

Master in Chemical Engineering

***Optimization of Component A Using Rubber
Process Analyser Data of ContiSeal Compound***

Master dissertation

of

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Abstract

This master thesis reports the progress of a project carried out at ContiSeal, a department of Continental Mabor at Lousado, in cooperation with the Faculty of Engineering at the University of Porto (FEUP).

The ContiSeal tire consists of a tire where a sealant layer is applied in the internal part that prevents the loss of air when the tire is perforated. The sealant is made of a mixture of two components, Component A and Component B. Component A is a mixture of rubber, polybutene and oil which is produced in a mixing extruder, Component B is made of organic peroxides, a chemical compound with double oxygen bounds (R-O-O-R) and polybutene prepared in a mixing tank. The reaction that occurs between Components A and B originates the sealant.

The main goal of this project is to assess rheology parameters, elastic shear modulus (G'), viscous modulus (G'') and the damping factor ($\tan(\delta)$) of rubber compound masterbatch, obtained with a rheometer (Rubber Processing Analyser (RPA), from Alpha Technologies), and relate them with the viscosity @ 0.02 Hz and 120 °C displayed by Component A. The project is divided in three objectives: i) assess correlation of each rheology parameter, G' , G'' and $\tan(\delta)$, and the viscosity of Component A; ii) understand the interactions between those properties and determine their ranges for originating a Component A with the target viscosity; and iii) determine how the composition of the ContiSeal masterbatch is related to its rheology properties and assure the stipulated specification on the second objective.

To assess correlation of each rheology parameter and the viscosity of Component A it was performed a design of experiments. The properties displaying the highest correlation with the viscosity of Component A are the elastic modulus module at 1 % and 10 % of strain amplitude ($G'1\%$, $G'10\%$) and the damping factor at 10 % and 100 % of shear amplitude ($\text{TAN}(\delta)10\%$, $\text{TAN}(\delta)100\%$), standing out $G'10\%$ and $\text{TAN}(\delta)100\%$. For obtaining the target viscosity @ 0.02 Hz and 120 °C of Component A, 555 Pa·s, these properties should be $280 \text{ Pa} < G'1\% < 290 \text{ Pa}$, $230 \text{ Pa} < G'10\% < 235 \text{ Pa}$, $0.34 < \text{TAN}(\delta)10\% < 0.36$ and $0.69 < \text{TAN}(\delta)100\% < 0.70$. In this project, it was found that to make G' to decrease, the concentration in carbon black of the rubber must be smaller or the added oil must be high, the same applies to increase $\tan(\delta)$.

Keywords: sealant; Component A; Rubber Processing Analyser (RPA); viscosity; design of experiments

Resumo

A presente tese de mestrado descreve o desenvolvimento de um projeto realizado no ContiSeal, um departamento da Continental Mabor em Lousado, em parceria com a Faculdade de Engenharia da Universidade do Porto (FEUP).

O pneu ContiSeal consiste num pneu em que uma camada de selante é aplicada na parte interna, que previne a perda de ar quando o pneu é perfurado. O *sealant* é produzido a partir de uma mistura de dois componentes, Componente A e Componente B. Componente A é uma mistura de composto de borracha, polibuteno e óleo produzido numa extrusora de mistura, enquanto que o componente B é composto por peróxidos orgânicos, composto químico com ligações duplas de oxigénio (R-O-O-R) e polibuteno produzido num tanque de mistura. A reação que ocorre quando os Componentes A e B são misturados dá origem ao *selante*.

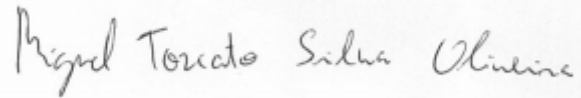
O objetivo principal deste projeto é medir os parâmetros reológicos, módulo de armazenamento (G'), módulo de perda (G'') e fator de amortecimento ($\tan(\delta)$) do composto de borracha do ContiSeal obtidos com um reómetro (Análise de Processamento de Borracha (RPA) da Alpha Technologies) e relaciona-los com a viscosidade @ 0,02 Hz and 120 °C do Componente A. O projeto foi dividido em três objetivos: i) medir a correlação de cada parâmetro reológico G' , G'' e $\tan(\delta)$, com a viscosidade do Componente A; ii) perceber as interações entre essas variáveis e determinar os seus intervalos para originar um Componente A com a viscosidade pretendida; iii) determinar como a composição do composto de borracha do ContiSeal está relacionada com as suas propriedades reológicas e assegurar a especificação estipulada no segundo objetivo.

Para avaliar a correlação de cada parâmetro reológico e da viscosidade do Componente A, foi realizado um desenho de experiências. As propriedades que mostram uma maior correlação com a viscosidade do componente A são o módulo de elasticidade com 1 % e 10 % de deformação ($G'_{1\%}$, $G'_{10\%}$), e o fator de amortecimento com 10 % e 100 % de deformação ($\text{TAN}(\delta)_{10\%}$ e $\text{TAN}(\delta)_{100\%}$), destacando-se $G'_{10\%}$ e $\text{TAN}(\delta)_{100\%}$. Para obtenção da viscosidade pretendida @ 0,02 Hz and 120 °C do Componente A, 555 Pa·s, estas propriedades devem estar entre 280 Pa < $G'_{1\%}$ < 290 Pa, 230 Pa < $G'_{10\%}$ < 235 Pa, 0,34 < $\text{TAN}(\delta)_{10\%}$ < 0,36 and 0,69 < $\text{TAN}(\delta)_{100\%}$ < 0,70. Neste projeto, foi encontrado que para diminuir G' a concentração de negro de fumo na borracha deve ser pequena ou a adição de óleo deve ser grande, o mesmo aplica-se para aumentar a $\tan(\delta)$.

Palavras-chave: selante; Componente A; Análise de Processamento de Borracha (RPA); viscosidade; desenho experimental

Declaration

I hereby declare, on my word of honor, that this work is original and that all non-original contributions were properly referenced with source identification.



Miguel Torcato Silva Oliveira

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Notation and Glossary

G'' - Viscous Module

G' - Elastic Shear Module

S^* - Complex Torque

S' - Elastic Component

S'' - Viscous Component

Greek Letters

δ - Buffer Factor

γ - Deformation Angle

a - Angle Between The Two Blocks

η - Viscosity

List of Acronymys

BPO - Dibenzoyl Peroxide

BR - Polybutadiene rubber

EPDM - Ethylene-Propylene-Diene-Monomer

ETO - Experimental Tire

MDR - Moving Die Rheometer

MU - Mooney Units

NBR- Nitrile Rubber

NR - Natural Rubber

Phr - Parts Per Hundred of Rubber

QDO - Quinone Dioxime

RPA - Rubber Process Analyser

Rpm - Rotation Per Minute

SBR - Styrene Butadiene Rubber

TSE - Twin-Screw Extruder

1 Introduction

1.1 Framing and presentation of the work

At ContiSeal, a department of Continental Mabor at Lousado, Portugal, a sealant coat is produced and applied inside tires.

This auto-sealant layer is a viscoelastic product that envelops and adheres to penetrating objects and avoids air loss. This product is made of a mixture of two components, called Component A and Component B.

Component A is a mixture of a rubber compound masterbatch, polybutene and paraffinic oil mixed in a twin screw extruder (TSE) acting as a continuous rubber mixer. The feeding of each compound is done with extreme accuracy by different dosing systems. This study focuses on this component and the rubber masterbatch that is used to make it.

Component B is a mixture of polybutene (indopol h-25) and organic peroxides (luperox), is produced in a mixing tank with a stirring paddle at ambient temperature due to the extreme reactivity of luperox.

To assure that Component A displays the required quality it is necessary to characterize it and to compare the results with the specifications. The quality control of Component A is based on its viscosity read at 0.02 Hz and 120 °C.

Dynamic rheometry tests are performed to assure the quality of both components and of the sealant. The rubber masterbatch is produced mixing natural and synthetic rubber and other groups of raw materials such as, fillers, vulcanizing agents and processing helpers. The rubber mixing is done in vertical mixers that are heated up for plasticizing the rubber and disperse the other chemical substances (carbon black, resin, oils, sulfur, etc.). The tests for the rubber compound for ContiSeal process are based on rheometry analysis, but these tests can not fully predict the behaviour on the compounds during the productive process, neither they are sensitive enough to measure with accuracy the variation level that wants to be achieved.

Nowadays these tests have come to be supplemented by fast, sensitive and efficient methods with the purpose to improve the productivity and reduce operation costs. In this way, the Rubber Process Analyser (RPA) emerge. Through the measure of the rubber dynamic properties (elastic shear modulus G' , viscous modulus G'' and the damping factor $\tan(\delta)$) the RPA is able to characterize the compounds in a more comprehensive way and to predict more rapidly its behaviour.

This thesis is about crossing the rheometric properties of rubber compound (G' , G'' and $\tan(\delta)$), obtained with an oscillating rheometer (RPA), with the viscosity of Component A to understand what information these properties can give about the compound to improve the viscosity of Component A.

1.2 Presentation of the company

Continental was founded in October of 1871 in Hannover, started with the production of rubber articles and solid tires for bicycles and carriages. Over the years, this German company was strengthening its position all over the world with the purchase of many tires manufacturers and with the entrance on the automotive industry. Nowadays, the Continental Group belongs to the top 5 world suppliers in the automobile industry, and is number 2 in Europe.

Besides tires, Continental also produces and delivers brake systems, chassis components, instrumentation and vehicle electronics. It employs around 178 000 people and has branches in 49 countries.

Its works politics is based on four values: trust, passion to win, freedom to act and one for all. Its vision is to search for the best solutions and to create the most developed technologies of transport and mobility without neglecting safety, because tires are the beginning of the stability of a vehicle, and the environment. Its goal is to render a safer, more sustainable, more comfortable, individual and accessible mobility.

On July 1st, 1990, Continental AG made a *joint-venture* of the Portuguese company Mabor - Manufatura de Borracha, S.A, located in Lousado and founded at 1946. In 1993, the German company purchased 100 % of the capital, renaming the brand Continental Mabor - Indústria de Pneus, S.A.

The areas involved for the develop of this thesis, in these 5 months in Continental Mabor, were in ContiSeal - Laboratory and Process, Product Industrialization (PI), Mixing Department and the Laboratory of analysis and processing of raw materials.

1.3 ContiSeal Process

The ContiSeal is a technology designed to seal a damaged tire tread; it uses a sealant layer applied over the innerliner that prevents the loss of air when the tire is perforated (figure 1). The ContiSeal factory was built in Lousado, in 2008, and this unit become the second with this type of technology in Continental group [1].

The main advantages are:

- Mobility increase;
- Safety;
- Avoids the need of spare tires;
- Less load for the vehicle;
- Does not need special rims;
- Seals 80 % of all the tires punctures



Figure 1 - ContiSeal™ layer - extracted from [1]

At ContiSeal, the production of the sealant consists in a sequential and continuous flow of tires through certain stations that prepare the tire for the application of the sealant (figure 2). The sealant, as mentioned before, is made of two components, Component A and Component B, which are produced separately.

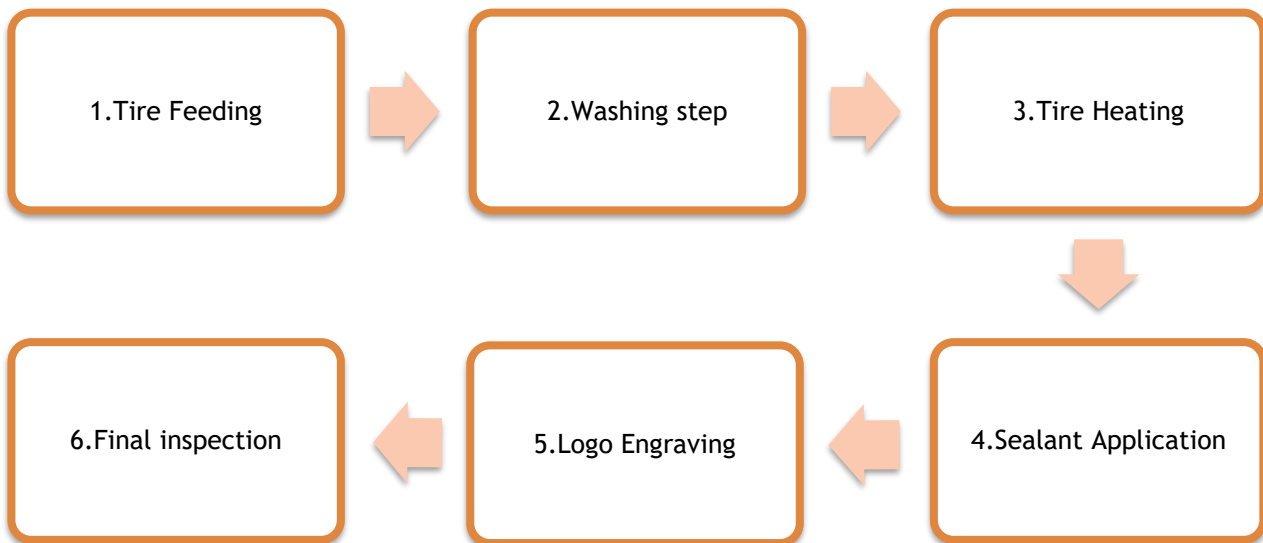


Figure 2 - ContiSeal sequential process

The first step, the input of the tire into the line, is an important step, where certain conditions must be observed.

After the introduction of the tire, the conveyors direct the tires towards two types of washing machines that clean the inside of the tires by two different processes, one with the use of mechanical brushes and soap, and the other with a laser jet, this last is called laser cleaning. The purpose of this step is to clean the inside of the tire and to remove undesirable substances that are present inside the tire.

Following the washing process, the tires are transported into a heating tunnel which heats the tires up to 90 °C, for about 30 minutes to remove the humidity of the tires after the washing machine.

The next step is the application process what is accomplished in three robots. In the membrane dosing system of these applicators, Component A and Component B are pumped into the mixing chamber and exit through a small nozzle. The robots (figure 3) apply a sealant layer while the tire rotates. It is possible to control the throughput of the material through the nozzle, the amount of sealant that should be applied in each tire article and the temperature. The temperature of the sealant in the mixing chamber should be around 113 ± 3 °C. After the application, the tire is send to the rotators which keep the tires spinning around 15 minutes.



Figure 3-ContiSeal's sealant application robot

After the sealant application, the tire goes to laser engraving. The laser engraving selectively removes part of the rubber, burning it to draw the ContiSeal logo.

The final step is the final inspection when the tire exits the line and it is verified by an operator that checks the appearance of the sealant, the logotype and the uniformity of the tire. Components A and B, which establish the sealant, are produced in a process apart from the tire flow.

1.4 Objectives of the Project

The main goal of this project is to evaluate the RPA results (G' , G'' and $\tan(\delta)$) of the rubber compound and cross these results with the Component A viscosity to ensure the stability of Component A.

To attain this objective, as a first instance, it was important to study the testing equipment, RPA, and to understand what it means, theoretically, each variable this equipment provides us. In a second step, evaluate which variable of all the RPA variables, has the biggest influence on the Component A viscosity. The third step is to define the best value of that variable to assure the stability of Component A viscosity inside the desired tolerance. The final step is to study the mixing

process of the rubber compound to control the variable defined on the second step and assuring the specification stipulated on the third step.

1.5 Contributions of the Work

Sometimes ContiSeal have a lot of trouble dealing with the viscosity of Component A, because the mixing in the extruder is not good, we have bad homogeneity and not stable viscosities, sometimes lower or higher than the tolerance. One think we know is that the rubber compound that is used to make the Component A has a big influence on the mixing because the physical properties are not always the same.

With this project, it will be possible to ensure the viscosity of Component A that is essential for the ContiSeal process obtaining a better control on the extruder as an improved rubber compound for ContiSeal. Beside this, this will contribute to a better final product with a good performance and it can increase the process efficiency, reducing time to obtain a good homogeneity with the extruder and reducing scrap too.

1.6 Organization of the thesis

This thesis is organized in seven different chapters, which will be made a brief presentation of each one.

Chapter 1. Introduction

This chapter, presents ContiSeal process, explaining what is Component A and sealant, about the RPA and physical tests of rubber compound and the tool used to the treatment of the results. The aim of the project is presented as well as the company where it was developed.

Chapter 2. Context and State of the Art

All the theoretical fundamentals for understanding this work are presented, such as the types of rubber vulcanization, mixing equipment giving more enface to the Twin-Screw extruder, about Component A, how this is made and the conditions for producing it, as well as the chemistry of ContiSeal and about rheometry given more enface to RPA, since it is the principal of this project.

Chapter 3. Materials and Methods

In this chapter, the materials and methods used through the project are presented and explained.

Chapter 4. Results and discussion

In this chapter, the results obtained for this study are presented and discussed

Chapter 5. Conclusion

The principal conclusions about the results obtained are summarized.

Chapter 6. Project Assessment.

In this chapter, is made a general evaluation of the work developed and the points and suggestions for the future are delineated.

Bibliography

Here are presented the references where the theory was found, some experimental methods specifications of the company for the assays done through the project and scientific papers.

Appendix

It is presented the tables with the data used to reach the results, tools for helping to explain some results and some of the results obtained.

2 Context and State of the art

This chapter provides the context of the work. An introduction to rubber materials, mixing processes, given emphasis to the twin-screw extruder, working principles of ContiSeal™ and rheometer analysers and rheology is provided given more enface to the RPA rheometry.

2.1 Rubber Materials

Elastomer and rubber are terms that sometimes are used with the same meaning. Elastomers can be defined as viscoelastic polymers that can recover their shape relatively quickly after being submitted to a certain amount of deformation. This term could also be applied to rubber but this material is usually considered a cured elastomer that can be changed to a state which is insoluble [2].

