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TRABAJO FIN DE GRADO
Rheological superposition of oriented polymers

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Abstract

Since the beginning of the processing of the polymers, these materials have been analysed with rheological techniques. Oscillations were implemented to obtain viscoelastic spectra, and the evolution of the viscosity was observed by the application of shear. Up to recently, oscillations and shears have been performed separately. However, nowadays there is possible to do both at the same time. These techniques are called superpositions. This work is directed to the analysis and comparison of poly-L-lactic acid (PLLA) and polypropylene (PP) regarding their rheological properties. To do that, apart from the conventional rheology, parallel and orthogonal superpositions are performed and contrasted. In the case of PP, it has been used as a reference and the viability of both superpositions has been verified. The most outstanding improvement over the conventional rheology has been the opportunity to perceive the effect of the flow in the viscoelastic properties, and more precisely, in the relaxation time. There was interest in the orientation of the chains in PLLA because its piezoelectric response. After the superpositions it was not reached to a conclusion with the chosen parameters. Comparing the superpositions, higher properties and cleaner changes have been achieved with the orthogonal one.

Resumen

Desde el principio del procesado de los polímeros, estos materiales han sido analizados con técnicas reológicas. Oscilaciones fueron implementadas para obtener espectros viscoelásticos, y la conversión de la viscosidad y el estrés fueron observados mediante la aplicación de cizalla. Hasta hace poco, las oscilaciones y la cizalla eran realizadas separadas. Sin embargo, hoy en día está la posibilidad de hacer las dos al mismo tiempo. Estas técnicas son llamadas superposiciones. Este trabajo está dirigido al análisis y comparación del ácido poli-L-láctico (PLLA) y polipropileno (PP) con respecto a sus propiedades reológicas. Para eso, aparte de la reología convencional, superposiciones paralelas y ortogonales son realizados y contrastados. En el caso del PP, se ha usado como referencia y la viabilidad de ambas superposiciones ha sido verificada. La mejora más destacada sobre la reología convencional ha sido la oportunidad de percibir el efecto del flujo en las propiedades viscoelásticas. Había interés en la orientación de las cadenas de PLLA debido a su respuesta piezoeléctrica. Después de las superposiciones, no se llegó a una conclusión clara con los parámetros elegidos. Comparando las superposiciones, propiedades más altas y cambios más limpios.

Acronyms

PP → Polypropylene

PLLA → Poly-L-lactic acid

β → Beta

G′ → Storage modulus

G″ → Loss modulus

DSC → Differential Scanning Calorimetry

T_g → Glass-transition temperature

T_m → Melting temperature

PSP → Parallel Superposition

OSP → Orthogonal Superposition

1. Introduction

Rheology is part of the science that studies the deformation and flow behaviour of materials [1]. So that, it is close to the material mechanics. The basis of the mechanics is known since the XVIII century: The ideal elastic solid and the ideal viscous liquid. However, multiple materials behave with an intermediate behaviour, that is, they behave as viscoelastic materials. Those are the materials of interest of Rheology.

In the Polymer field the rheology has been stablished as a powerful tool to analyse the relation between the structure, the processing and the application [2]. When a product wants to be made, a plastic bottle for example, rheology can be used to define how the properties of the material will change during the creation of it. The material, for instance, should not change a lot internally if a good and homogeneous product is wanted [2].

It is possible to do this relation in the opposite way. If a product with specific properties is demanded, we should select the most appropriate polymer structure and the processing method that fits those properties. In order to produce such structure-processing-properties correlation, it is necessary to consider the rheological properties in each step.

There are many processing techniques, and the conditions to perform them are affected by the type of process, the material and the final application, they are somehow interconnected (Fig. 1) [3].
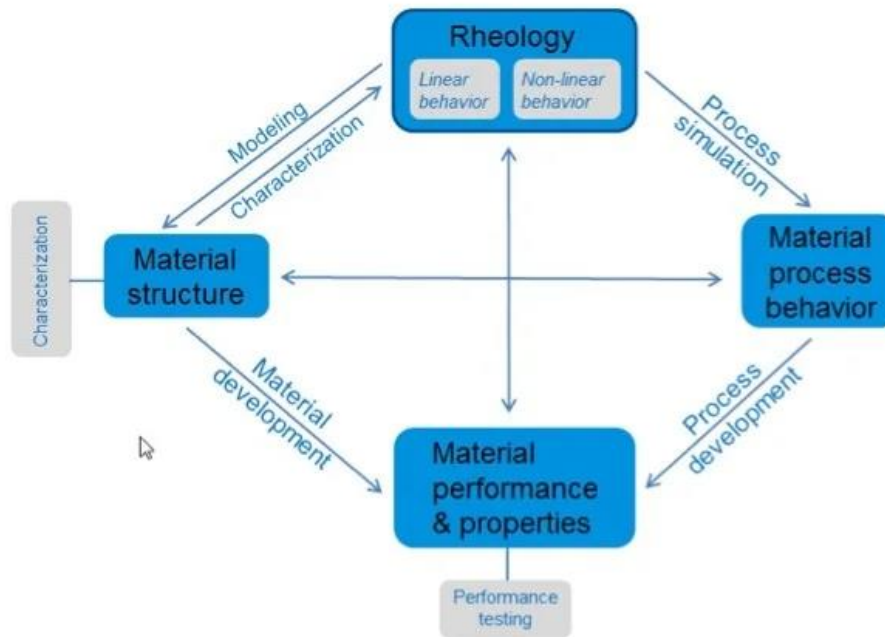
Fig. 1: Material-Rheology-Processing-Application relationship [4].

With a deep understanding of the rheological features of materials and processing techniques, it would be possible to predict the final performance of a material.

1.1 Determination of rheological properties: Linear and non-linear viscoelasticity

The determination of the rheological properties is usually carried out in two different conditions: Continuous flow and linear viscoelasticity measurements [5]. Three types of flow are mainly used in the rheological measurements of polymer blends: steady state shearing, dynamic shearing, and elongation [5]. These models are varied regarding their shear rate and the uniformity of the stress and strain. Focusing on steady state shearing and dynamic shearing, it could be said that steady state shearing (flow measurements) allows to determine the effect of the structure on the processing conditions while the dynamic shearing (oscillation measurements) gives information about molecular parameters.

Each one of them gives different information about the material, but each one lacks what the other one offers: steady state shearing lacks the information

regarding the morphology or the structure of the material while the dynamic shearing lacks the effect of suffered stress and real viscosity.

In the conventional rheology, both of them are performed separately. However, the steady state shearing can change the viscoelastic properties of a material (determine in dynamic shearing). So, conventional rheology does not give the real overview that the material would have in the processing.

The solution to this is doing both steady shear and dynamic measurements simultaneously. That procedure is called a superposition, which can be classified as part of non-linear viscoelasticity. In this work we are going to focus two kinds of superposition: the parallel and the orthogonal superpositions. This is a type of testing that has not been carried out so far in the group, so this work has been devoted to fine-tuning them.

