Improving paint characteristics

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Si para recobrar lo recobrado,
debí perder primero lo perdido.
Si para conseguir lo conseguido,
tuve que soportar lo soportado.

Si para ahora estar enamorado,
fue menester haber estado herido
Tengo por bien sufrido lo sufrido,
tengo por bien llorado lo llorado

Porque después de todo he comprobado
que no se goza bien de lo gozado
sino después de haberlo padecido

Porque después de todo he comprendido
que lo que el árbol tiene de florido
vive de lo que tiene sepultado

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ABSTRACT

In this work, the rheological properties of coatings, produced by the company "Tintas Europa", were studied and compared with the coating of a competitor company, in order to improve their characteristics.

The company approached to the IPB with a problem to be "solved"; they wanted to know the reason why costumers prefer the competitor coating instead of theirs, assuming they are sold as identical products and therefore should have the same reception.

Based on this premise the following objectives were established: evaluate the rheological properties of the paint samples that were provided; investigate the properties of ideal paints; modify the components of the samples to alter their rheological properties; study the effect of modifications on the rheological properties of paints

To achieve the proposed objectives, experimental tests were carried out. Six samples were tested, including the competitor's sample, Newplaste and Supramate, which are paints that are currently sold by the company, and three Supramate modifications named A, C and D, with different percentages of thickeners in their composition. All tests were performed with a rheometer that allowed to know the main rheological differences between paintings. Those tests were: Viscosity curve, Amplitude Sweep, Frequency Sweep and Three-Interval-Thixotropy-Test (3ITT).

It was found that the samples had similarities in their viscous and elastic behaviors, but a difference in thixotropy behaviors was found. Finally, the sample that, rheologically, most closely resembled the competitor's sample, and is expected to have a similar behavior in practice, was sample A that was a modified coating, and had the least percentage of thickener in its composition.

Keywords: Coatings. Paints Rheology. Rheology Tests. Rheology Mathematical Models.

RESUMO

Neste trabalho, foram estudadas e comparadas as propriedades reológicas de tintas produzidos pela empresa "Tintas Europa", com a tinta de uma empresa concorrente, por forma a melhorar as suas características.

A empresa abordou o IPB com um problema a "resolver"; queriam saber por que razão os clientes preferem a tinta da concorrên em vez da sua, assumindo que são vendidas como produtos idênticos e, portanto, deveriam ter a mesma aceitação.

Com base nessa premissa, foram estabelecidos os seguintes objetivos: avaliar as propriedades reológicas das amostras das tintas fornecidas; investigar as propriedades de tintas ideais; modificar os componentes das amostras para assim alterar as suas propriedades reológicas; estudar o efeito dessas modificações nas propriedades reológicas das tintas.

Para atingir os objetivos propostos, foram realizados testes experimentais. Foram testadas seis amostras: a da concorrência, a Newplaste, a Supramate, que são as tintas atualmente comercializadas pela empresa, e três modificações do Supramate denominadas por A, C e D, com diferentes percentuais de espessantes na sua composição. Todos os testes foram realizados com um reómetro que permitiu perceber quais as principais diferenças reológicas entre as diversas tintas. Esses testes foram: Teste rotacional para obtenção da curva da Viscosidade, Teste dinâmicos com varrimento da amplitude, Teste dinâmico com varrimento da freqüência e Teste da tixotropia de Três Intervalos (3ITT).

Verificou-se que as amostras apresentavam comportamentos viscoso e elástico semelhantes, mas foi encontrada diferença no comportamento da tixotropia. A amostra que, reologicamente, se assemelhava mais concorrente, e que se espera que tenha um comportamento semelhante na prática, foi a amostra A, que eé uma tinta modificada com menor percentagem de espessante na sua composição.

Palavras-chave: Revestimentos. Paints Rheology. Testes de reologia. Modelos matemáticos de reologia.

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LIST OF SYMBOLS

$\boldsymbol{\eta_B}$. Bingham Viscosity

$\boldsymbol{\eta_C}$. Casson Viscosity

$\boldsymbol{\eta_{HB}}$. Herschel-Bulkley Viscosity

$\boldsymbol{\dot{\gamma}}$. Shear Rate

$\boldsymbol{\tau_B}$. Bingham Yield Point

$\boldsymbol{\tau_C}$. Casson Yield Point

$\boldsymbol{\tau_{HB}}$. Herschel-Bulkley Yield Point

$\boldsymbol{\eta}$. Viscosity

$\boldsymbol{\tau}$. Shear Stress

LIST OF ABREVIATIONS

3ITT. Three Interval Thixotropy Test

A. Area

F. Force

G' Elastic Modulus

G'' Viscous Modulus

h. Thickness between the plates

Hz. Hertz

Lin. Lineal Scale

Log. Logarithmic Scale

LVER. Low Viscoelastic Range

p. Parameter

Pa. Pascal

s. Second

v. Velocity

1. INTRODUCTION

A paint coating can be defined as a liquid material which, when spread over a surface as a relatively thin film, subsequently dries to form a solid, cohesive, adhesive protective layer.

Since the beginning of human history, thirty-thousand years ago, primitive people started creating and developing what us know today as coatings. Of course, they weren't aware about that and it wasn't exactly the same as it's today but it was a beginning. Chemical analysis of these first paintings showed that they were made with iron and manganese oxides as pigments and egg white, animal fats, plant sap, or water as solvent. This mix was then applied to cave walls as a form of art to leave a graphic representation of their life.

Along the time, many paint making advances were made by the different cultures, but it was really expensive to produce them so not everyone had access to them. They were produced in small batches and carefully guarded.

It wasn't until the Industrial Revolution and the mass production of automobiles influenced the coatings industry, in the late eighteenth and early nineteenth century, that paints and coatings began to get relevance enough to start producing them in large scale, so the first paint and varnish factories were stablished. But this wasn't for their color that they were needed, they discovered that coatings could have anti-corrosive properties as well as others that were really important for the time, these properties helped to accelerate the rate of scientific discovery.

Later, after the middle of the twentieth century, synthetic resins replaced the natural oils that were used in coatings formulations.

Coatings developed slowly from artistry to technology, today coatings manufacturers offer products that can decorate, protect and perform special functions on the surfaces where they are applied. From cars and children's toys up to spacecraft coatings are needed in a very wide range of applications. (V. Mannari, 2015)

2. THEORETICAL BACKGROUND

2.1. ANATOMY OF COATINGS

As there is a wide variety of materials and surfaces that have a wide range of physical and chemical characteristics, it's not a surprise that we need a diverse range of coatings with different properties. These properties are achieved by varying the nature and quantity of the components.

A paint is composed by a mixture of a solid part, which gives origin to an adhesive film, and a volatile part. When the paint is applied, a thermoplastic material and a thermostable material are formed; the thermoplastic one is formed spontaneously without any chemical reaction, and to form the thermostable one, chemical reactions are needed to modify one of the components usually made by the action of a catalyst (Lambourne, 1999).

All coatings will contain a film-forming material. This material may be organic or inorganic and, after application, may form a hard film, an impervious film, a soft porous film, or combinations in between. Furthermore, the film-forming material may be clear (unpigmented) or filled with a variety of different pigments, depending on its function and that should not destroy the surface where it is applied.

When the film-forming material (resin) contains pigments, it is called a binder. Pigments are finely divided in-soluble particles that provide color and opacity when dispersed into a medium. The binder will hold the pigment particles together and in turn adhere to the substrate over which it has been applied. The binder must be dissolved in a solvent to become a liquid, also known as vehicle, the term vehicle comes from the ability to transport and apply the liquid to the surface being coated. This is other component that the coating must have, otherwise the viscosity would not be appropriate to be applied, so, the role of the solvent is to provide a suitable consistency to the pigment-resin solution such that it can be applied uniformly as a thin layer. Once on the surface, the solvent evaporates and the mixture becomes a pigment-resin system. Application properties of the paint usually are characterized by the vehicle in a liquid condition. The viscosity, rate of solvent evaporation, and consistency of the wet coating are most important during application. After application, the pigments determine the corrosion-inhibitive properties and, generally, the color and some flow control properties of the applied coating. To control other properties such as viscosity, opacity or storage stability the additives are added in small amounts. The binder determines the weatherability of the coating, its environmental resistance, and the coating's ability to function in a given environment. The required surface preparation, and often the application equipment and techniques, are also determined by the binder (Lambourne, 1999), (US Army Corps of Engineers, 1995).

The composition of a paint is indicated in Table 2.1 Composition of paints (Lambourne, 1999) which also indicates the function of the main components.

Table 2.1 Composition of paints (Lambourne, 1999)

	Components	Typical Function
Vehicle (continuous phase)	Polymer or resin (Binder)	Provides the basis of continuous film, sealing or otherwise protecting the surface to which the paint is applied. Varies in chemical composition according to the end use
	Solvent or diluent	The means by which the paint may be applied. Avoided in a small number of compositions such as powder coatings and 100% polymerizable systems.
Pigments (discontinuous phase)	Additives	Minor components, wide in variety and effect, e.g. catalyst driers, flow agents.
	Primary pigment (fine particle organic or inorganic)	Provides opacity, colour, and other optical or visual effects. Is thus most frequently used for aesthetic reasons. In primers the pigment may be included for anti-corrosive properties.
	Extender (coarse particle inorganic matter)	Used for a wide range of purposes including opacity/obliteration (as an adjunct to primary pigment); to facilitate sanding, e.g. in primer surfaces.

2.2. RHEOLOGY

The term rheology comes from the Latin words *Rheos* & *Logos* and means "Flux study", more exactly it is the science that studies the deformation and the matter flow. This science has a wide importance in a lot of materials, but in paints and coatings specially, is critical to the understanding and improvement of things like coating use, dispersion, application, thickness, stability, and quality control (Tracton, 2005) (Lambourne, 1999).

Figure 2.1 shows two parallel infinite plates with a fluid in between. If a uniform force is applied (F) on the higher plate, this one will start to move in constant velocity (v); the bottom plate is held rigid and the distance between the plates is h. Every layer of the liquid moves in the Y direction. The immediately adjacent liquid layer of the higher plate moves at the same velocity of that plate, but the next lower layer moves at a little bit lower velocity, and this goes on up to the latest layer if the layers are crossed in X direction. This phenomenon happens because of the molecules, the ones that are in the fastest layers tend to be more disorganized and some of them end up in the slower layer. Higher-speed molecules collide and accelerate the slower ones, just as the latter slow down faster molecules. The force (F) is proportional to the velocity (v) and the area (A) of the plates is inversely proportional to the thickness between the plates (h). If the liquid between the gap is ideal, the plate will continue to move at steady velocity (v) for as long as the force F is applied (Tracton, 2005) (Lambourne, 1999).

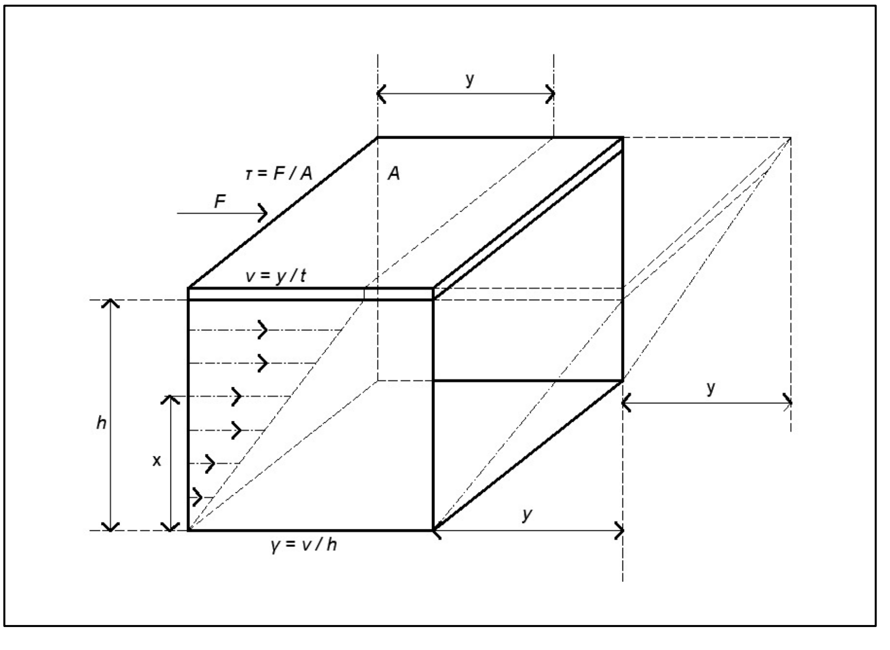

Figure 2.1 Simple shear experiment.

In 1687 Sir Isaac Newton established a hypothesis in his book "Principia" saying "The resistance which arises from the lack of slipperiness of the parts of the liquid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another", that is shown in Equation 2.1.

$$\frac{F}{A} = -\eta \frac{v}{h} \qquad (2.1)$$

Where η is the "lack of slipperiness" called viscosity of the fluid. This constant is a measure of the resistance of a liquid to flow, it is related with the coercion forces between the molecules. The more viscous is a fluid more difficult it would be to it to flow. New symbols are defined in Equation 2.2.

$$\tau = -\eta\dot{\gamma} \qquad (2.2)$$

This equation is the Newton's Law for viscosity, the force per unit area is called shear stress (τ). And the gradient of velocity is called shear rate ($\dot{\gamma}$) (Tracton, 2005) (Lambourne, 1999).