The rubber compounds have many characteristics that makes them unique comparing to other materials, such as elasticity, the damping factor and abrasion resistance. There are two types of rubber used in this process, natural rubber (NR) and synthetic rubber [3].

Natural rubber (NR) is a natural polymer deriving from the latex coagulation of the Seringueira tree. Its characteristics are based in high tensile strength, rupture resistance and fatigue resistance. It also has a good abrasion resistance and dynamic properties, also it has a good adherence and high green strength which are very important in the tire industry since it keeps the shape intact during tire construction. However, NR has low resistance to ozone, high temperatures, oxidation, oils and concentrated acids and bases. To avoid these drawbacks, it is usual to use blends of natural and synthetic rubbers [4].

Synthetic rubber consists not only of one type of units but can also be co-polymeric, which means that different monomers can be conjugated. The double bounds in the structure are crucial for the vulcanization reaction since it is due to these bounds that the crosslinking reaction occurs. One of the most important synthetic rubber for the tire industry is the styrene-butadiene rubber (SBR) because it has a good traction properties and abrasion resistance [4].

Polybutadiene rubber (BR) is known for its resistance to low temperatures but it has the disadvantage of having a significant cold flow at room temperature. This rubber also does not possess the durability, toughness and cut-grow resistance of NR [4].

The butyl rubber is an isobutylene copolymer (98 %) and isoprene (2 %), the higher the degree of unsaturation, the greater the rate of vulcanization and the resistance to heat, but the resistance to ozone decreases. The main property of the butyl rubber is the high impermeability to gases and air. Besides this, it as a good heat resistance, good bending properties, good resistance to aging caused by the weather and ozone and good electrical properties. The rubber used in ContiSeal is a butyl rubber [5].

Rubber Vulcanization

Vulcanization or curing is the rubber conversion through a chemical process of crosslinking formation, in other words, is a process whereby the chemical structure of rubber, the raw material, is altered by the conversion of the molecules of the independent polymer into a three-dimensional structure where they are linked together (figure 4) [6].

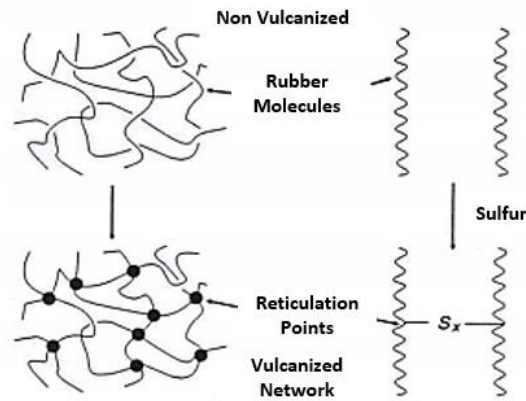


Figure 4 - Scheme of the formation of the three-dimensional network due to the vulcanization reaction - adapted from [6]

In a system of curing process, it is used a combination of accelerators, activators and a vulcanization agent. Vulcanization agents are chemical products such as sulfur, organic peroxides or resins, metal oxides or urethanes. Accelerators such as metallic oxides are also added to the mixture to improve the reaction rate. The use of inorganic accelerators gives a cure long enough for the rubber to develop heat-resistance properties [7].

Sulfur is the best well-known vulcanization agent. It is generally used with NR, SBR and BR because they are highly unsaturated elastomers. When a mixture of natural rubber with sulfur is subjected to the action of heat, the sulfur atoms act in this double bond and establish, through covalent bonds, the three-dimensional structure, represent in the figure 4 [7].

Another process in rubber curing is the peroxide cure system. This process is based on organic peroxides, chemical compounds with double oxygen bounds (R-O-O-R) that are used as vulcanizing agents for rubbers with the main saturated hydrocarbon chain or other main chains (siloxane chains in the case of silicone rubber). Although they may also be used in the vulcanization of conventional rubbers (NR, SBR, NBR, EPDM, etc.) [4,8].

Vulcanization with peroxides is explained by a mechanism involving the formation of free radicals, according to the scheme shown in figure 5.

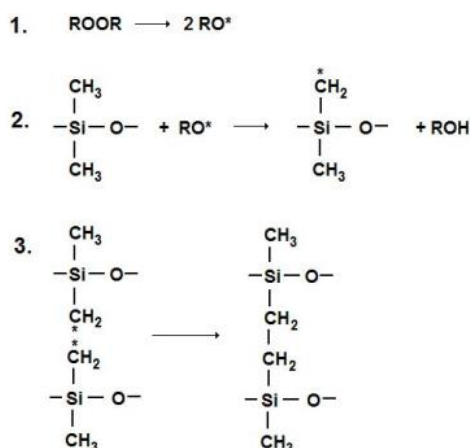


Figure 5 - Peroxide side reactions with the rubber chains - extracted from [8]

When a free radical is produced, it will react with the rubber chains and create crosslinks between them (figure 5), by hydrogen abstraction and/or addition to double bonds. When selecting a peroxide compound as a curing agent there are certain factors that should be considered, namely the peroxide half-life activity, minimum cure time, free radical energies and maximum storage temperature [4].

The crosslink reaction that originates the ContiSeal compound is based on a peroxide curing system. One common rubber cure peroxide is used, the dibenzoyl peroxide (BPO). BPO usually has a low half-life, but it harvests one of the highest energy free peroxides. Peroxides present some advantages in comparison with sulfur. They create strong carbon-carbon type crosslink bonds with increased heat stability and heat aging properties [4].

Besides peroxides, the crosslinking in the ContiSeal compound is also due to another vulcanization agent, quinone dioxime (QDO). With this molecule, it is needed first an oxidizing agent, which, in this specific case are peroxides. The peroxides activate the QDO by forming the intermediate dinitrosobenzene. This intermediate can be added to two molecules of rubber with removal of two hydrogen radicals, which react with the polymer or with more dinitrobenzene, regenerating the QDO [7].

2.2 Twin Screws Extruder

Rubber mixing has mainly two purposes, the first is to attain a uniform blend of all the components in the mixture in order to have a final homogenized compound, and the second one is to effectively disperse all fillers [4].

It is usual not to mix just one type of rubber but different types as also the other chemical substances added, such as fillers, oils, different vulcanization agents. This makes rubber mixing a complex process yielding a multifaceted final compound [9].

Since rubber and most of the other additives are not mutually soluble substances, the mixing procedure has to enclose four steps: mastication, incorporation, dispersion and distribution.

Mastication shortens rubber molecular chains, resulting in a reduced molecular weight, reducing its viscosity. Incorporation refers to the process where the filler particles become included inside the rubber and dispersion is the breaking down of the filler agglomerates into their primary units. Finally, distribution corresponds to mixing in the usual sense except that it is homogenized on the macro-scale [9,10].

Rubber is usually mixed in batch system mixers. There are two types of mixing equipment, a roll mill and an internal mixer. During the batch mixing, the quantities of different components are feed into the internal mixer according to fixed recipes. The advantage of this process is the high flexibility regarding different recipes and mixing orders. The disadvantages of the discontinuous rubber mix are the lower quality control and the waste of raw material during the starting up. It is well known, for example, that the first batch of a run yields a material with less quality due to the initial lower temperatures of the chamber. A further disadvantage of the discontinuous process is that, due to the rising temperature of the mixture in the internal mixer the crosslinking chemicals must be added in cost intensive separate stages. With the help of continuous mixing processes, differences in the quality between batch processes can be prevented by a constant dosage of the mixture components and constant process conditions [11].

The extruders used to produce at ContiSeal act as continuous mixers. Instead of extruding rubber material in a specific profile, they act as mixers and blend the rubber compound with polybutene. The mixing behaviour in Twin Screws, known as TSE, depends on the screw configuration and the design of its different elements. These factors allow a variation in the mixing efficiency from the feeding zone to the tip [12,13].

TSE may have a large variety of configurations including co-rotating, counter-rotating, partially or fully intermeshing crews as well with constant or variable mixing angle. Since, even with the multitude of different designs, TSE's were primarily designed for processing plastics, it was a challenge to transfer the overall extrusion technology to rubber processing. Even though both process include similar steps, in terms of rubber processing the procedure is more classic since the higher viscosity of rubber requires specific control in temperature and in the machine parameters. The most difficult issue is rubber feeding with a constant throughput [12,14]

Extruding temperature also plays an important role and it is fundamental to maximize the extruder output from low to moderate temperatures for scorching safety. This means it is necessary to have enough mechanical energy to not compromise the mixing. But, should not be too higher to avoid pre-crosslinking. Since temperature plays an important role in continuous mixing in TSE, to improve the cooling control a special barrel geometry was designed in which a helical cooling chamber is milled into the liner where the cooling water is in counter flow to the compound. This leads to higher cooling efficiency and may help to reduce compound temperature, which can be conclusive to avoid scorching [13,14].

With continuous mixing, energy demand is always constant, which assumes also a product with constant quality. The mechanical energy input comes usually from the kneading elements, since they generate shear flow. In the tip area of the kneading block the shear is suggestively higher than in the rest of the cross-section [14].

2.3 Component A

Sealant results from a chemical reaction between two important components, Component A and B.

As stated above, Component A is the most complex. It is a mixture of rubber compound, polybutene and paraffinic oil and its mixed in the TSE acting as continuous rubber mixing. The rubber is firstly blended in a small single screw extruder and then it is pumped to the TSE through a gear pump (figure 6). Gear pumps use a very simple mechanism to generate flow, which consists of two gears counter rotating and, since the material only stays in the fixed space volume between the gears and the wall, it is assured that only the specified quantity of material exits the pump. Also, gear pumps can be operated at high rates and it can be used in applications where the operating pressures are low to moderate and the throughput is controlled by its rate [15].

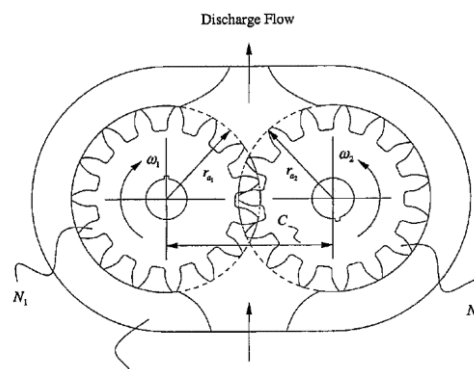


Figure 6-Gear pump configuration - extracted from [15]

The polybutene and the paraffinic oil are dosed through a gravimetric system feeding system. Above the extruder there are four weighting scales, three for each polybutene entrance and one at the end for the paraffinic oil. These scales have pumps attached that feed the materials to the extruder. The TSE used for the mixing of Component A is co-rotating.

With the purpose of having a good mixture, several process parameters must be controlled. The throughput and the speed of the screw are among the most important, they must be coordinated so that a good mixture can be obtained without scorch or pre-crosslinking of the material. The specific energy of the extruder is a good property of this relation. The throughput of the extruder is not constant because there must always be a compromise between the sealant applicator need and the stock in the accumulators. If the throughput of the extruder is too high, the accumulators can reach their maximum capacity and the extruder will stop, oppositional, if

the throughput is too low, the quantity of Component A in the accumulators will decrease to minimum which will cause a break in production due to the absence of material.

Another important parameter is the temperature. There is a gradient of temperatures along the length of the extruder, where the initial temperature must be around 60 °C because it is the melting point of the rubber, in the middle, temperatures should be lower because that is where the polybutene is added, at the end, the temperatures increase to process and to keep Component A at high temperatures (around 120 °C) when it is in the accumulators. This high temperature is needed to the crosslinking reaction may occur.

Pressure is another parameter that must be considered. Pressures throughout the screw is dependent on the extruder speed. The higher the speed, the higher the pressure will be in the sections where the mixing elements are placed.

2.4 The Working Principles of ContiSeal

To be able to enclose the piercing objects and maintain a strong seal, the sealant must have a balance between its viscous and elastic properties (Figure 7).

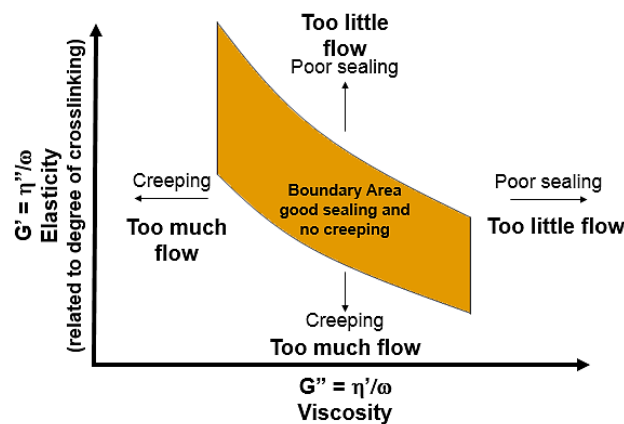


Figure 7 - ContiSeal performance vs creeping - extracted from [16]

The viscosity part is responsible for allowing the sealant to adhere to the tire and to flow enough so it is possible for it not only to stick to the puncturing object but also to create another strong seal at the puncture site when the object is removed. The elastic component is what assures the long term seal integrity, avoiding the flow of material away from the applied area and through the large holes left behind by displaced objects and also assures the high air impermeability [16].

To get these specific properties, the sealant is composed of several materials each of one imparting it with an important characteristic for its function. These materials are presented in table A.1 on Appendix A.

The start of crosslinking reaction is essential for the sealing function. As mentioned before, in the ContiSeal process, an organic peroxide is used, the BPO which has an activation temperature around 90 °C [16].

The sealant crosslinking reaction starts with formation of peroxide radical due to the heat. These radicals then convert the para-quinone dioxime (QDO) into para-dinitrosobenzene (figure 8). This agent will be responsible for the crosslinking reaction of the isoprene chains (figure 9). Even though the peroxide activation must occur at high temperatures, the reaction of the QDO with the rubber chains takes place at 50 °C, therefore there is no need for a post heating temperature. This lower reaction temperature also accounts for the enhancement in the crosslinking degree that can be observed after a certain time, during the storage of the tire [16].

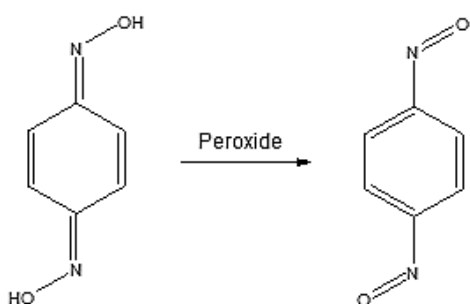


Figure 8 - Conversion of QDO into para-dinitrosobenzene - extracted from [16]

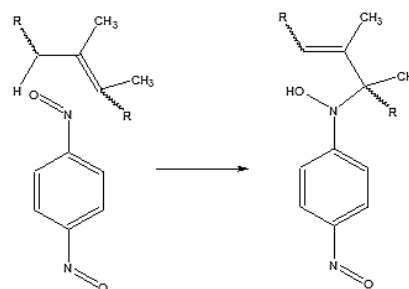


Figure 9 - The crosslink reaction of the isoprene chains due to QDO - extracted from [16]

Peroxides can also react directly with the rubber double bonds either by addition, where a fragment of the peroxide radical will be added to the chain, or by hydrogen abstraction, which will result in a subsequent recombination of the rubber chains [16].

However, peroxides can also have the opposite effect. If, instead of reacting with the QDO, the peroxides react with the rubber chains, this will result in chain separation. Since this also creates more unsaturated bounds, which act as crosslinking sites for the quinone cure, the chain breaks is compensated by newly formed bonds [16].

2.5 Rheology and Rheometry

In this project are performed rheological tests, to the compounds, aiming the evaluation of the rheological properties, using rheometers as Rubber Process Analyser (RPA). Therefore, to understand the fundamental application of each test, it will be made a little approach of each rheological test, giving more emphasis to the rheological tests performed in the RPA.

Rheology is the science that addresses the study of the flow matter. Usually matter does not behave as an ideal solid (elastic behaviour) or fluid and it has simultaneously viscous and elastic properties. Polymeric materials are mostly viscoelastic with some cured rubbers being the only exception, since they show an elastic behaviour at least regarding small distortions.

When a shear stress is applied to a material it will react with a shear strain that is related to the displacement of the layers close to the source of the shear stress. Viscosity is the resistance of a fluid, such as rubber, to flow under that stress. Mathematically, viscosity (η) is the shear stress divided by shear rate as shown below in equation 1 [17].

$$\eta = \frac{\text{Shear stress}}{\text{Shear rate}} \quad (1)$$

Viscosity is very dependent on temperature being that at higher temperatures the material is normally less viscous. The viscosity can be measured by two methods [17].

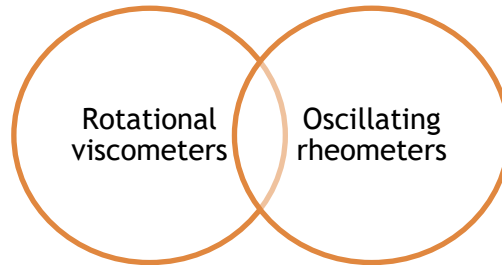


Figure 10 - Methods to measure viscosity

Rotational viscometers

The most commonly used rotational viscometer in the rubber industry is the Mooney viscometer. Melvin Mooney of U.S. Rubber Co. developed this instrument in the 1930s. Since then, it has become one of the most widely used test methods in the industry. It is used for testing fluids, raw rubber and mixed stocks [17].

Two pre-cut rubber test pieces are placed into a two-part compression cavity mold. With the dies closed, a sealed, pressurized cavity is formed, in which a special rotor is imbedded in the rubber. This rotor and dies are grooved to help prevent the rubber from slipping at the rotor or die interface while the rotor is running [17].