On one hand, in the parallel superposition, both continuous flow and dynamic measurements are carried out in the same axis and direction. In contrast, in the orthogonal superposition, both of them are also done simultaneously but in a perpendicular axis. Parallel superposition is the most common superposition, but as the overlapped shear and oscillation occurs in the same axis the results can be affected by the other. In this way, orthogonal superposition could increase the resolution of the results.

The main advantages of the superpositions are that it is possible to measure viscoelasticity in flow and predict the viscoelastic behaviour of the material during the processing.

1.2 Importance of the flow viscoelasticity for the final application

One of the most direct applications of measuring flow viscoelasticity is the characterization of anisotropy. The processing of film, by melt-blowing, for example, can lead to an orientation of the chains and a subsequent improvement in the mechanical properties [6]. In this case result essential to understand the

viscoelastic properties in flow in order to establish the causes and conditions for molecular alignment.

An interesting material to analyze this relation is the Poly-L-lactic acid (PLLA). PLLA is a biodegradable thermoplastic polymer that has been mainly used in biomedical applications, and it has started to be a material of interest for other applications such as agricultural and even general ones that other more used polymers have [7]. This is due to the good properties like high modulus and strength. However, it has a bad property that makes it difficult to handle: brittleness [8]. The improvement of the toughness of PLLA has become a challenge for many research groups.

The toughening can be achieved by the addition of different plasticizers or by the control of the crystallization, which is improved with the orientation. Conventionally, crystalline α-form is responsible for its brittleness. However, a higher performance has been found in its β-form, a morphology where there is a good orientation of the crystalline parts (Fig. 2).
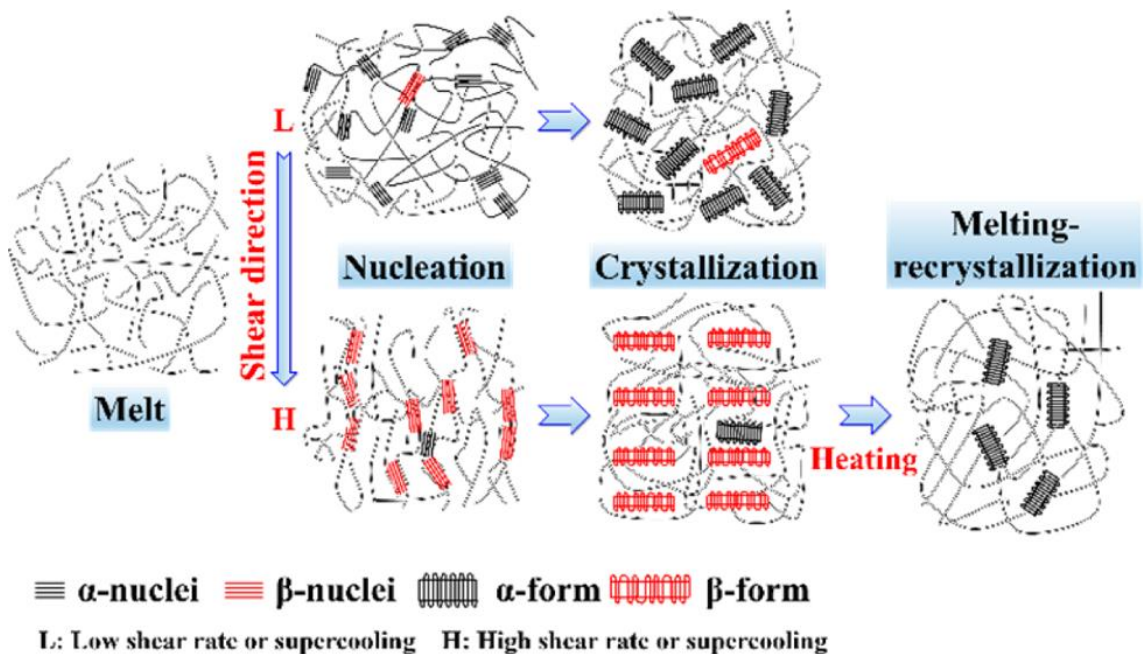

Fig. 2: Morphological forms of PLLA [8].

It was found that a shear-induced crystallization can produce large amounts of β-PLLA. In an ambient pressure the form can be induced with shear rates higher than $13.6s^{-1}$ [8]. Also, in general, higher orientation is accomplished at higher drawing temperatures for semicrystalline PLLA [9]. More interestingly, the presence of β-form in PLLA makes the material piezoelectric [10], that is, when stress is applied, an electrical charge is obtained. Because of that, the PLLA has been considered a good candidate for the work-up of superposition protocols in this work.

However, since we are starting from scratch in this type of test, it was considered appropriate to include in the study a model material, such as polypropylene, whose flow properties and viscoelastic properties have been extensively studied over the years. For this reason, the viscoelastic flow properties of two materials will be analysed in this work: polypropylene (PP) and poly-L-lactic acid (PLLA).

1.3 Objective

The general objective of this project is to establish a rheological protocol that allows determining the viscoelastic features of polymer flow.
In order to achieve this general objective, some specific objectives have been defined:

- Correlate empirically flow properties and viscoelastic properties.
- Evaluate the possibilities and limitations of the parallel and orthogonal superposition tests.
- Evaluate the influence of the studied parameters on the rheological properties of different materials.

2. Rheology: General Concepts

2.1 Conventional rheology

2.1.1 Study of the materials under flow conditions

In general terms, it is considered that the flow happens when the relative position of two molecules changes under precise deformation fields, usually at high temperatures [11]. It is a specific type of deformation that is defined by the stress and strain rate. The stress (σ) is the group of forces that act in a specific surface, and the strain rate (γ) is the difference of distance that happen between two points after a deformation is implemented in certain amount of time [12].

