

Trial- 25 < 27

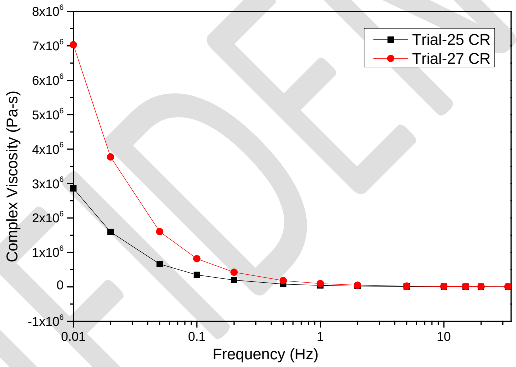


Figure 27: Complex viscosity measurements in a frequency sweep of samples made with different spindles

The sol content between the different batches made with the two types of cooling spindles (Table 6) shows a low sol content for the samples with a low outlet temperature: TT-3 spindles offer better cooling compared to igel spindles.

Table 6: Sol content and measured outlet temperature of batches made with different cooling spindles

Batches	Sol content, %	Measured outlet temperature, (^{0}C)
Trial-25 CR	28.8	205
Trial-27 CR	17.3	145

4. General conclusions

For a 4 module setup, and on the basis of sol content and mechanical properties, Trial-3 and 19 possess overall good devulcanizate properties. However, in terms processability these samples do not perform best: the viscosity is rather high due to a low DBD concentration or a low devulcanization temperature. This indicates once again that a balance has to be found between degree of devulcanization and degradation of the polymer. Besides, 4 modules do not provide sufficient residence time; 5 or 6 modules are necessary for a sufficient degree of devulcanization.

In a 5 module setup, extensive cooling by a low module temperature and a low energy input by a low screw speed result in better devulcanizate properties.

Some general conclusions are:

- The repeatability of the extruder conditions is a critical factor
- TT-3 spindles have a higher cooling efficiency than igel spindles.
- The devulcanization aid is crucial in controlling the pressure in the modules
- The starting temperature should be low for a good grinding effect
- However, a low starting temperature delays the onset of the devulcanization reaction
- From visual inspection, the presence of nitrogen, or in other words the absence of oxygen, had no effect on the devulcanization
- There are indications, that DBD causes degradation of the polymer, which results in low delta torque values and low tensile strength
- A decrease in DBD content reduces the sheet forming ability
- Residence time is a dominant factor
- Regarding the after-treatment: there is not much difference between cold rolling and dry ice cooling
- Plain rubber granulate as the starting material without oil and DBD gives good devulcanizate properties

Appendix-4

Rumal
06820t0002

TP-WE 70/1600 M4 Devulkanisation of Rubber

2016-02-24-26

☒ Auftragstammblatt	☒ Termin	
	☒ Stempelkarte	
☒ Materialeingang	☒ Anlieferung	EB 4379
☒ Aufgabenstellung	☐ Fragenkatalog	
	☐ Versuchsplanung	
☒ Vorbereitung	☐ Sonderanfertigung	
	☒ Extruder	
	☒ Nachfolge	
	☒ Halle/Besucherraum	
	☐ Versuchsunterlagen	
☒ Dokumentation	☒ Versuchsprotokoll	
	☒ Nachbesprechung	
	☐ Versuchsbericht	
	☐ Auswertung	
	☐ Ablage Muster	
	☐ Gesamtprotokoll	
☒ Materialausgang	☒ Entsorgt (Kunststoffmüll)	610kg
	☐ Rücklieferung	
	☒ Einlagerung	4 Paletten
☒ Abbau/Reinigung	☒ Extruder	
	☒ Dosierwerk	
	☐ Nachfolge	
☒ Kosten der Versuche	☒ trägt der Kunde	☐ werden intern verrechnet
☒	☒ Extruder TP-WE 70	2400/M6
	☒ Zusätzliche Dosierwerke	2x Feststoff; 1x Flüssig
	☐ Wasserbad	
	☒ Entgasung	
	☐ sonstiges	KB 70
	☐ Zus. Wasseranschluß	
	☐ Radialgranulierung	
	☒ reinigungsintensive Materialien	
☒ Versuchsabmeldung	☒ Verteiler	Kunde; BKF; Fr.: Pietrek

test report

TP-WE 70/1600 M4

company: **Rumal**

commission no.: **06820t0002**

present: **Mrs. Dr. Ir. Dierkes; Mr. van Swaaij, Mr. Rajendran** **(Universit of Twente)**
Mr. Wallis **(BKF)**
Mr. Gerdon **(ENTEX**

leading: M.Gerdon
date: 2016-02-24-26

		1					
setting no:		**1**	**2**	**3**	**4**	**5**	**6**
setup		**1**					
date		**24.02.**	**24.02.**	**24.02.**	**24.02.**	**24.02.**	**24.02.**
time		11:00	11:25	12.00	13:25	13:55	14:15
Extruder							
power Extruder (P-max = 46 KW)	KW	11,7	14,5	16,3	11,2	6,9	5,5
torque Extruder min.	Nm	134	117	129	157	95	148
torque Extruder max. (M-max motor = 170 Nm)	Nm	137	118	134	152	93	150
speed Extruder (n-max = 250 min-1)	min-1	70	100	100	60	60	30
dosing units							
dosing of rubber granulat	%	100	100	100	100	100	100
dosing of rubber granulat	kg/h	25,00	25,00	25,00	25,00	12,50	12,50
dosing of pepton	%	0	0	0	0	0	0
dosing of pepton	kg/h	0,00	0,00	0,00	0,00	0,00	0,00
dosing of TDAE	%	0	0	0	0	0	0
dosing of TDAE	kg/h	0,00	0,00	0,00	0,00	0,00	0,00
capacity set	kg/h	25	25	25	25	12,5	12,5
temperature control							
temp. cooling water	°C	8	8	8	8	8	8
temp. feed section	°C	8	8	8	8	8	8
setting temperature cylinder 1	°C	120	120	90	120	120	120
temp. cylinder 1 oil flow	°C	120	121	91	118	121	121
temp. cylinder 1 oil return	°C	118	118	90	120	118	118
mass flow cylinder 1 oil	m³/min	0,048	0,048	0,048	0,048	0,048	0,048
heat flow cylinder 1	kW	2,9	4,3	1,4	-2,9	4,3	4,3
setting temperature cylinder 2	°C	150	150	100	150	150	150
temp. cylinder 2 water flow	°C	150,1	150,4	101	150,3	150,4	150,4
temp. cylinder 2 water return	°C	150,1	150,5	100,8	150,2	150,1	150
mass flow cylinder 2 water	m³/min	0,04	0,04	0,04	0,04	0,04	0,04
heat flow cylinder 2	kW	0,0	-0,2	0,4	0,2	0,5	0,6
setting temperature cylinder 3	°C	150	150	100	150	150	150
temp. cylinder 3 water flow	°C	149	149,4	100	149,4	149,8	149,6
temp. cylinder 3 water return	°C	148,2	149,1	100,6	149,1	148,9	145,8
mass flow cylinder 3 water	m³/min	0,04	0,04	0,04	0,04	0,04	0,04
heat flow cylinder 3	kW	1,3	0,5	-1,3	0,5	1,4	6,2
setting temperature cylinder 4	°C	150	150	100	150	150	150
temp. cylinder 4 water flow	°C	151,5	151,4	102,2	151,5	151,8	151,5
temp. cylinder 4 water return	°C	150,9	151	102,5	150,8	150,8	150,3
mass flow cylinder 4 water	m³/min	0,054	0,054	0,054	0,054	0,054	0,054
heat flow cylinder 4	kW	1,3	0,9	-0,9	1,5	2,1	2,6
total heat flow	kW	5,5	5,5	-0,3	-0,7	8,4	13,7
mass temperature/pressure							
T-1 melt temp. between cylinder 1 & 2	°C	213	227	188	212	170	183
T-2 melt temp. between cylinder 2 & 3	°C	222	231	203	217	186	183
T-3 melt temp. between cylinder 3 & 4	°C	198	206	182	200	199	184
T-4 melt temp. between cylinder 4 & 5	°C	185	190	173	186	181	173
T-5 melt temp. outlet manuel	°C	204	215	197	206	204	194
P-1 melt pressure cylinder 1 & 2	bar	32	31	32	38	28	37
P-2 melt pressure cylinder 2 & 3	bar	5	2	1,6	7	0	3
P-3 melt pressure cylinder 3 & 4	bar	15	13	17	20	18	24
P-4 melt pressure cylinder 4 & 5	bar	15	11	15	17	14	25
Vacuum							
Vacuum at M2	mbar	200	200	200	200	200	200
Vacuum at M3	mbar	50	50	50	50	50	50
output							
specific energy	KWh/kg	0,468	0,58	0,652	0,448	0,552	0,44

remark

Target: devulkanisation of rubber

setting 1 setup 1
using preblended material
This setting is similar to setting 26 from last trials.
We decrease the temperture in the first module, because of a much higher mass temp. than last trials.

setting 2 setup 1
using preblended material
increase the speed of the csp.
the temperture of the material rais abut 20K over the total process.

setting 3 setup 1
using preblended material
reduce the temperature in all barrels to prevent the material of overheating.

setting 4 setup 1
using preblended material
using same temperature setting like setting 1 and try to reduce the speed to the min. possible speed.
At 60 rpm the max. torque is reached.

setting 5 setup 1
using preblended material
reduce the output to 12,5kg/h.
The temperature decreasing direktly but the pressure is nearly the same.