Usually there is a pre-heat time after the dies are closed to allow the rubber to approach the temperature of the instrument. Then the specification calls the rotor to turn at two revolutions per minute (2rpm) for a special time. The instrument records viscosity in Mooney Units (MU) which are units based on torque. Generally, the measured viscosity of the rubber under test decreases with running time because of the thixotropic effects of the rubber tested. However, depending on the type of rubber and the test temperature, the rate of decrease in the measured Mooney viscosity with time should slow down greatly (figure 11) [17,18].

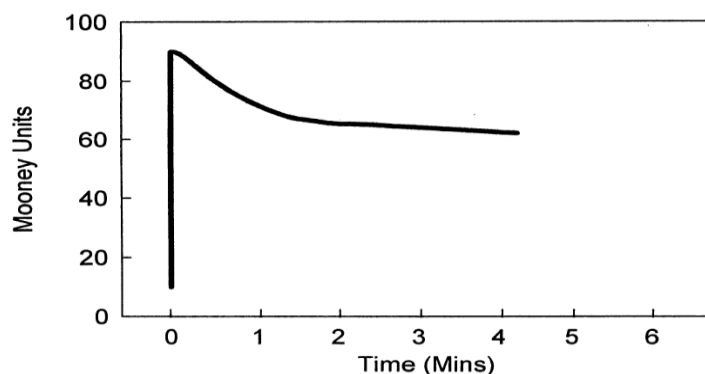


Figure 11 - Mooney viscosity of raw rubber - Extracted from [17]

Mooney Viscosity crudely relates to the average molecular weight of raw rubber and to the state-of-mixing or quality-of-mix for masterbatch or final uncured rubber stock. When the rubber specimen is too tough, slippage and tearing may occur. One basic problem with the Mooney viscometer is that it measures viscosity at a low shear rate of only 1 s^{-1} , which is far lower than many rubber manufacturing processes [17].

Oscillating rheometers

Oscillating rheometers measures dynamic viscosity through the application of a sinusoidal strain to an uncured rubber specimen molded in a sealed, pressurized cavity [17].

One example of oscillating rheometers is the RPA, a new dynamic mechanical rheological tester which can analyse raw polymers and masterbatches as well as rubber compounds before, during and after cure. It requires no special samples preparation, is easy to operate, and can apply a wide range of dynamic test conditions to a rubber sample, including very high strains, temperatures and frequencies [19].

RPA contains two cone shaped dies as show in figure 12. The conical shape produces a uniform shear strain on the entire sample. This is especially important when testing filled elastomer systems because their modulus strongly depends on the shear strain. Two seal plates with their respective seals complete a pressurized sample cavity. The two dies can separate for ease of sample loading. The sample is loaded on the lower die and then the dies are closed [20,21].

The upper die closes onto the sample to form a constant volume compression mold while exceed sample is extruded into a spew channel. At the end of a test, the dies are opened and the sample is removed (figure 13) [20,21].

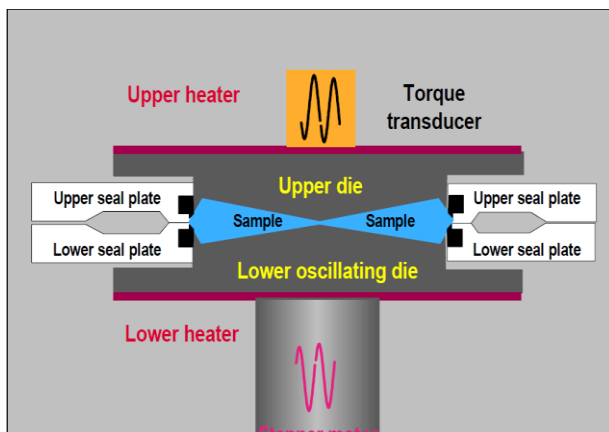


Figure 12 - Cross section view of the RPA die design - extracted from [20]



Figure 13 - RPA staging platform and film system - extracted from [21]

Rubber, as told before, has both a viscous and an elastic response to deformation. The viscous response is proportional to the rate of deformation while the elastic response is proportional to the amount of deformation. A viscous response is often modeled by a dashpot

while an elastic response is modeled by a metal spring, measuring both these properties helps characterize rubber behaviour in processing and final product performance.

Oscillating rheometers are designed to measure both elastic and viscous properties of elastomers and compounds. The upper die is attached to a torque transducer to eliminate noise from the lower die drive system and to measure the torque transmitted through the sample. If in the conditions of the test it is assumed linear viscoelastic behaviour, a sinusoidal deformation produce a response of a sinusoidal torque (figure 14). This torque is called the complex torque or S^* and it is not in phase with the applied strain due to the viscoelastic nature of rubber. The S^* torque signal is transformed by the RPA computer into an elastic (S') torque (in phase with strain) and a viscous (S'') torque (90 degrees out of phase with strain) by applying a Fourier Transform to the S^* signal. The elastic susceptibility is parameterized by the complex shear modulus (G^*) which determines the stress induced in a material upon application of an oscillatory shear strain. Torque values (S^*) are directly converted to the shear modulus (G^*) by multiplying the appropriate die form factor and dividing by the strain. The elastic component of the stress is in phase with the applied strain; the ratio of this stress to the strain is the elastic shear modulus G' (equation 2). The viscous component of the stress is out of phase with the strain; the ratio of this stress with the strain is the viscous modulus G'' (equation 3). The damping factor ($\tan(\delta)$) is calculated by equation 5 and explains the relative contribution of the viscous and elastic components of viscoelastic materials [19,22,23,24]

$$G' = \frac{K S'}{\text{Strain}} \quad (2)$$

$$G'' = \frac{K S''}{\text{Strain}} \quad (3)$$

where, S' is elastic torque, S'' is viscous torque and K is a constant related to the geometry of the dies and sample cavity. The damping factor $\tan(\delta)$ is given by [22]:

$$\tan \delta = \frac{S''}{S'} = \frac{G''}{G'} \quad (4)$$

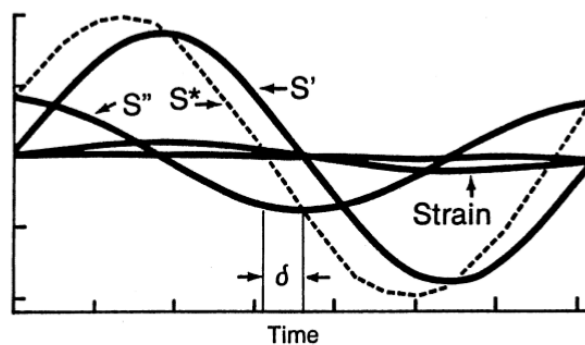


Figure 14 - Applied sinusoidal strain and resulting stress response - extracted from [17]

Oscillating rheometers can measure the elasticity of rubber, as mentioned above, the elastic shear modulus G' and viscous modulus G'' are measured from the testing of rubber. G' is a direct measure of elasticity. A higher G' response means a higher elastic quality at a defined temperature, frequency and strain. Dividing G'' by G' gives the $\tan(\delta)$ as shown in equation 4 [17].

$\tan(\delta)$ is the tangent of the phase angle as shown in figure 14. The $\tan(\delta)$, as a processability parameter, has been found to be at least twice as sensitive to real differences in rubber processability than the Mooney Stress Relaxation. Also, an RPA $\tan(\delta)$ as a parameter is more reliable and can be measured at a wider range of shear rates. Therefore, $\tan(\delta)$ and G' are both very effective processability measurements. An example of comparing viscoelastic properties with the RPA is shown in figure 15. Here two different sources of SBR have almost the same Mooney viscosity but have quite different $\tan(\delta)$ values [17].

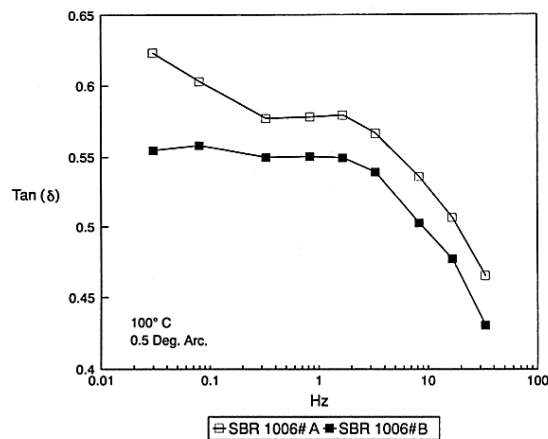


Figure 15 - Uncured $\tan(\delta)$ response from the RPA for two SBR polymers with the same Mooney viscosity - extracted from [17]

Another application of this equipment is the prediction of the influence of the oil, carbon black and the fillers in the performance and processing of the different rubber compounds, through the G' and G'' modules. With these applications, the RPA can be used in different thematic, such as, in the characterization of the quality of raw material, in the optimization of the mixing process, in predicting the dynamic behaviour of the compounds and in the study of the reinforcement given by the fillers [25].

The amount and type of carbon black and oil used in rubber compound greatly affects its processing characteristics and cured physical properties. Carbon black surface area, structure, and loading levels all affect a compound's processing behaviour and final cured and uncured properties. Above a "threshold loading", carbon black forms an aggregate-aggregate network when mixed into a rubber compound. Applied strain will break down this network, after a sufficient relaxation time, the network will reform. The nature of the breakdown and reformation of this network affects a compound's processability in the uncured state and its mechanical properties in the cured state. In appendix A, figure A.1, A.2 and A.3 it is possible to see the

behaviour of G' , G'' and $\tan(\delta)$ while increasing carbon black concentrations and temperatures [19].

Processing oil also affects both uncured and cured compound properties, these physical plasticizers act as “intermolecular lubricants”, allowing rubber chains to move past each other during processing. When oil is added to a rubber compound with carbon black, the oil dilutes the carbon black networking effects discussed earlier. Naturally, when a processing oil is added to a rubber compound, it never improves the processing characteristics and reduces the hardness of the cured stock. Processing oils may also lower the glass transition temperature and increase the molecular free volume of a rubber compound. In appendix A, figure A.4, A.5 and A.6 it is possible to see the behaviour of G' , G'' and $\tan(\delta)$ while increasing oil concentrations and temperatures [19].

A method to determine the interaction between fillers in function of the deformation amplitude, given by the RPA, is through the curve that represents the Payne effect. With this curve it is possible to visualize the viscoelastic behaviour of the compounds as shown in figure 16 [26,27].

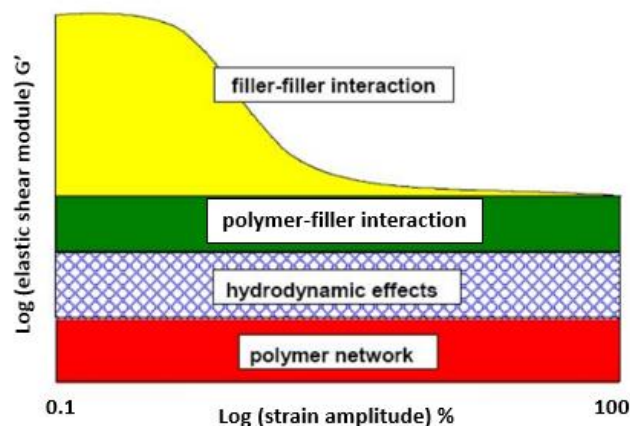


Figure 16 - Payne Curve for viscoelastic behaviours - adapted from [27]

When the rubber compound contains fillers (carbon black, silica and oil), the physical properties change. According to Payne, the dynamic performance of the elastomers is due to the tridimensional structure derived from aggregation of the fillers particles.

In figure 16, the different contributions, such as: hydrodynamic effects, polymer network and the interaction of polymer-filler structure do not depend of the applied deformation. In relation to the contribution of the polymeric structure, this one is related to the density of crosslinking and the nature of the polymer. The hydrodynamic effects are related with the greatness of deformation, due to the dilution of the filler particles on the rubber. The polymer-filler is due to the combination of the filler with the rubber and chemical nature of the polymeric matrix. The increasing of the module is due to the filler presence, since there are Van der Waals

connections and hydrogen bridges, in case of the carbon black and silica. As the first three contributions do not depend on the deformation, the Payne effect could be characterized by the interactions of filler-filler that occur at low deformations.

With the deformation scanning, promoted by the RPA, it is possible to define the dynamic properties - G' e G'' , as the $\tan(\delta)$ of the compounds. In this way, through the data of the RPA, it is possible to evaluate and quantify the Payne effect in the interactions filler-filler of the rubber compounds [26].

The important advantages of the RPA in measuring rubber viscosity over the methods discussed are its versatility in measuring viscosity at both low and high shear rates, ease of use, and excellent repeatability [4].

2.6 Design of Experiments

Optimizing refers to improving the performance of a system, a process or a product to obtain the maximum benefit from it. To overcome this problem, the optimization of analytical procedures has been carried out by using multivariate statistical techniques as design of experiments (DOE) which has been used to overcome the main disadvantages of a methodology known as one-variable-at-time (OVAT), which leads to non-optimized final products or process. This may be explained by factor interactions that OVAT methodology does not consider: different variables can interact and be responsible for a specific system behavior [28,29].

Among the most relevant multivariable statistical methods, the response surface methodology (RSM) is the most used. RSM is a collection of mathematical and statistical techniques based on the fit of a polynomial equation to the experimental data, which must describe the behaviour of a data set with the objective of making statistical previsions. It also can be applied when a response or a set of responses of interest are influenced by several variables. The objective is to simultaneously optimize the levels of these variables to attain the best system performance [28,29].

Before applying the RSM technology, it is first necessary to choose an experimental design that will define which experiments should be carried out in the experimental region being studied. There are some experimental matrices for this purpose. Experimental designs for first-order models (e.g., factorial designs) can be used when the data set does not present curvature [28].

However, to approximate response function to experimental data that can not be described by linear functions, experimental designs for quadratic response surfaces should be used, such as three level factorials, Box-Behnken, Central Composite and Doehlert designs [28].

The simplest model which can be used in RSM is based on a linear function. For its application, it is necessary that the responses obtained are well fitted to the equation 5 [28].

$$y = \beta_0 \sum_{i=1}^k \beta_i x_i + \varepsilon \quad (5)$$

Where k is the number of variables, β_0 is the constant term, β_i represents the coefficients of the linear parameters, x_i represents the variables, and ε is the residual associated to the experiments.

To evaluate curvature, a second-order model must be used. The next level of the polynomial model should contain additional terms, which describe the interaction between the different experimental variables. This way, a model for a second order interaction presents the next terms [28]:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{1 \leq i < j}^k \beta_{ij} x_i x_j + \varepsilon \quad (6)$$

Where β_{ij} represents the coefficients of the interaction parameters.

To determine a critical point (maximum, minimum, or saddle), it is necessary for the polynomial function to contain quadratic terms according to the equation presented below [28].

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{1 \leq i < j}^k \beta_{ij} x_i x_j + \varepsilon \quad (7)$$

Where β_{ii} represents the coefficients of the quadratic parameter.

3 Materials and Methods

In this chapter, the materials and methods used through the project are presented and explained. A reference of the materials and equipment used in the project is given first and, then the procedures that were used to address the objectives of the project are provided.

3.1 Materials

Masterbatch

The ContiSeal masterbatch is a mixture of butyl polymers, carbon black, oil, zinc oxide, aliphatic tackifiers, QDO and sulfur.

The masterbatch is produced in a batch mixer.

Component A

Component A is produced in TSE from the masterbatch, polybutene and paraffinic oil.

3.2 Equipment

Twin Screw Extruder (TSE)

The extruders used to produce ContiSeal work as continuous mixers. Instead of extruding rubber material in a specific profile, they act as mixers and blend the rubber compound with polybutene. The mixing behaviour in twin screws, depends on the screw configuration and the design of its different elements.

The TSE used for the mixing of Component A is co-rotating. The design of the TSE incorporates mixing and conveying elements (figure 17).



Figure 17 - Twin Screw Extruder (TSE) at ContiSeal

With the purpose of having a good mixture, several process parameters must be controlled. The throughput, temperature and the speed of the screw are among the most important, they

must be coordinated so that a good mixture can be obtained without scorch or pre-crosslinking of the material.

To measure the viscosity of Component A, it is taken a sample to a can when the throughput on the extruder is stable and it is registered all the extruder parameters.

Dynamic Rheometer Analyser

The rheometers used within this work are ThermoScientific RheoStress 6000 and Rubber Process Analyser (RPA).

ThermoScientific RheoStress 6000 (figure 18) is a rotation rheometer and the tests performed were only dynamic measurements. One of the rheometers was coupled to a UTC and the other to UTMC. The software used to collect the data was RheoWin Job Manager. The assays, or “jobs” (figure 19), performed were named according to the type of measurement. The rheometer software always provides the rheometric quantities that can be calculated with the values measured according to the job.



Figure 18 - ThermoScientific RheoStress 6000

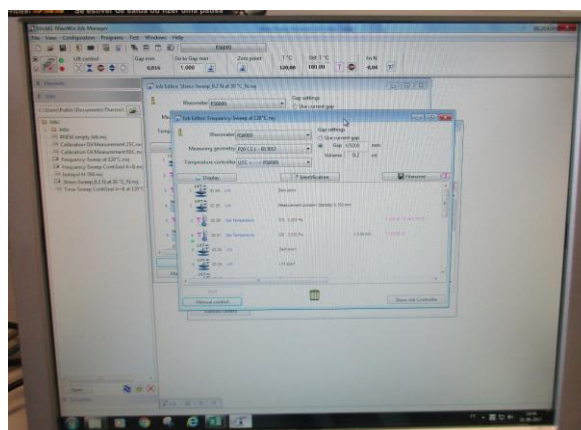


Figure 19 - RheoWin Job Manager

At ContiSeal there are two rheometers, the last time they were calibrated was last year, in November of 2016 by the company ThermoScientific. Normally they must be calibrated every two years.