The flow is usually measured under shearing conditions. In shear rheology, the stress is tangential to the surface from which the stress is applied. (Fig. 3). The most relevant parameters are the shear stress (σ) and shear rate ($\dot{\gamma}$) [13]. In this sense, the ration between the sear stress and shear rate defines the viscosity (η) of the material (Fig. 4).
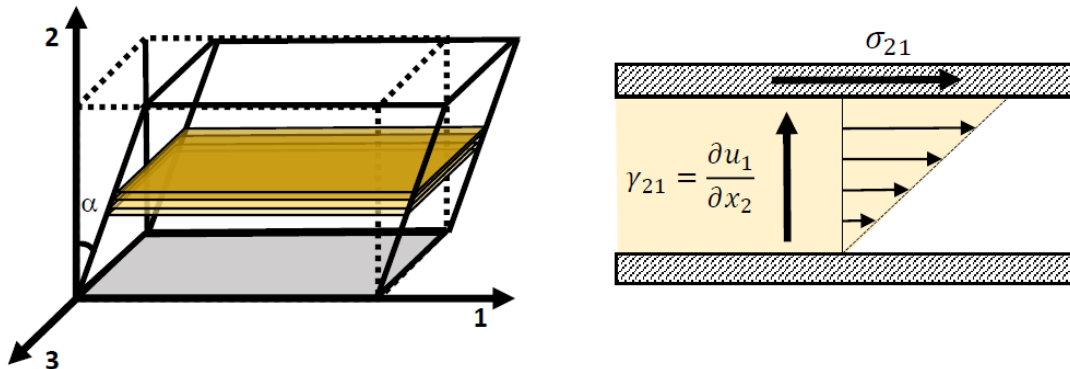

Fig. 3: Simple shear flow.

$$\eta(\dot{\gamma}) = \frac{\sigma_{21}(\dot{\gamma})}{\dot{\gamma}_{21}}$$

Fig. 4: Viscosity equation.

The shear viscosity is a very important rheological parameter as it describes the resistance of a material to the flow [14]. In some materials, when they flow the

viscosity remains constant, meaning that the shear stress and shear rate are proportional to each other [15]. The fluids that follow this behaviour are called Newtonian fluids. In the case of polymers, other behaviours are possible: Shear thickening (or dilatant), that is, the increase of viscosity with the increase of shear rate [16]; and shear thinning (or pseudoplastic), that is, the decrease of viscosity with the shear rate. Shear thickening is very usual in colloidal dispersions [16], and shear thinning is usual in polymer melts [17] (Fig. 5).
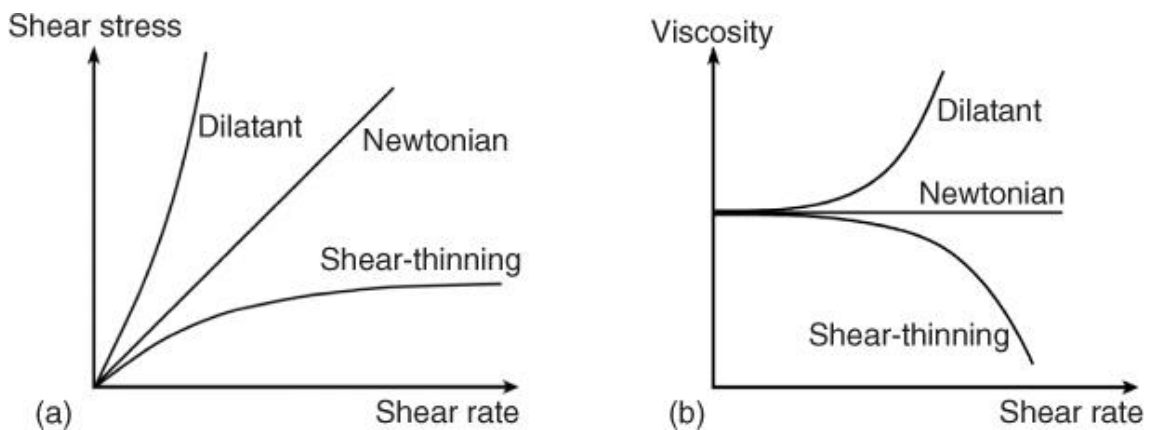

Fig. 5: Flow curves for Newtonian, shear thinning and shear thickening: a) shear stress vs shear rate b) viscosity vs shear rate [18].

The dynamic of entanglements is the responsible of the Newtonian or non-Newtonian behaviour in polymers. In Newtonian, the applied shear does not affect the entanglements, and so the shear stress increases constantly with the shear rate and the viscosity remains constant. However, if the material is non-Newtonian, the entanglement density changes and the properties of the material are altered. For pseudoplastic materials, the entanglement density decreases and, consequently, the necessary energy to flow [19]. The transition from Newtonian to pseudoplastic behaviour in polymers occurs progressively due to a transition from an entangled to a disentangled morphology. The characteristic time that polymer chain needs to entangle (or disentangle) is called relaxation time.

The relaxation time is possible to be measured through viscosity flow curves. There are several approaches or models to fit experimental data that take into account both, the Newtonian viscosity and the relaxation time. In this work the model that best fits the experimental results is the one developed by Cross-William-Landel-Ferry model (Fig. 6). It considers the effect of shear rate and

temperature on the viscosity, and describes both Newtonian and pseudoplastic behaviour.

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\alpha_c \dot{\gamma})^m}$$

Fig. 6: Cross model.

Where η_0 is the Newtonian viscosity, η_∞ the viscosity at infinite shear rate, α_c the relaxation time and m the pseudoplasticity index.

2.1.2 Dynamic determination (oscillation): viscoelasticity

The viscoelastic analysis is one of the most important areas of rheology. The analysis is nondestructive and usually is carried out through dynamic shear test, also called oscillatory tests. These experiments consist of an oscillatory deformation due to the application of an oscillatory stress to the material. From the analysis of these waves and the phase difference between them, the following parameters can be determined (Fig. 7).

$$G' = \frac{\sigma_{21}^0}{\gamma_{21}^0} \cos \delta \qquad G'' = \frac{\sigma_{21}^0}{\gamma_{21}^0} \operatorname{sen} \delta \qquad \tan \delta = \frac{G''}{G'}$$

Fig. 7: Measurement of G', G'' and $\tan \delta$.

σ_{21}^0 and γ_{21}^0 are the amplitudes of the oscillation (oscillation stress and oscillation strain, respectively), and δ is the phase difference between them, G' (storage modulus) represents the energy stored elastically in each cycle and defines the solid character of the material, and G'' (loss modulus) is the energy lost as heat and defines the liquid character.