test report **TP-WE 70/1600 M4**

company: **Rumal**	**commission no.:**	**06820t0002**

present: **Mrs. Dr. Ir. Dierkes; Mr. van Swaaij, Mr. Rajendran** **(Universit of Twente)**
Mr. Wallis **(BKF)**
Mr. Gerdon **(ENTEX**

leading: M.Gerdon
date: 2016-02-24-26

		2						**remark**
setting no:		**7**	**8**	**9**	**10**	**11**	**12**	**Target:** devulkanisation of rubber
setup		**1**						
date		**24.02.**	**24.02.**	**24.02.**	**24.02.**	**24.02.**	**24,02,**	
time		15:20	15:45	16:15	16:30	16:55	17:10	
Extruder								**setting 7 setup 1**
power Extruder (P-max = 46 KW)	KW	7,1	6,3	9,5	8,7	6	5,8	change to seperate components feeding
torque Extruder min.	Nm	95	85	127	117	71	46	Same setting like setting 4 with other feeders.
torque Extruder max. (M-max motor = 170 Nm)	Nm	96	89	128	122	76	47	The torque is much lower, because of libricaton by
speed Extruder (n-max = 250 min-1)	min-1	60	60	60	60	70	100	the oil in the 1st barrel. Also all temperatures
dosing units								are much lower than bevor.
dosing of rubber granulat	%	90	90	95	90	90	90	
dosing of rubber granulat	kg/h	22,50	22,50	23,75	22,50	22,50	22,50	
dosing of pepton	%	5	5	0	0	5	5	**setting 8 setup 1**
dosing of pepton	kg/h	1,25	1,25	0,00	0,00	1,25	1,25	use seperate comonents feeding
dosing of TDAE	%	5	5	5	10	5	5	Increase the temperature of the 1st module to 150°C
dosing of TDAE	kg/h	1,25	1,25	1,25	2,50	1,25	1,25	to get the same settings like etting 26 in the last
capacity set	kg/h	25	25	25	25	25	25	trials, because the material wich comes ot of the
temperature control								machine is verry dry and not sticky.
temp. cooling water	°C	8	8	8	8	8	8	
temp. feed section	°C	8	8	8	8	8	8	
setting temperature cylinder 1	°C	120	150	150	150	150	150	**setting 9 setup 1**
temp. cylinder 1 oil flow	°C	119	151	151	151	151	151	Switch of the peption and the pressure at the 1st ring
temp. cylinder 1 oil return	°C	121	148	148	147	147	148	rais directly fom 10 to 40bar and also the temperature
mass flow cylinder 1 oil	m³/min	0,048	0,048	0,048	0,048	0,048	0,048	raises very fast.
heat flow cylinder 1	kW	-2,9	4,4	4,4	5,9	5,9	4,4	
setting temperature cylinder 2	°C	150	150	150	150	150	150	
temp. cylinder 2 water flow	°C	150,4	150,1	150,2	150,2	149,3	150,2	**setting 10 setup 1**
temp. cylinder 2 water return	°C	150	149,9	150,1	150,2	149,3	149,8	increase the amount of oil to see if the low presure
mass flow cylinder 2 water	m³/min	0,04	0,04	0,04	0,04	0,04	0,04	is an effect of lubricaton in the 1st barrel.
heat flow cylinder 2	kW	0,6	0,3	0,2	0,0	0,0	0,6	the pressure is still high. That means, that
setting temperature cylinder 3	°C	150	150	150	150	150	150	the low pressure is not an effect of lurrication
temp. cylinder 3 water flow	°C	149,8	149	149,1	149,1	149	149	in the first modul and should be an effect of the peption.
temp. cylinder 3 water return	°C	149,6	148,5	148,6	148,6	148,3	148	
mass flow cylinder 3 water	m³/min	0,04	0,04	0,04	0,04	0,04	0,04	
heat flow cylinder 3	kW	0,3	0,8	0,8	0,8	1,1	1,6	**setting 11 setup 1**
setting temperature cylinder 4	°C	150	150	150	150	150	150	change back to setting 8 too see if the pressure drops
temp. cylinder 4 water flow	°C	151,5	151,6	151,4	151,6	151,5	151,3	again down to 10 bars, Than it is defently an effect of
temp. cylinder 4 water return	°C	151	151,1	151,1	151,1	151	151	peption. We saw the same pressure drop like bevor.
mass flow cylinder 4 water	m³/min	0,054	0,054	0,054	0,054	0,054	0,054	So Peption makes this effect.
heat flow cylinder 4	kW	1,1	1,1	0,6	1,1	1,1	0,6	Increas the sped to 70rpm like setting 1
total heat flow	kW	-0,9	6,6	6,0	7,8	8,1	7,3	
mass temperature/pressure								
T-1 melt temp. between cylinder 1 & 2	°C	140	151	206	203	144	148	**setting 12 setup 1**
T-2 melt temp. between cylinder 2 & 3	°C	179	177	200	195	174	155	same like setting 2
T-3 melt temp. between cylinder 3 & 4	°C	204	202	211	208	204	200	
T-4 melt temp. between cylinder 4 & 5	°C	190	192	202	201	193	189	
T-5 melt temp. outlet manuel	°C	148	185	204	212	205	197,2	
P-1 melt pressure cylinder 1 & 2	bar	18	13	43	42	14	10	
P-2 melt pressure cylinder 2 & 3	bar	3	1,3	0	0	2	0	
P-3 melt pressure cylinder 3 & 4	bar	27	28	28	27	22	16	
P-4 melt pressure cylinder 4 & 5	bar	23	22	22	22	21	8	
Vacuum								
Vacuum at M2	mbar	200	200	200	200	200	200	
Vacuum at M3	mbar	50	50	50	50	50	50	
output								
specific energy	KWh/kg	0,284	0,252	0,38	0,348	0,24	0,232	

test report **TP-WE 70/1600 M4**

company: **Rumal**	commission no.: **06820t0002**
present: **Mrs. Dr. Ir. Dierkes; Mr. van Swaaij, Mr. Rajendran** (Universit of Twente) **Mr. Wallis** (BKF) **Mr. Gerdon** (ENTEX	leading: M.Gerdon date: 2016-02-24-26

		3						remark
setting no:		**13**	**14**	**15**	**16**	**17**	**18**	**Target:** devulkanisation of rubber
setup		**1**				**2**		
date		**24.02.**	**24.02.**	**24.02.**	**24.02.**	**24.02.**	**24,02,**	
time		17:30	17:50	18:10	18:40	19:20	19:40	
Extruder								**setting 13 setup 1**
power Extruder (P-max = 46 KW)	KW	4,7	3,5	4,7	9,9	11,4	10,7	same setting like setting 5
torque Extruder min.	Nm	63	95	126	80	91	89	
torque Extruder max. (M-max motor = 170 Nm)	Nm	65	97	130	83	93	88	
speed Extruder (n-max = 250 min-1)	min-1	60	30	30	100	100	100	**setting 14 setup 1**
dosing units								same setting like setting 6
dosing of rubber granulat	%	90	90	90	90	90	90	
dosing of rubber granulat	kg/h	11,25	11,25	22,50	22,50	22,50	22,50	
dosing of pepton	%	5	5	5	5	5	5	**setting 15 setup 1**
dosing of pepton	kg/h	0,63	0,63	1,25	1,25	1,25	1,25	we increase the output by this speed, bacause we saw
dosing of TDAE	%	5	5	5	5	5	5	that the particels in the material are smaler with lower
dosing of TDAE	kg/h	0,63	0,63	1,25	1,25	1,25	1,25	speed than with high speed.
capacity set	kg/h	12,5	12,5	25	25	25	25	
temperature control								
temp. cooling water	°C	8	8	8	8	8	8	**setting 16 setup 1**
temp. feed section	°C	8	8	8	8	8	8	same setting like setting 3
setting temperature cylinder 1	°C	150	150	150	90	90	90	
temp. cylinder 1 oil flow	°C	150	151	151	89	91	91	
temp. cylinder 1 oil return	°C	147	148	148	90	89	89	**setting 17 setup 2**
mass flow cylinder 1 oil	m³/min	0,048	0,048	0,048	0,048	0,048	0,048	change to setup 2 with a lomg dispersion ring at the end
heat flow cylinder 1	kW	4,4	4,4	4,4	-1,4	2,8	2,8	The torque is a little bit higher than bevor
setting temperature cylinder 2	°C	150	150	150	100	100	100	The material at the outlet looks finer.
temp. cylinder 2 water flow	°C	150,3	150,3	150,2	100,3	100,6	100,7	
temp. cylinder 2 water return	°C	150,2	150,2	149,8	100,4	100,8	100,8	
mass flow cylinder 2 water	m³/min	0,04	0,04	0,04	0,04	0,04	0,04	**setting 18 setup 2**
heat flow cylinder 2	kW	0,2	0,2	0,6	-0,2	-0,4	-0,2	we give in some nitrogen by the injection ring
setting temperature cylinder 3	°C	150	150	150	100	100	100	to reduce the amount of oxigen in the machine.
temp. cylinder 3 water flow	°C	148,9	149	148,8	100,1	99,6	99,6	no differenc in parameter.
temp. cylinder 3 water return	°C	148	147,7	147,8	100,6	100,5	100,4	
mass flow cylinder 3 water	m³/min	0,04	0,04	0,04	0,04	0,04	0,04	
heat flow cylinder 3	kW	1,5	2,1	1,6	-1,1	-1,9	-1,7	
setting temperature cylinder 4	°C	150	150	150	100	100	100	
temp. cylinder 4 water flow	°C	151,6	151,3	151,5	102,3	102	102	
temp. cylinder 4 water return	°C	150,5	150,3	150,7	102,9	102,4	102,5	
mass flow cylinder 4 water	m³/min	0,054	0,054	0,054	0,054	0,054	0,054	
heat flow cylinder 4	kW	2,4	2,1	1,7	-1,7	-1,1	-1,4	
total heat flow	kW	8,4	8,8	8,4	-4,4	-0,7	-0,6	
mass temperature/pressure								
T-1 melt temp. between cylinder 1 & 2	°C	185	177	147	135	136	136	
T-2 melt temp. between cylinder 2 & 3	°C	179	174	170	139	161	160	
T-3 melt temp. between cylinder 3 & 4	°C	187	178	185	182	185	183	
T-4 melt temp. between cylinder 4 & 5	°C	176	168	180	172	171	172	
T-5 melt temp. outlet manuel	°C	192	178	186	186	178	170	
P-1 melt pressure cylinder 1 & 2	bar	18	26	17	15	15	15	
P-2 melt pressure cylinder 2 & 3	bar	0	0,9	7	0	0	0	
P-3 melt pressure cylinder 3 & 4	bar	13	18	32	18	19	18	
P-4 melt pressure cylinder 4 & 5	bar	12	19	31	15	0	0	
Vacuum								
Vacuum at M2	mbar	200	200	200	200	200	200	
Vacuum at M3	mbar	50	50	50	50	50	50	
output								
specific energy	KWh/kg	0,376	0,28	0,188	0,396	0,456	0,428	

test report **TP-WE 70/1600 M4**

company: **Rumal**

commission no.: **06820t0002**

present:
Mrs. Dr. Ir. Dierkes; Mr. van Swaaij, Mr. Rajendran **(Universit of Twente)**
Mr. Wallis **(BKF)**
Mr. Gerdon **(ENTEX**