The RPA (figure 20) is an oscillating rheometer that was designed to analyse in a single test the raw elastomers and rubber compounds before and after vulcanization. This equipment is composed by a pressurized and sealed chamber, in which the rubber sample is automatically transferred directly to the lower oscillating die. Besides this provides a huge range of different deformations, frequencies and temperatures face to the results.



Figure 20 - Rubber Process Analyser (RPA)

3.3 Experimental Procedure

Frequency Sweep

The “Frequency Sweep” method was applied to measure the viscosity of Component A, that is used to check the feeding systems of the extruder, if are dosing the correct amount of polybutene and rubber masterbatch, it also gives an indication of the degree of pre-crosslink in the Component A. The range of frequencies spans from 100 Hz to 0.01 Hz. The rotor used is a plate-plate with a 20 mm diameter. The stress is kept constant at 100 Pa and the system is at 120 °C. The measurement gap is 0.5 mm. This method allows to obtain the complex viscosity, $|\eta^*|$ at 0.02 Hz (equation 8) and the frequency that corresponds to the maximum in the η'' function, related to the elastic shear modulus (G')

$$|\eta^*| = (\eta'^2 + \eta''^2)^{\frac{1}{2}} \quad (8)$$

where η' is the viscosity related to the loss modulus, or dynamic viscosity, and η'' , as mentioned above, is related to the elastic modulus. η'' can thus be calculated according to the Equation (9).

$$\eta'' = \frac{G'}{\omega} \quad (9)$$

To be possible to assess the quality of Component A, target values and tolerances and action limits were established based on the testing results of experimental tires (ETO), which showed good sealing performance (table 1).

Table 1 - Target and Limits of Frequency-Sweep A

Target and Tolerances	$ \eta^* $ [Pa·s]	η'' max.
	0.02 Hz	Hz
LTL lower limit	405	
LAL lower action limit	425	
Target	555	0.20
UAL upper action limit	685	0.38
UTL upper limit	705	0.40

Oscillating Rheometer RPA

The rheometric characterization by the oscillating rheometer (RPA) is composed by 9 phases, is made through a study of strain scan. In the first four phases occurs two interspersed relaxation with deformation scanning, one of conditioning and other of measurement, before the sample vulcanizes. The relaxations have a duration of 1 minute and an operating temperature of 70 °C and the deformation scanning operate in a range of 0.1 % to 100 % at the same temperature and relaxation. The conditioning scanning has as purpose reducing the noise that can arise the flocculation (formation of agglomerates and fillers) - according to the deformation scanning. In the fifth phase, occurs the sample eating till reach a temperature of 170 °C and for 10 minutes happens the vulcanization of it, follow by a cool down to the 70 °C.

At least, in the last for phases occurs the analysis after the vulcanization, in the same conditions expressed in the first four phases. The period of the analysis of a sample on the RPA, counting with the preparation of the sample and the length of these nine phases, take over 40 minutes.

The phases of the RPA that are more important for ContiSeal, are the first four phases, before the vulcanizations occurs, because in the extruder the rubber do not vulcanize, it only reaches at 70 °C inside the extruder, so the data more relevant of the RPA for the ContiSeal compound are the uncured data. In total, the RPA gives twelve variables of data (figure B.1 Appendix B), G' at three points of the curve (1 %, 10 %, 100 %) and $\tan(\delta)$ (1 %, 10 %, 100 %). For this study were selected the most important variables for the ContiSeal Process, inside those twelve variables, were selected six variables. These variables are part of the uncured phases after the non-conditioning phase. These are the parameters that were selected for this study and have more influence for this process

3.4 Design of Experiments

After having established the variables of the RPA to study, it was necessary proceed to the realization and study of the experiments, obtaining the information about the selected variables with the response of the process, which is the viscosity of Component A. To achieve this objective, it was made a design of experiments using a statistical software called Minitab 17. With this

program, it was possible to understand how the RPA variables influence the viscosity of Component A and which RPA data the rubber compound must have to maximize the viscosity.

To assure that only the variables of the RPA are the ones that have influence in the viscosity and do not have other variables at stake, the samples of Component A were always taken at the same conditions on the extruder, same temperature, same density, same throughput and same rpm. The temperature that the samples were taken on the extruder was at 124 °C. The throughput selected was at 5000 cm³min⁻¹ (289 kg.h⁻¹) because the mixing is more stable and is one of the most used throughput on the extruder for the production so it is easier to take samples in this conditions without affecting the production. The rpm corresponding to this throughput is 354 rpm and density was at 1.123 gdm⁻³.

3.5 Waste treatment

For the accomplishment of the project it was necessary to take samples of Component A of the extruder to steel containers of 250 mL. After the analysis of the samples they were keep in the lab for one month and at the end of the month the samples were put back inside a barrel of 200 L and when the barrel was full, the material was scraped and taken to a landfill.

4 Results and discussion

By using the RPA, it was possible to understand more about the variables that it gives to us, the meaning of each one and to quantify the influence that those variables have in the viscosity of Component A.

This chapter has the objective to show the impact of the variables in the mixing of the rubber compound in the extruder and see which variables have the most effect on the viscosity of Component A.

4.1 Optimization of the viscosity of component A

With the purpose of maximize the viscosity of Component A, it was made an experimental design resorting response surface methodology, more specifically a Box-Behnken design. This design was used to determine what factors or interactions are more important and what factors or combination of factors maximize the response. The Box-Behnken design not contain an embedded factorial or fractional factorial design. Box-Behnken designs have treatment combinations that are at the midpoints of the edges of the experimental domain and require at least three factors. Figure 21 shows a three-factor Box-Behnken design. Points on the diagram represent the experimental runs that are performed:

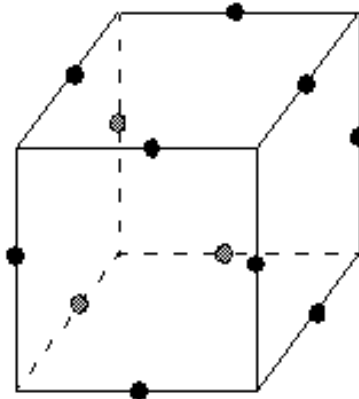


Figure 21 - Illustration of the Box-Behnken model - extracted from [28]

This design allows estimation efficient of the first- and second-order coefficients. Because Box-Behnken designs often have fewer design points, they can be less expensive to run than central composite designs with the same number of factors.

Box-Behnken designs also prove to be useful if it is known the safe operating zone for the process. Central composite designs usually have axial points outside the "cube." These points may not be in the region of interest, or may be impossible to run because they are beyond safe operating limits. Box-Behnken designs do not have axial points, thus, it can be sure that all design

points fall within the safe operating zone. Box-Behnken designs also ensure that all factors are never set at their high levels simultaneously.

To complete this design it was gathered, over these months at ContiSeal, a lot of samples and results of the viscosity of Component A with different rubber batches and the corresponding RPA results, in a total of 64 samples. The samples were all measured in the same extruder conditions. The RPA values and viscosity results, with the related conditions, are shown in table B.2, on the appendix B. To obtain these results it was asked the department of mixing to take one sample for each table of the rubber compound masterbatch and test it in the oscillating rheometer (RPA) on the quality laboratory and then they were introduced in a program call “Quality Data Viewer” (appendix B, table B.1)

The first part of the design of experiments was to know what RPA properties have the main effect on the viscosity of Component A. To attain this, it was collected 64 results of the viscosity of Component A and were selected 6 variables of the RPA as mentioned above, these results are present in table B.2 on appendix B. The figure 22, shows the effects for the viscosity @ 0.02 Hz and 120 °C of Component A.

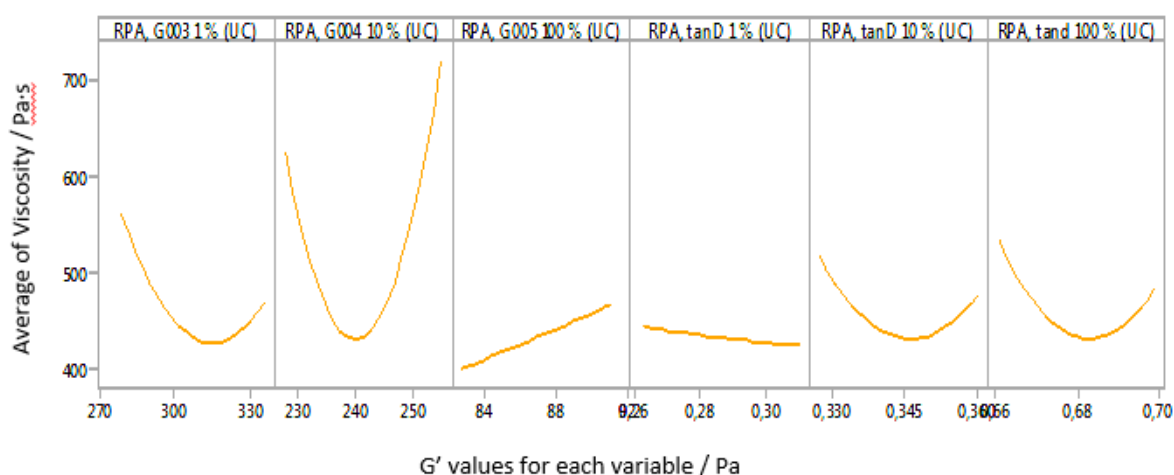


Figure 22 - Main effects design for viscosity

The figure 22 shows the influence of each study variable on the viscosity, in the ordinates axes are the values for the viscosity and in the axes of abscissas are the values for each variable that were collected. By the observation of the graph the variables that have more effect on the viscosity are the G'1%, G'10%, TAN(δ)10% and TAN(δ)100%, but the ones that have more influence are G'1% and G'10% because they have the highest slope. The variable G'100% and TAN(δ)1% do not have any effect because it does not show a curve, only a straight line which means that it will not have influence in the viscosity. Another conclusion that is observed is that G'10 % have highest effect in comparison to G'1%, which means that when the rubber has a shear amplitude of 10 % it has more effect on the viscosity of Component A. One last observation is, for example, when G'10% is higher it can have highest viscosities, but this is not certain because this design only

serves to understand the variables that influence the response but it will be show for which data the viscosity is higher.

The second part of the design was to find the interaction between all rheometric parameters in this project, figure 23 shows the interactions of all parameters with the viscosity.

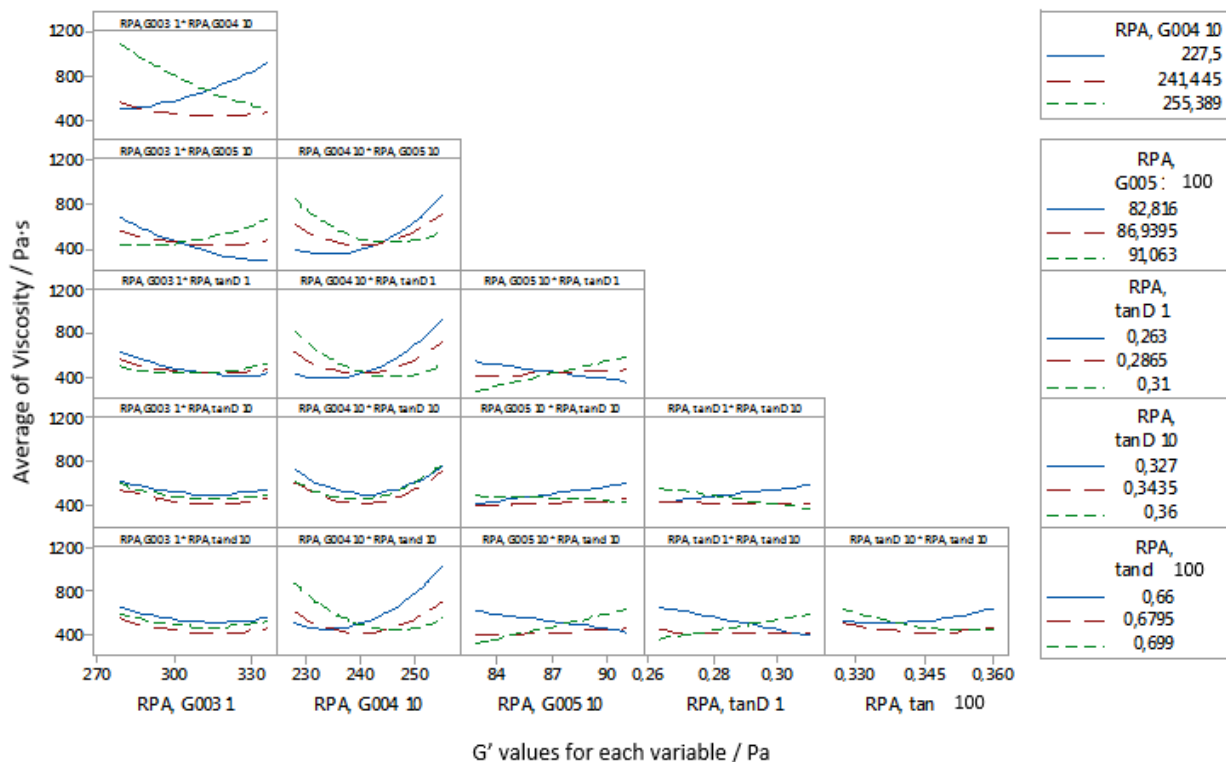


Figure 23 - Interaction graph for viscosity

By observing the figure 23, it is seen all the interactions between the variables and the effect that they have in the viscosity when interacting with each other. In the ordinates axes it is revealed the viscosity values and in the abscissae axe are the values of each variable. The green lines are the maximum values for each variable, the red ones are for the middle values and the green for the maximums as shows the key figure.

When focus on the variable $G'1\%$ (G003 1), the principal interactions are, with $G'10\%$ (G004 10), $G'100\%$ (G005 10) and the minor interaction is $TAN(\delta)1\%$ because the three lines intersect with each other, being that $G'10\%$ has the main interaction. $TAN(\delta)10\%$ and $TAN(\delta)100\%$ has no interaction since the three lines are parallel with each other. The interaction with $G'10\%$ has two points of intersections, when $G'1\%$ is close to the minimum and the viscosity is minimum there is interaction when $G'10\%$ is maximum or intermediate. The other interaction is near the central value of $G'1\%$ when $G'10\%$ has maximum values or minimum and then the viscosity is higher which is the best for the process. With $G'100\%$ there is only interaction when the viscosity is minimum and $G'1\%$ is at the central value, but there is no cross point for higher viscosity's, which means if $G'1\%$ is at the middle point the viscosity will be minor.

The variable $G'_{10\%}$ interacts with $G'_{100\%}$, $TAN(\delta)_{1\%}$ and $TAN(\delta)_{100\%}$, but the interaction with these three variables only happens when the viscosity is minimum which has no interest because the purpose is to have the higher viscosity, so it is represented in figure 23 that when $G'_{10\%}$ is near the central point or higher there is interaction with minimum, medium and maximum of each variable but the viscosity is minimum. With the variable $TAN(\delta)_{10\%}$ there is absolutely no interaction between any value.

Related to the variable $G'_{100\%}$ it interacts with $TAN(\delta)_{1\%}$ and $TAN(\delta)_{100\%}$ but in a linear way, which means that the interaction is not so significant, even so $G'_{100\%}$ has one interaction with the three curves of the variable $TAN(\delta)_{1\%}$ when the value for that variable is in the middle, but the viscosity is minimum too. With $TAN(\delta)_{100\%}$ there are two interactions, when $G'_{100\%}$ is near the minimum and the viscosity is minimum, there is interaction between the middle or the maximum value of $TAN(\delta)_{100\%}$. The other interaction is with the maximum value and with the minimum value of $TAN(\delta)_{100\%}$ and occur when $G'_{100\%}$ is near his center point and the viscosity is higher, which means that when $G'_{100\%}$ is higher and $TAN(\delta)_{100\%}$ is minimum or maximum the viscosity can be highest which is the purpose.

Observing the variable $TAN(\delta)_{1\%}$ it is shown that interacts with the variable $TAN(\delta)_{10\%}$ and $TAN(\delta)_{100\%}$, but again with a little significance. The interaction with $TAN(\delta)_{10\%}$ occurs when the value of $TAN(\delta)_{1\%}$ is between the minimum and the middle and the viscosity is minimum. With $TAN(\delta)_{100\%}$, when the viscosity is minimum and $TAN(\delta)_{1\%}$ is near the minimum there is interaction when $TAN(\delta)_{100\%}$ is minimum or intermediate. When there is interaction with the maximum value and the minimum of $TAN(\delta)_{100\%}$ and $TAN(\delta)_{1\%}$ is near the maximum the viscosity has tendency to be higher.

Finally, the interaction between $TAN(\delta)_{10\%}$ and $TAN(\delta)_{100\%}$, occurs when the viscosity is minimum and when $TAN(\delta)_{100\%}$ is between the minimum and the middle point, this occurs with the maximum value or the minimum value of $TAN(\delta)_{100\%}$. Once again, the interaction occurs for lower viscosities.

After this discussion, the principal variables that must be taken into consideration and have a highest influence in the viscosity are $G'_{1\%}$ that has many interactions with most variables specially with $G'_{10\%}$, that is clear the intersection of the curves for the other variables, $TAN(\delta)_{10\%}$ that despite not have having defined curves as the other ones, has clear points of intersection and finally $TAN(\delta)_{100\%}$ that interacts with all variables except with $G'_{1\%}$.

After the discovery of the rheometric variables that have the most influence on the viscosity of Component A and the principal interactions between them, it was made a response surface plot and a contour plot to have an idea what values for each variable allow higher viscosity or the target viscosity.