This experiment can be carried out in two ways: using small amplitude sinusoidal waves called SAOS (Small Amplitude Oscillation Shear), or using a large amplitude sinusoidal wave, called LAOS (Large Amplitude Oscillation Shear). Other way to call the SAOS range is the LVE (Linear Viscoelastic) range (Fig. 8).
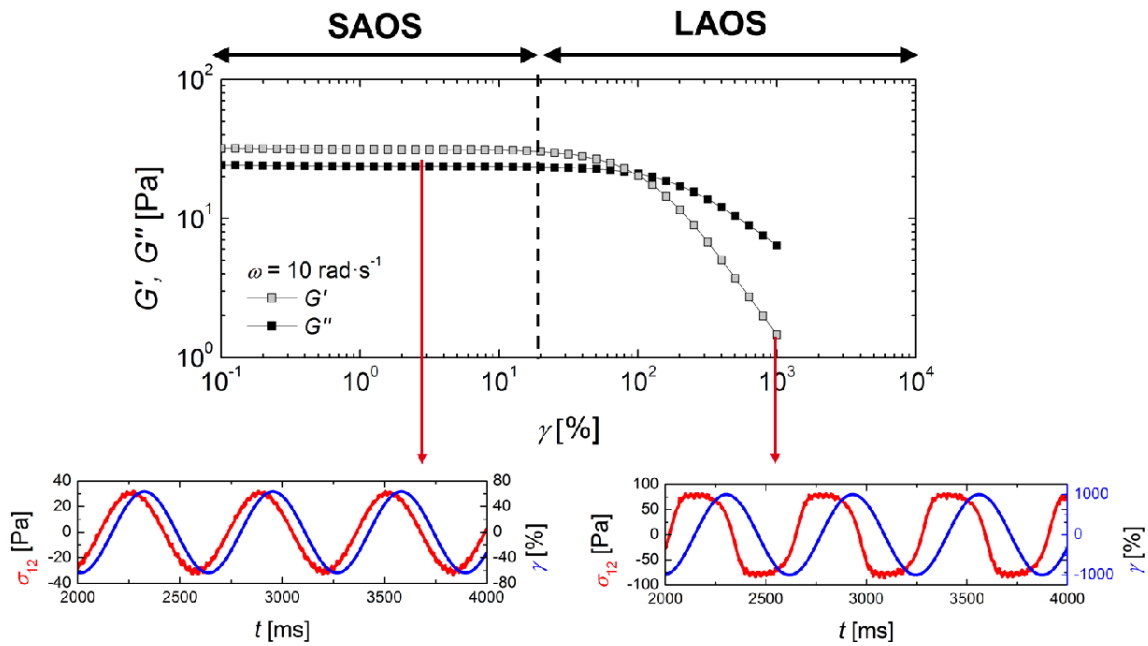
Fig. 8: SAOS and LAOS regions with the comparison of the waves [20].

Although LAOS analysis can give us structural information, the experiments in conventional rheology are carried out in LVE conditions.

The viscoelastic behaviour, as explained before, is defined as being able to have both elastic and viscous behaviours, and the parameters that define the behaviour are G' and G''. That means that when G'>G'' it can be said that the material will have a solid-like behaviour whereas when G'<G'' it will have liquid-like behaviour [21]. The point at which G' and G'' cross is called the crossover point, and the modulus of that transition is the crossover modulus (G_x).

In such LVE condition, different tests can be made:

- **Strain Sweep:** Oscillatory measurements while strain amplitude (%) is increased at a constant frequency. In those determinations the LVE will be identified.

- **Frequency Sweep (Oscillation Frequency):** The strain is constant but the frequency is changed throughout the test. It is used to calculate how the viscoelastic properties change with the experimental time and make the viscoelastic spectrum.

- **Temperature Sweep:** The strain and frequency are maintained constant, the only variable being the temperature. These experiments are adequate to identify thermal transitions.

- **Time Sweep:** All the variables are fixed and the change on the properties is analysed in order to describe the evolution of the material (for example, cross-linking or degradation reactions).

While the viscoelastic analysis does not give information about the behaviour during the processing, the analysis can give an approximation of the behaviour in flow. For this purpose, complex viscosity is used. Complex viscosity is a mathematical approach to the resistance to flow of a material [22], and it follows the equation of Fig. 9.

$$|\eta^*(\omega)| = \sqrt{(G'/\omega)^2 + (G''/\omega)^2}$$

Fig. 9: Complex viscosity equation.

Where $\eta^*(\omega)$ is the complex viscosity and ω the angular frequency, which goes in rad/s.

2.1.3 Relations between flow and viscoelastic properties: The Cox-Merz Rule.

As explained, the measurement conditions for both flow and viscoelasticity differ. However, it is possible to correlate both the continuous flow viscosity and complex viscosity functions.

The Cox-Merz rule is an empirical relationship to determine the shear viscosity using the complex viscosity values acquired with an oscillation test [23]. The rule states that there is an equivalence between viscosity measured during oscillatory tests at low frequencies and the viscosity measured using steady shear at low rates of deformation. complex viscosity as a function of frequency is equal to the steady shear viscosity as a function of shear rate [24]. The rule only is fulfilled in *thermorheologically simple* samples, which are polymer melts and solutions [25,26]. The equation is shown in Fig. 10.

$$|\eta^*(\omega)| = \sqrt{\eta'(\omega)^2 + \eta''(\omega)^2} = \eta(\dot{\gamma})|_{\dot{\gamma}=\omega}$$

Fig. 10: The Cox-Merz rule.

Where $\eta'(\omega) = \frac{G'}{\omega}$, $\eta''(\omega) = \frac{G''}{\omega}$ and $\eta(\dot{\gamma})|_{\dot{\gamma}=\omega}$ is the viscosity measured in the flow ramp.

2.2 Influence of shear flow on the viscoelastic properties of materials

The determination of flow and viscoelastic properties of materials in conventional rheology is analysed in separate experiments, although the results can be correlated through the Cox-Merz Rule in some cases. However, the influence of the addition of a steady shear flow to the viscoelastic parameters is not possible this way.

Some rheometers have the option to apply simultaneously a shear rate in the parallel or perpendicular direction of an oscillation. When the shear is applied in the same direction as the oscillation it is called *Parallel superposition*, and when it is in the perpendicular is *Orthogonal superposition*. The applied stress (or strain) fields are different [27], and a visual comparison of them is in Fig. 11.
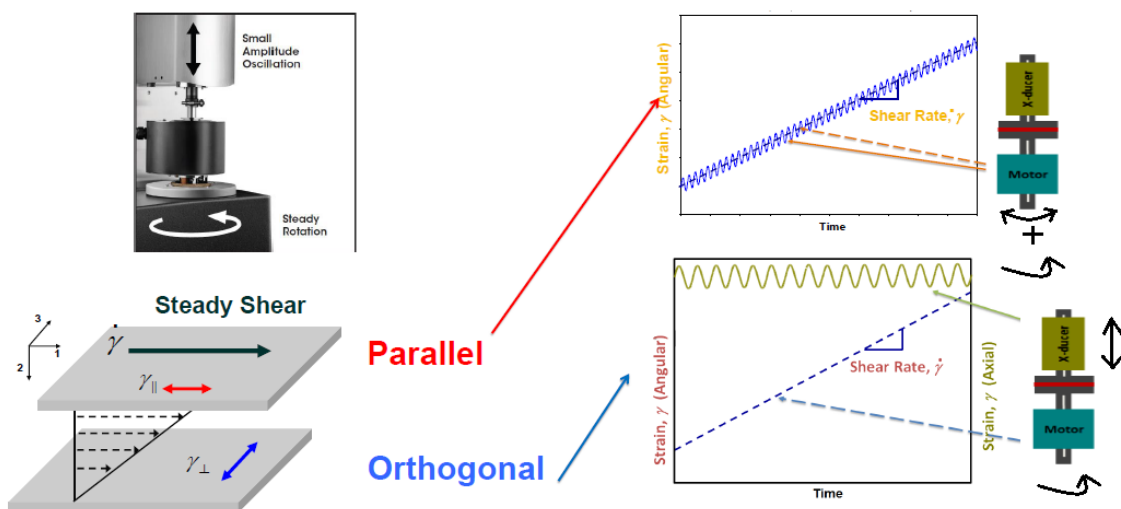
Fig. 11: Parallel and orthogonal superpositions [28].