leading: M.Gerdon
date: 2016-02-24-26

		4					
setting no:		**19**	**20**	**21**	**22**	**23**	**24**
setup		**4**	**5**	**6**			**7**
date		**25.02.**	**25.02.**	**26.02.**	**26.02.**	**26.02.**	**26.02.**
time		15:45	18:50	09:20	10:00	10:30	11:50
Extruder							
power Extruder (P-max = 46 KW)	KW	11	12,6	14	13	13,7	13,8
torque Extruder min.	Nm	85	97	115	152	160	160
torque Extruder max. (M-max motor = 170 Nm)	Nm	87	101	116	153	160	163
speed Extruder (n-max = 250 min-1)	min-1	100	100	100	70	70	70
dosing units							
dosing of rubber granulat	%	90	90	90	90	90	90
dosing of rubber granulat	kg/h	22,50	22,50	22,50	22,50	22,50	22,50
dosing of pepton	%	5	5	5	5	5	5
dosing of pepton	kg/h	1,25	1,25	1,25	1,25	1,25	1,25
dosing of TDAE	%	5	5	5	5	5	5
dosing of TDAE	kg/h	1,25	1,25	1,25	1,25	1,25	1,25
capacity set	kg/h	25	25	25	25	25	25
temperature control							
temp. cooling water	°C	9	9	9	9	9	9
temp. feed section	°C	15	15	15	15	15	15
setting temperature cylinder 1	°C	90	90	90	90	90	90
temp. cylinder 1 oil flow	°C	91	91	91	91	91	91
temp. cylinder 1 oil return	°C	90	90	90	90	90	90
mass flow cylinder 1 oil	m³/min	0,047	0,047	0,048	0,048	0,048	0,048
heat flow cylinder 1	kW	1,4	1,4	1,4	1,4	1,4	1,4
setting temperature cylinder 2	°C	100	100	100	100	100	100
temp. cylinder 2 water flow	°C	100,8	100,8	100,8	100,8	100,5	100,6
temp. cylinder 2 water return	°C	100,9	101	101	100,9	100,4	100,8
mass flow cylinder 2 water	m³/min	0,04	0,04	0,04	0,04	0,04	0,04
heat flow cylinder 2	kW	-0,2	-0,4	-0,4	-0,2	0,2	-0,4
setting temperature cylinder 3	°C	100	100	100	100	100	100
temp. cylinder 3 water flow	°C	100,9	100,8	100,3	100	99,7	100
temp. cylinder 3 water return	°C	101,3	101,1	101	100,4	100,2	100,4
mass flow cylinder 3 water	m³/min	0,04	0,04	0,04	0,04	0,04	0,04
heat flow cylinder 3	kW	-0,9	-0,6	-1,5	-0,9	-1,1	-0,9
setting temperature cylinder 4	°C	100	100	100	100	100	100
temp. cylinder 4 water flow	°C	102,1	102,1	99,7	100,5	100,2	100,5
temp. cylinder 4 water return	°C	102,6	102,8	100,1	100,6	100,5	100,5
mass flow cylinder 4 water	m³/min	0,054	0,054	0,054	0,054	0,054	0,054
heat flow cylinder 4	kW	-1,4	-2,0	-1,2	-0,3	-0,9	0,0
setting temperature cylinder 5	°C	-	-	100	100	70	70
temp. cylinder 5 water flow	°C	-	-	101,3	102	71	72,8
temp. cylinder 5 water return	°C	-	-	101,4	102,3	73	74
mass flow cylinder 5 water	m³/min	-	-	0,04	0,04	0,04	0,04
heat flow cylinder 5	kW	-	-	-0,2	-0,6	-4,8	-2,8
total heat flow	kW	-1,1	-1,7	-1,9	-0,6	-5,1	-2,7
mass temperature/pressure							
T-1 melt temp. between cylinder 1 & 2	°C	134	134	134	133	132	133
T-2 melt temp. between cylinder 2 & 3	°C	160	160	159	154	152	151
T-3 melt temp. between cylinder 3 & 4	°C	182	186	183	175	175	173
T-4 melt temp. between cylinder 4 & 5	°C	152	208	162	161	154	152
T-5 melt temp. between cylinder 5 & 6	°C	-	-	187	170	163	163
T-6 melt temp. outlet manuel	°C	173	224	200	195	188	190
P-1 melt pressure cylinder 1 & 2	bar	12	17	15	20	18	22
P-2 melt pressure cylinder 2 & 3	bar	0	0	4	3	4	4
P-3 melt pressure cylinder 3 & 4	bar	18	21	19	24	21	21
P-4 melt pressure cylinder 4 & 5	bar	0	0	0	0	0	0
P-5 melt pressure cylinder 5 & 6	bar	-	-	0	0	0	0
P-6 melt pressure at the die	bar	0	0	-	-	-	-
Vacuum							
Vacuum at M2	mbar	50	50	20	20	20	200
Vacuum at M3	mbar	50	50	20	20	20	20
Vacuum at M5	mbar	-	-	20	20	20	20
output							
specific energy	KWh/kg	0,44	0,504	0,56	0,52	0,548	0,552

remark

Target: devulkanisation of rubber

setting 19 setup 4
try to reproduce the setting 17 from the 1st day.
The process is repoducable but the particels at the end
are not so soft like yesterday.
reduce the diameter of the last ring to 35mm
Dwelltime is 116sec.

setting 20 setup 5
the torque and the outlet temp are much higer
than with the other dispergen ring.
Because of the high outlet temp. We change to an 36 mm
ring for setup 6
Dwelltime is 121sec.

setting 21 setup 6
assemble the 5th module to get more dwell time.
dwelltime 125sec.

setting 22 setup 6
reduce the speed to 70rpm to increase the dwelltime
and recuce the shear stress.
dwelltime is 170sec.

setting 23 setup 6
reduce the temperature in th 5th barrel to coll down the
material. At 70°C maximum torque is reached.
The temperature drops about 7K

setting 24 setup 7
no differenz in outlet temp. and torque with this setup.

test report **TP-WE 70/1600 M4**

company:	**Rumal**	commission no.:	**06820t0002**
present:	**Mrs. Dr. Ir. Dierkes; Mr. van Swaaij, Mr. Rajendran**	**(Universit of Twente)**	
	Mr. Wallis	**(BKF)**	
	Mr. Gerdon	**(ENTEX**	leading: M.Gerdon
			date: 2016-02-24-26

		5					
setting no:		**25**	**26**	**27**	**28**	**29**	**30**
setup		**7**	**8**	**9**	**10**		
date		**26.02.**	**26.02.**	**26.02.**	**26.02.**	**26.02.**	**26.02.**
time		12:10	13:55	15:15	16:50	17:25	18:00
Extruder							
power Extruder (P-max = 46 KW)	KW	12,8	10,6	9,7	12,8	11,7	16
torque Extruder min.	Nm	144	122	114	145	94	128
torque Extruder max. (M-max motor = 170 Nm)	Nm	145	124	116	147	96	130
speed Extruder (n-max = 250 min-1)	min-1	70	70	70	70	100	100
dosing units							
dosing of rubber granulat	%	90	90	90	90	90	92,5
dosing of rubber granulat	kg/h	22,50	22,50	22,50	22,50	22,50	23,13
dosing of pepton	%	5	5	5	5	5	2,5
dosing of pepton	kg/h	1,25	1,25	1,25	1,25	1,25	0,63
dosing of TDAE	%	5	5	5	5	5	5
dosing of TDAE	kg/h	1,25	1,25	1,25	1,25	1,25	1,25
capacity set	kg/h	25	25	25	25	25	25
temperature control							
temp. cooling water	°C	9	9	9	9	9	9
temp. feed section	°C	15	15	15	15	15	15
setting temperature cylinder 1	°C	90	90	90	90	90	90
temp. cylinder 1 oil flow	°C	90	90	90	90	89	90
temp. cylinder 1 oil return	°C	91	91	91	91	90	91
mass flow cylinder 1 oil	m³/min	0,048	0,048	0,048	0,048	0,048	0,048
heat flow cylinder 1	kW	-1,4	-1,4	-1,4	-1,4	-1,4	-1,4
setting temperature cylinder 2	°C	150	150	150	150	150	150
temp. cylinder 2 water flow	°C	150	150,3	150,2	150,4	150,3	150,3
temp. cylinder 2 water return	°C	149,6	150	149,9	149,9	149,9	150,1
mass flow cylinder 2 water	m³/min	0,04	0,04	0,04	0,04	0,04	0,04
heat flow cylinder 2	kW	0,6	0,5	0,5	0,8	0,6	0,3
setting temperature cylinder 3	°C	100	100	100	100	100	100
temp. cylinder 3 water flow	°C	99,9	99,8	99,5	99,9	99,8	100
temp. cylinder 3 water return	°C	100,4	100,2	99,8	100,4	100,4	101,1
mass flow cylinder 3 water	m³/min	0,04	0,04	0,04	0,04	0,04	0,04
heat flow cylinder 3	kW	-1,1	-0,9	-0,6	-1,1	-1,3	-2,4
setting temperature cylinder 4	°C	100	100	100	100	100	100
temp. cylinder 4 water flow	°C	99,3	100,6	99,2	99,8	100,7	100,3
temp. cylinder 4 water return	°C	99,4	100,6	99,3	99,9	100,8	100,5
mass flow cylinder 4 water	m³/min	0,054	0,054	0,054	0,054	0,054	0,054
heat flow cylinder 4	kW	-0,3	0,0	-0,3	-0,3	-0,3	-0,6
setting temperature cylinder 5	°C	70	70	70	70	70	70
temp. cylinder 5 water flow	°C	72,6	72	72,3	70,7	73,1	70,5
temp. cylinder 5 water return	°C	73,3	72,2	72,6	70,9	73,2	70,5
mass flow cylinder 5 water	m³/min	0,04	0,04	0,04	0,04	0,04	0,04
heat flow cylinder 5	kW	-1,7	-0,5	-0,7	-0,5	-0,2	0,0
setting temperature cylinder 6	°C	-	-	-	70	70	70
temp. cylinder 6 water flow	°C	-	-	-	69	69	70
temp. cylinder 6 water return	°C	-	-	-	72	70	71
mass flow cylinder 6 water	m³/min	-	-	-	0,021	0,021	0,021
heat flow cylinder 6	kW	-	-	-	-3,8	-1,3	-1,3
total heat flow	kW	-3,8	-2,3	-2,6	-6,2	-3,8	-5,3
mass temperature/pressure							
T-1 melt temp. between cylinder 1 & 2	°C	138	139	139	139	139,8	181
T-2 melt temp. between cylinder 2 & 3	°C	157	158	150	157	161	189
T-3 melt temp. between cylinder 3 & 4	°C	173	172	170	172	180	187
T-4 melt temp. between cylinder 4 & 5	°C	151	152	151	150	154	155
T-5 melt temp. between cylinder 5 & 6	°C	179	133	128	126	105	123
T-6 melt temp. at the die	°C	-	-	-	106	111	120
T-7 melt temp. Outlet manuel	°C	205	175	145	166	170	191
P-1 melt pressure cylinder 1 & 2	bar	20	19	18	21	16	27
P-2 melt pressure cylinder 2 & 3	bar	0	0	0	0	0	0
P-3 melt pressure cylinder 3 & 4	bar	21	24	24	22	18	17
P-4 melt pressure cylinder 4 & 5	bar	0	0	0	0	0	0
P-5 melt pressure cylinder 5 & 6	bar	0	0	0	0	0	0
P-6 melt pressure at the die	bar	-	-	-	2	1	2
Vacuum							
Vacuum at M2	mbar	200	50	50	50	50	50
Vacuum at M3	mbar	20	50	50	50	50	50
Vacuum at M5	mbar	20	50	50	50	200	200
output							
specific energy	KWh/kg	0,512	0,424	0,388	0,512	0,468	0,64

remark

Target: devulkanisation of rubber

setting 25 setup 7
increase the barrel temperatur in the 2nd module to get an faster reaction. The masstemp. there is still the same. but the torque becomes lower.