The response surface model generates either a response surface plot for a single pair of variables or separate surface plots for all possible pairs of variables. Surface plots show how the

fitted response relates to two continuous variables. A surface plot displays the three-dimensional relationship in two dimensions, with the variables on the x and y scales, and the response (z) variable represented by a horizontal surface. Minitab generates the graph by calculating fitted responses (z-values) using the x and y variables while holding any additional variables constant at the values that were specified.

Contour plots show how the fitted response relates to two continuous variables. A contour plot provides a two-dimensional plot where all points that have the same response are connected to produce contour lines of constant responses.

As mentioned above, seeing figure 22, the variables that have most effect on the viscosity are $G'1\%$, $G'10\%$, $TAN(\delta)10\%$ and $TAN(\delta)100\%$. For each of these variables it was selected the best results that show in a visible way what rheometric values the rubber must have to achieve the viscosity results showed on table 1 in chapter 3. All the surface plots and contour plots for all the variables are showed in table B.3 in appendix B.

So first in figure 24 and 25, are showed the surface plot and contour plot for the relation between the variable $G'1\%$ and $TAN(\delta)100\%$.

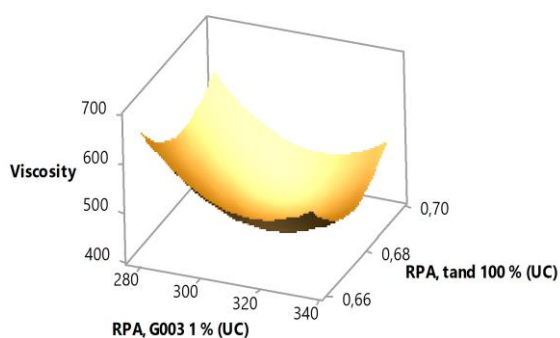


Figure 24 - Surface lot of viscosity vs $TAN(\delta)100\%$ (UC) and $G'1\%$ (UC)

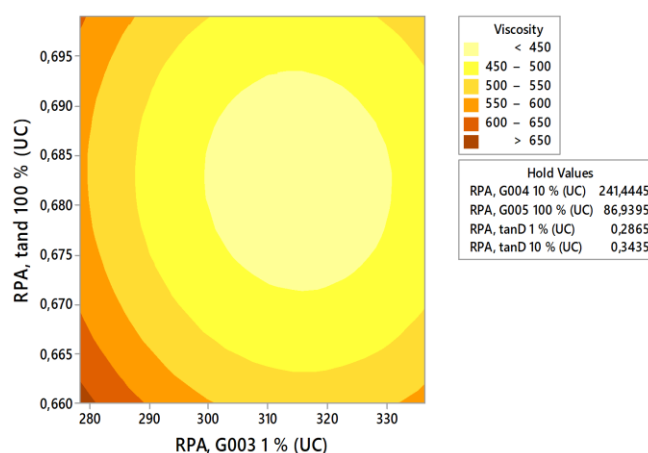


Figure 25 - Contour plot of viscosity vs $TAN(\delta)100\%$ (UC) and $G'1\%$ (UC)

Figure 24, is represented a minimum for viscosity with the variable $G'1\%$ and $TAN(\delta)100\%$, despite of the purpose is to maximize the viscosity, the minimum of this graph presents the results desired for the process, which are values around 550 Pa·s. This happens because in ContiSeal the maximum values that are obtained are below the 500 Pa·s so, the results that were collected were around the 400 Pa·s and 500 Pa·s and the results that are best for the process are between 550 Pa·s and 600 Pa·s as shown in table 1 in chapter 3. With figure 24 it can be predicted that when $G'1\%$ is around 300 Pa and 320 Pa and $TAN(\delta)100\%$ is around 0.68, the viscosity is at the minimum, around 450 Pa·s. When $G'1\%$ and $TAN(\delta)100\%$ move away from the center point the viscosities can be much higher, than 550 Pa·s, which is the target viscosity for ContiSeal process.

The analysis of figure 25, shows the different areas for different ranges of viscosity, with this it is possible to see for which values of each variable the viscosity is the desired. The area more transparent, in the middle, represents the minimum of the viscosity in accordance with the plot from figure 24, which means that if $G'1\%$ is around 310 Pa to 330 Pa and the $TAN(\delta)100\%$ is 0.68 to 0.69 the viscosity is within the area of lower viscosity, below the 450 Pa·s, so the rubber compound can not have these properties values, because for sure the viscosity will be low. To ensure a good viscosity of Component A, the results must be inside the orange line (550-600 Pa·s) or in the dark colors, which means that $G'1\%$ must be in the minimum, around 280 to 290 Pa, and $TAN(\delta)100\%$ among the minimum and maximum value. If $G'1\%$ is near the maximum values, for sure the viscosity trends to be lower.

In the figure 26 and 27 are shown the surface and contour plots for the RPA variables $G'1\%$ and $G'10\%$.

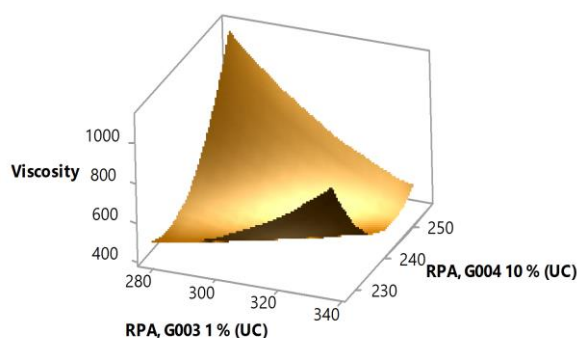


Figure 26 - Surface plot of viscosity vs $G'10\%$ (UC) and $G'1\%$ (UC)

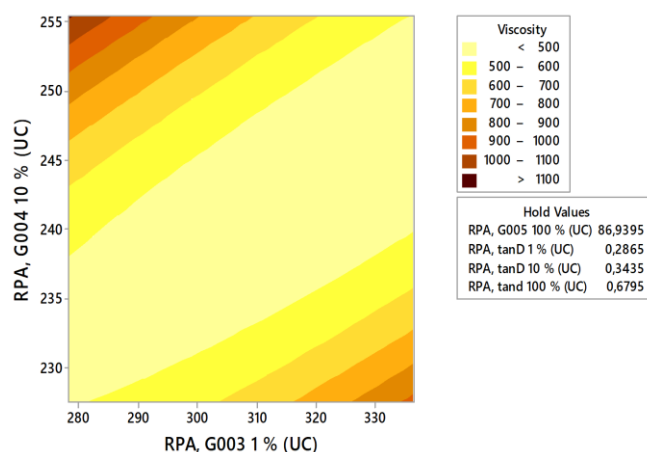


Figure 27 - Contour plot of viscosity vs $G'10\%$ (UC) and $G'1\%$ (UC)

Figure 26 shows the rheometric parameters, $G'1\%$ and $G'10\%$, obtained by the RPA equipment. This surface plot does not represent a straight minimum, this occurs because of the domain, the limit values for the variables should be other. Here it is seen that the minimum is around the 450 Pa·s for viscosity, and some parts of the graph have tendency to go to higher viscosities. These two variables were the ones that have the greatest interaction, but because of the minimum is not so understandable, it is difficult to know the values of this rheometric variables for higher viscosities, but looking for figure 26 it is easier to see for which value the viscosity it is better.

In figure 27, the biggest area is the one with lighter color, that represents the values for viscosity lower than 500 Pa·s, that occurs when the values of the variables are between the minimum and the maximum so, $G'1\%$ and $G'10\%$ can have any value and the viscosity will always be lower than 500 Pa·s. It is impossible to conjugate the two variables for the viscosity value of interest, because when looking for the more darkest areas, that represent higher viscosities, only

occurs between maximums and minimums for these variables, which means that if the rubber compound presents these properties of $G'1\%$ and $G'10\%$ the viscosity can be higher than 500 Pa·s or lower than 500 Pa·s.

This behaviour goes according to what shows in figure 23 for these two variables, that it is possible to have lower viscosities or higher viscosities for maximum, intermediate and minimum values for $G'1\%$ and $G'10\%$.

In figure 28 and 29 it is represented the surface and contour plot of viscosity for $TAN(\delta)10\%$ and $G'10\%$.

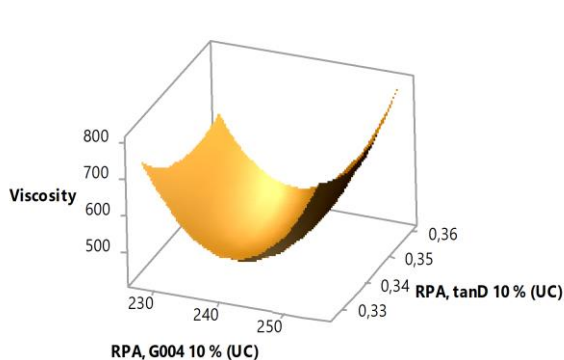


Figure 28 - Surface plot of viscosity vs $TAN(\delta)10\%$ (UC) and $G'10\%$ (UC)

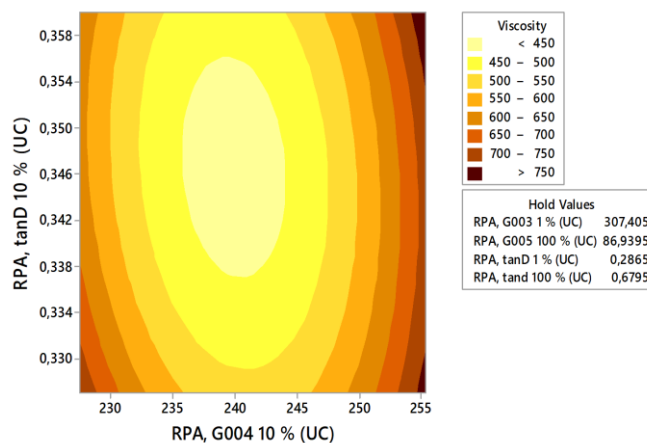


Figure 29 - Contour plot of viscosity vs $TAN(\delta)10\%$ (UC) and $G'10\%$ (UC)

Figure 28 shows the minimum of viscosity with the values for each of these variables. The minimum is around 450 Pa·s for viscosity when $G'10\%$ and $TAN(\delta)10\%$ are in the middle points, as 240 Pa and 0.34, respectively. When these variables move away the values for viscosity increase steadily, for viscosities around the 550 and 600 Pa·s which is good for ContiSeal™. This means that the rubber compound can not have values in the middle points for these two variables because it will always give smallest viscosities.

Analysing figure 29 the middle area is the minimum for viscosity that represents results lower than 450 Pa·s, this happens when $G'10\%$ is between 238 and 245 Pa, the middle points and when $TAN(\delta)10\%$ is between 0.34 and 0.35 which means that when these RPA variables are within these values the viscosity will be low and not in the target. To have a good viscosity (550 to 600 Pa·s), $G'10\%$ has to be between 232 and 235 Pa or 246 and 250 Pa and $TAN(\delta)10\%$ in all the range of values between maximum and minimum. If $G'10\%$ is at the maximum or minimum the viscosity will be higher than the maximum limit and that is bad for the ContiSeal process, because with a too viscous material it will cause problems in the applicators dosing the material and in sealant performance, so the rubber compound can not have $G'10\%$ at the maximum or minimum values, but close to the middle points as discussed.

These two variables are the ones that have most influence on the viscosity as shown in figure 22. The relation between these two variables is great as seen in figure 28 and 29 with a perfect minimum.

In figure 30 and 31 are shown the surface plot and contour plot obtained for the RPA variables TAN(δ)100% and G'10%.

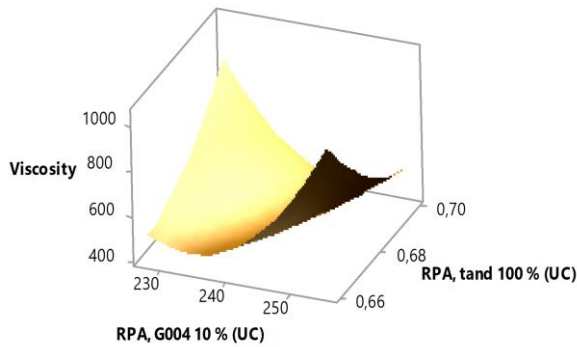


Figure 30 - Surface plot of viscosity vs TAN(δ)100% (UC) and G'10% (UC)

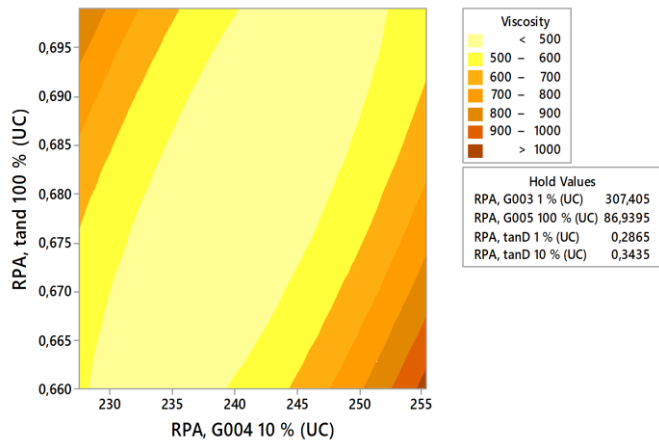


Figure 31 - Contour plot of viscosity vs TAN(δ)100% (UC) and G'10% (UC)

Figure 30 shows a minimum for viscosity, but not a perfect one because of the limits of the values for the rheometric variables. So, when G'10% is between 230 Pa and 240 Pa and TAN(δ)100% is 0.67 to 0.70 the viscosity will be around 450 and 500 Pa·s, this is the minimum, but looking for figure 30 it is more understandable to know the best variables values for higher viscosities.

According to figure 31, the highest lighter area corresponds to the minimum point of figure 30, the small values for viscosity, it occurs when G'10% is between 230 to 250 Pa, but specially at the 235 Pa and when TAN(δ)100% is in all the range of values, between the maximum and minimum. This behaviour is the same as the rheometric variables G'1% with G'10% (figure 26 and 27) and it is difficult to have a global conclusion, because the variables are conjugated. Even so, with TAN(δ)100% and G'10% it is more likely to have higher viscosities, because observing figure 31, when G'10% it is at minimum or maximum, not at center, and TAN(δ)100% is only at minimum or maximum too, the viscosity has tendency to be higher around the 550 and 650 Pa·s which is very good for the process. With these two variables values it is more likely to have minimums than maximums for viscosities.

Next, figure 32 and 33 corresponds to the behaviour of viscosity with the rheometric variables TAN(δ)100% and TAN(δ)10%, these are presented in a surface and contour plot.

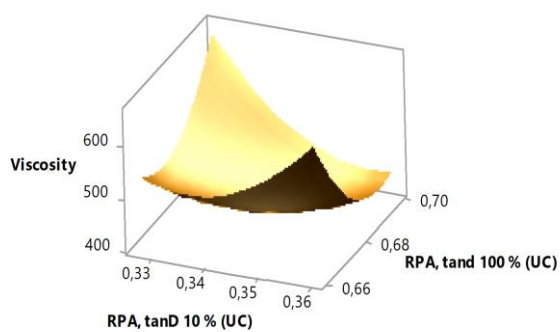


Figure 32 - Surface plot of viscosity vs $TAN(\delta)100\%$ (UC) and $TAN(\delta)10\%$ (UC)

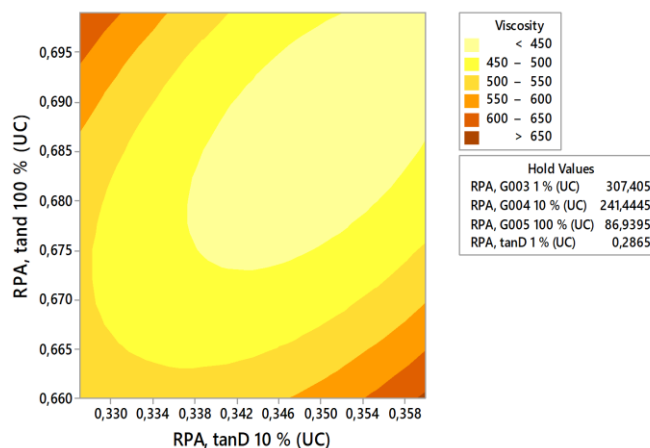


Figure 33 - Contour plot of viscosity vs $TAN(\delta)100\%$ (UC) and $TAN(\delta)10\%$ (UC)

Analysing figure 32 the RPA $TAN(\delta)100\%$ and $TAN(\delta)10\%$ have a good relation for the viscosity because it is represented a minimum in the surface plot and it is possible to see that the minimum is around higher viscosities. Still is not enough having the viscosity desired for Component A, but when $TAN(\delta)10\%$ and $TAN(\delta)100\%$ move away the middle points, it is possible to conclude that the viscosity increases for values higher than 500 Pa·s which is good. These theory is proven by seeing figure 33.

Observing figure 33 it is possible to see that the minimum point is basically in the middle points of these RPA variables. So, if the values for $TAN(\delta)10\%$ are in the center or the maximum and $TAN(\delta)100\%$ is in the middle and maximum, for sure the viscosity will be lower than 450 Pa·s, especially if the variables have values in the middle points. For having viscosities higher than 500 Pa·s or 550 Pa·s, $TAN(\delta)100\%$ must be at the maximum values, around 0.69 to 0.70 and $\tan(\delta) 10\%$ must be at the minimum values around 0.33. If $TAN(\delta)100\%$ is at the minimum and $TAN(\delta)10\%$ is at the maximum it is possible to obtain higher viscosities too, but the variables can not have intermediate values because the viscosity of Component A will be low.