There are several test geometries to carry out those kinds of experiments, being the most widely employed the concentric cylinders [29] (Fig. 12b). However, in this work the parallel plate geometry is going to be used (Fig. 12a) due to the relatively high viscosity of the polymeric melt.
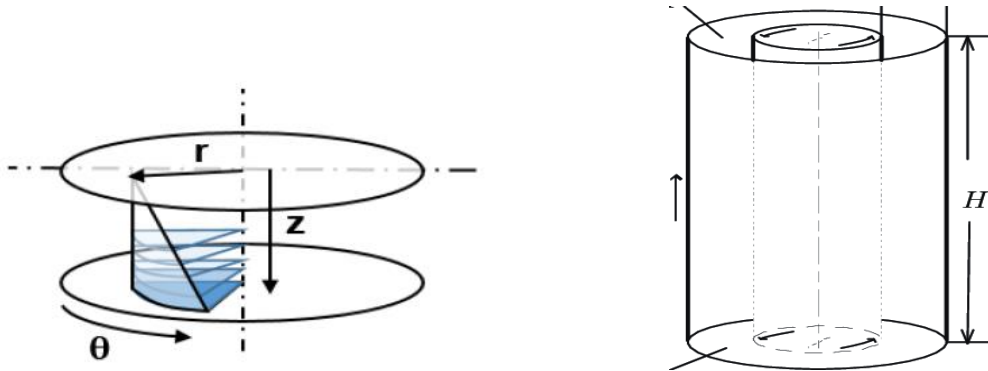

Fig. 12: a) Parallel plates b) Concentric cylinder [29].

This is to note that, in parallel plates, considering simple shear, the movement of both plates in parallel superposition leads to a shear-shear superposition. However, in orthogonal superposition, where the upper plate moves up and down, the produce effect is a compression. This is not the case of concentric cylinders. As it is claimed in literature, the orthogonal superposition would be only viable with the use of concentric cylinders [27,30,31]. The inside cylinder would rotate while the other would move vertically. This way, the shear would be formed rotationally and the oscillation vertically.

As explained, all the measurements are carried out in parallel plates. So, although a not shear-shear superposition is produced, the deformation is still orthogonal due to the fact that we apply forces in the perpendicular direction. However, this effect is to take in mind when looking at the obtained results.

3. Experimental

3.1 Materials

Polypropylene (PP) and Poly-L-lactic acid (PLLA) were the materials used in this project: two PP of different molecular weight and two PLLA, with different molecular weights (Table 1). PP is a semicrystalline polyolefin whose molecular structure is Fig. 12a, and PLLA a biodegradable polyester whose molecular structure is Fig. 12b.

The low molecular weight PP is PP 070 G2M, supplied by Repsol [32]; and high molecular weight PP is PP HP400H, supplied by Moplen [33]. Both PLLAs (PLLA L130 and PLLA L175) have been supplied by Purac (Corbion) [34].

Table 1: General information of the materials.

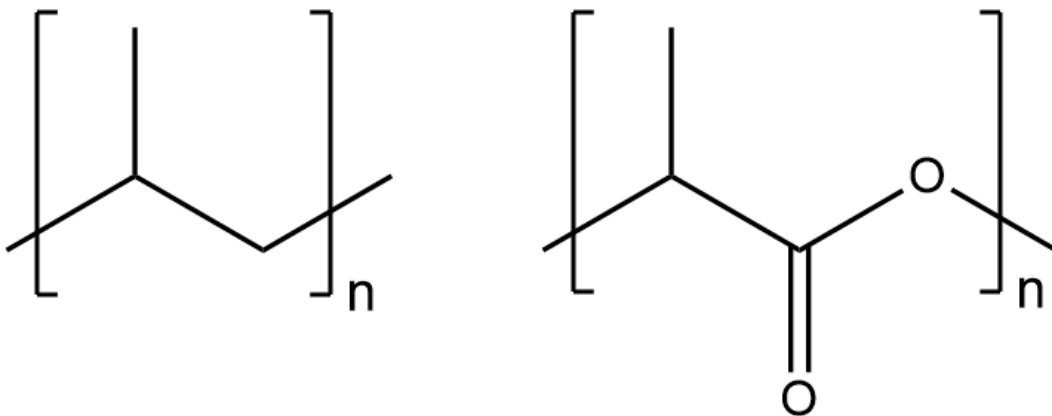| Name	Commercial name	Supplier	M_w (g/mol)	PDI
PP L	PP 070 G2M	Repsol	-	-
PP H	PP HP400H	Moplen	473000	6,3
PLLA L	PLLA L130	Purac (Corbion)	109170	1,62
PLLA H	PLLA L175	Purac (Corbion)	209000	1,85

Fig. 13: Molecular structure of a) PP b) PLLA.

3.2 Techniques

3.2.1 Compression moulding

This processing technique has been used to make the sample available in the form required for rheological determination. Generally, in rheology, we work with 1-2 mm thick sheets, from which the samples are stamped with the dimensions appropriate to the geometry of the test, which is why it has been necessary to obtain these sheets from the material pellets. To do that the *Collin Laboratory Platen Press Type P 200 E* (Fig. 14) has been used.

Fig. 14: Collin Laboratory Press Type P 200 E.

The steps were the following:

1) First, the pellets were introduced in a mould of 1 cm thickness between two Teflon sheets.

2) The mould was then introduced in the press at different temperature depending on the material. For PP the material was added at 190 ºC and for PLLA at 185 ºC.

3) Then, the pressure was increased slowly to150 bars and kept for at least 2 minutes.

4) Finally, the pressure was released and the press opened for the release of the mould. After the cooling in the air, the mould was opened and the plate obtained.

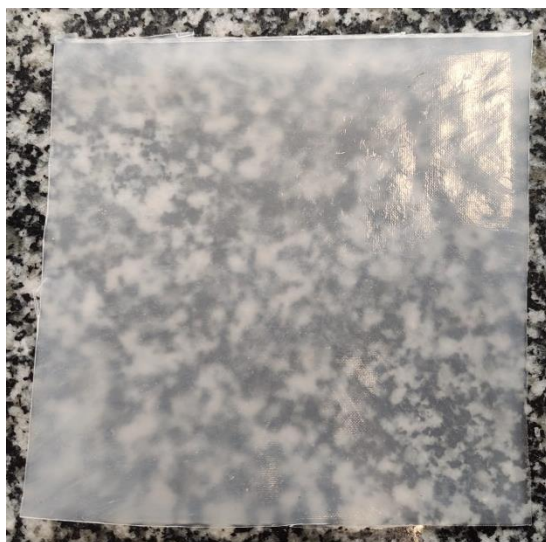An example of the obtained plate is shown in Fig. 15.