setting 26 setup 8
Chang the diameter of the last dispergen ring The outlet temp. is much lower, but the material is not so sticky anymore.

setting 27 setup 9
The outlet temp. is pretty low.

setting 28 setup 10
Ther is no solide strand comming out of the die. The material is verry brittle. After cooling down it becomes sticky.

setting 29 setup 10
increase the speed for more shear. If we reduce the vaccum under 200mbar the flow speed is so high that we suck out the material by the vaccum pump.

setting 30 setup 10
reduce the amount of Pepton to find the right quantity. dwelltime over all modules is 150sec.

test report **TP-WE 70/1600 M4**

company: **Rumal**
commission no.: **06820t0002**

present: **Mrs. Dr. Ir. Dierkes; Mr. van Swaaij, Mr. Rajendran** **(Universit of Twente)**
Mr. Wallis **(BKF)**
Mr. Gerdon **(ENTEX**

leading: M.Gerdon
date: 2016-02-24-26

		6					
setting no:		**31**	**32**	**33**			
setup		**10**					
date		**26.02.**	**26.02.**	**26.02.**			
time		18:35	18:53	19:15			
Extruder							
power Extruder (P-max = 46 KW)	KW	13,8	14,7	16,4			
torque Extruder min.	Nm	158	119	132			
torque Extruder max. (M-max motor = 170 Nm)	Nm	160	122	133			
speed Extruder (n-max = 250 min-1)	min-1	70	100	100			
dosing units							
dosing of rubber granulat	%	90	100	100			
dosing of rubber granulat	kg/h	22,50	25,00	25,00			
dosing of pepton	%	5	0	0			
dosing of pepton	kg/h	1,25	0,00	0,00			
dosing of TDAE	%	5	0	0			
dosing of TDAE	kg/h	1,25	0,00	0,00			
capacity set	kg/h	25	25	25			
temperature control							
temp. cooling water	°C	9	9	9			
temp. feed section	°C	15	15	15			
setting temperature cylinder 1	°C	90	90	90			
temp. cylinder 1 oil flow	°C	91	92	90			
temp. cylinder 1 oil return	°C	90	91	92			
mass flow cylinder 1 oil	m³/min	0,048	0,048	0,048			
heat flow cylinder 1	kW	1,4	1,4	-2,8			
setting temperature cylinder 2	°C	150	150	150			
temp. cylinder 2 water flow	°C	150,3	150,4	150,3			
temp. cylinder 2 water return	°C	150	150,4	150,4			
mass flow cylinder 2 water	m³/min	0,04	0,04	0,04			
heat flow cylinder 2	kW	0,5	0,0	-0,2			
setting temperature cylinder 3	°C	100	100	100			
temp. cylinder 3 water flow	°C	99,7	100	99,9			
temp. cylinder 3 water return	°C	100,4	100,7	100,8			
mass flow cylinder 3 water	m³/min	0,04	0,04	0,04			
heat flow cylinder 3	kW	-1,5	-1,5	-1,9			
setting temperature cylinder 4	°C	100	100	100			
temp. cylinder 4 water flow	°C	100,4	100,4	100,4			
temp. cylinder 4 water return	°C	100,4	100,4	100,5			
mass flow cylinder 4 water	m³/min	0,054	0,054	0,054			
heat flow cylinder 4	kW	0,0	0,0	-0,3			
setting temperature cylinder 5	°C	70	70	70			
temp. cylinder 5 water flow	°C	72	72	72,2			
temp. cylinder 5 water return	°C	73,2	72,2	72,3			
mass flow cylinder 5 water	m³/min	0,04	0,04	0,04			
heat flow cylinder 5	kW	-2,9	-0,5	-0,2			
setting temperature cylinder 6	°C	70	70	70			
temp. cylinder 6 water flow	°C	70	69	68			
temp. cylinder 6 water return	°C	72	71	70			
mass flow cylinder 6 water	m³/min	0,021	0,021	0,021			
heat flow cylinder 6	kW	-2,5	-2,5	-2,5			
total heat flow	kW	-5,0	-3,1	-8,0			
mass temperature/pressure							
T-1 melt temp. between cylinder 1 & 2	°C	181	210	206			
T-2 melt temp. between cylinder 2 & 3	°C	188	197	204			
T-3 melt temp. between cylinder 3 & 4	°C	168	165	173			
T-4 melt temp. between cylinder 4 & 5	°C	150	147	152			
T-5 melt temp. between cylinder 5 & 6	°C	121	116	117			
T-6 melt temp. At the die	°C	116	114	116			
T-7 melt temp. Outlet manuel	°C	185	175	175			
P-1 melt pressure cylinder 1 & 2	bar	30	19	24			
P-2 melt pressure cylinder 2 & 3	bar	5	1	4			
P-3 melt pressure cylinder 3 & 4	bar	21	14	15			
P-4 melt pressure cylinder 4 & 5	bar	0	0	0			
P-5 melt pressure cylinder 5 & 6	bar	0	0	0			
P-6 melt pressure at the die	bar	2	2	2			
Vacuum							
Vacuum at M2	mbar	50	50	50			
Vacuum at M3	mbar	50	50	50			
Vacuum at M5	mbar	200	200	200			
output							
specific energy	KWh/kg	0,552	0,588	0,656			

remark

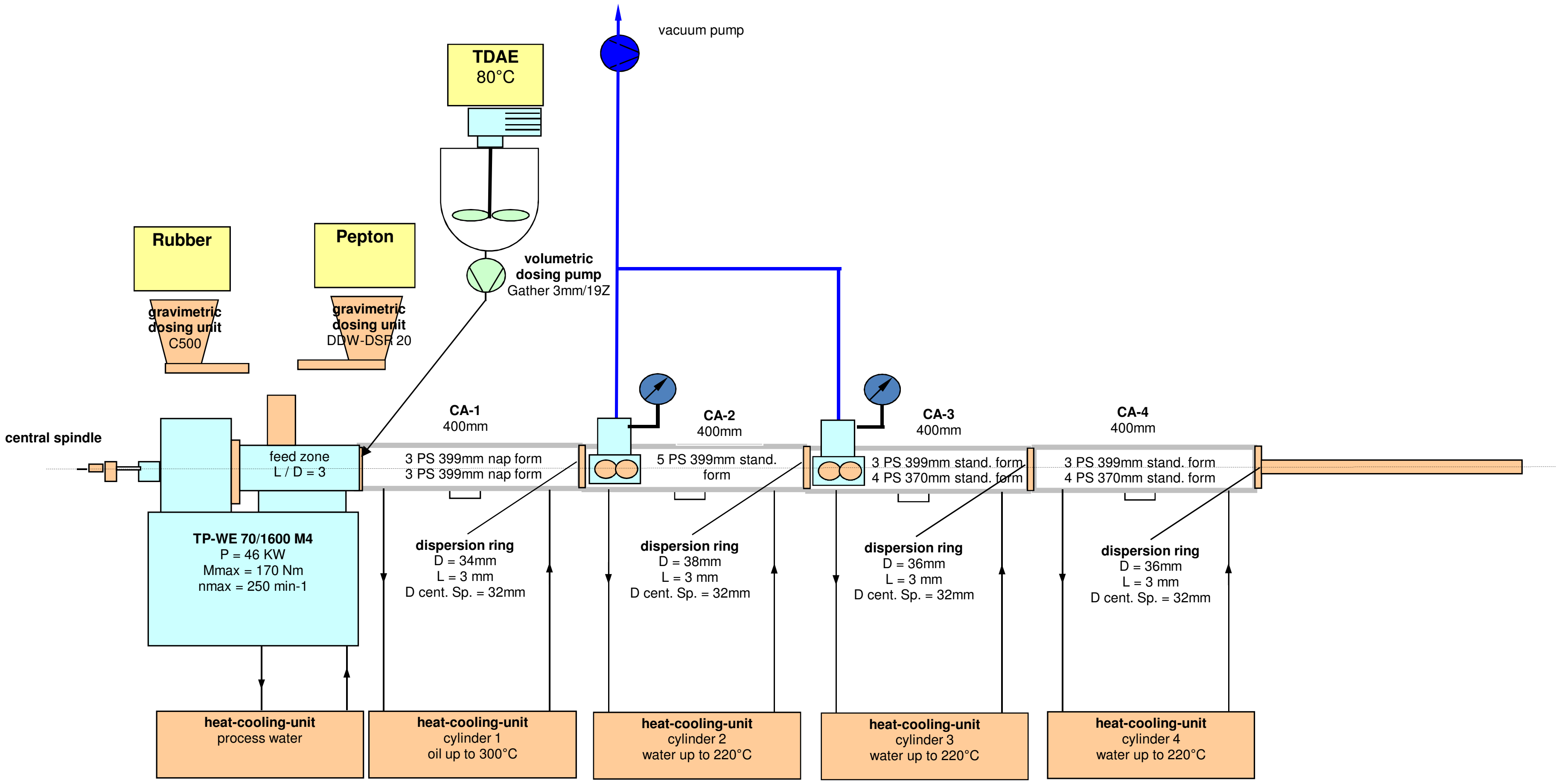
Target: devulkanisation of rubber

setting 31 setup 10
cahnge to the smaler grinded material with a particle size of 0.8-2mm

setting 32 setup 10
change to preblend material with particle size of 0.8-2mm.
there is no compact strand anymore with this material.

setting 33 setup 10
change to preblend material with particle size of 2-7mm.
Wwhen we change the material we see that the torque rise directly, but keeps stable after that.
That means, that the total extra enery we need in ths setup, is just for grinding the material in the first barrel.