Figure 34 and 35 show an example of a surface plot and a contour plot with two rheometric variables, TAN(δ)1% and G' 10%, that it is impossible to obtain a good viscosity.

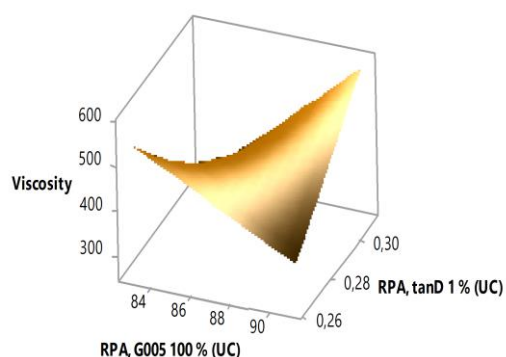


Figure 34 - Surface plot of viscosity vs TAN(δ)1% (UC) and G' 100% (UC)

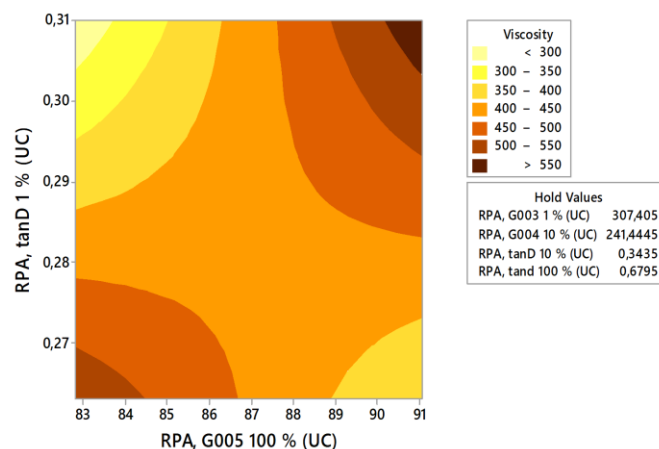


Figure 35 - Contour Plot of viscosity vs TAN(δ)1% (UC) and G' 100% (UC)

Figure 34, represents a small minimum but not a perfect one, this minimum corresponds to the low viscosities with these two variables, but here the viscosities are very low around the 300 Pa which are very bad for the ContiSeal™. If G' 100% moves away for lower values the viscosity has tendency to be higher, the same happens when TAN(δ)1% move away for higher values, but is possible to see that is difficult to obtain viscosities higher than 550 Pa·s.

Figure 35 shows the difficult of obtaining higher viscosities with these two variables, because the area for viscosity higher than 550 Pa·s are the darkest ones and it is very small. The biggest area in the middle corresponds to viscosities between 400 to 450 Pa·s which have no interest, because the purpose is to have higher viscosities. These results are in accordance to what is shown in figure 22 that G' 100% and TAN(δ)1% are the rheometric variables that have no influence in the viscosity and in figure 34 the minimum is not so defined. In figure 35 it is observed that with these variables the viscosity will be always low.

In figure 36 and 37 it is represented the surface and contour plot for the rheometric variables $TAN(\delta)100\%$ and $G'100\%$. These graphs show what is defined as saddle point. It does not have a minimum or maximum so it is impossible to have results about these two variables. The saddle point is a point over a surface in which the declivity is null and the elevation is maximum in a direction and minimum in a perpendicular direction.

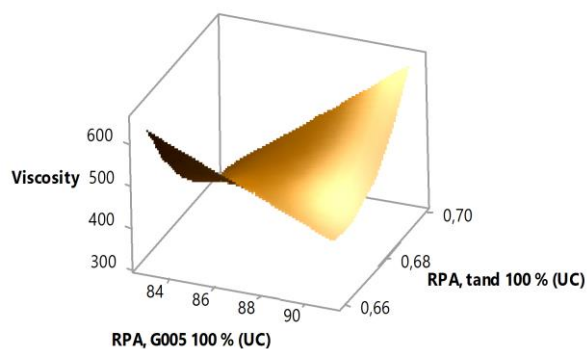


Figure 36 - Surface plot of viscosity vs $TAN(\delta)100\%$ (UC) and $G'100\%$ (UC)

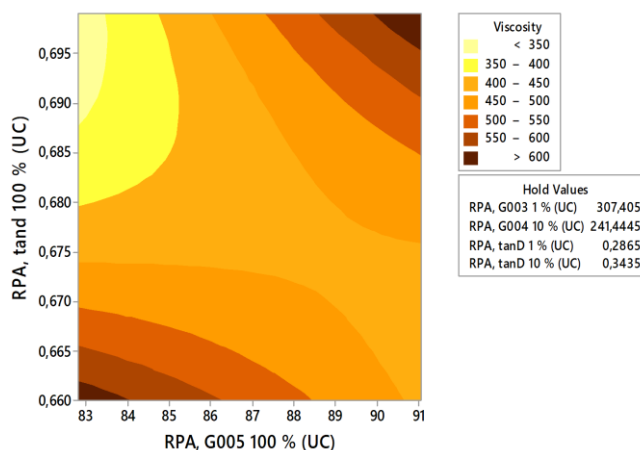


Figure 37 - Contour plot of viscosity vs $TAN(\delta)100\%$ (UC) and $G'100\%$ (UC)

In figure 36 it is not possible to see a minimum but a saddle point, to not have this, the domain of these variables must be change. This means that for the values obtained to $G'100\%$ and $TAN(\delta)100\%$ it is impossible to have a response, the levels of the variables had to be changed. In figure 37 it is seen that the viscosity is always very low, and because of the shell point it is impossible to conclude anything. The color areas with the viscosity desired are very small, for sure with these two variables it is not possible to optimize the response.

After this discussion of the surface and contour plot it can be conclude that the rheometric variables that have highest influence on the optimization of the viscosity are $TAN(\delta)100\%$ with $G'1\%$, $TAN(\delta)10\%$ with $G'10\%$ and $TAN(\delta)100\%$ with $TAN(\delta)10\%$. These variables match the ones that were obtained in figure 22 and show that they have the most influence in viscosity. To obtain better viscosities, around the target viscosity (555 Pa·s) these rheometric properties for the rubber compound must be inside some values, for example, for $TAN(\delta)100\%$ it must be in the maximum (0.69 to 0.70) or in the minimum values, not at the center, $G'1\%$ must be between 280 Pa and 290 Pa, close to the minimum, $G'10\%$ between 230 and 235 Pa or 246 and 250 Pa and finally $TAN(\delta)10\%$ must be close to 0.34 or 0.36.

Figure 38 represents the response optimizer for the viscosity. This graphic shows the values for each variable to reach the target. The response optimizer does not use the data in the worksheet, instead, the program estimates the optimal variable based on stored models, which helps to determine if the correct model of optimization of the response is being used.

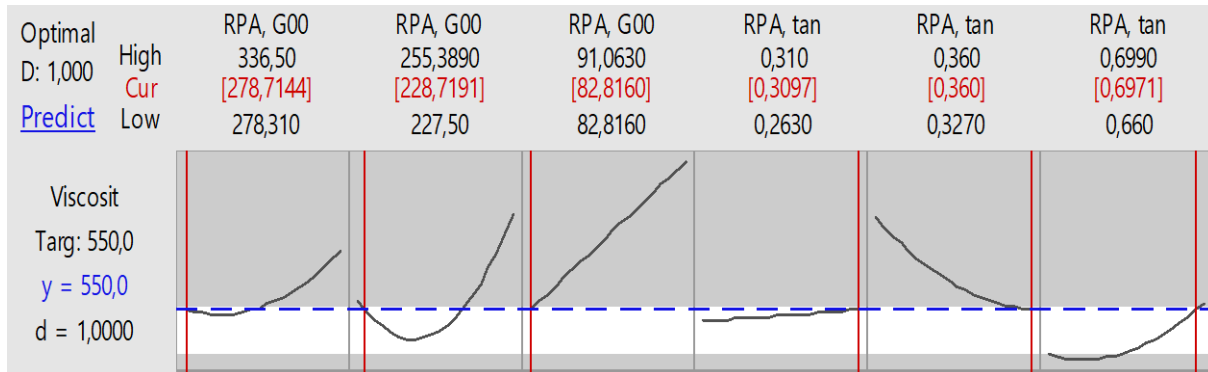


Figure 38 - Response optimization for viscosity

The first thing it is easy to repair is that the variables that have the same behaviour, (curve lines) as shown in figure 22, are the same that show in the response optimizer, which are $G'1\%$, $G'10\%$, $TAN(\delta)10\%$ and $TAN(\delta)100\%$. The $TAN(\delta)1\%$ and $G'100\%$ are straight lines, it means that these last ones will not have any effect on the viscosity whatever the value they have.

The second thing to discuss and the purpose of this graph are the values for each variable to reach the target viscosity. The target is 550 Pa·s represented by blue streak in the graph and the values for each variable are the ones represented with red. With these it is possible to compare with the results obtained for contour and surface plot to know if the values are agreeable. So, for $G'1\%$ the best value to reach the target viscosity is around 278 Pa, and in the contour plot, the values that were seen to reach the same viscosity for this variable are between 280 Pa and 290 Pa which is exactly the one obtained in the optimizer. With $G'10\%$ the value the optimizer gives is around 228 Pa, the one obtained in contour plot for the same variable is between 230 Pa and 235 Pa, meeting the same value of the optimizer. Looking for $G'100\%$ and $TAN(\delta)1\%$, that value do not matter for the viscosity, because in figure 22 and 38 the lines are straight and in the contour plot and surface plot it was impossible to reach a correct value since the plots do not have a minimum or a maximum but a shell point. With $TAN(\delta)10\%$ the value shown in the optimizer is around 0.36 and the ones found in the contour plot were between 0.34 and 0.36 which match the response optimizer. Finally, $TAN(\delta)100\%$ has a value of 0.697 obtained by the response optimizer and in contour plot this variable was around 0.69 to 0.70 which once again match the result obtain with the response optimizer.

After this it is possible to say that this model is correct for this problem, because all the values and behaviours obtained in DOE were precisely the same as the response optimizer.

After all this discussion, the important part now is to know what it is possible to do to change the values of the rheometric variables for the rubber to have the parameters desired to get a good viscosity for the process and to understand why the effects are bigger than others on Component A.

As it was mentioned, the variables that have the most effect in viscosity are $G'1%$, $G'10%$, $TAN(\delta)10%$ and $TAN(\delta)100%$, inside this four the best ones are $G'10%$ and $TAN(\delta)100%$. As show in figure 16, chapter 2, with 1 % of strain amplitude the rubber is on the filler-filler interaction and the greater the amplitude the interaction between filler-filler will decrease. With 10 % of strain amplitude this interaction does not have a huge difference than 1 %, but the interaction with rubber is bigger and there is less interaction between fillers. In this phase, the viscous module (G'') is bigger, that is why $G'10%$ has a little more effect than $G'1%$ in the viscosity of Component A, because it is more viscous. $TAN(\delta)10%$ has the same effect too, because $\tan(\delta)$ is G'' divided by G' and this factor is a good representation of the plastic and elastic components and the best indicator for state of mixture. $TAN(\delta)100%$ has basically the same effect as $TAN(\delta)10%$, but with $TAN(\delta)100%$ the interactions between the other variables is bigger, because in 100 % of strain amplitude the fillers are more reacted to the rubber so the viscosity module rises and the elastic module decreases, that is why with bigger values for $TAN(\delta)100%$ the viscosity of Component A is better.

With the surface plot, contour plot and the response optimizer it was possible to know which values, the rheometric variables must have, to obtain the target viscosity 555 Pa·s @ 0.02 Hz and 120 °C of Component A. For $G'1%$ the best value is the minimum of that variable, the same happen to $G'10%$ and for $TAN(\delta)10%$ and $TAN(\delta)100%$ the values must be higher close the maximum. So, the purpose is to decrease G' uncured and increase $\tan(\delta)$ uncured to optimize the response. To accomplish this, it is needed to change the concentrations of the fillers in the rubber, especially of carbon black or oil as represent the figures A.1, A.3, A.4 and A.6 in appendix A, respectively. Observing the figure A.1 and A.2, the uncured elastic shear module (G') and viscous module (G'') will increase with the increasing of carbon black in the rubber, it means that for having a minimum value for $G'1%$ and $G'10%$ the quantity of carbon black must be reduced when mixing the rubber. It is possible to see that with an increasing of temperature, G' and G'' decrease too. When looking for uncured $\tan(\delta)$ (figure A.3) with a reduced concentration of carbon black this variable will be higher, because carbon black loadings increased the density of the carbon black aggregate-aggregate network and with the increasing of temperature it will be higher too. So, to decrease elastic module (G') and increase $\tan(\delta)$, the concentration of carbon black must be reduced for having a good viscosity.

In relation to the amount of oil in the rubber (figure A.4, A.5 and A.6) it is the opposite of carbon black, so for decreasing G' and G'' , the concentration of oil in the rubber should be higher

with an increase of temperature. Relatively to $\tan(\delta)$, according to figure A.6, as process oil concentration increase the values increase too, because they reduced the concentration of carbon black and the aggregate-aggregate network. So, when changing the oil in the rubber, the concentration must be increased to have low G' and G'' and higher $\tan(\delta)$.

5 Conclusion

Sealant is made of Component A and Component B, while Component A is made of rubber compound masterbatch and polybutene. The goal of this project was to understand the influence of rheometric properties G' , G'' and $\tan(\delta)$ of rubber compound masterbatch on the viscosity @ 0.02 Hz and 120 °C displayed by Component A. This component is very complex and displays a low reproducible viscosity. To attain this goal, the first thing was to discover the variables that have the major influence on the viscosity of Component A, to know the best values of these variables to obtain the target viscosity and learn what it should be done to reach these values.

Using the response surface methodology, rheometric variables G' @ 1 % of strain amplitude (named $G'1\%$), G' @ 10 % of strain amplitude (named $G'10\%$), $\tan(\delta)$ @ 10 % (named TAN(δ)10%) and $\tan(\delta)$ @ 100 % (named TAN(δ)100%) of strain amplitude were selected from G' @ 1 % ,10 % and 100 % of strain amplitudes, $\tan(\delta)$ @ 1 % , 10 % and 100 % of strain amplitudes as displaying the highest correlation with the viscosity displayed by Component A. These results were obtained based on 64 experiments.

For obtaining the target viscosity 555 Pa·s @ 0.02 Hz and 120 °C of Component A, the selected rheologic properties should take the values of 280 Pa < $G'1\%$ < 290 Pa, 230 Pa < $G'10\%$ < 235 Pa, 0.34 < TAN(δ)10% < 0.36 and 0.69 < TAN(δ)100% < 0.70. These values were obtained based on the empirical model from the response surface methodology, a second order polynomial (appendix B). In this project, it was found that G' decreases as the concentration in carbon black decreases and the oil concentration increases; the same applies to increase $\tan(\delta)$. This study shows that it is possible to control the viscosity of Component A by controlling four rheologic variables of rubber compound masterbatch - $G'1\%$, $G'10\%$, TAN(δ)10% and TAN(δ)100%.

It was also found how these variables correlate with the rubber compound masterbatch composition, namely on its content in carbon black and oil. Rheologic properties of polybutene were found to be quite constant.

6 Assessment of the work done

This chapter has the purpose to give a global evaluation of the executed work. This is divided by three sections, the objectives achieved, the limitations and future work and the final assessment.

6.1 Objectives Achieved

The main goal of this project is to evaluate the rheometric properties (G' , G'' and $\tan(\delta)$) of rubber compound masterbatch and cross these results with the Component A viscosity to improve it.

To attain this goal there were three principal objectives to be achieved. The first objective was to, evaluate which variable of the rheometric variables, has the biggest influence on the Component A viscosity. The second was to define the best value of that variables to assure the stability of Component A viscosity inside the desired tolerance. The final objective was to study the mixing process of rubber compound to control the variables defined on the first objective and to assure the specification stipulated on the third objective.

Relatively to the founding of the rheometric properties, using RPA, that have most influence on the viscosity of Component A and their respective values, they were accomplished. The last objective could not be complete because there was not time to change the recipes in the rubber and to test at ContiSeal to see if the values for each variable could be achieved and to know if the viscosity desired could be reached. The only thing it was possible to do was to understand what can be made in the raw materials of the rubber to achieve does values.

6.2 Limitations and Future Work

The biggest limitation faced during the development period of the project was time. The main obstacle for this study was the collection of samples. Due to the nature of the design of experiments there was a need of a lot of samples to be taken at the same conditions on the extruder. The problem was that, the extruder runs at the condition required by the production plan and they were not always in adjusted to the condition established in this study. This was the main issue, on top of that I had the challenge to work as a lab technician in ContiSeal while performing all the task related with this project.

For future developments, we should continue this study focusing on our last objective. Understand if it is possible to produce masterbatch with the optimal RPA values and crosscheck it with the Component A viscosity. For that is necessary to change the recipe of the production of the rubber compound. Another study that could be made is to study the influence of each extrusion parameter, temperatures, throughput, rpm and the density, to know the best values for each of

these parameters the viscosity is better. Finally, another important study to be made is testing the mixing temperature of the rubber and the storage time of it at ContiSeal, if with the past of the days the properties of the rubber will decrease and influence viscosity.

6.3 Final Assessment

During the development of this project, over these 5 months at Continental, was very important for me because it made me evolve in different levels, academic, professional and personal. This study was very important for ContiSeal, because the RPA is a new technology and gives a lot of information about the rubber compounds and no one has ever made a crosscheck with the viscosity of Component A. Our colleagues from the Continental in Hannover were very interested too about this study so it is very good for the process and we learn more about it.