Fig. 15: Polymer plate accomplished with the plate press.

3.2.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is an analytical method used to characterize the thermal properties of materials [35]. In the case of polymers, it is generally possible to determine transitions such as T_g and T_m. For this purpose, heating and cooling sweeps were carried out at 20°C/min and in an inert atmosphere. The sample was placed in standard aluminium capsules, in quantities of 7-12 mg. Air is used as a reference and the temperatures are identified by the heat flow rates [36].

The used calorimeter is *Perkin Elmer DSC 7*, and the applied protocol was the following one:

1) 1 minute at 30°C
2) Ramp from 30°C to 200°C at 20°C/min (first scan)
3) Hold at 200°C for 3 minutes, to erase the thermal history
4) Ramp from 200°C to 30°C at 20°C/min (cooling)
5) Hold at 30°C for 1 minute
6) Ramp from 30°C to 200°C at 20°C/min (second scan)

3.2.3 Rheometry

The used rheometer is *Ares G2* of TA Instruments (Fig. 16). It is a rotational rheometer with the ability to obtain very accurate results under linear and non-linear conditions [37].

In rheometers, different geometries of plates exist, which are not interchangeable. One or the other is used depending on the characteristics and response of the material. In this project, parallel plates are used. For the PP materials, aluminium plates of 12 mm diameter were used, and for PLLA stainless steel of 25 mm diameter. The temperatures for the experiments and the corresponding protocols are indicated in the text.
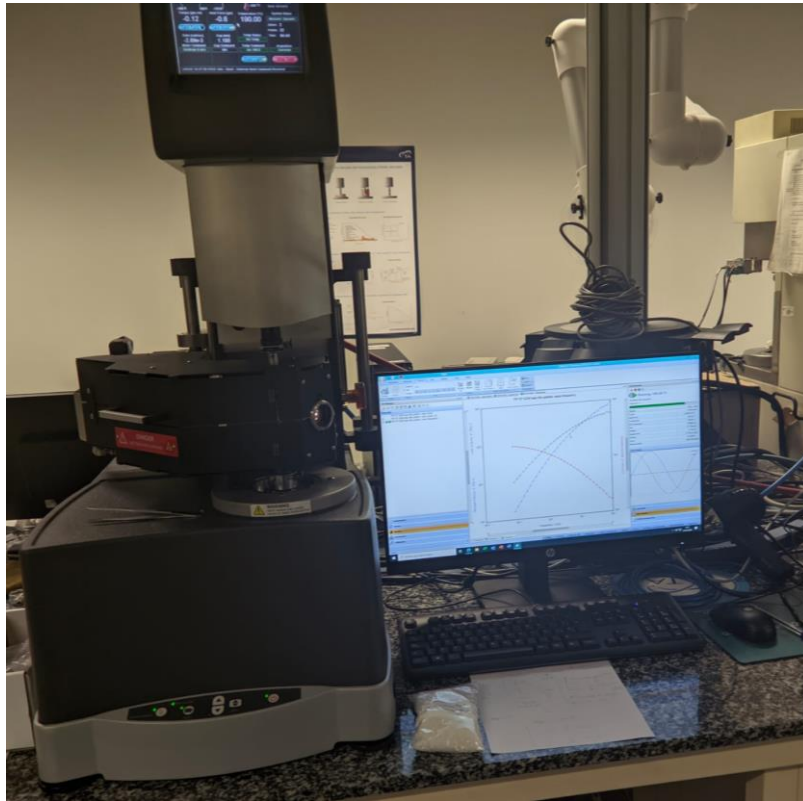
Fig. 16: Ares G2 rheometer.

4. Results and discussion

The main objective of this work is to establish a measurement protocol capable to determine precisely the viscoelastic behaviour of polymers in flow. The different steps that have been carried out for this purpose will be described in this section.

4.1 Determination of the measurement conditions

Before the rheological procedures, the Differential Scanning Calorimetry (DSC) was performed in both PP and PLLA to acquire the characteristic temperatures of them (T_g and T_m).

The thermograms corresponding to the first heating scan are shown in Fig. 17, Fig. 18, Fig. 19 and Fig. 20, and the T_g and T_m values are represented in Table 2.

Table 2: T_g and T_m of the materials achieved by DSC.

Name	T_g (ºC)	T_m (ºC)
PP L	-	174
PP H	-	173
PLLA L	72	183
PLLA H	74	180

*The equipment used does not have the necessary cooling capacity for the determination of the T_g of PP.

The rheological determinations are carried out in melt, therefore, in view of these results, it has been decided to carry them out at 190ºC for PP. It is at a temperature higher than Tm to ensure that they will be completely molten. However, in the PLLA case, it has been decided to carry out at 185ºC because of the sensibility to degradation. This phenomenon reduces the molecular weight by the change in chemical and/or physical structure [38]. Also, the PLLA has to be dried due to it being hygroscopic [39].
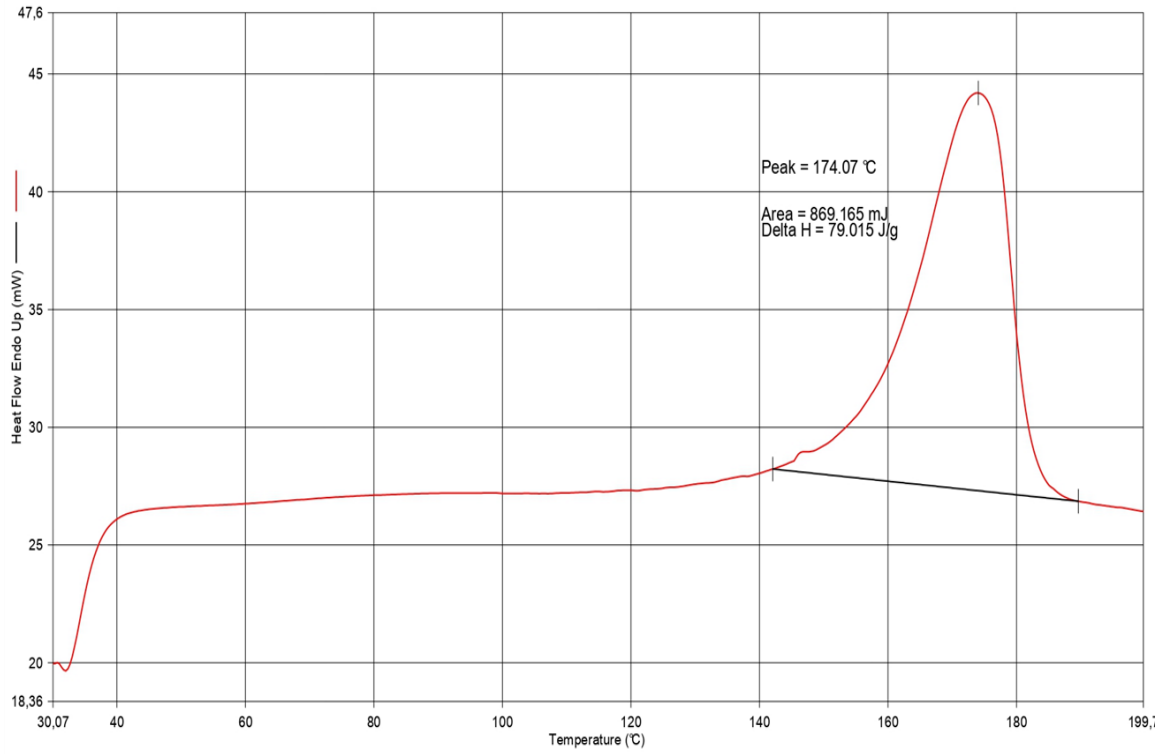
Fig. 17: DSC of PP L.