setup 1



Firma:	Rumal	
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Datum:	2016-02-24-26	
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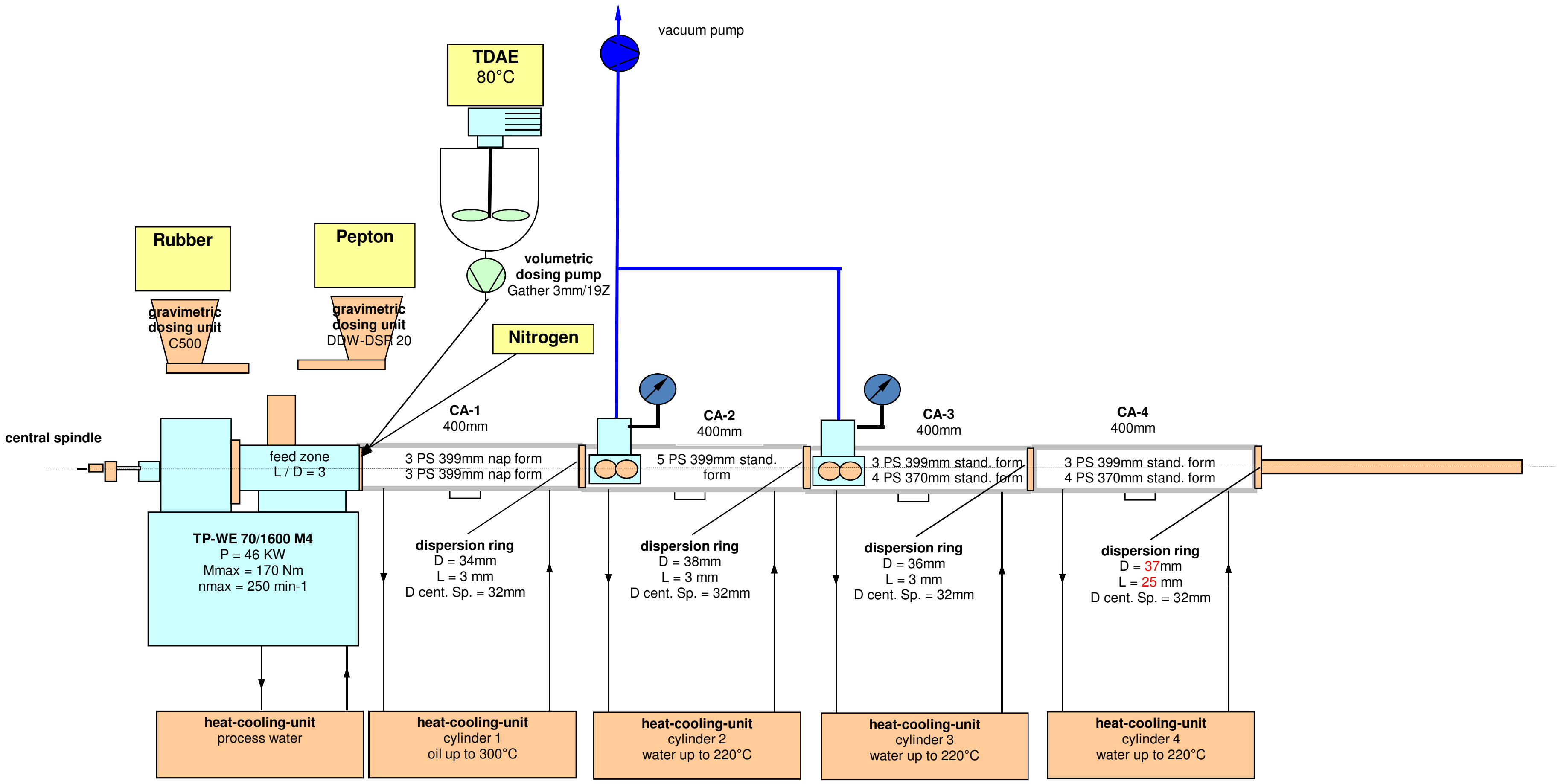
setup 2



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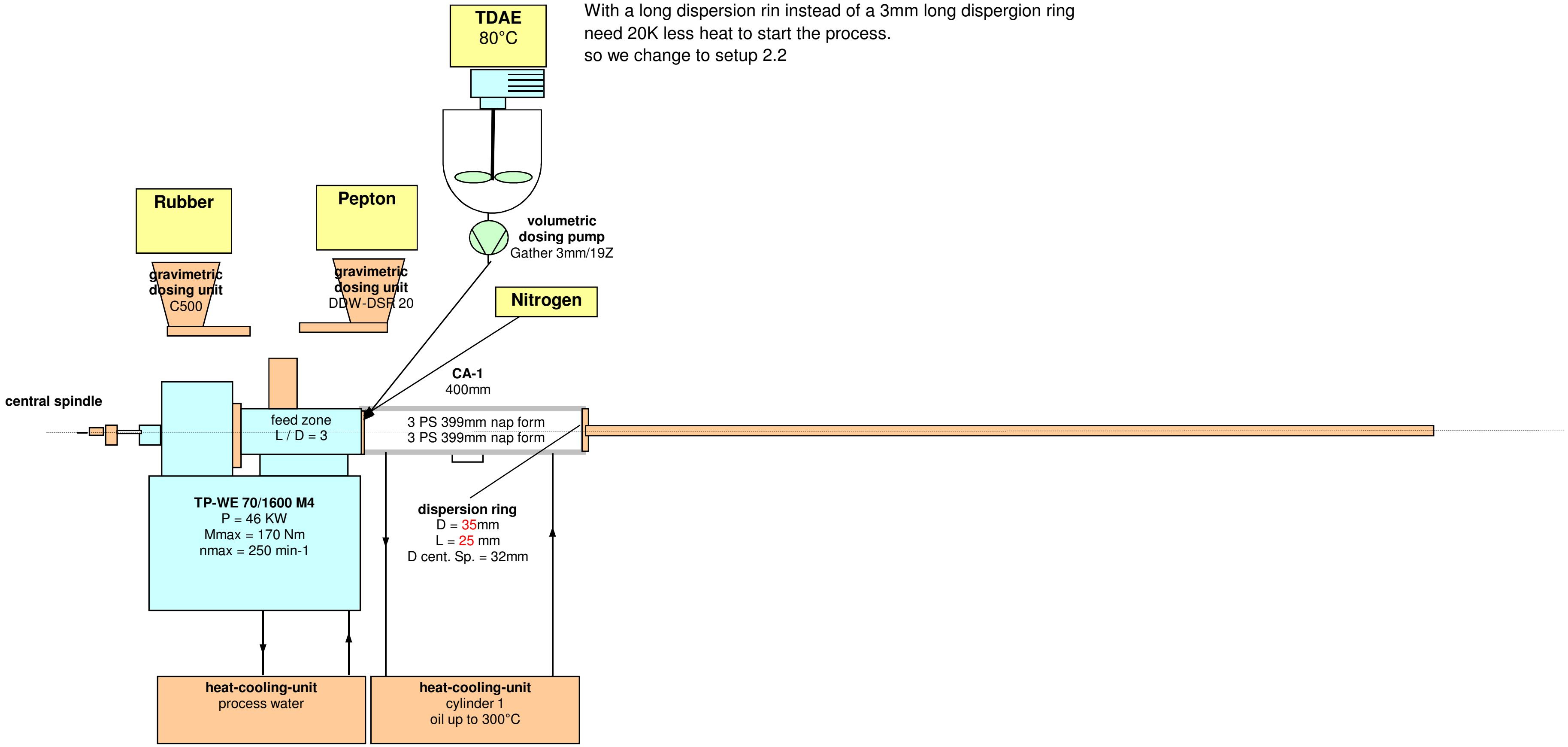
setup 2.1

This setup was used to find the best length of the dispergion ring.
With a long dispersion rin instead of a 3mm long dispergion ring
need 20K less heat to start the process.
so we change to setup 2.2



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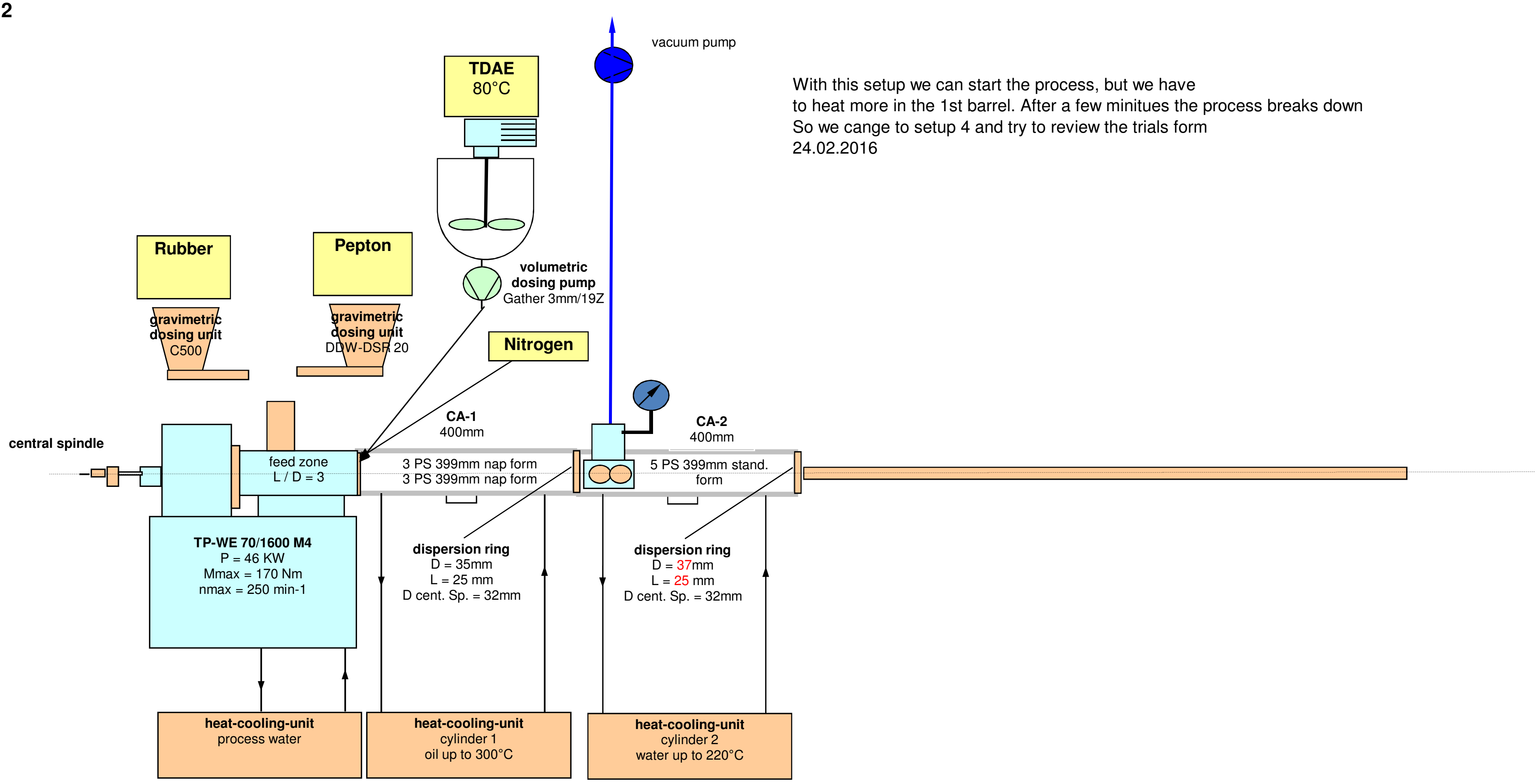
setup 2.2