This project has the potential to move on and to be continued for a lot of years and a lot of people will be very interested. If this objective is completed and we obtain a constant viscosity of Component A in the desired tolerance, the performance of sealant will be perfect and it will reduce scrap, problems on the machine and time.

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Appendix A

As said in the Context and State of Art (chapter 2), in table A.1 are all the materials that form the sealant

Table A.1 - The materials that composed the ContiSeal sealant - extracted from

Material	Sealant Relevant Properties
Butyl Polymers	High air impermeability, resistance to flow at high temperature and resistance to oxidative aging
Carbon black	Low loading of black provides reinforcement at low strain without loss of ultimate elongation and reaction sites for the quinone curing system
Paraffinic oil	Process aid to improve flow of material through equipment
Aliphatic tackifier	Provides adhesion of sealant to tire and of sealant to penetrating objects
Liquid polymer tackifiers	Provides extremely high tack over a wide temperature range and insures optimum flow properties needed for seal performance
Peroxide activated QDO	Provides age resistant crosslinks which maintain material properties over long service life of tire
ZnO and sulfur	Provides high temperature stability to the crosslink network

In figure A.1 is shown the behaviour that elastic module (G' uncured) has when increasing the carbon black concentration in the rubber and in temperature sweeps of SBR models.

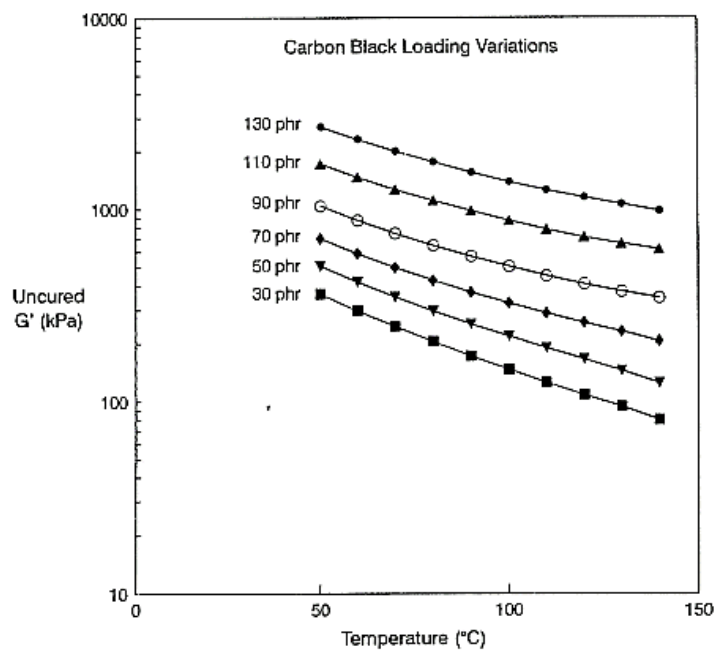


Figure A.1 - Changes in RPA elastic modulus (G') response in temperature sweeps of SBR models with different carbon black concentrations - extracted from

In figure A.2 is shown the behaviour that viscous module (G'' uncured) has when increasing the carbon black concentration in the rubber and in temperature sweeps of SBR models.

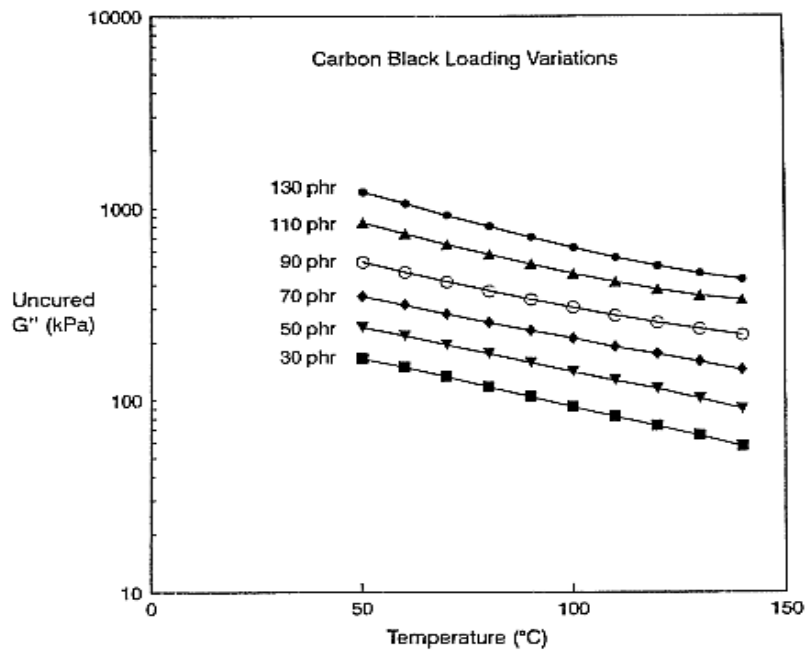


Figure A.2 - Changes in RPA viscous modulus (G'') response in temperature sweeps of SBR models with different carbon black concentrations - extracted from

In figure A.3 is shown the behaviour that $\tan(\delta)$ has when increasing the carbon black concentration in the rubber and in temperature sweeps of SBR models.

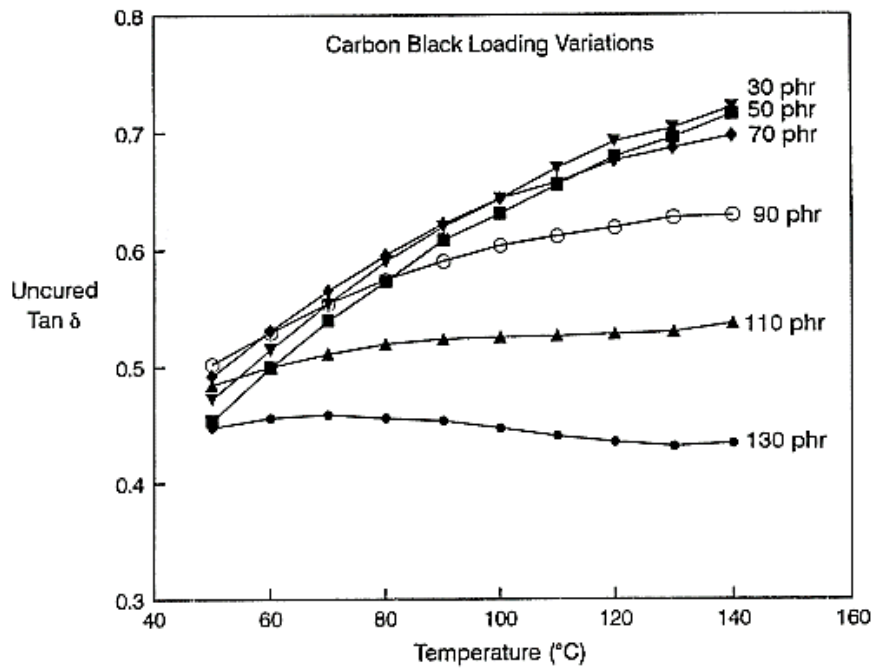


Figure A.3 - Changes in RPA $\tan(\delta)$ response in temperature sweeps of SBR models with different carbon black concentrations - extracted from

In figure A.4 is shown the behaviour that elastic module (G' uncured) has when increasing the oil concentration in the rubber and in temperature sweeps of SBR models.

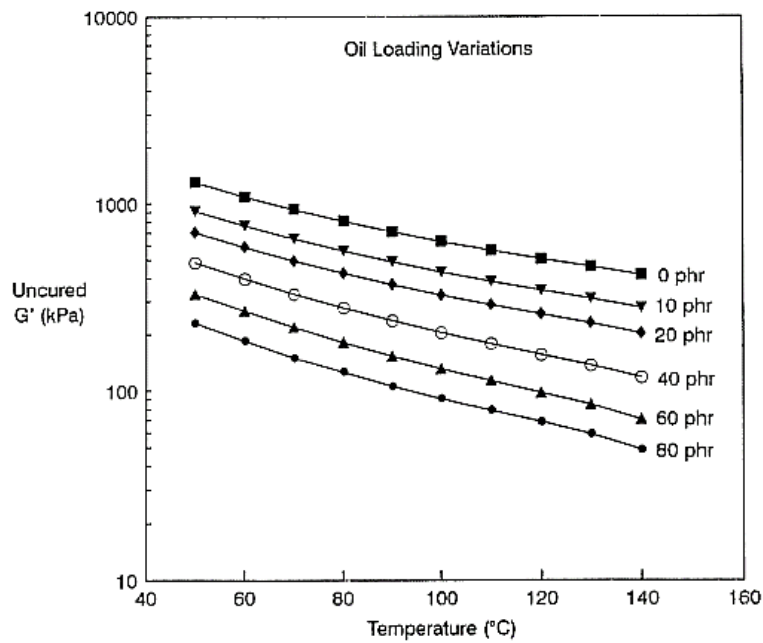


Figure A.4 - Changes in RPA elastic modulus (G') response in temperature sweeps of SBR models with different oil concentrations - extracted from

In figure A.5 is shown the behaviour that viscous module (G'' uncured) has when increasing the oil concentration in the rubber and in temperature sweeps of SBR models.

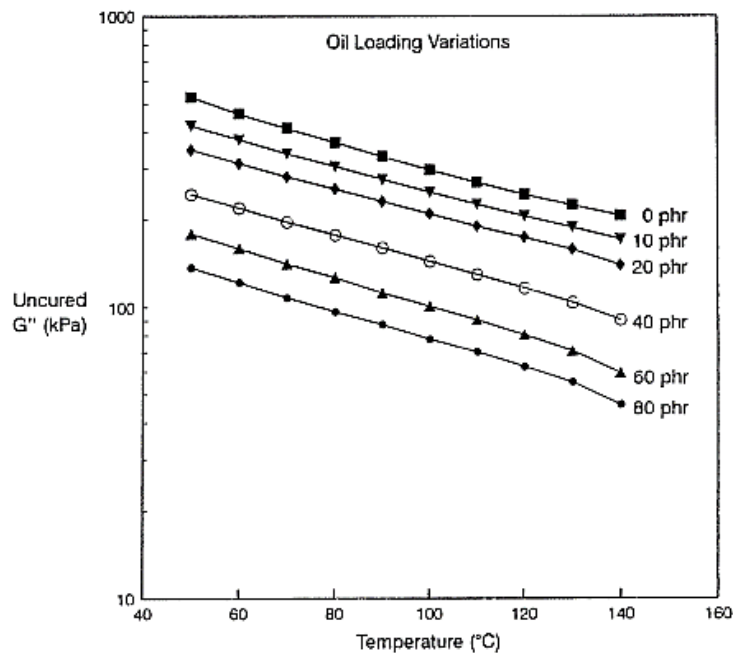


Figure A.5 - Changes in RPA viscous modulus (G'') response in temperature sweeps of SBR models with different oil concentrations - extracted from

In figure A.6 is shown the behaviour that $\tan(\delta)$ has when increasing the oil concentration in the rubber and in temperature sweeps of SBR models.

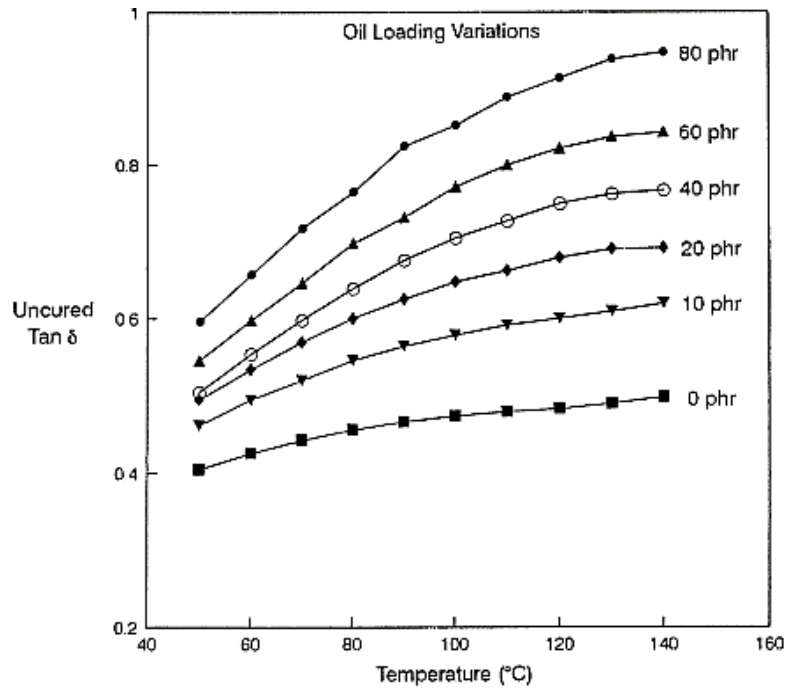



Figure A.6 - Changes in RPA $\tan(\delta)$ response in temperature sweeps of SBR models with different oil concentrations - extracted from

Appendix B

In this appendix it will be presented some information that was essential for the achievement of the results of this thesis, and some results obtain of DOE.

In the table B.1 are presented some of the RPA uncured results for the rubber compound masterbatch that were necessary for the results in chapter 4. In this table is presented the data for the variables in study for this project.

Table B.1 - RPA uncured data for ContiSeal compound

Continental Mabor Lousado	Chart type: Stat. table Single values Controll plan: Final Lab order: 20170512-0004	M08161 Composto para ContiSeal								
Criteria	RPA,G'@1.00	RPA,G'@10.0	RPA,G'@100	RPA,G'@1 %	RPA,G'@10	RPA,G'@100	RPA,tanD@1	RPA,tanD@10	RPA,tanD@10	RPA,DeltaG' (
	Mean Std.	Mean Std.	Mean Std.	Mean Std.	Mean Std.	Mean Std.	Mean Std.	Mean Std.	Mean Std.	Mean Std.
000 - 024	351.99 5.04	265.72 3.32	92.869 0.648	326.94 6.69	252.425 2.942	90.205 0.560	0.2813 0.0090	0.3382 0.0013	0.6856 0.0072	236.74 6.44
025 - 035 FIM	348.60 5.23	264.88 1.12	93.489 0.801	324.59 3.80	251.361 1.438	90.882 0.966	0.2828 0.0175	0.3370 0.0022	0.6733 0.0131	233.70 4.65
Batch:										
025 / MDRO / 001 Online 02:11:04										
026 / MDRO / 001 Online 02:11:04										
027 / RPA1 / 001 NogueiraJ 14:32:25	353.42	266.49	93.054	323.49	253.120	90.429	0.2820	0.3360	0.6860	233.06
028 / MDRO / 001 Online 02:11:04										
029 / MDRO / 001 Online 02:11:04										
030 / RPA1 / 001 NogueiraJ 14:58:15	352.39	264.22	92.683	329.72	251.151	90.002	0.2590	0.3400	0.6800	239.72
031 / MDRO / 001 Online 02:11:04										
032 / MDRO / 001 Online 02:11:04										
033 / RPA1 / 001 NogueiraJ 01:28:59	342.39	264.83	93.711	324.52	251.553	90.867	0.2900	0.3350	0.6710	233.65
034 / MDRO / 001 Online 02:11:04										
035 / RPA1 / 001 NogueiraJ 01:56:08	346.19	264.00	94.506	320.62	249.621	92.230	0.3000	0.3370	0.6560	228.39
035 FIM / MDRO / Online 02:11:04										

The table B.2 shows all the 64 results of the viscosity of Component A (Frequency Sweep A) that were collected for this study as the conditions that the samples were taken from the extruder (throughput, density and rpm) and it shows the RPA values that correspond to the table of the rubber compound that was being used in the extruder when taking the sample.

The data of Frequency Sweep A and RPA were used on the treatment of the results in DOE.