2.2.1. *Types of rheological behavior*

Fluids that obeys the Newton law of viscosity (Equation 2.1) are called "*Newtonian fluids*" where exist a linear relation between the shear stress (τ) and the shear rate ($\dot{\gamma}$). This means that the viscosity (η) is independent of the shear stress (τ) applied to cause the liquid to flow. In the case of "*Non-Newtonian fluids*" the relation between the shear stress (τ) and shear rate ($\dot{\gamma}$) is not linear, that means that the viscosity (η) does not stay constant and instead of it they are in function of the shear stress (τ).

There are different types of non-Newtonian fluids according to the relation "*shear stress/shear rate*". Figure 2.2 shows the shear stress-shear rate curve for Newtonian and non-Newtonian fluids (Tracton, 2005).

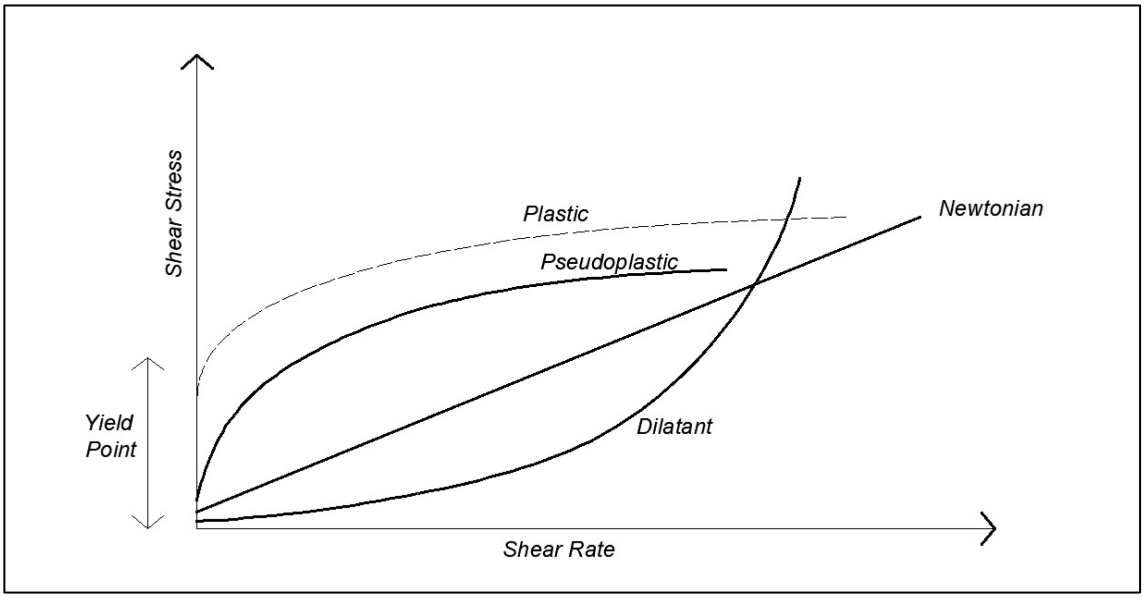

Figure 2.2 Diagram of the shear stress-shear rate for Newtonian fluids and non-Newtonian fluids independent of time.

These behaviors can also be represented as a relation between the viscosity and the shear rate to obtain the viscosity curve, this representation was shown in Figure 2.3.

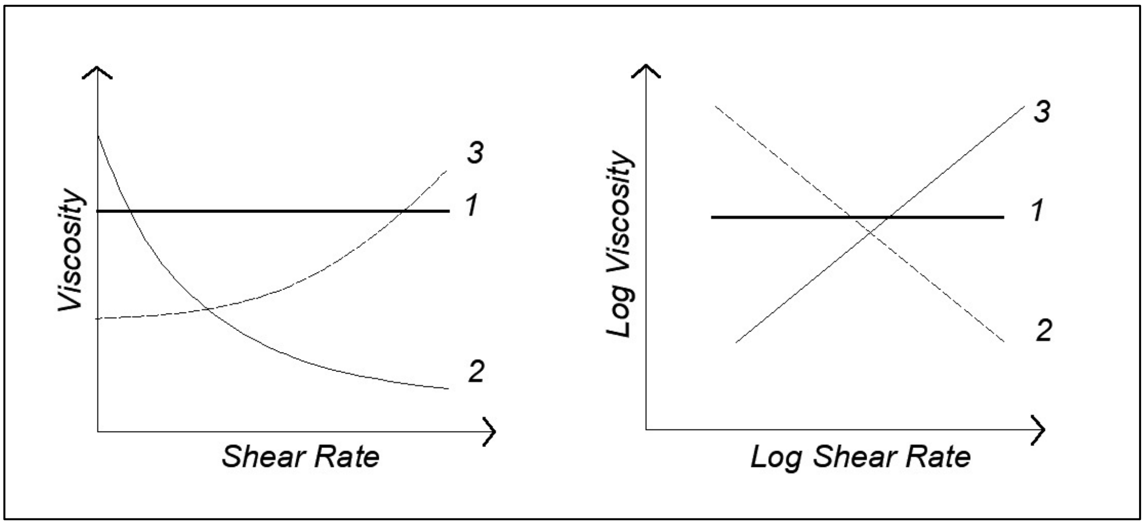

Figure 2.3 Viscosity curve for 1) Newtonian, 2) Pseudoplastic and 3) Dilatant substances.

Plastic

Rheologically speaking, are the easier kind of fluids to study, they behave more like plastic solids until the yield point is reached, the yield value is the minimum shear stress needed to produce that a liquid flow. If the shear stress applied is less than the value of yield point the liquid will deform but it will not flow, behaving as an elastic solid; the value of viscosity will tend to infinite. This value is of great importance to produce "no-drip paints", and to understand the behavior of coatings after they have been used. If the yield value is greater than the shear stress that gravity produces it will behave as a solid and it will not flow (Tracton, 2005). In Figure 2.2 was shown its behavior.

Pseudoplastic

Pseudoplastics drops in viscosity as shear stress is applied, just like plastic fluids without the yield point. As the shear rate is reduced, viscosity increases at the same rate. There is not hysteresis, the curve of shear rate-shear stress is the same increasing and decreasing.

Many coatings exhibit this type of behavior, with the particularity that they are time dependent (Tracton, 2005). This pseudoplastic behavior is shown in Figure 2.2 and Figure 2.3.

Dilatant

These ones are defined as the fluids that increase their viscosity value as shear stress is increased. There are very few liquids that possess this property. In Figure 2.2 and Figure 2.3 is shown their behavior (Tracton, 2005).

Thixotropic

This is a special case of pseudoplasticity because it is time dependent. As shear rate is reduced, viscosity increases at a lesser rate to produce a hysteresis loop. This property is used to produce "no-drip paints". In Figure 2.4 the hysteresis loop is shown (Tracton, 2005).

Rheopectic

This property is the opposite of thixotropy. It is time dependent too but an increase of shear stress produces an increase of viscosity, it has a hysteresis loop too and as a proper opposite it is useless as a characteristic for paints and coatings. In Figure 2.4 the hysteresis loop is shown (Tracton, 2005).

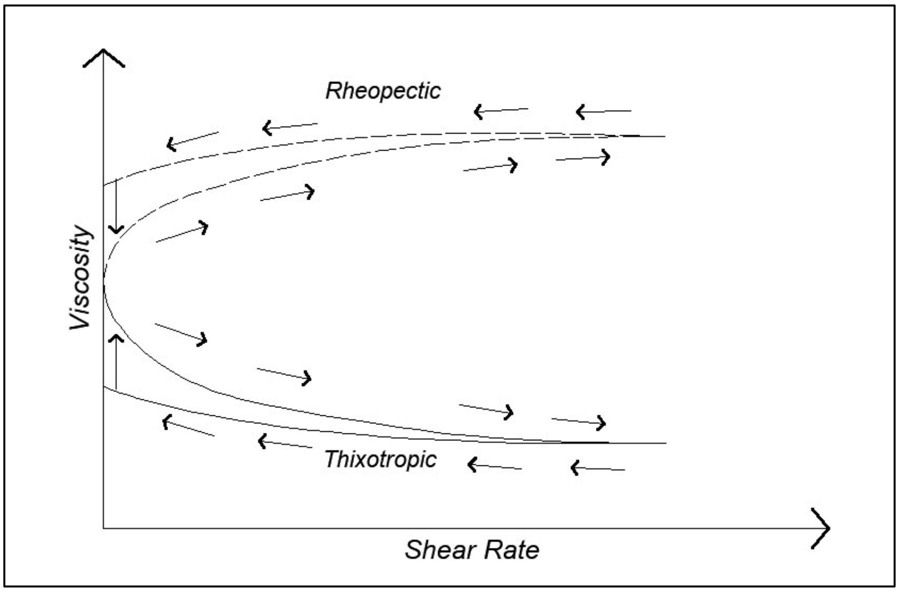

Figure 2.4 Viscosity vs Shear Rate curves: hysteresis loops.

2.2.1.1. Mathematical models

To compare samples that are similar the mathematical models are used, that are functions that approximates to the curve and are used to describe the viscosity curve using a small number of curve parameters. Using this mathematical model, the comparison between the samples is reduced to just compare these parameters, instead of comparing point by point. (Bohlin Instruments, 1994) (Moolman, 2003)

There are a few of different models but not everyone can be used in every case, that is why is important to pay attention to the correlation ratio, if this indicates that there was not enough agreement between the test data and the model function it is better to try another model. It is important to not forget that the parameters that comes out of the function are purely mathematical variables, and, even if the correlation ratio is high, they could not directly represent rheological parameters (Moolman, 2003) (Bohlin Instruments, 1994).

A wide number of models exists; therefore, the type of flow behavior should be examined first to determinate which model to adopt. As paints are pseudoplastic fluids that exhibits an “infinite” viscosity until sufficiently high stress is applied to pass the Yield Point, the most common models used in this area are the Bingham, Casson and Herschel-Bulkley Models (Moolman, 2003) (Bohlin Instruments, 1994).

In this work these three models were adjusted to the curves that were obtained in order to be able to compare them.

- **Bingham Model**

The Bingham Model follows the Equation 2.1

$$\tau = \tau_B + \eta_B \dot{\gamma} \qquad (2.1)$$

This is a flow curve model function where the shear stress is a function of the shear rate, including the "Bingham yield point" τ_B

η_B should not be confused with a viscosity value, it is only a calculated coefficient used for the curve approximation and is referred to as the "Bingham flow coefficient". (Moolman, 2003) (Bohlin Instruments, 1994)

The Casson Model

The Casson model is given by the Equation 3.2

$$\tau^{\frac{1}{p}} = \tau_C + (\eta_C \dot{\gamma})^{\frac{1}{p}} \qquad (3.2)$$

This is a flow curve model function where the shear stress is a function of the shear rate, including the "Casson yield point" τ_C, and the "Casson viscosity" η_C that follows the same consideration of the "Bingham flow coefficient" that was mentioned before (Moolman, 2003)

- **The Herschel-Bulkley Model**

The Herschel-Bulkley model is given by the Equation 3.3

$$\tau = \tau_{HB} + \eta_{HB} \dot{\gamma}^p \qquad (3.3)$$

This is a flow curve model function where the shear stress is a function of the shear rate, including the "Herschel-Bulkley yield point" τ_{HB}, and the "Herschel-Bulkley viscosity" η_{HB} and the exponent p also called "Herschel-Bulkley index" (Moolman, 2003)

2.3. VISCOELASTICITY

Most materials are not purely viscous and often show significant elastic behavior. In the nineteenth century, some scientist began to have doubt about matter that did not behave ideally viscous or ideally elastic because their behavior could not be described by Newton's law (liquid-like) neither by Hooke's law (solid-like). These intermediate substances have a key parameter, time, that determines whether viscous or elastic behavior will prevail. Those substances are the viscoelastic, also called complex fluids or, in more moderns-day terms, Maxwell fluids; coatings are Maxwell fluids. (A. Franck, TA Instruments Germany, 1993) (Moolman, 2003).

Measurements in the elastic region provide information about the materials internal structure, e.g. molecular or physical structure; and in the viscous region information about the flow behavior, important for processing (e.g. extrusion, mixing, pumping, leveling, etc.) is obtained (A. Franck, TA Instruments Germany, 1993).

The rheological material behavior can be measured as a function of time, temperature, strain or stress amplitude and frequency. The results obtained provide information about the sample structural properties such as molecular weight, molecular weight density, concentration, crosslinking density for polymers or particle/domain size, shape, interface properties, etc. for multiphase fluids. This information is important in product development to predict product performance and processing behavior of new or modified materials. The general rheological behavior in an oscillation experiment can be described with the Maxwell model (A. Franck, TA Instruments Germany, 1993).