Fig. 18: DSC of PP H.
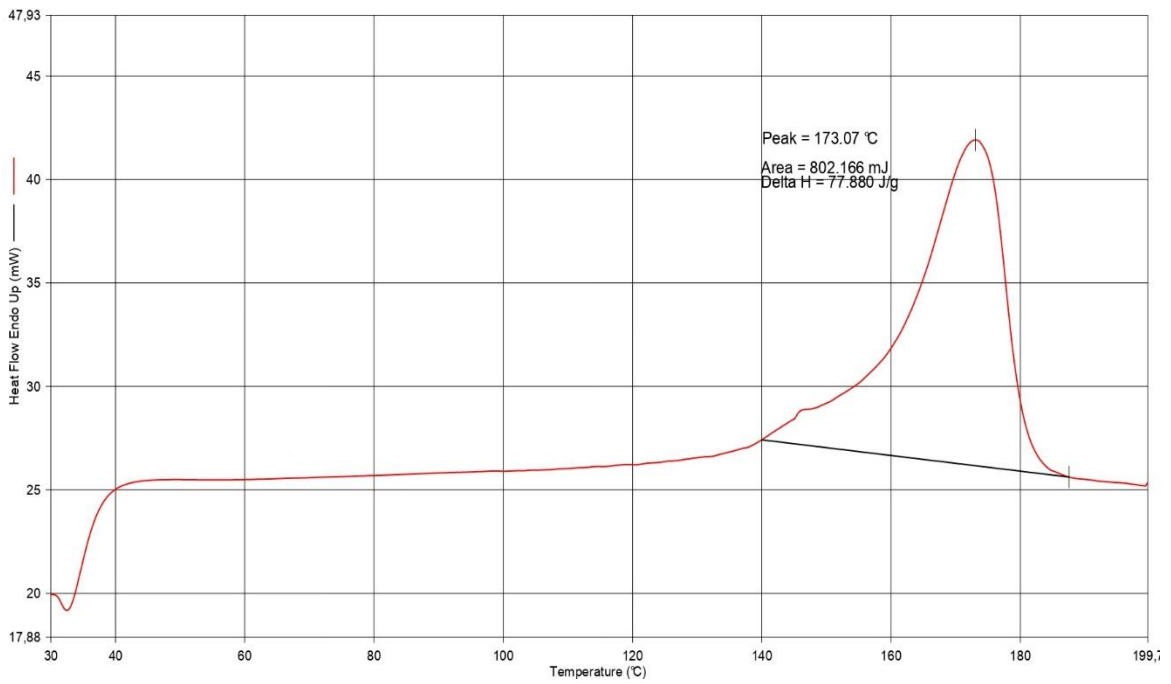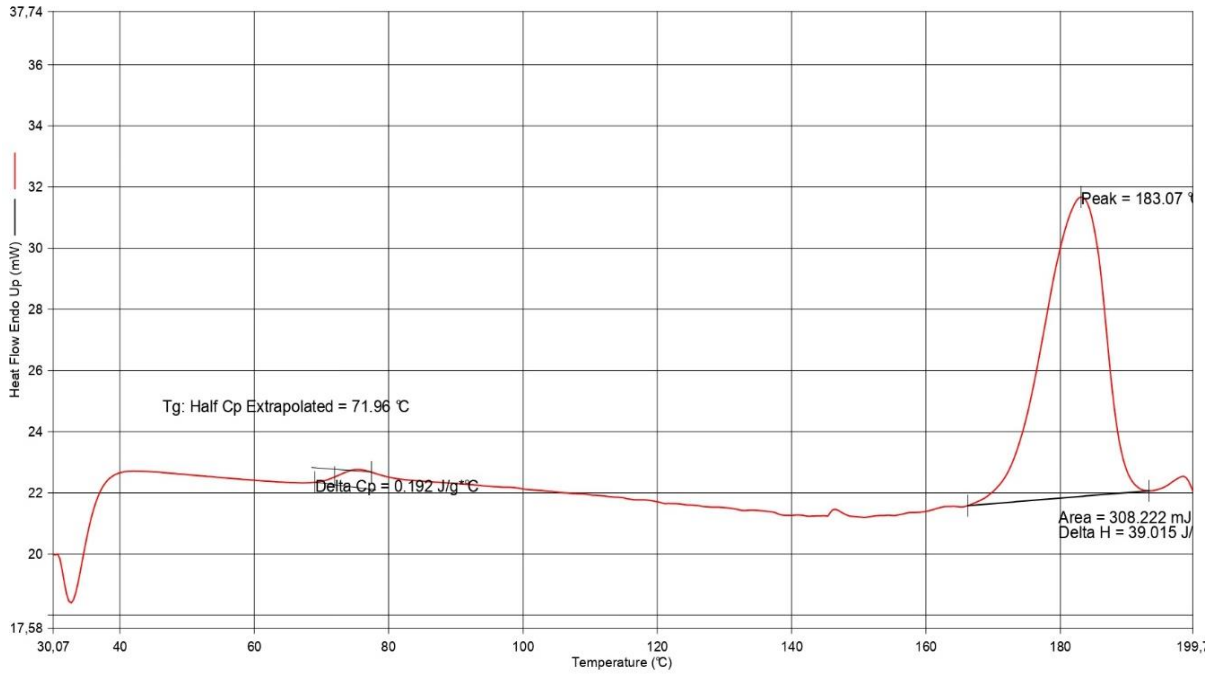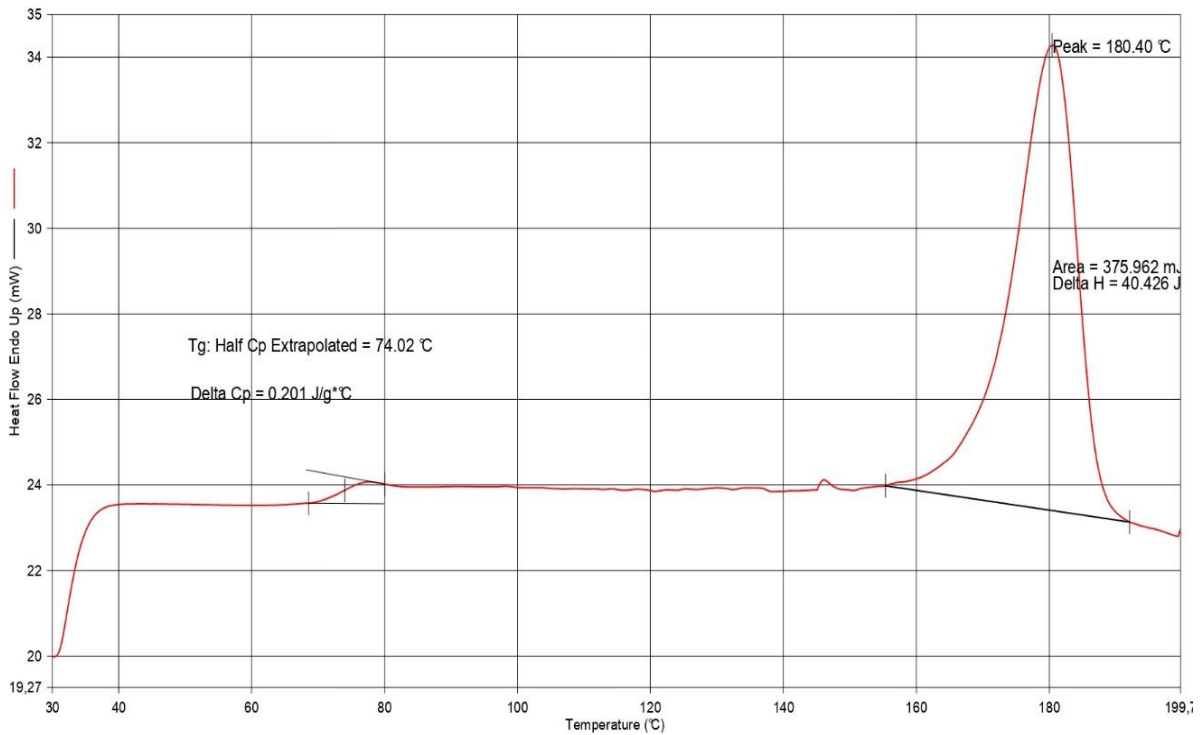
Fig. 19: DSC of PLLA L.