Table B.2 - Results of "Frequency Sweep A" and RPA

Dia	Extruder					Masterbatch (RPA Properties)								
	CCM/min	Caudal	RPM	Densidade	Frequency Sweep A	Dia	Carga	RPA, G003 1% (UC)	RPA, G004 10% (UC)	RPA, G005 100% (UC)	RPA, tanD1 % (UC)	RPA, tanD10 % (UC)	RPA, tanD100 % (UC)	
18-03-2017	5000	289	354	1,123	442,01	0,19	14-03-2017	4 a 6 (6)	299,69	237,65	85,60	0,292	0,346	0,691
19-03-2017	5000	289	354	1,123	453,12	0,18	14-03-2017	16 a 18 (18)	286,65	228,50	82,82	0,290	0,352	0,692
21-03-2017	5000	289	354	1,123	444,05	0,23	14-03-2017	25 a 27	278,31	228,29	84,06	0,285	0,347	0,676
22-03-2017	5000	289	354	1,123	431,26	0,23	21-03-2017	4 a 6 (6)	296,75	236,89	87,71	0,300	0,350	0,680
23-03-2017	5000	289	354	1,123	459,13	0,30	21-03-2017	10 a 12 (12)	294,10	235,90	87,11	0,310	0,360	0,680
24-03-2017	5000	289	354	1,123	479,72	0,20	21-03-2017	16 a 18 (18)	295,91	236,79	86,15	0,304	0,360	0,690
24-03-2017	5000	289	354	1,123	472,84	0,31	21-03-2017	19 a 21 (21)	296,62	236,23	86,64	0,281	0,347	0,680
25-03-2017	5000	289	354	1,123	452,78	0,31	24-03-2017	1 a 3 (3)	299,81	239,88	86,17	0,290	0,350	0,690
26-03-2017	5000	289	354	1,123	432,31	0,27	24-03-2017	10 a 12 (12)	296,91	242,59	87,55	0,300	0,360	0,690
28-03-2017	5000	289	354	1,123	434,64	0,30	24-03-2017	25 a 27 (27)	295,90	244,11	90,10	0,296	0,347	0,673
28-03-2017	5000	289	354	1,123	432,35	0,34	24-03-2017	28 a 30 (30)	290,15	236,46	87,03	0,290	0,350	0,680
28-03-2017	5000	289	354	1,123	430,42	0,20	24-03-2017	28 a 30 (30)	290,15	236,46	87,03	0,290	0,350	0,680
28-03-2017	5000	289	354	1,123	455,92	0,23	27-03-2017	4 a 6 (6)	308,06	237,30	86,56	0,285	0,360	0,680
29-03-2017	5000	289	354	1,123	481,14	0,35	27-03-2017	7 a 9 (9)	310,12	238,78	87,31	0,300	0,350	0,680
30-03-2017	5000	289	354	1,123	430,07	0,31	27-03-2017	13 a 15 (15)	310,90	239,65	88,15	0,280	0,350	0,680
30-03-2017	5000	289	354	1,123	441,66	0,18	27-03-2017	16 a 18 (18)	312,18	240,52	87,37	0,290	0,350	0,690
31-03-2017	5000	289	354	1,123	425,41	0,29	27-03-2017	25 a 27 (27)	310,02	241,84	87,91	0,280	0,350	0,690
01-04-2017	5000	289	354	1,123	428,91	0,21	30-03-2017	1 a 3 (3)	302,40	240,90	86,45	0,278	0,348	0,680
02-04-2017	5000	289	354	1,123	427,51	0,30	30-03-2017	4 a 6 (6)	298,40	238,40	86,37	0,292	0,348	0,695
02-04-2017	5000	289	354	1,123	439,28	0,25	30-03-2017	10 a 12 (12)	310,90	240,10	88,48	0,280	0,349	0,680
03-04-2017	5000	289	354	1,123	450,24	0,24	30-03-2017	22 a 24 (24)	307,30	238,60	88,27	0,285	0,347	0,684
04-04-2017	5000	289	354	1,123	482,24	0,29	30-03-2017	28 a 30 (30)	299,40	234,20	87,61	0,280	0,350	0,675
04-04-2017	5000	289	354	1,123	440,73	0,34	30-03-2017	31 a 33 (33)	300,40	234,50	88,41	0,281	0,350	0,668
05-04-2017	5000	289	354	1,123	426,70	0,33	30-03-2017	34 a 36 (36)	291,20	227,50	85,98	0,284	0,350	0,670
06-04-2017	5000	289	354	1,123	433,51	0,21	30-03-2017	37 a 39 (39)	289,40	229,60	86,41	0,290	0,350	0,670
06-04-2017	5000	289	354	1,123	485,10	0,24	04-04-2017	4 a 6 (6)	305,34	241,48	87,79	0,290	0,350	0,690
07-04-2017	5000	289	354	1,123	428,08	0,17	04-04-2017	7 a 9 (9)	310,89	242,96	88,27	0,290	0,350	0,690
07-04-2017	5000	289	354	1,123	481,06	0,23	04-04-2017	10 a 12 (12)	311,29	244,90	89,25	0,290	0,350	0,690
07-04-2017	5000	289	354	1,123	459,87	0,27	04-04-2017	19 a 21 (21)	301,34	236,08	87,59	0,293	0,349	0,675
10-04-2017	5000	289	354	1,123	412,70	0,10	04-04-2017	28 a 30 (30)	308,57	240,07	88,76	0,280	0,350	0,690
08-04-2017	5000	289	354	1,123	435,55	0,29	04-04-2017	31 a 33 (33)	298,17	235,30	88,75	0,281	0,345	0,660
09-04-2017	5000	289	354	1,123	436,34	0,20	06-04-2017	7 a 9 (9)	314,44	242,89	88,79	0,301	0,353	0,673
11-04-2017	5000	289	354	1,123	451,30	0,33	06-04-2017	16 a 18 (18)	317,98	239,94	86,92	0,296	0,356	0,684
12-04-2017	5000	289	354	1,123	426,30	0,28	06-04-2017	28 a 30 (30)	316,10	241,10	88,17	0,307	0,354	0,674
13-04-2017	5000	289	354	1,123	430,20	0,18	11-04-2017	7 a 9 (9)	321,16	248,58	89,73	0,290	0,345	0,679
20-04-2017	5000	289	354	1,123	425,47	0,26	18-04-2017	4 a 6 (6)	311,98	239,52	86,15	0,295	0,342	0,683
20-04-2017	5000	289	354	1,123	405,82	0,26	18-04-2017	10 a 12 (12)	305,12	234,15	85,23	0,294	0,344	0,678
21-04-2017	5000	289	354	1,123	441,90	0,19	18-04-2017	13 a 15 (15)	311,98	238,42	86,63	0,273	0,342	0,677
21-04-2017	5000	289	354	1,123	448,71	0,22	18-04-2017	19 a 21 (21)	315,03	237,29	86,75	0,286	0,344	0,671
21-04-2017	5000	289	354	1,123	456,60	0,30	18-04-2017	22 a 24 (24)	315,14	245,09	87,37	0,283	0,342	0,685
21-04-2017	5000	289	354	1,123	444,33	0,25	18-04-2017	25 a 27 (27)	307,29	240,32	87,12	0,275	0,338	0,672
23-04-2017	5000	289	354	1,123	442,75	0,24	21-04-2017	4 a 6 (6)	304,14	242,62	86,31	0,265	0,327	0,690
23-04-2017	5000	289	354	1,123	501,37	0,20	21-04-2017	7 a 9 (9)	304,36	244,76	88,07	0,268	0,327	0,682
25-04-2017	5000	289	354	1,123	433,09	0,19	21-04-2017	19 a 21 (21)	313,36	247,57	87,85	0,263	0,328	0,694
25-04-2017	5000	289	354	1,123	521,93	0,17	21-04-2017	22 a 24 (24)	308,26	245,05	87,05	0,268	0,328	0,694
27-04-2017	5000	289	354	1,123	496,42	0,14	21-04-2017	13 a 15 (15)	305,34	242,36	87,10	0,274	0,332	0,690
28-04-2017	5000	289	354	1,123	450,74	0,22	25-04-2017	4 a 6 (6)	321,38	251,93	88,83	0,281	0,337	0,694
28-04-2017	5000	289	354	1,123	469,58	0,22	25-04-2017	7 a 9 (9)	316,36	252,01	88,84	0,269	0,334	0,699
28-04-2017	5000	289	354	1,123	434,02	0,23	25-04-2017	10 a 12 (12)	318,34	250,22	89,04	0,297	0,342	0,691
02-05-2017	5000	289	354	1,123	474,28	0,21	25-04-2017	19 a 21 (21)	319,14	252,30	89,65	0,263	0,338	0,691
02-05-2017	5000	289	354	1,123	425,25	0,25	28-04-2017	4 a 6 (6)	310,30	246,10	88,44	0,272	0,336	0,683
02-05-2017	5000	289	354	1,123	456,58	0,17	28-04-2017	7 a 9 (9)	309,70	247,40	88,54	0,285	0,340	0,690
05-05-2017	5000	289	354	1,123	558,60	0,13	28-04-2017	1 a 3 (3)	311,41	248,54	89,03	0,290	0,338	0,683
05-05-2017	5000	289	354	1,123	504,49	0,19	28-04-2017	4 a 6 (6)	319,25	251,18	88,72	0,287	0,338	0,698
05-05-2017	5000	289	354	1,123	532,32	0,14	28-04-2017	7 a 9 (9)	320,29	253,50	89,82	0,273	0,338	0,691
05-05-2017	5000	289	354	1,123	448,60	0,17	28-04-2017	10 a 11 (11)	313,27	249,99	89,27	0,286	0,339	0,687
09-05-2017	5000	289	354	1,123	506,04	0,29	05-05-2017	19 a 21 (21)	308,37	245,98	89,490	0,291	0,333	0,670
09-05-2017	5000	289	354	1,123	479,91	0,23	05-05-2017	22 a 24 (24)	308,20	241,80	89,580	0,272	0,335	0,663
11-05-2017	5000	289	354	1,123	433,98	0,25	09-05-2017	4 a 6 (6)	315,79	249,76	88,384	0,274	0,337	0,698
12-05-2017	5000	289	354	1,123	411,57	0,31	09-05-2017	10 a 12 (12)	317,43	247,77	89,156	0,266	0,337	0,685
13-05-2017	5000	289	354	1,123	463,56	0,17	09-05-2017	22 a 24 (24)	313,60	249,00	88,845	0,272	0,335	0,684
16-05-2017	5000	289	354	1,123	464,10	0,14	12-05-2017	7 a 9 (9)	326,53	252,59	90,335	0,271	0,339	0,684
17-05-2017	5000	289	354	1,123	497,76	0,27	12-05-2017	10 a 12 (12)	336,50	255,39	91,063	0,280	0,339	0,685
19-05-2017	5000	289	354	1,123	520,31	0,26	12-05-2017	22 a 24 (24)	327,55	252,35	90,267	0,291	0,336	0,686

The figures B.3 and B.4 shows the surface and contour plot for the viscosity of each RPA variable. It is explained in chapter 4 some of these plots, the ones that have the major influence on viscosity.

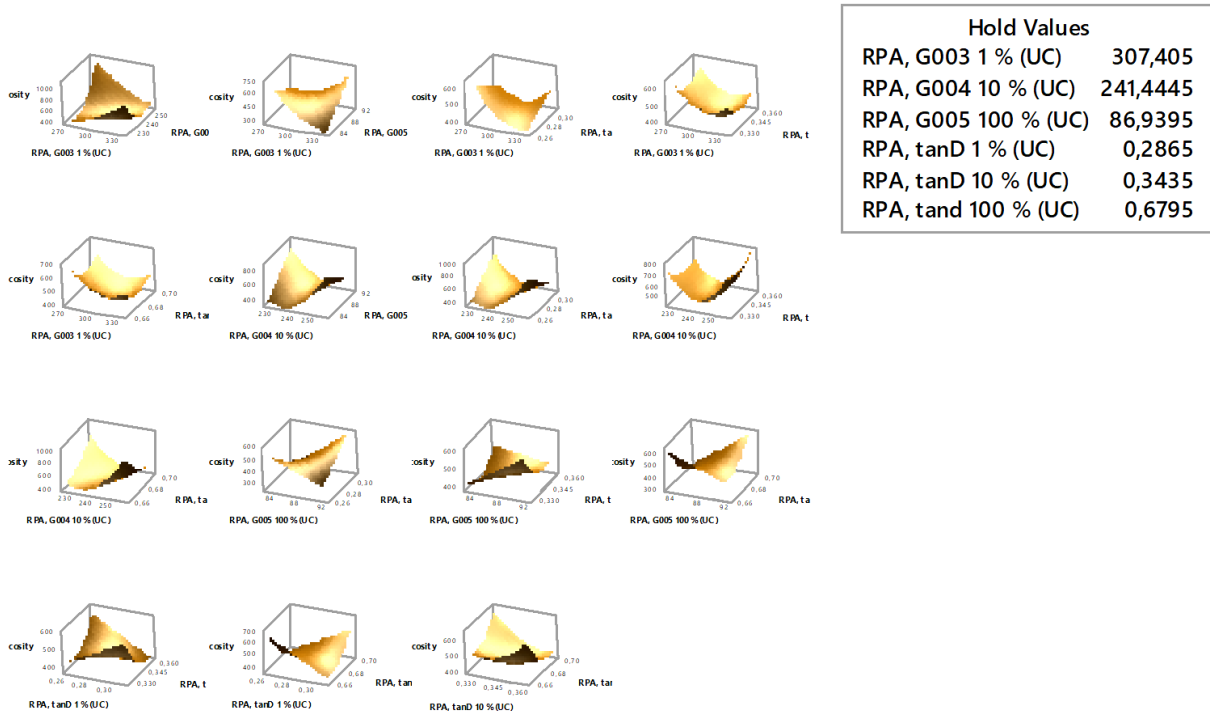


Figure B.3 - Surface plots for viscosity to all the RPA variables

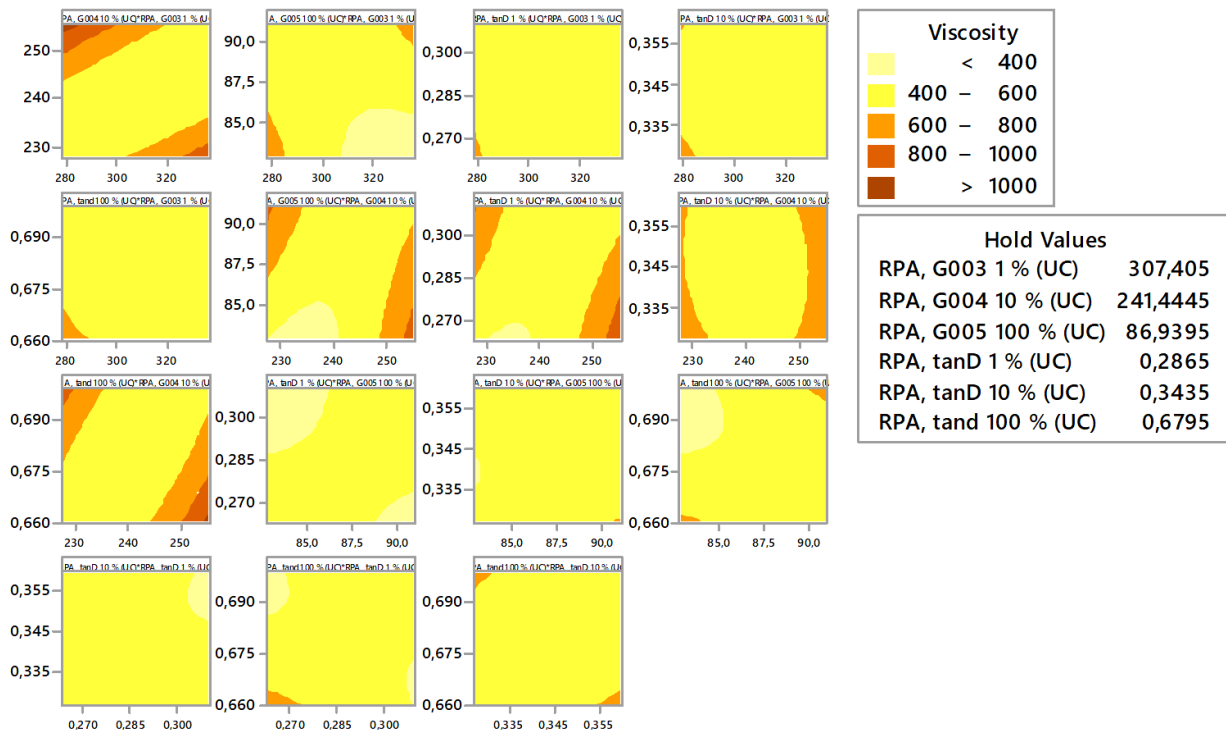


Figure B.4 - Contour plots for viscosity to all the RPA variables

The following equation is a second order polynomial for the viscosity of Component A.

Regression Equation in Encoded Units:

$$\begin{aligned}
 \text{Viscosity} = & 40556 - 52 \text{ RPA, G003 1 \% (UC)} + 574 \text{ RPA, G004 10 \% (UC)} - 748 \text{ RPA, G005 100 \% (UC)} \\
 & - 100650 \text{ RPA, tanD 1 \% (UC)} + 113635 \text{ RPA, tanD 10 \% (UC)} - 217456 \text{ RPA, tand 100 \% (UC)} \\
 & + 0,099 \text{ RPA, G003 1 \% (UC)*RPA, G003 1 \% (UC)} + 1,24 \text{ RPA, G004 10 \% (UC)*RPA, G004 10 \% (UC)} \\
 & + 0,0 \text{ RPA, G005 100 \% (UC)*RPA, G005 100 \% (UC)} + 2305 \text{ RPA, tanD 1 \% (UC)*RPA, tanD 1 \% (UC)} \\
 & + 236508 \text{ RPA, tanD 10 \% (UC)*RPA, tanD 10 \% (UC)} + 202366 \text{ RPA, tand 100 \% (UC)*RPA, tand 100 \% (UC)} \\
 & - 0,647 \text{ RPA, G003 1 \% (UC)*RPA, G004 10 \% (UC)} + 1,34 \text{ RPA, G003 1 \% (UC)*RPA, G005 100 \% (UC)} \\
 & + 85 \text{ RPA, G003 1 \% (UC)*RPA, tanD 1 \% (UC)} - 9 \text{ RPA, G003 1 \% (UC)*RPA, tanD 10 \% (UC)} \\
 & + 12 \text{ RPA, G003 1 \% (UC)*RPA, tand 100 \% (UC)} - 3,42 \text{ RPA, G004 10 \% (UC)*RPA, G005 100 \% (UC)} \\
 & - 621 \text{ RPA, G004 10 \% (UC)*RPA, tanD 1 \% (UC)} + 137 \text{ RPA, G004 10 \% (UC)*RPA, tanD 10 \% (UC)} \\
 & - 800 \text{ RPA, G004 10 \% (UC)*RPA, tand 100 \% (UC)} + 1306 \text{ RPA, G005 100 \% (UC)*RPA, tanD 1 \% (UC)} \\
 & - 846 \text{ RPA, G005 100 \% (UC)*RPA, tanD 10 \% (UC)} + 1591 \text{ RPA, G005 100 \% (UC)*RPA, tand 100 \% (UC)} \\
 & - 223369 \text{ RPA, tanD 1 \% (UC)*RPA, tanD 10 \% (UC)} + 273701 \text{ RPA, tanD 1 \% (UC)*RPA, tand 100 \% (UC)} \\
 & - 250078 \text{ RPA, tanD 10 \% (UC)*RPA, tand 100 \% (UC)}
 \end{aligned}$$