The shear storage modulus or elastic modulus (G') gives information about the amount of structure present in a material. It represents the energy stored in the elastic structure of the sample. If it is higher than the shear loss modulus o viscous modulus (G'') the material can be regarded as mainly elastic. The shear loss modulus (G'') represents the viscous part or the amount of energy dissipated in the sample. The 'sum' of the shear loss and storage modulus is the so-called shear complex modulus G*. In Figure 2.5 is graphically represented how the shear storage modulus (G') and the shear loss modulus (G'') contributes in a vector way to the shear complex modulus (G*) (A. Franck, TA Instruments Germany, 1993).

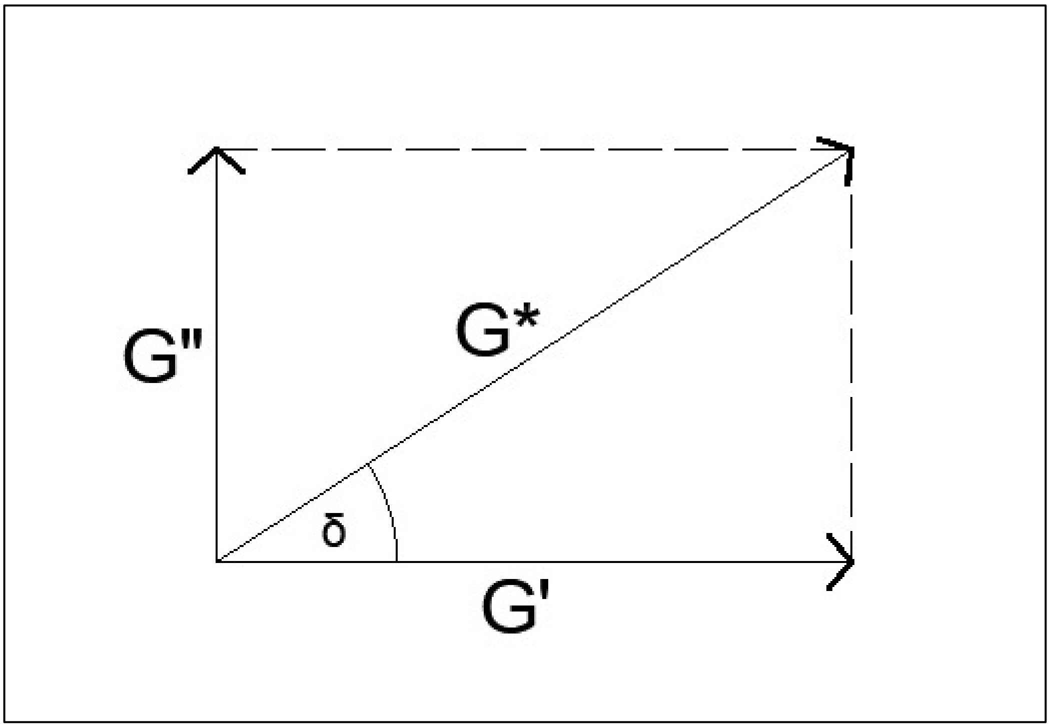

Figure 2.5 Sumatory of the loss modulus (G'') and storage modulus (G') results in complex modulus (G).*

The phase angle (δ) is a measure of the amount of elasticity present in a sample. A material is equally elastic and viscous if the phase shift is 45^{o} or tan δ =1; for an elastic material it would be zero, and for a totally viscous material it would be 90 ^{o}. For a viscoelastic material the phase shift for the strain is between 0^{o} and 90^{o} (A. Franck, TA Instruments Germany, 1993) (Bohlin Instruments, 1999).Tests Types

2.4. TESTS

Using the rheometer, there is a lot of information that can be taken besides the viscosity of a substance, this data can provide information about the character of the sample as well.

Some behavior of coatings that can be predicted from rheometric data are:

- Sedimentation of particles in a suspension
- Levelling due to surface tensions
- Sagging under gravitational forces
- Tube or pipe-line flow

- Mixing, stirring
- Painting, brushing, spraying
- Wet grind of pigments
- Rolling and high-speed coating.

As it was explained before, during the life of a coating, since it is manufactured until it is completely dried on a surface, there are different forces that acts over it that variates from very small shear rates of $10^{-6}s^{-1}$ to very high shear rates of $10^{6}s^{-1}$. To simulate them accurately, several rheometric techniques exist (Moolman, 2003).

There are enough tests type to obtain representative information about the different properties of each sample but the results obtained could be inconclusive if the parameter settings are not performed properly. Some of the parameter that must be taken into consideration during the test are: time duration of the test, temperature profile and data point distribution.

2.4.1. Standard rotational test

This test was mostly used to obtain the flow and viscosity curves, it relates the flow and viscosity behavior to a wide range of shear rates. The test consisted in the deformation of the sample by confining the material between the walls of the measuring instrument and by setting up a velocity gradient across the thickness of the material causing it to flow. In more practical words it showed the behavior of the samples when they were exposed to different conditions, simulating the ones to which the coatings are exposed during their life. It is a destructive tests that impose a constant shear rate or stress or an increasing form and it is possible to see how it resists to flow (Barnes, 2000) (Lambourne, 1999).

2.4.2. Standard oscillatory test

When what it is wanted was to test the viscoelastic behavior to investigate the character of the sample it was advisable to use an oscillatory technique. This technique applied a stress or strain whose value is changing continuously according to a sine wave equation; the response followed a sine wave too. During the test, the sample is continuously excited but is not destructed because a certain value of strain, indicated by the end of the low viscoelastic range (LVER), is never exceeded. If the strain were exceeded the elastic internal structure of the material would be destructed, so it was important to keep the strain low (Bohlin Instruments, 1994) (Moolman, 2003).

2.4.2.1. Amplitude Sweep test

Using a standard oscillatory test it was possible to see the amplitude sweep, graphicly shown in Figure 2.6, this allows to investigate the character of the sample, it helped to saw if in the small amplitudes, along the low viscoelastic range (LVER), the sample would behave more as a solid when G’>G’’ or as a liquid if G’’>G’. It was also helpful to determinate the limit of the LVER, that value was of great importance because it means that, from this point on, the internal structure of the sample was destructed. Finally, this would be used to determinate in a more accurate way the yield point of the sample, there are two interpretations of the yield point (Moolman, 2003) (Bohlin Instruments, 1999)

- τ_{Y1}: When there was a deviation of 10% of the G' curve from the constant plateau values in the LVER
- τ_{Y2}: When there was a cross-over point between the two modulus, when G" > G'.

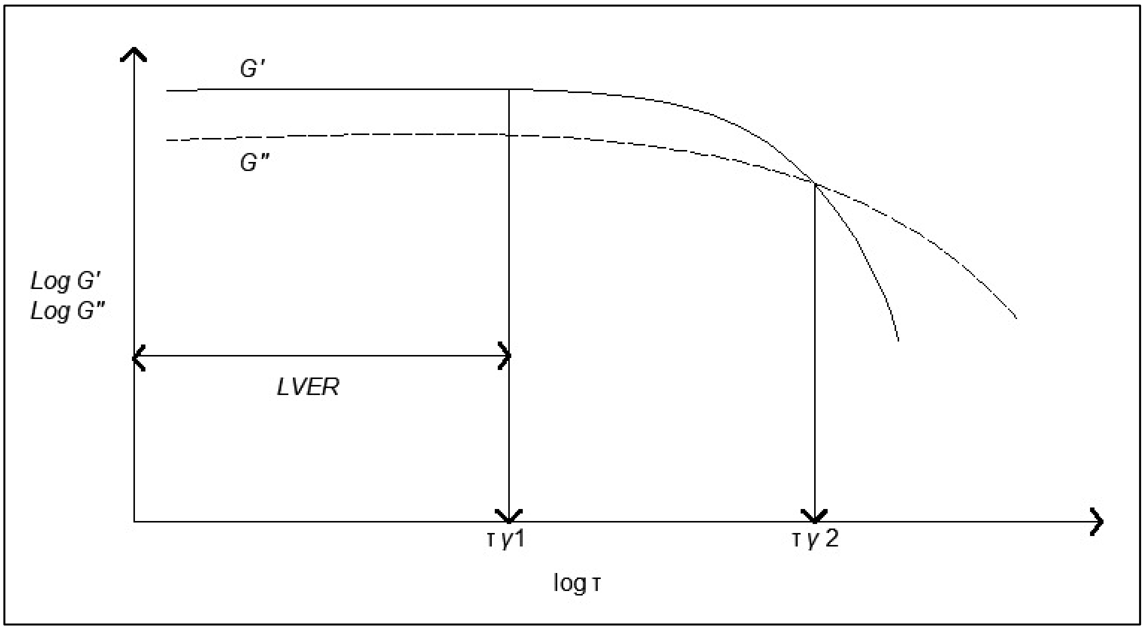

Figure 2.6 Determination of the yield point from amplitude sweep.

2.4.2.2. Frequency Sweep test

As it was explained before, it is not accurate to state that a substance is purely elastic or purely viscous, because when a wide variety of stress is applied over a wide variety of time or frequency, is possible to observe a liquid like behavior in solids and a solid like behavior in liquids. This type of test provides information about the internal structure of a sample studying the viscoelastic properties as a function of frequency (Moolman, 2003) (Bohlin Instruments, 1999).

As standard rotational tests are not that accurate at low shear stress, the frequency sweep can be used instead of it to determinate the behavior of the sample below its yield point. It provides several information of G’ that can be used to determinate the behavior of the sample at rest (Moolman, 2003).

The relation between G’ and G’’ gives an indicative of the character of the sample the liquid like behavior of a substance (G’’) and the solid like behavior (G’) in the low and high frequency ranges. The high frequencies have implications on the short time scale behavior, and the low frequencies has implications on the long-time scale behavior Coatings suffers of both of frequencies low and high, during storage (long time) and application (short time), therefore the correct interpretation is the great importance in the paint industry.

2.4.3. Combinations

In some cases, the combined use of the rotational and oscillatory tests is needed, using their advantages to obtain important data, as it is the case of the three-interval-thixotropy-test.

2.4.3.1. Three-Interval-Thixotropy-Test (3ITT)

This test is special because, in order to perform it is necessary to mix the oscillatory and the rotational tests, and it allowed to investigate the thixotropy behavior of the sample. It is a simulation of the application process of a coating, and the three intervals went as follows:

1. Low shearing: to investigate the original structure of the sample before the application using a standard oscillatory test.
2. High shearing: a high shear load is applied to simulate the process of application of the coating, the internal structure is destructed and the original viscosity fall. For this stage it was used a standard rotational test, because it can apply a high shear load in short time.

3. Low shearing: to investigate the recovery along time of the internal structure without destroying it was used a standard oscillatory test.

The oscillatory mode in the low shearing phases, one and three, gives values of the elastic and viscous modulus that gives information about the character of the sample. The other advantage that this mode presented is that an almost zero shear load can be applied that does not destruct the internal structure and the sample is “at rest”.

The rotational mode presents the advantage that it can perform better the interval of high shear simulating more accurately the application of the coating.

In Figure 2.7 a typical graphical representation of this test is shown.

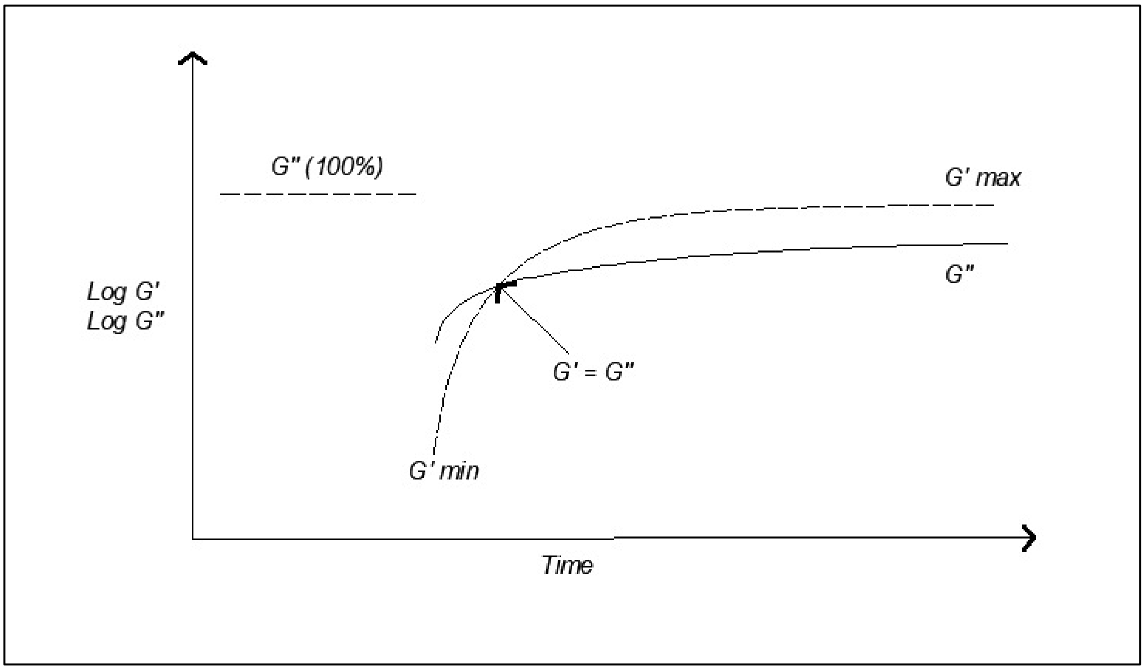

Figure 2.7 Typical G’ and G’’ representation of a Three-Interval-Thixotropic-Test.