With this setup we can start the process, but we have
to heat more in the 1st barrel. After a few minitues the process breaks down
So we cange to setup 4 and try to review the trials form
24.02.2016

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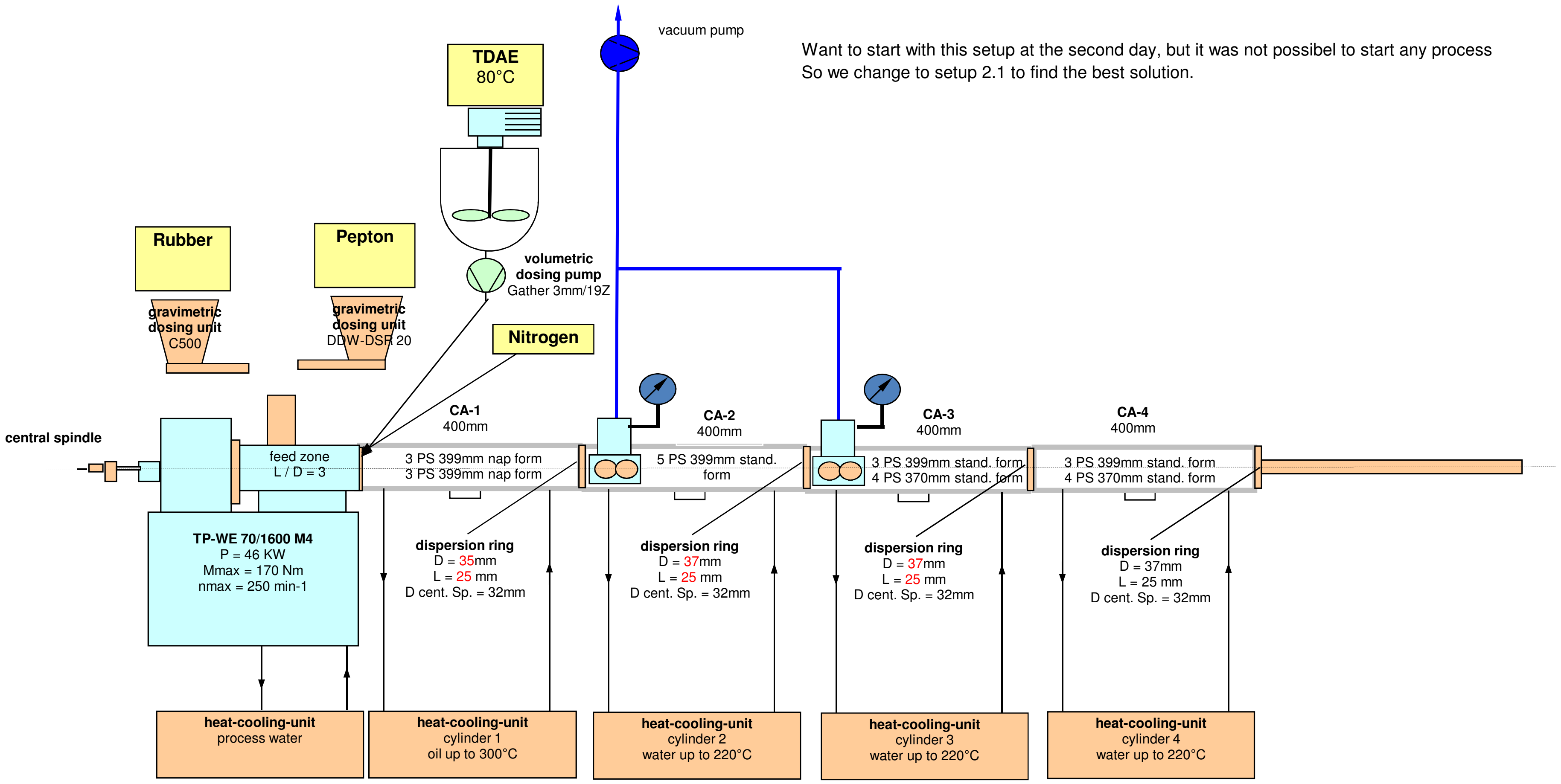
setup 3

Want to start with this setup at the second day, but it was not possibel to start any process
So we change to setup 2.1 to find the best solution.



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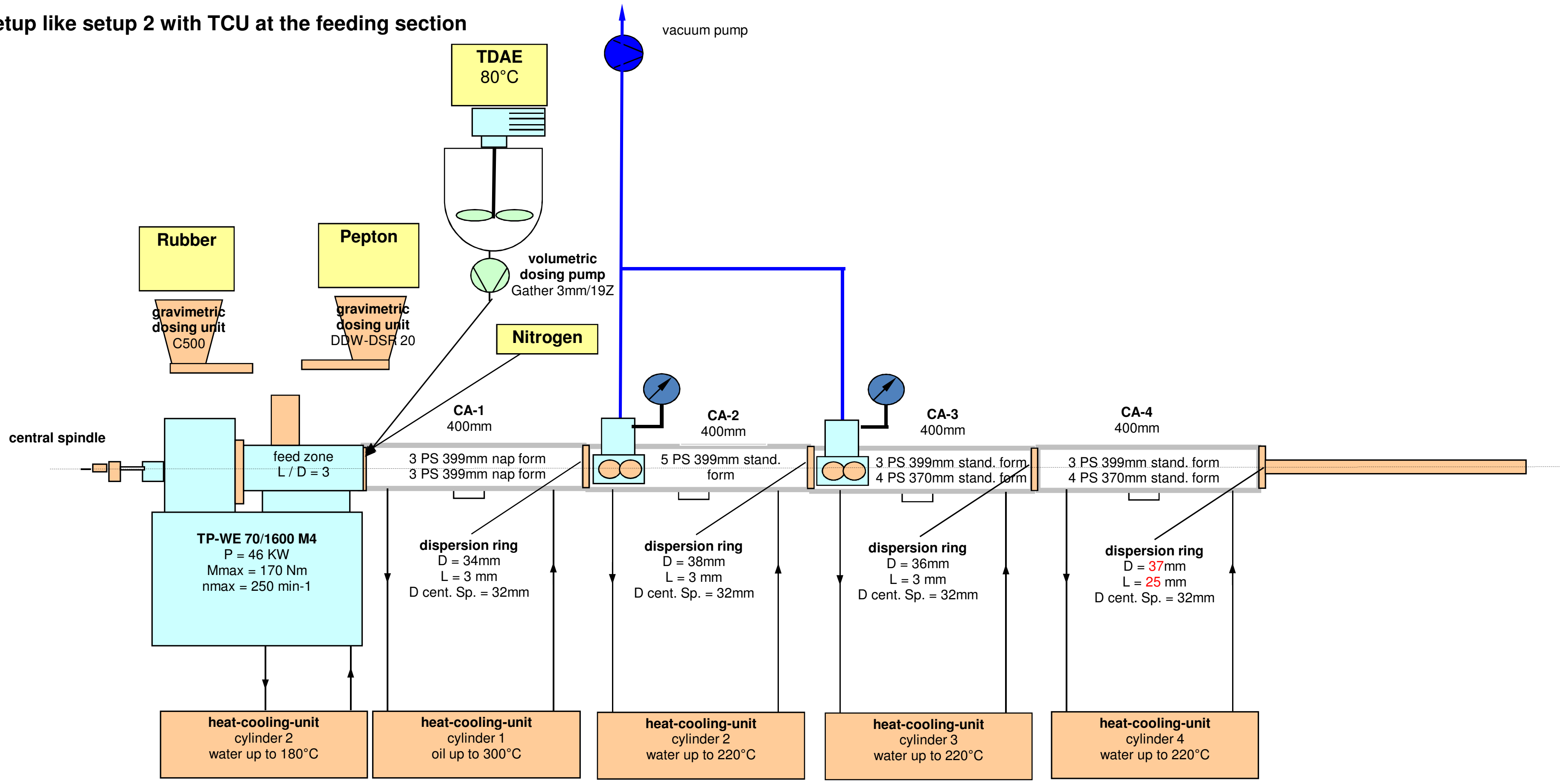
setup 4
same setup like setup 2 with TCU at the feeding section