The data interpretation is as follows:

- If on the third interval exists a crossover point (G’=G’’) it is important to know the time until the crossover point. If during the first interval the solid like behavior predominates over the liquid like behavior (G’>G’’) and during the third interval is the contrary in the beginning is important to examine this in order to explain the levelling and sagging behavior of the paint.
- On the third interval, when G’’>G’ a liquid like character predominates over the solid like character, this means that the sample can flow over its own gravity to fill hollow spaces, can flow after the application and avoid brush marks, allows to

the air to scape to achieve a proper degasification the film. This could be bad also, because it could lead to dripping paints, so the period while G’’>G’ shouldn’t be long, but a structural recovery that is too fast could lead to poor levelling and insufficient layer thickness.

- When G’>G’’ a solid like character predominates and sagging of paint is limited on the third interval, the layer thickness is ensured and the separation of the components is prevented.
- Exists various methods to analyze the structural recovery of a sample, in this case it was taken in account the percentage of regeneration after a predetermined time, comparing the values of G’ after one minute of applying the high shear load with the ones obtained during the first interval.

3. AIMS OF THE WORK

Paints and coatings are not free of optimizing process for their end use performance, in practice, to achieve this outcome it must be improved their rheological behavior. This includes optimizing their leveling behavior, pigment dispersibility, sag resistance, applicator loading and film thickness (Lambourne, 1999) (Moolman, 2003).

Besides the influence of the shear rate on rheology behavior, there are also shear rate dependent phenomena that have to be considered which are time dependent, such as thixotropic behavior. In addition, elastic behavior may occur, which can influence the flow properties (Lambourne, 1999) (Moolman, 2003).

After all that said, it is proper to assume that paint will respond very differently to these different forms of stress. Rheology is used to investigate and improve all these properties in the different processes in the coating industry (Lambourne, 1999) (Moolman, 2003).

In addition, there is new legislation to control emission to the atmosphere and safety at work is also increasing. Such legislative pressure is increasing in industry throughout the world. In Portugal, the use and disposal of organic solvents is subject to a set of legal requirements related to health, safety and environment issues. It is the Decree-Law no. 127/2013, of 30 August the one that establishes that the industrial emissions regime has limitation of the emission of volatile organic compounds resulting from the use of organic solvents, as well as the rules intended to avoid or reduce emissions to air. The consequence of such pressure is to limit the freedom of choice of both paint formulators and users. Two trends which have emerged from such limitations are the move towards higher and higher solids paints, to decrease the solvent to be eliminated in the formation of the solid paint film, and towards water-based paints. The inevitable result of such trends is paint with more complex rheological properties than before, both in the bucket and in the film (Lambourne, 1999) (Moolman, 2003). (Ministério da Agricultura, do Mar, do Ambiente e do Ordenamento do Território, 2013)

The objectives of this work were:

- Evaluate the rheological properties of the sample coatings that were provided by the company “Tintas Europa”.
- Investigate the properties that an ideal coating should have.

- Modify the composition of the provided coatings in order to improve their performance.
- Study the effect of the modification of some components (additives) over the rheological properties of the coatings.

4. MATERIALS AND METHODS

4.1. THE SAMPLES

The company “Tintas Europa” provided us samples of two lines of coatings that they produce, called “Supramate” and “Newplaste”. This samples were extensively tested in order to know the differences between them and try to approach to the competitor’s one, that was also tested.

In order to protect the privacy of the company and the safety of the formulation of the coatings, the exact compositions of “Newplaste” and “Supramate” are not specified in this document.

4.1.1. Supramate Sample

The coating “Plastine SupraMate” is based in water dispersions of synthetic resins and pigments of good resistance to light and alkalis. This product is ideal, because its characteristics of beauty and the property of being easy to clean make of this product a perfect option to be used as interior decoration. Is easy to apply, with a fast drying, and a good white color. It can be applied over any kind of indoor and outdoor surfaces of cement or cast as long as they were properly prepared to be painted (Tintas Europa, 2017).

In its composition it had an 0.8478% of a mixture of three thickeners, “Hecellose B 15K”, “Tafigel Pur 44” and “Aquaflow NHS 300”.

Hecellose B 15K, is a nonionic, water-soluble polymer from wood pulps or cotton linters that can be used for rheological modifier in water-based paints. It has excellent bio-stability in solution against enzymatic attack. It provides good pseudoplastic flow and wide compatibility with colored pigments, emulsion polymers, surfactants, emulsifiers, defoamers, and preservatives. (Lotte Fine Chemical)

Tafigel Pur 44 is a rheology modifier that is designed as an “associative thickener” which builds up and stabilizes viscosity by forming a network between polyurethane, binder molecules and pigment particles. (Munzing Chemie GmbH, 2017)

Aquaflow NHS300 is a solvent-free, nonionic synthetic associative thickener designed for waterborne paints and coatings, it provides efficient viscosity development, excellent film build and favorable brush drag. (Ashland Speciality Ingredients, 2013)

4.1.2. Newplaste Sample

The coating “Newplaste” is based in a water dispersion of synthetic resins, that allows the client to obtain a matte finishing with decorative properties. This product is ideal because of its beauty, it is easy to clean to use as indoor decoration, and because of its properties of resistance to atmospheric agents and a high resistance to light is also a good option to outdoor decorations. Is easy to apply, fast drying that allows the client to give even two layers of product per day, good cover, it also has antifungal and antibacterial properties. (Tintas Europa, 2017)

In its composition it has an 0.6123% of a mixture of two thickeners, “Hecellose B 15K”, and “Rheolate 278”.

Rheolate 278 is a thickener that improves the rheology of the coating, giving superior high-shear viscosity, enhances the film building and provides an excellent brush drag. It also imparts a superior flow and levelling, reduces spattering during roller application, gives a good colour acceptance, is enzyme resistant and is also easy to incorporate. (Elementis Specialties, Inc., 2018)

4.1.3. Sample A

The sample named A was a modification of Supramate. Only the percentage, quantity and variety of thickener varied, while the other components remained in the same proportion as those present in the Supramate sample. Sample A had just 0.36% of “Hecellose B 15 K” as a thickener, so it is expected to not have a high viscosity.

4.1.4. Sample C

The sample named C was a modification of Supramate. Only the percentage, quantity and variety of thickener varied, while the other components remained in the same proportion as those present in the Supramate sample. Sample C had 0.36% of "Hecellose B 15 K" and an added 0.54% of "Tafiguel Pur 44" that is a rheology modifier for aqueous systems as thickeners. It had in total 0.9% of thickener in its composition.

4.1.5. Sample D

The sample named D was a modification of Supramate. Only the percentage, quantity and variety of thickener varied, while the other components remained in the same proportion as those present in the Supramate sample. Sample C had 0.36% of "Hecellose B 15 K" and an added 1.4% of "Rheolate 278" that is an associative polyurethane-based thickener for Latex Paints. It had in total 1.76% of thickener in its composition, so it is expected to have the highest viscosity of all samples that are produced by the company.

4.1.6. Competitor Sample

The sample of the competitor is from a paint that has similar characteristics to Supramate and Newplaste. But, according to the clients opinion that was proportionated to the company, they choose first the competitor brand instead of the ones form Tintas Europa because it is easier to use.

4.1. THE RHEOMETER

All tests were made using a CVO Bohlin Rheometer that is an instrument designed to provide accurate rheological measurements on a wide variety of materials.

This sophisticated machine, shown in Figure 4.1, consists of a small unit, capable of taking a number of different measuring geometries and also has a temperature control unit. It offers a wide range of measurement capabilities in a single integrated package. The control of this instrument is by software application that works on a standard computer connected to the electronics control box (Bohlin Instruments, 1999).

Figure 4.1 CVO Bohlin Rheometer that was used to do all the measures

4.1.1. Measuring system

The nature of the sample and the type of test determine the ideal measuring system. In the case of coatings, the cone and plate system is recommended (Moolman, 2003).

In practice this is the ideal measuring system, it is really easy to clean, it has homogeneous shear conditions because in the entire conical gap the shear rate is constant and also it just requires a little amount of sample volume. (Moolman, 2003) (Bohlin Instruments, 1994).

As it is shown in Figure 4.2 this measuring system consists of a bob with a conical surface and a fixed plate with a flat surface. The CP4/40 is a 40mm diameter cone that has an angle of 4°. The cone is truncated, because by removing the tip of the cone a more robust measuring geometry is produced. (Bohlin Instruments, 1994).

Since strain and shear rate are calculated using the angular displacement and the gap it follows that the smaller the cone angle, the greater the error is likely to be in gap setting and hence the results, by using a relatively large angle (4°) it becomes easier to get reproducibility of gap setting (Bohlin Instruments, 1994).

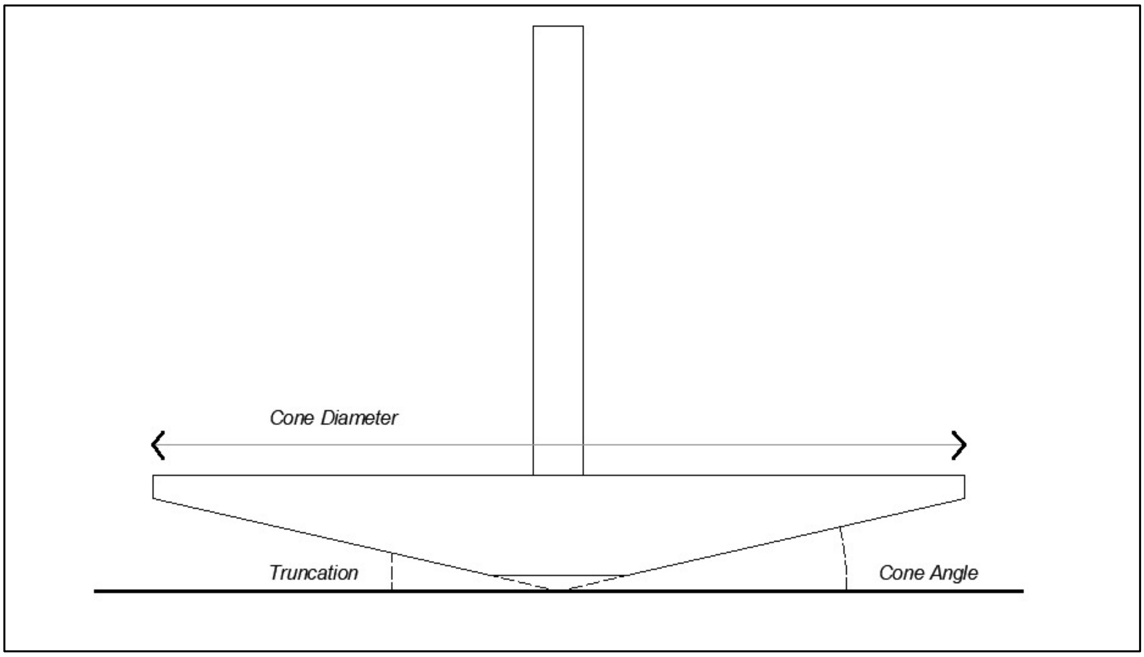

Figure 4.2 The cone and plate measuring system.

4.2. THE TESTS

Before the tests are even performed is important to know the samples and its chemicals and physical specifications, in order to apply the proper parameters and avoid the misleading of the interpretation of the data that was obtained. (Moolman, 2003)

Below, the data interpretation of the most frequently used test types:

4.2.1. Viscosity curves

Coatings have complex structures and therefore complex flow behavior; they cannot be described by only one viscosity value, because most coatings show pseudoplastic behavior (Moolman, 2003). To perform this test, all samples were stirred two minutes before starting it, to simulate the process before application that was done by the clients. The test was repeated six times to ensure that the results were constant. It was used a standard rotational test in the rheometer, using as parameters a controlled shear rate with a minimum of 0.0716 s^{-1}, the minimum shear rate admissible in the system, and a maximum of 900 s^{-1} at a temperature of 25ºC. The tests lasted ten minutes where the shear rate increased logarithmically from the minimum to the maximum.

4.2.1.1. Influence of thixotropy in the viscosity curves

To investigate the influence of the thixotropy and evaluate the performance of the coating at low shear rates when it was at rest, simulating the storage phase, a similar test was performed. In that case, three samples, Supramate, Newplaste and Competitor, were stirred 24 hours before performing the test, to guarantee the homogeneity of the samples, and it stayed at rest until the test was performed. In a different day the same samples were stirred for 5 minutes and had 2 minutes of rest before the test was made. The conditions of the rheometer were the same as the previous phase, it was used the viscometry test in the rheometer using as parameters a controlled shear rate with a minimum of 0.0716 s^{-1}, the minimum shear rate admissible in the system, and a maximum of 900 s^{-1} at a temperature of 25ºC. The tests lasted ten minutes where the shear rate increased logarithmically from the minimum to the maximum.

4.2.2. Amplitude sweeps test

To obtain the limits of the low viscoelastic range (LVER) the viscous and elastic modulus were measured, the samples were stirred for two minutes before performing the test to simulate the conditions of the coating before being applied. This test was repeated six times in each sample to guarantee the representativeness of the obtained data. In a standard oscillatory test mode and a controlled strain, the conditions were: a minimum deformation of 1% and a maximum of 100%, a frequency of 1Hz and a temperature of 25ºC. The tests lasted three and a half minutes each.

4.2.3. Frequency sweeps test

In order to evaluate the solid and liquid-like behavior of the samples and therefore their internal structure, the frequency sweep test was performed. To perform it, the samples were stirred for two minutes before being tested to simulate the conditions of the coating before being applied. This test was repeated six times in each sample to ensure the representativeness of the data. Using a standard oscillatory test, the parameters were: a minimum frequency of 0.1 Hz and a maximum of 20 Hz, and a controlled stress of 6 Pa, in a temperature of 25 ºC. The test lasted four minutes and twenty seconds each.

4.2.4. *Three-Interval-Thixotropy-Test (3ITT)*

This test allows to investigate the thixotropy behavior of the sample, that refers to the decrease of the viscosity while a constant shear load is applied and after recovery of the sample during a rest phase. This test was repeated six times for each sample in order to guarantee that the data was reliable. This test in the end simulates the application process of a coating using three intervals as follows: (Moolman, 2003)

1. Low shearing: to investigate the original structure of the sample before the application. A standard oscillatory test was used, with a maximum shear stress of 6 Pa in order to not destroy the internal structure of the sample at rest, simulating the stage where the paint was stored in the can or waiting to be used, and also to knew the initial elastic modulus to compare with the one that was obtained in the 3rd interval.
2. High shearing: a high shear load is applied to simulate the process of application of the coating, the internal structure is destructed and the original viscosity fall. A standard rotational test was used, applying a shear rate of 1000 s^{-1} for 1 minute it was possible to simulate the application process that was performed by the painters.
3. Low shearing: to investigate the recovery along time of the internal structure. A standard oscillatory test was used, with a maximum shear stress of 6 Pa in order to not destroy the internal structure of the sample that is being recovered by the thixotropy.

In Figure 4.3 the input data of the test is given:

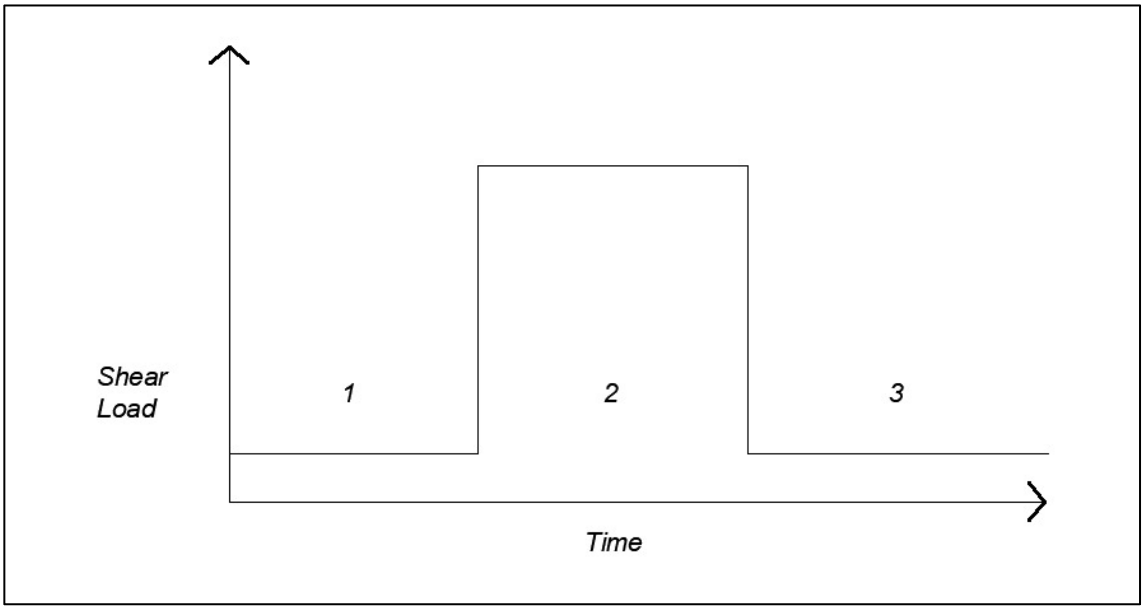

Figure 4.3 Test method of the three-interval-thixotropic-test.

This test is special because, to perform it, is necessary to mix the oscillatory and the rotational test, for the low shear intervals the oscillatory mode is used and for the high shear interval a rotational mode is used. The advantage of performing this test in this combined mode is that the oscillatory mode gives values of G' and G'' so it is possible to obtain more information about the character of the sample; it also has the advantage that, during the low shear interval, an almost zero shear can be applied so the sample is "at rest", the structure is not destructed and the measure of the recovery is better. On the other hand, the rotational mode has the advantage that can perform better the high shear interval simulating more accurately the application of the coating.

5. RESULTS AND DISCUSSIONS

5.1. VISCOSITY CURVES

Traditionally, the viscosity curve is always regarded to be the most important parameter in rheology as it immediately gives an indication of the substance's resistance to flow. As paints are viscoelastic fluids just this parameter is not enough but is always useful.

The viscosity curves of the coatings were presented in Figure 5.1

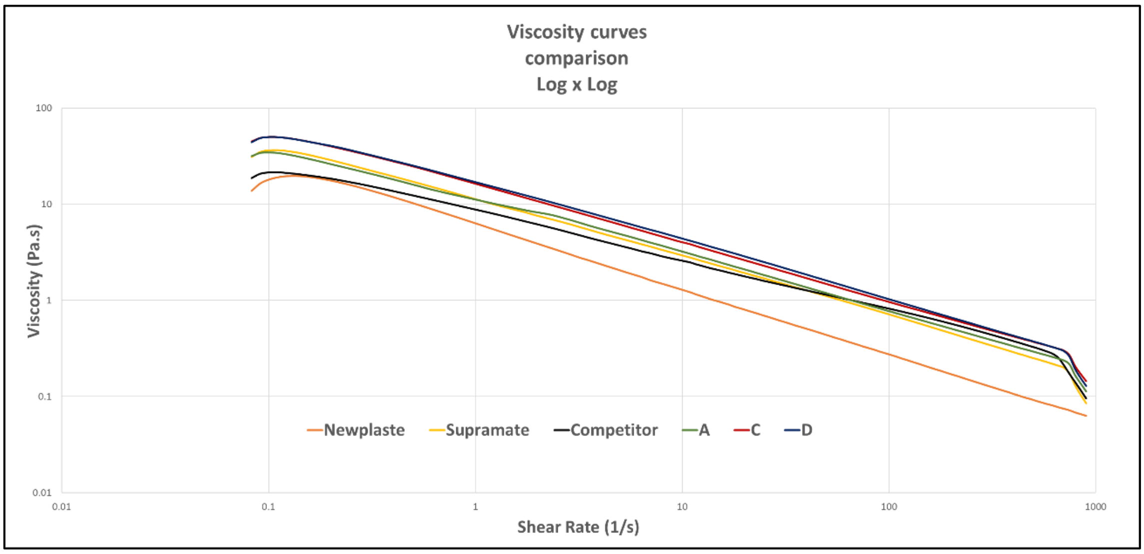

Figure 5.1 Viscosity curves comparison. Viscosity vs Shear Rate.

The test was stopped at a maximum value of shear rate of 900s^{-1} because, as it is possible to see in the graphic in samples Supramate, Competitor, A, C and D, the curves fell, but they fell because the sample that was charged in the rheometer started to spatter, so in the end there was no sample under the cone plate.

The slopes of the samples Supramate, A, C and D were equals, as it was the same sample with just some modifications in their composition. As it was expected, the viscosity of A is lower than C and D, because it has a lower thickener percentage.

The slope of Newplaste was also similar to Supramate and its modifications but a little bit higher, its viscosity was visibly the lowest, even lower than the sample A.

The slope of the Competitor was similar but a little bit higher than all the other samples, it is possible to see this because there is a cross over point between the lines at high shear rates.

As it was shown in (Thermo Fisher Scientific Inc, 2019), the commercial paints exhibited a significant shear thinning behavior. As it happened in their experiment, our coatings had a relatively high viscosity at the beginning of the experiment, close to 200Pa.s in theirs and to 100Pa.s in ours, and its viscosity continued to decrease as the shear rate was increased, arriving to values that were close to 0.5Pa.s in both cases.

During the life of a coating this will go through different shear rates, the viscosity curve represented how the viscosity reacted to these forces. The differences along the low and high shear rate was explained in (Malvern Instruments Worldwide, 2015), that states that a higher viscosity along low shear rates implies that the sample is more stable after the application, that means that it would be less likely to drip.

In (Thermo Fisher Scientific Inc, 2019) was stated that during processing, the pumpability and energy required for mixing and transport directly correlates with its viscosity at medium-to-high shear rates (10 to 1000 s-1). Finally, during application (brushing, rolling, spraying, etc.), the paint will be subjected to high shear rates (>100 s^{-1}) where it is expected to behave as a relatively low viscosity, free-flowing liquid

In Figure 5.1 the sample Competitor presents a lower viscosity at low shear rates, compared to samples Supramate, A, C and D; so according to the characteristics explained before, the samples with the higher viscosity would be better than sample Competitor. At higher shear rates there is a cross over point, where the viscosity of Competitor is higher than the viscosity of samples A, Supramate and Newplaste and very similar to samples C and D.

5.1.1. Influence of thixotropy in the viscosity curves

If a fluid has an internal microstructure it can present a thixotropic behavior, this will reflect the time that takes to move from one state of microstructure at rest to another and back. This time can be different in every sample, to prove this this comparison was made. This test had the same parameters as the test made in Section 4.1 and the graphic comparisons were shown in Figure 5.2

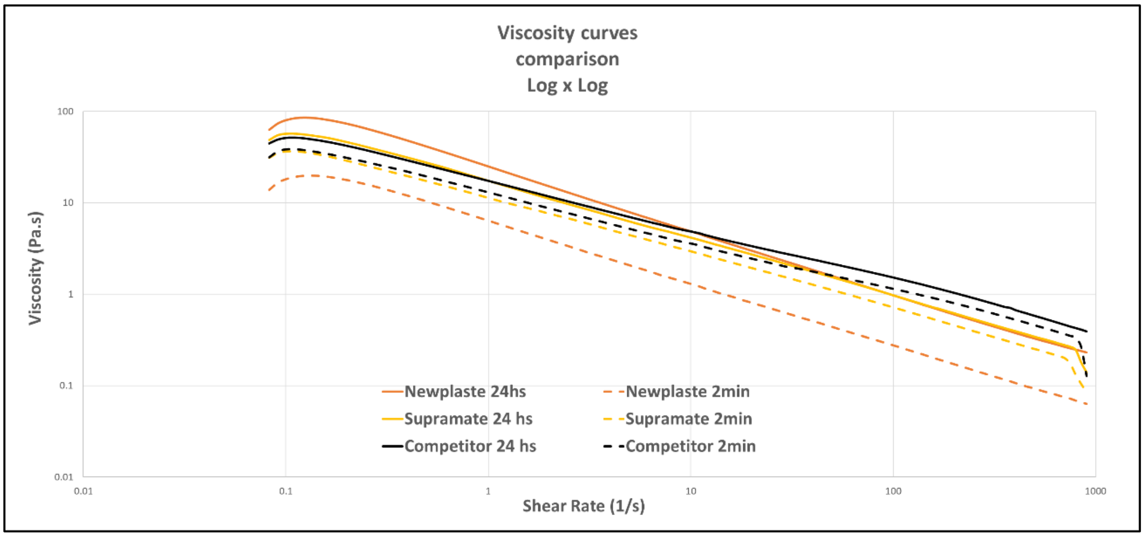

Figure 5.2 Comparison of the viscosity curves after 2 minutes and 24 hours of rest before the test, Viscosity vs Shear Rate

It is clear that there were differences between the viscosity curves when the time of rest was higher. The sample Newplaste presented a bigger difference between the two viscosity curves than the others. (Malvern Instruments Worldwide, 2015) says that applying shear to a structured material reduces its viscosity, and, in general the breakdown and subsequent recovery of any such structure does not occur instantaneously but can take some finite time - the longer the breakdown or recovery process takes, the more thixotropic the material is.