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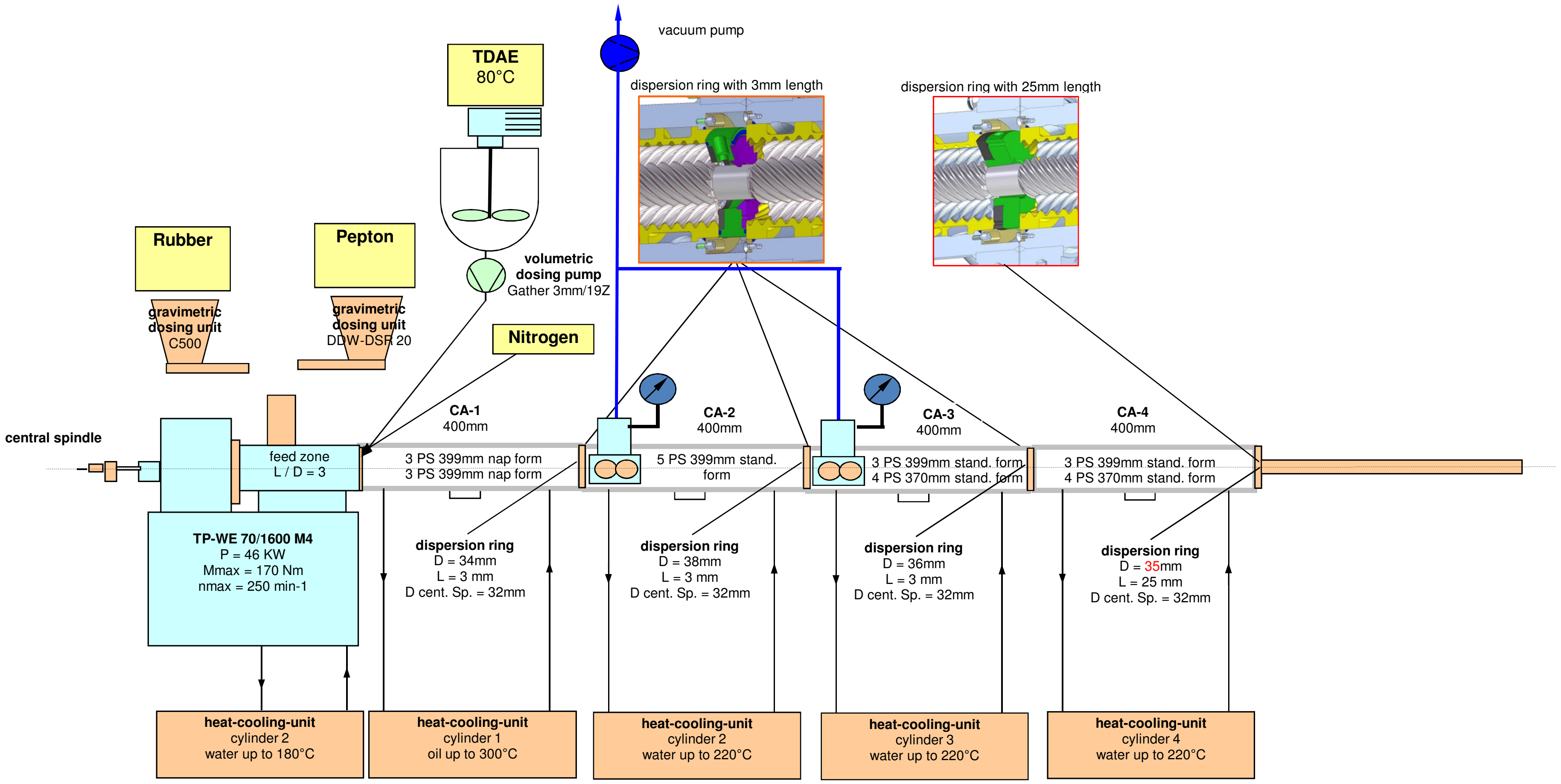
setup 5



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Kom.-Nr.: 06820t0002	
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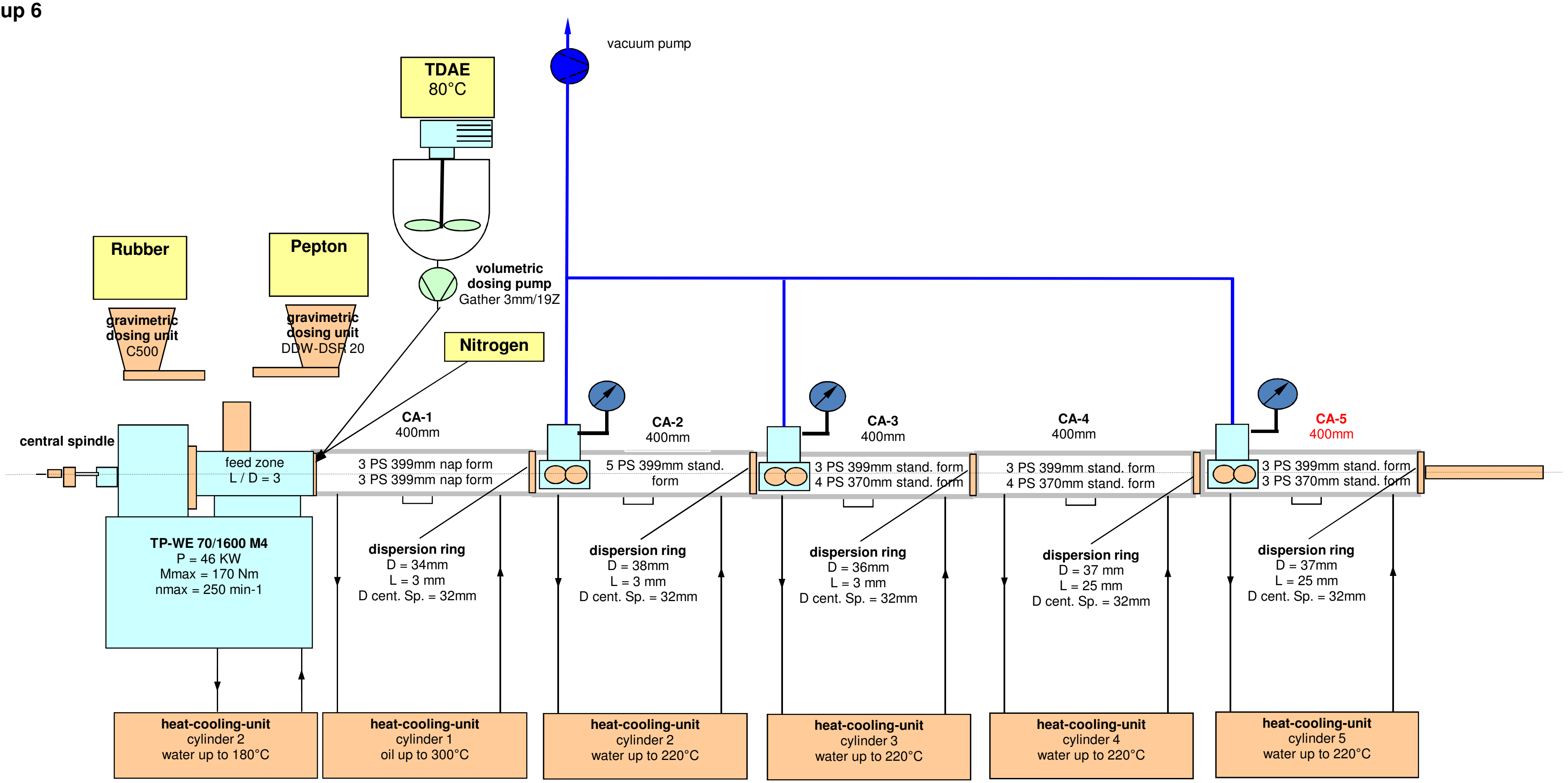
setup 6



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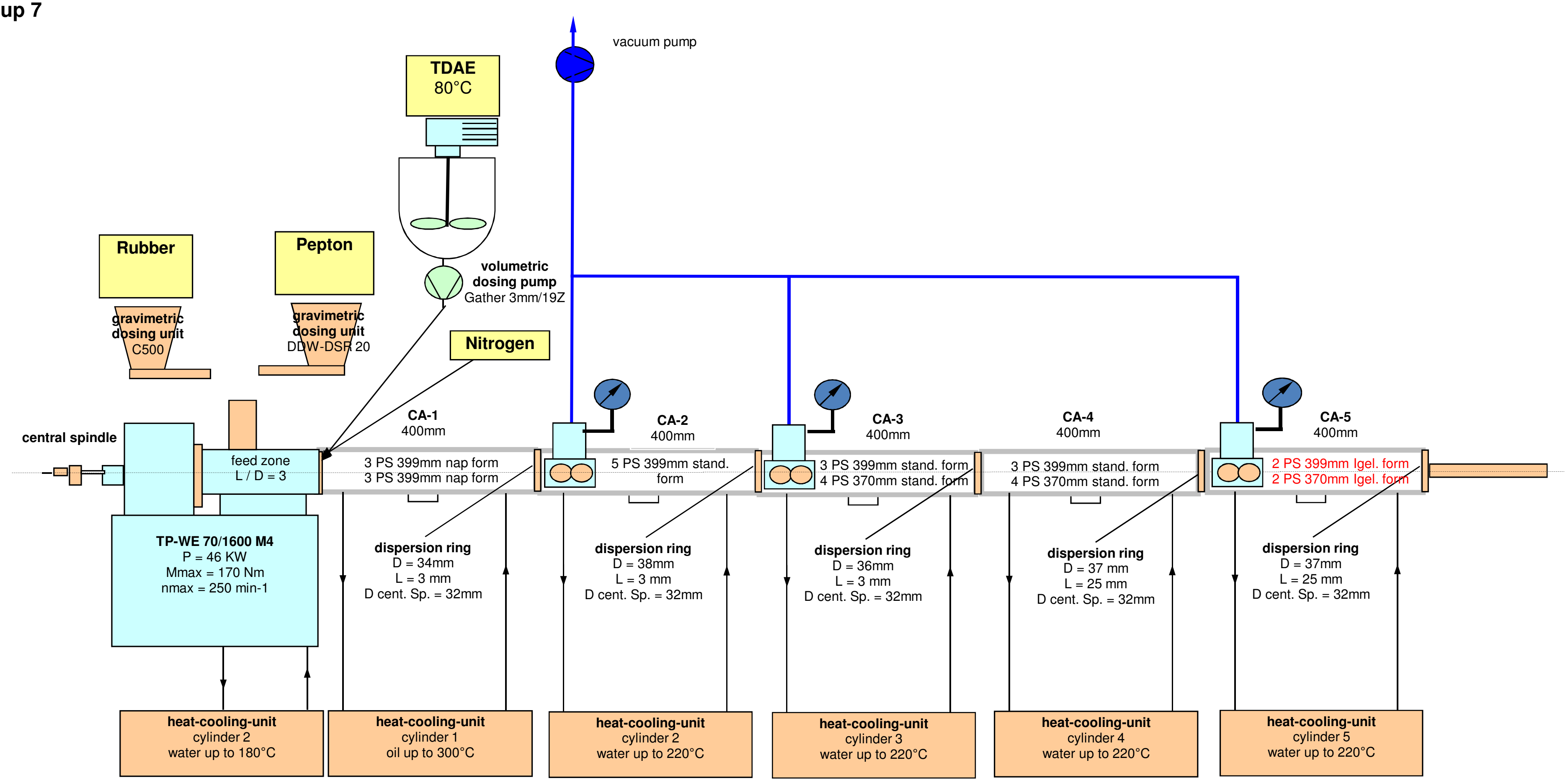
setup 7