As it is explained in (Thermo Fisher Scientific Inc, 2019), the shear thinning behavior of paint is crucial to its performance and products are formulated with this ideal flow behavior in mind. When exposed to low shear conditions (mainly due to gravity), as those experienced during transport and storage, having a high viscosity helps maintain product consistency and keep particles from settling out of suspension as it is the case of phase separation. Also, a higher viscosity at low shear helps prevent the paint from running or streaking after it has been applied to a vertical surface like a wall. However, contrastingly, under the intermediate shear conditions during processing, the paint should be readily flowable and exhibit a medium-to-low viscosity making it easy to mix, pump, transport, etc. Under high shear application, the paint should be even lower in viscosity making it relatively effortless to be applied using brushes and rollers, and should even have the ability to be sprayed through a nozzle. Studying the paint behavior over a broad, shear-rate range is essential for assessing its true quality across its entire lifespan from storage to final usage. In this test, to compare the behaviors of the coatings and to stablish the behavior of them at storage, the time of rest of the samples was different, one took 24 hours of rest and the other just 2 minutes. This graphic allows to state some important facts about the samples tested.

- When the sample is at rest, stirred 24 hours before, it could be stated that is a representation of the sample when is in storage, the viscosity at low shear rate should be high, to prevent sedimentation. In this case sample Newplaste presented the best characteristic
- When the paint is going to be applied by the costumer the viscosity should be low, for a better and easier process, when the sample was stirred two minutes before of performing the test, the moment when the costumer stirs the paint before applying was represented. In this case, the sample with the lowest viscosity after two minutes of rest was also Newplaste. This sample also had the highest slope in the curve, that meant that the viscosity would decrease faster during the application.

The thixotropy recovery after application was also important to study, because it is the responsible of the process of levelling and proper drying, that was explained in detail in Section 5.4

5.1.2. Modelling

After obtaining the flow and viscosity curves, it was possible to apply some mathematical models to know an approximate value of the yield point, it was important to state that those values were only mathematical and as it will be shown later, not always the ones with the highest value of correlation ratio were the most accurate.

As it is stated in (Malvern Instruments Worldwide, 2015) in the case of fluids that have a yield point there were three models that fitted properly, Herschel-Bulkley, Casson and Bingham.

5.1.2.1. The Herschel-Bulkley model

Using the viscosity curves the Herschel-Bulkley model was applied, and it was possible to see how they fitted in Figure 5.3, in this case the flow deformation of the competitor was used as example. The fit was almost perfect on most of the curve except when the values of deformation were low.

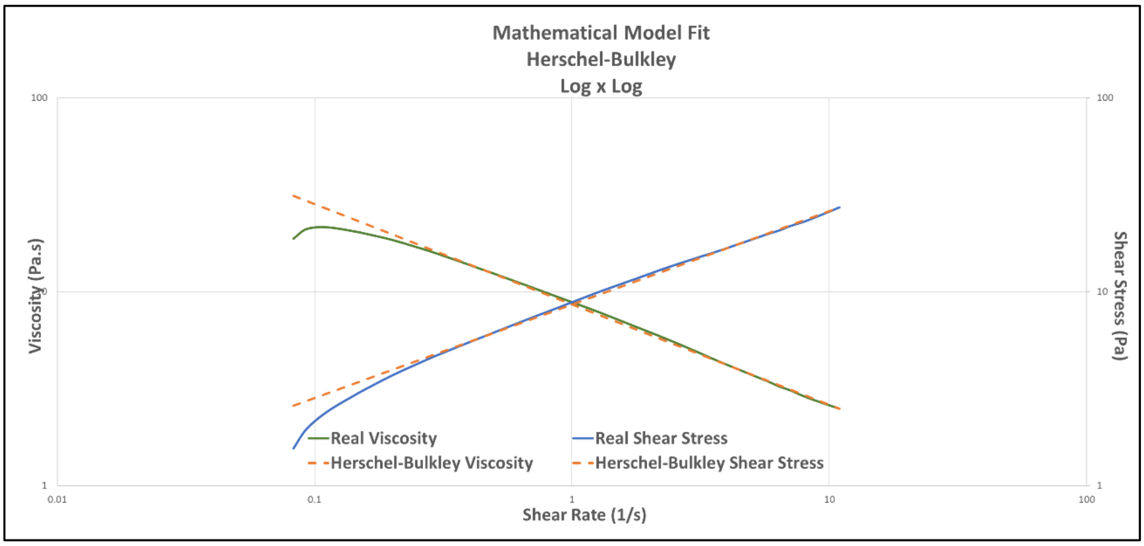

Figure 5.3 Herschel-Bulkley Model Fit, Viscosity and Shear Stress vs Shear Rate.

Each sample was fitted with this model and the parameters values that were obtained are the ones shown in Table 5.1.

Table 5.1 The Herschel-Bulkley model parameters

Sample	Herschel-Bulkley			
	τ_{HB} (Pa)	η_{HB} (Pa.s^p)	p	Correlation Ratio
Newplaste	0.664	12.627	0.324	0.995
Supramate	2.912	11.804	0.494	0.981
Competitor	0	9.439	0.485	0.998
A	0	12.635	0.415	0.999
C	0	17.202	0.430	0.998
D	0	16.474	0.430	0.998

Even with a correlation ratio close or over 99% in most of samples, it was not possible to state that the yield point of some samples was null, because coatings have a resistance to flow when the values of deformation are low, they behave as solids. But it was possible to state that the yield point of all samples are in the same order and that they had small values. Even graphically this model does not fit properly at low values so this error could be expected.

5.1.2.2. The Casson model

Following the same parameters that were used with the Herschel-Bulkley model, the Casson model was applied. The graphic representation of how it fitted was shown in Figure 5.4, the viscosity curves of the Competitor were used as example. As it occurs in the case of Herschel-Bulkley, the model fits better on high values of deformation.

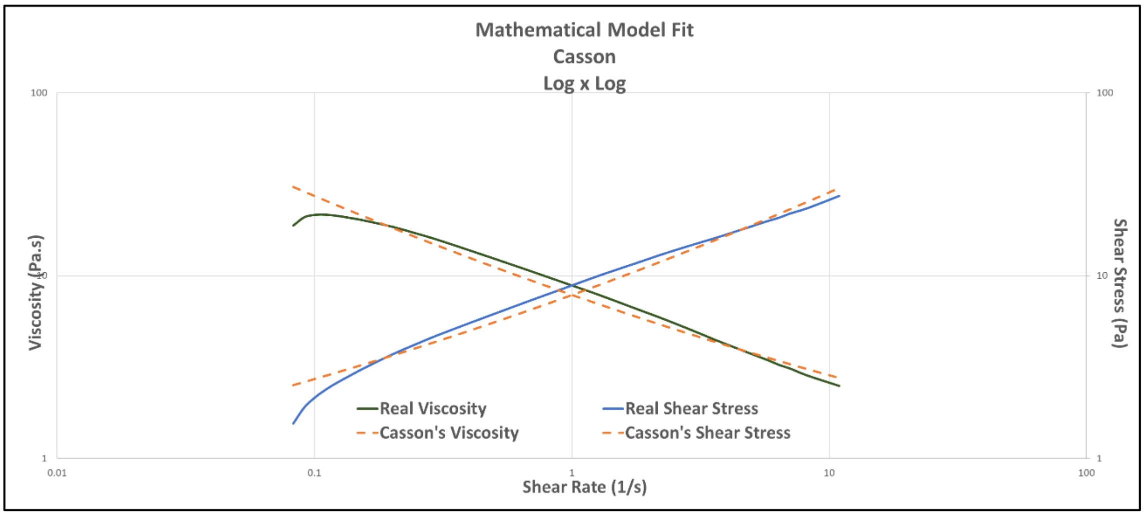

Figure 5.4 Casson Model Fit, Viscosity and Shear Stress vs Shear Rate.

All the samples were fitted with this model and the parameters were shown in Table 5.2.

Table 5.2 The Casson model parameters

Sample	Casson			
	τ_C ($Pa^{1/p}$)	η_C (Pa.s)	p	Correlation Ratio
Newplaste	0.978	0.024	9.813	0.996
Supramate	1.183	0.342	3.966	0.972
Competitor	0.845	0.444	4.302	0.993
A	1.072	0.431	3.895	0.997
C	1.054	0.549	4.210	0.997
D	1.039	0.553	4.211	0.997

In this case none of the samples has a null yield point, they are all in the same order and the correlation ratio was, in almost every case, superior to the 99%. In the other hand the model does not fit properly in the range of low values of shear rate. If the values of yield point were compared, that the sample that was closer to the Competitor's yield point was Newplaste. In (Thermo Fisher Scientific Inc, 2019) the Casson model was used to fit in a water-based coating, and the value of the yield stress was of 35Pa, the big difference may relay in the different formulation

5.1.2.3. The Bingham model

The Bingham model was applied to all the samples also and the graphical model fit was shown in Figure 5.5, the flow and viscosity curves of the competitor were used as example. This model was the one that fitted the less in the viscosity curves.

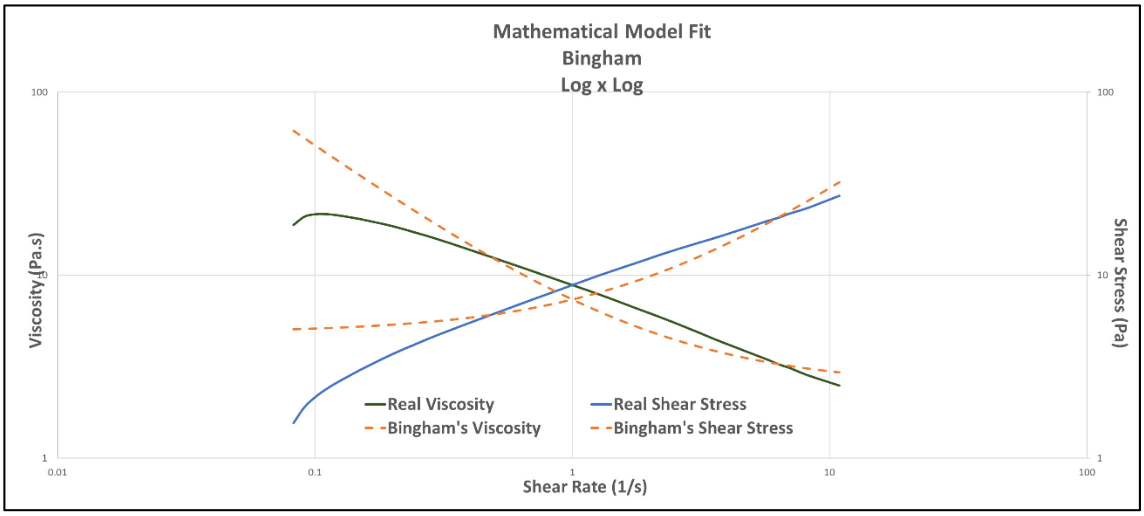

Figure 5.5 Bingham Model Fit, Viscosity and Shear Stress vs Shear Rate.

The model fit parameters are shown in Table 5.3

Table 5.3 The Bingham model parameters

Sample	Bingham		
	τ_B(Pa)	η_B(Pa.s)	Correlation Ratio
Newplaste	9.488	2.227	0.925
Supramate	9.585	3.492	0.954
Competitor	5.375	2.737	0.960
A	7.850	3.066	0.951
C	10.443	4.342	0.949
D	9.936	4.228	0.947

The yield point values obtained were higher than in the other models, and the correlation ratio was lower, the model fit graphicly follows the flow and viscosity curves but it did not fit properly.

5.2. AMPLITUDE SWEEP

To obtain the limits of the low viscoelastic range (LVER) the test of the amplitude sweep was used. The graphic results were shown in Figure 5.6.

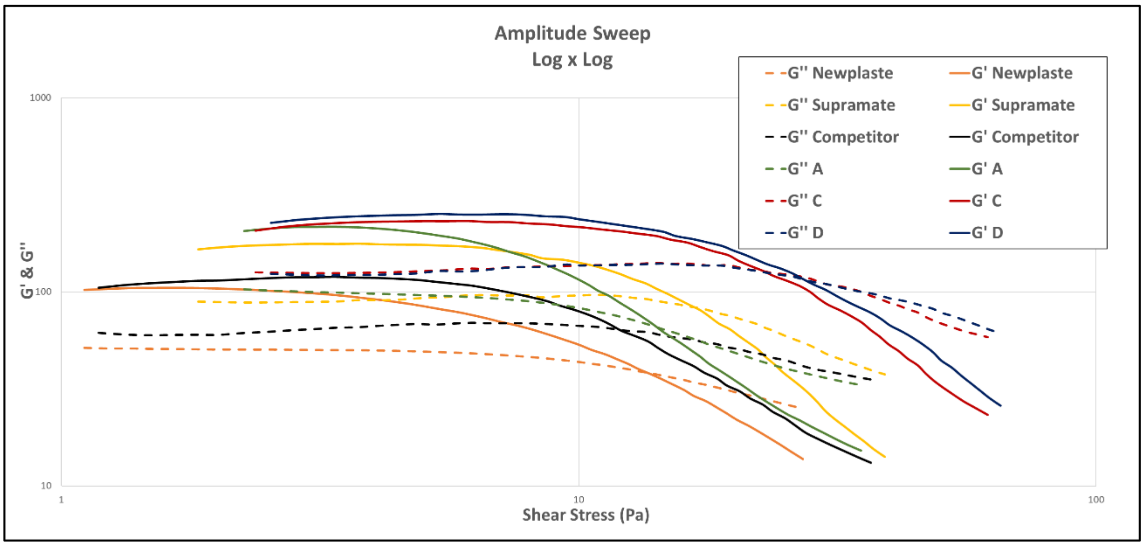

Figure 5.6 Amplitude Sweep, Elastic and Viscous modulus vs Shear Stress

In Figure 5.6 was possible to appreciate:

- All samples presented a solid-like behavior during the LVER, (G'>G''). And a liquid-like behavior after the cross over point.
- Samples C and D were almost equal, they both have different thickeners and they worked similarly.
- Sample A and Newplaste were the closest ones to the competitor, it was more similar to Newplaste at low stress and more similar to sample A when the stress was increased
- The three mixture of thickeners that has Supramate seems to interact and make the viscous modulus lower than C and D, as the concentration of thickener was higher in Supramate it would be expected that the elastic modulus of it to be bigger.

Using this method was also possible to obtain a more certain value of yield point of all samples. The values showed below in Table 5.4 were obtained assuming that the yield point value was equivalent to the point where the G'' curve had a deviation of 10% of the constant plateau as it was explained by (Moolman, 2003). This value also represented the limit of the LVER.

Table 5.4 Yield Point values and limit of the LVER (10% deviation)

	Newplaste	Supramate	Competitor	A	C	D
Yield Point (Pa)	3.657	6.961	6.221	4.895	13.362	13.722

There was another theory explained before and also by (Moolman, 2003) that assumed that the value of Yield Point was the stress when there was a cross-over point between the two modulus, G" > G'. In that case, the values of Yield Point were shown in Table 5.5

Table 5.5 Yield Point values (cross over point)

	Newplaste	Supramate	Competitor	A	C	D
Yield Point (Pa)	13.295	16.56	11.372	14.768	24.458	26.882

The difference between the two possible values of Yield Point went around 10 Pa, the ones obtained by the cross-over point had a higher value.

The comparison of all the Yield Point values obtained, using the amplitude sweep test and the mathematical models of Section 5.1.2 were shown in Table 5.6.

Table 5.6 Yield point values obtained by different methods in Pa

	Herschel-Bulkley	Casson	Bingham	10% deviation	Cross-over point
Newplaste	0.663	0.978	9.488	3.657	13.295
Supramate	2.912	1.183	9.585	6.961	16.560
Competitor	0	0.845	5.375	6.221	11.372
A	0	1.072	7.850	4.895	14.768
C	0	1.054	10.443	13.362	24.458
D	0	1.039	9.936	13.722	26.882

Comparing, the model that most approximates to the values of Yield Point obtained by performing the amplitude sweep, that was always advised by the bibliography to be the most accurate, was the Bingham Model, this model was the one with the lowest correlation ratio.

5.3. FREQUENCY SWEEP

In order to evaluate the solid and liquid-like behavior of the samples and therefore their internal structure, the frequency sweep test vas performed; the graphical results were shown in Figure 5.7

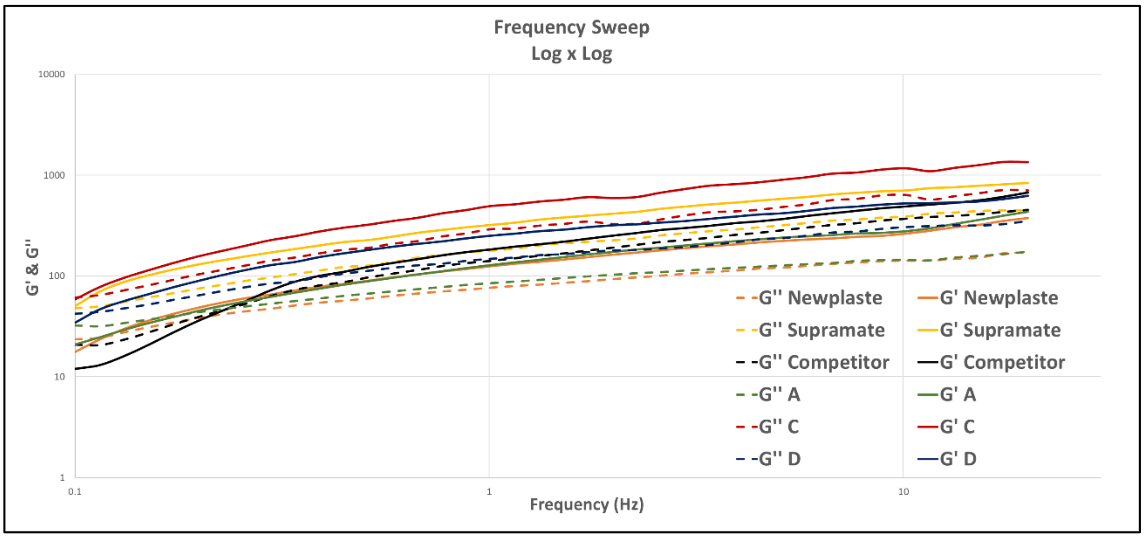

Figure 5.7 Frequency Sweep, Elastic and Viscous modulus vs Frequency.

Samples Supramate, C and D behaved in a really similar way and was shown in Figure 5.8. They all showed the same pattern, and there was a cross over point that showed up at really low frequencies and it happened at almost the same frequencies. The curve of Supramate was exactly in the middle of samples C and D that represents the co-participation of the mixture of thickeners action in Supramate.

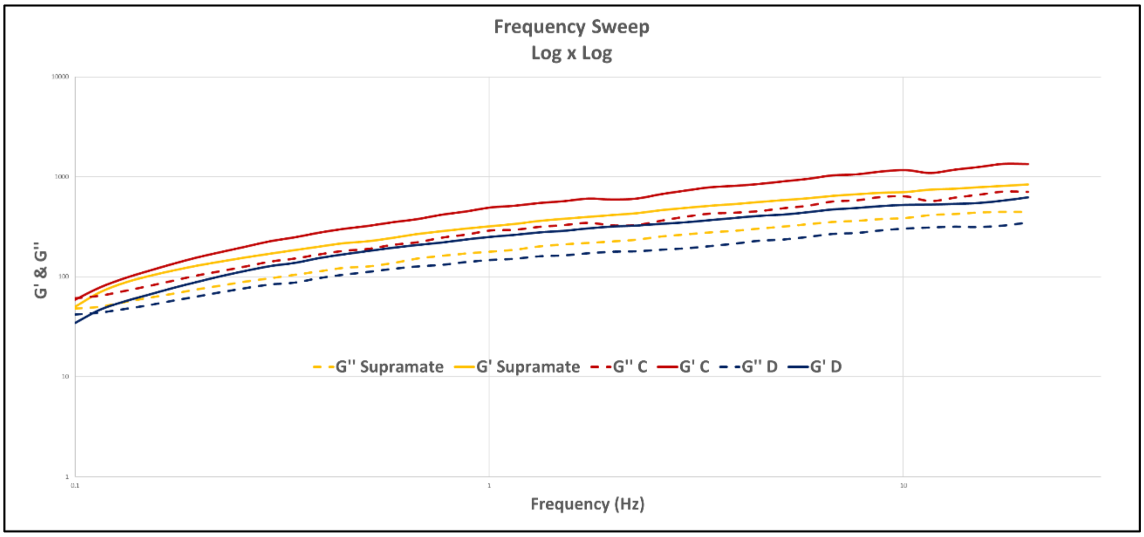

Figure 5.8 Frequency Sweep of samples: Supramate, C and D, Elastic and Viscous modulus vs Frequency.

Samples Competitor, Newplaste and A were different to the others, but presented similarities between them, this was explained graphically in Figure 5.9

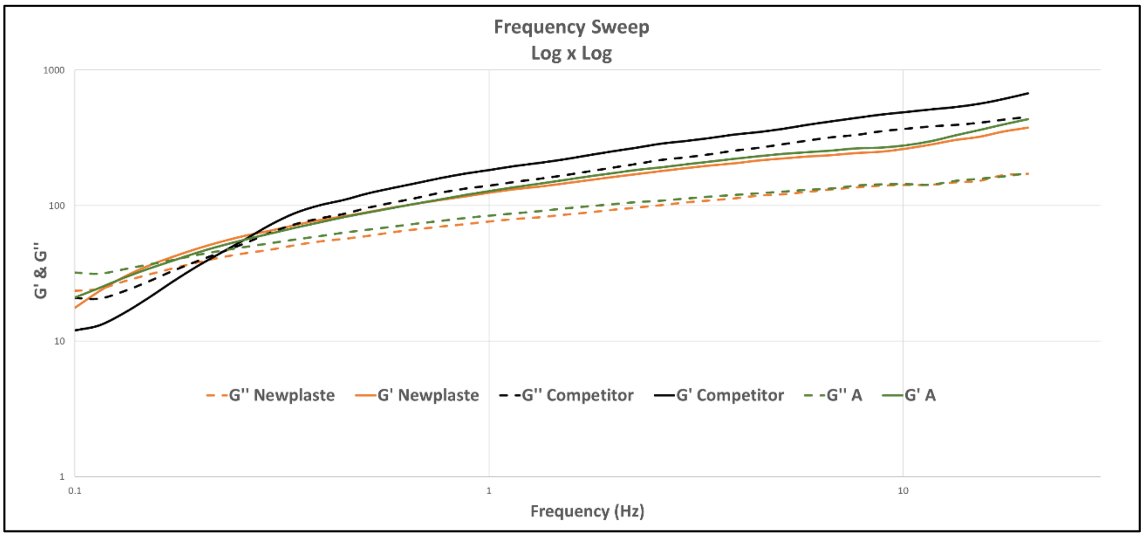

Figure 5.9 Frequency Sweep of samples Competitor, Newplaste and A, Elastic and Viscous modulus vs Frequency.

The samples presented a liquid like behavior at low frequencies (G’’>G’) until the cross-over point, that happened at a frequency of 0.2588Hz for the Competitor and at 0.1972Hz for sample A, the following closest one was Newplaste where the cross-over occurs at a frequency 0.1312Hz. The behavior of the curves for sample A and Newplaste were the same during almost all frequencies. The other difference that was possible to notice is the space between the curves of the Competitor, that was really small in comparison with samples A and Newplaste.

If the phase angle were evaluated along all frequencies the graphic shown in Figure 5.10 would be obtained.

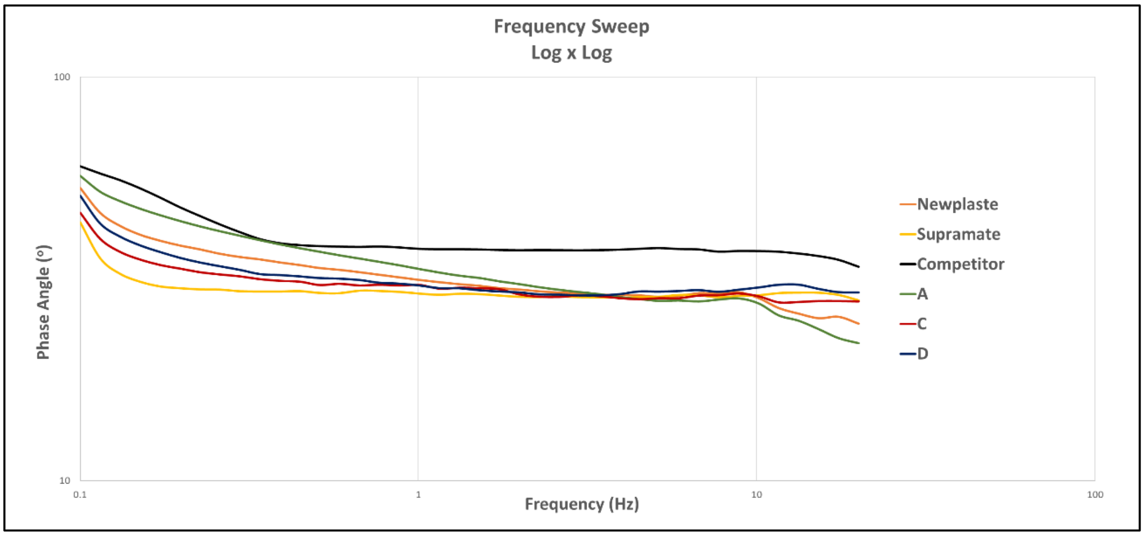

Figure 5.10 Phase Angle evaluation using the Frequency Sweep test

At low frequencies all samples showed a liquid-like behavior, the value of the phase angle was close to 90º, as the frequency increased the sample Competitor presented a plateau, that stayed stable over the whole range of frequencies with a value of 37º. Once again, the closest one to the competitor was sample A, but only along low frequencies, it presented a linear decrease, that means that the solid-like behavior of the sample will increase when the frequency increases. Samples Supramate, Newplaste, C and D behaved in a very similar way, they formed a plateau after 1 Hz of frequency, with a value that went between 28º and 31º, and it stayed stable until 10 Hz were reached. The value of the plateau angle was smaller than the Competitor's one and it meant that, at those frequencies, the competitor would be "more liquid" than the others.