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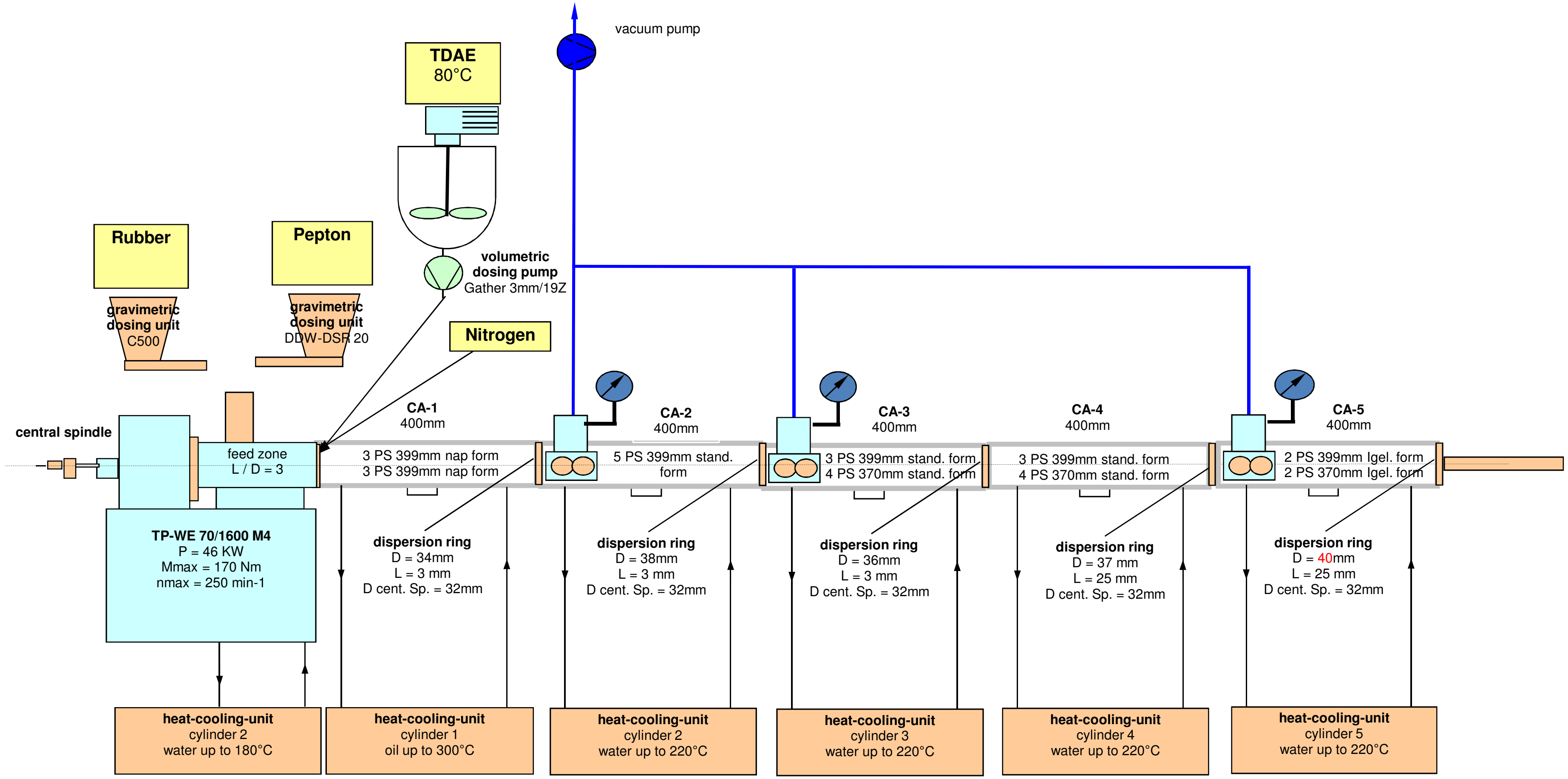
setup 8



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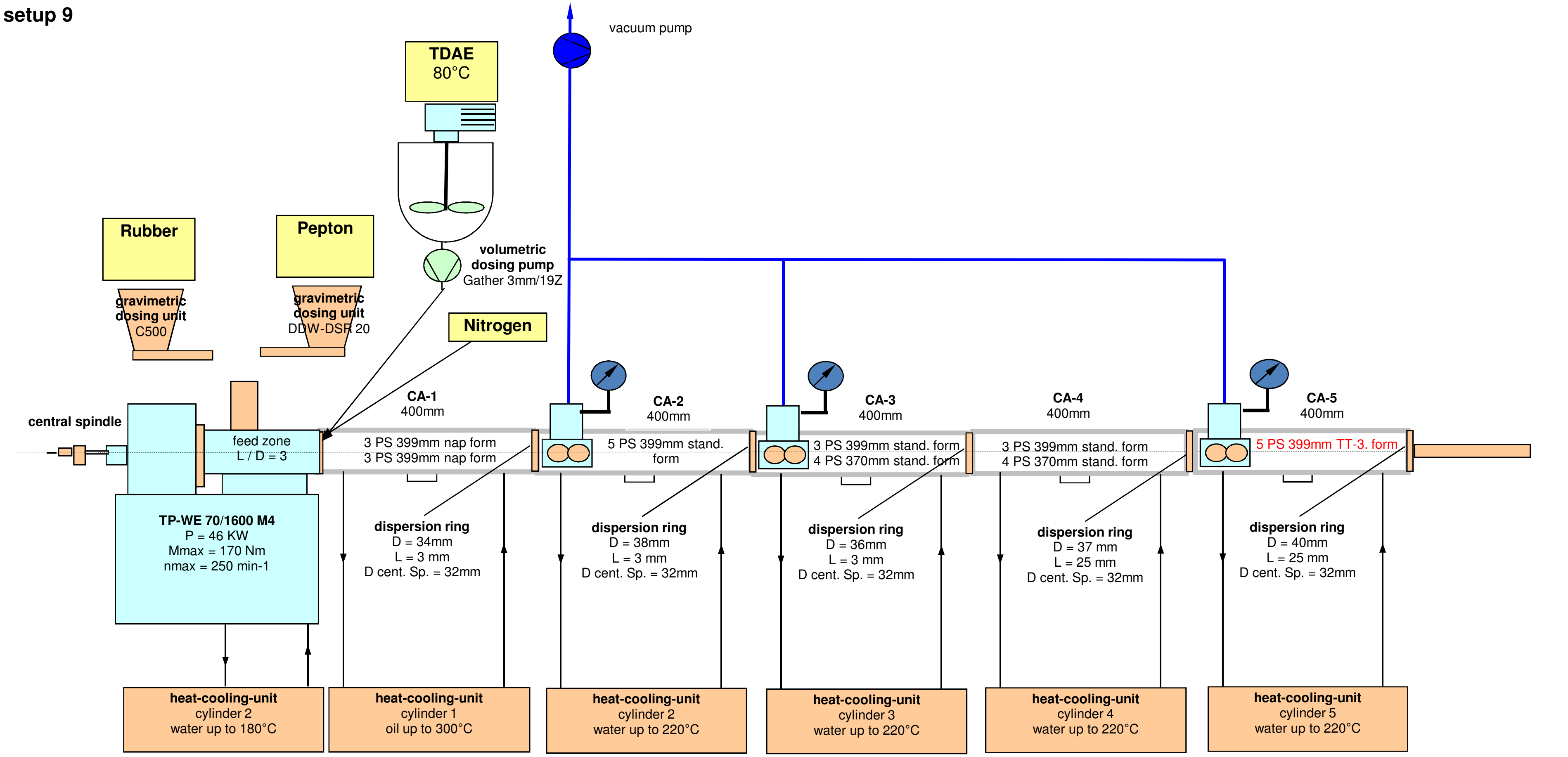
setup 9



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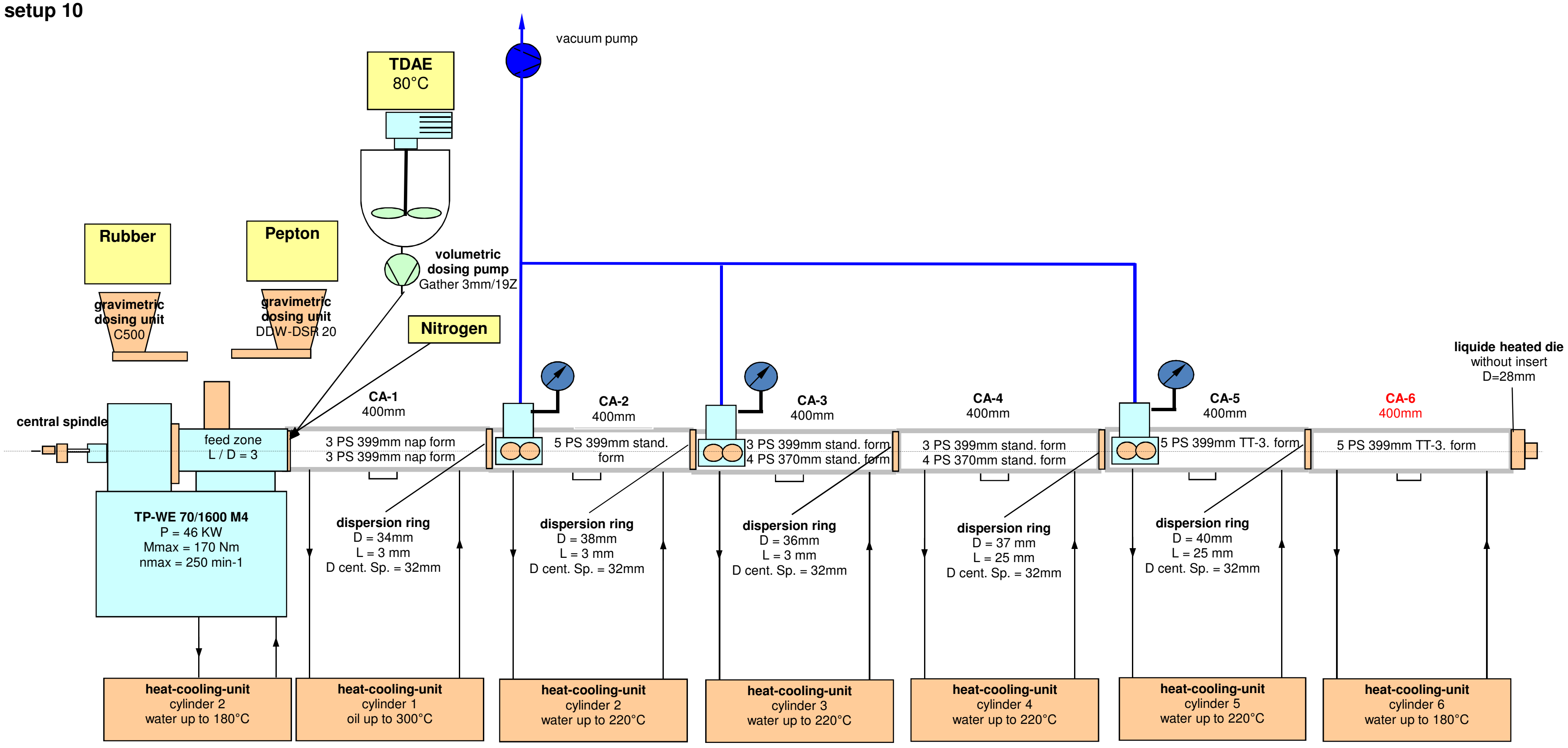
setup 10



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