5.4. THREE-INTERVAL-THIXOTROPY-TEST

To investigate the structural recovery of all samples, the three-interval-thixotropy-test (3 ITT) was performed. In order to do this the samples were not stirred before initiating the test to simulate better the process of application and the conditions of the three intervals were as follows:

5.4.1. 1st Interval

A standard oscillatory test was used, to simulate the stage where the paint was stored in the can or waiting to be used, and also to know the initial elastic modulus to compare with the one that will be obtained in the 3rd interval. The graphical results of this interval were shown in Figure 5.11.

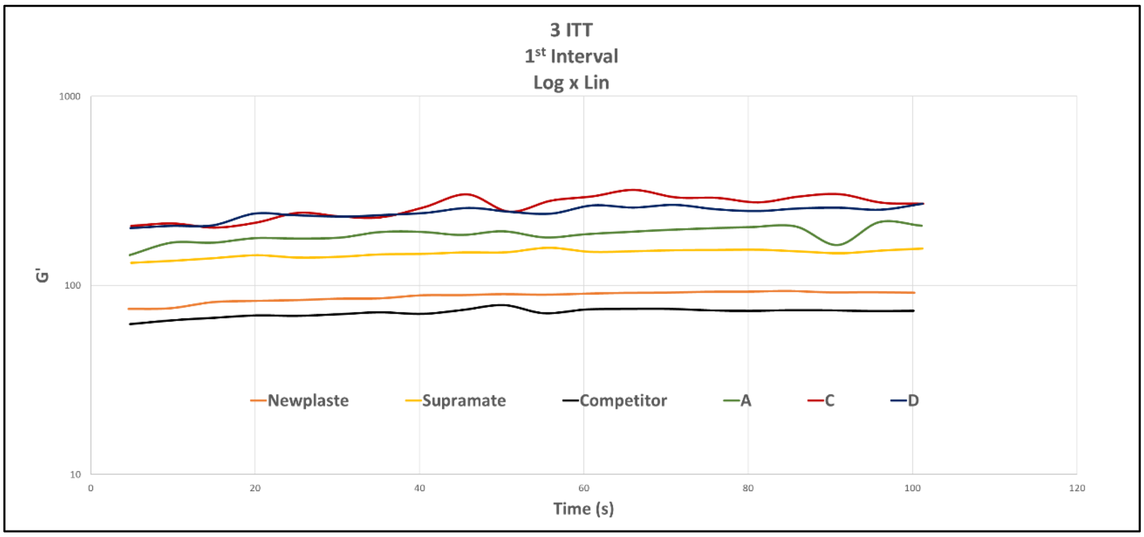

Figure 5.11 1st interval of the 3ITT, Elastic modulus vs Time.

As it was expected, all samples show a constant plateau, the lowest one was from the Competitor showing the least solid-like behavior, the closest one in this interval was sample Newplaste.

5.4.2. 2nd Interval

Shown in Figure 5.12, this process intended to destroy fully the internal structure of the paint, it also helps to the applicability because it makes the viscosity decrease.

In less than 20 seconds the minimum viscosity available for all samples was reached. The closest one to the Competitor is sample A that presented the same slope.

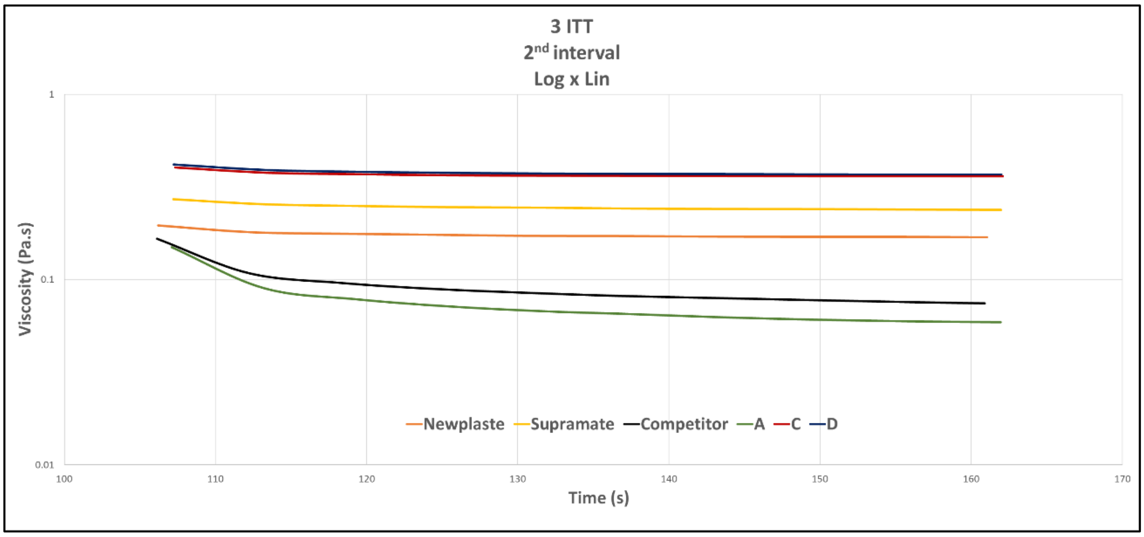

Figure 5.12 2nd interval of the 3ITT, Viscosity vs Time.

5.4.3. 3rd Interval

Using the same parameters used in the 1st interval to compare the values of the elastic modulus (G') and its recovery this final interval was performed. This stage, shown in Figure 5.13, intends to simulate the conditions after application, were the paint is supposed to do the levelling and dry properly, as it was explained before in Section 4.2.4, the thixotropy recovery was very important for this two final processes.

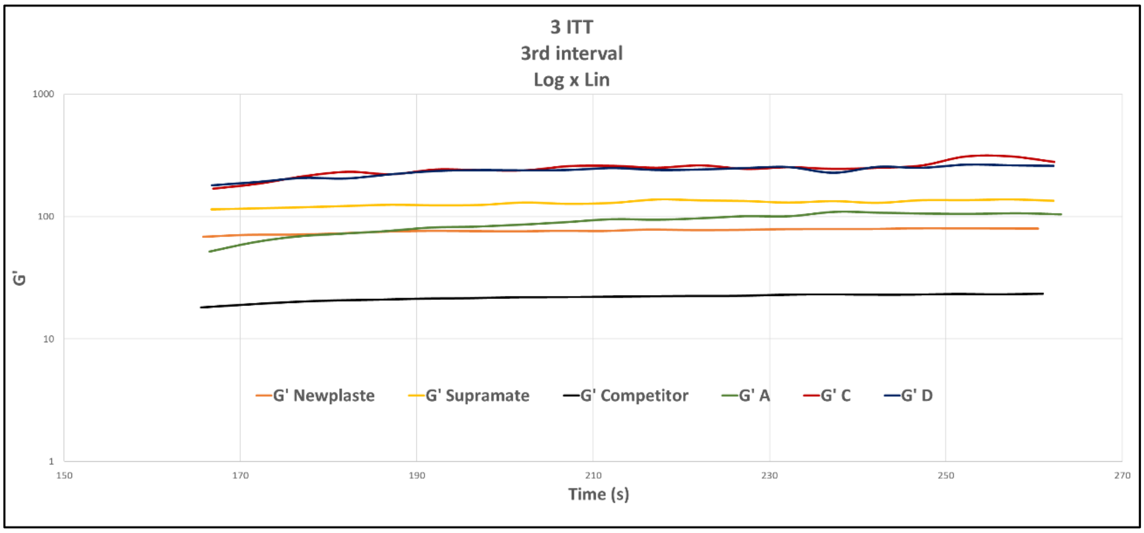

Figure 5.13 3rd interval 3ITT, Elastic modulus vs Time.

All samples presented, at least, a little increase in their elastic modulus during the time of the test, the one with the least G' is the Competitor and the closest ones were samples A and Newplaste. For a better appreciation of the decrease of G’ the 1st and 3rd intervals were compared in Figure 5.14.

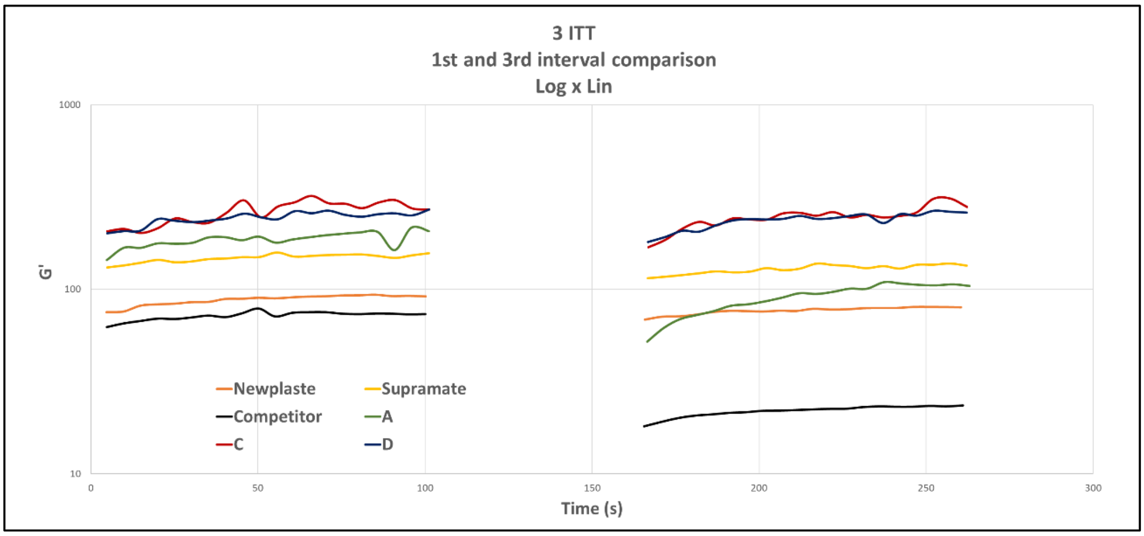

Figure 5.14 Comparison of intervals 1 and 3 of the 3ITT, Elastic modulus vs Time.

Graphicly it was easier to see the difference that existed before and after the application of a great deformation, all samples presented a decrease in their elastic modulus but they also recovered it really fast except for samples A and Competitor, the percentage of recovery after one minute of “rest” was shown in Table 5.7

Table 5.7 Comparison of recovery of all samples

	Initial G'	Final G'	Percentage of Recovery
Newplaste	92.43	78.51	84.94
Supramate	152.95	134.24	87.77
Competitor	73.56	22.68	30.83
A	199.22	100.41	50.40
C	284.90	251.02	88.11
D	256.00	243.26	95.02

The percentage of recovery of the G’ of the Competitor was really inferior in comparison with other samples, the only one that approaches to its level was sample A but the difference between them was still high.

As it was stated in (Thermo Fisher Scientific Inc, 2019) the importance of the recovery after application relayed in the possibility of dripping and leave droplets or streak marks after the paint has fully cured if the paint remains as an easily flowable liquid for too long.

On the other hand, if the paint recovers too quickly, the paint would be susceptible to showing brush or roller marks resulting in an unperfect final surface coating.

6. CONCLUSIONS

After all samples were tested and discussions were made it is possible to state

- The main difference between the samples that are sold by Tintas Europa and the Competitor relays on the thixotropy recovery, this was seen after the 3ITT was performed, graphicly there is a big difference in between the paints provided by the company and the Competitor. The percentage of recovery after one minute of the application of a big shear stress is, at least, 20% less than the ones provided by the company. Practically, this could mean that the Competitor coating has a liquid behavior after the application that lasts more than the rest of samples, this could lead to a better levelling and also a lighter coating during the application, with a lower viscosity during that period (but high enough to avoid dripping) and, therefore, easier to use.
- Sample A (that has only “Hecellose B 15 K” as thickener) presented a greater similarity to the competitor's sample, in terms of its behavior, in all the tests that were carried out.
- Samples C and D behave in the same way in all tests, so “Tafigel Pur 44” and “Rheolate 278” acts in the exact same form. As there is no big difference between them, it could be advised to the company to use the cheapest in other formulations, that in this case it would be “Tafigel Pur 44” which price is 6.08€ per kilogram.

Considering that Tintas Europa produces 120000 liters of Supramate per year, the cost of the mixture of thickeners that is used to produce it, Hecellose B 15 K in combination with Tafigel PUR 44 and AquaFlow NHS 300, that represents only the 0.8478% of the formula is of 5172.22€ each year.

In case the industry decides to start selling Sample A as a new formulation of Supramate, with only a 0.3629% of Hecellose B 15 K, the cost of the thickeners for the production will be only 2521.43€ each year.

Sample A is the one that most approaches to the sample of the Competitor, so it could be better received by the costumers. The next step in order to improve the formula could be to add a thixotropy modifier and a thickener for high shear rates, to make the percentage of recovery after one minute of application lower and athe viscosity at high shear rates slightly higher.

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