Fig. 20: DSC of PLLA H.

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4.2 Determination of the rheological protocol prior to superposition

4.2.1 Conventional rheology

In order to establish the rheological protocol for the superposition, the conventional characterisation of the PPs will be carried out first. In this section, all the frequency experiments were carried out at 190°C under linear viscoelastic (LVE) conditions.

However, in order to determine the linearity conditions, it is necessary to initially perform a strain amplitude sweep at the same temperature. The corresponding strain sweeps for both PP are represented in Fig. 21.
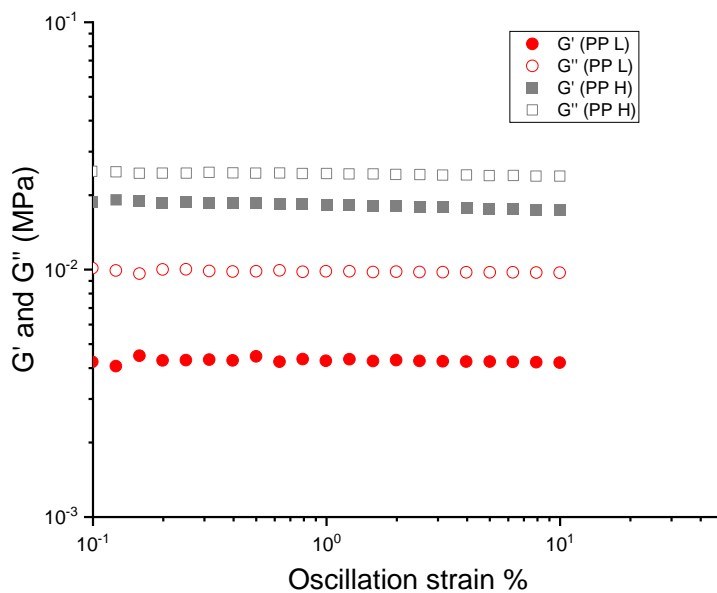

Fig. 21: Strain Sweep of PP L and PP H.

This experiment shows the evolution of G′ and G″ with the applied strain. As it can be seen, in both PPs G″ is higher than G′, meaning that the materials behave as a viscoelastic liquid at this temperature [40]. In addition, PP H presents higher moduli values, as expected due to its higher molecular weight. In both cases, a constant G′ and G″ values all over the analysed strain range is shown. So, all the experiment are in linear viscoelastic (LVE) conditions. Therefore, a 4% strain amplitude was chosen for the frequency measurements.

The viscoelastic spectra of both PP, in oscillation mode, in the range of 100 Hz to 0.01 Hz, at 190ºC are represented in Fig. 22.
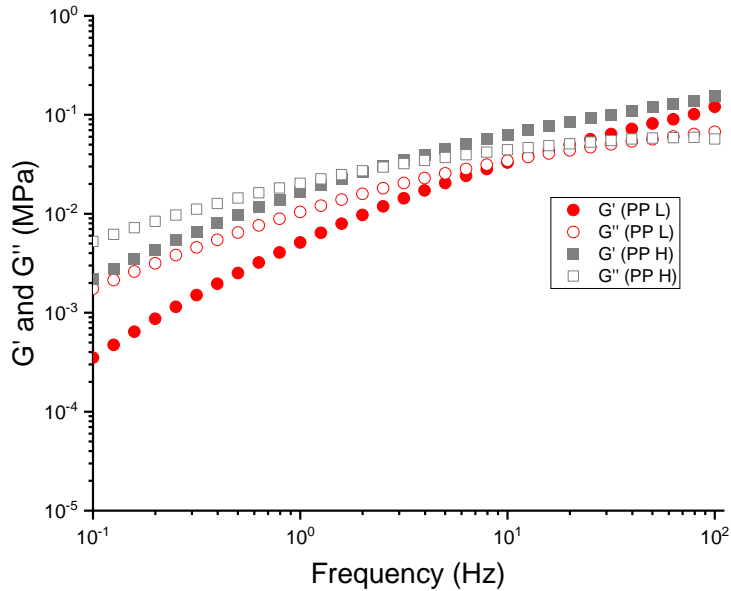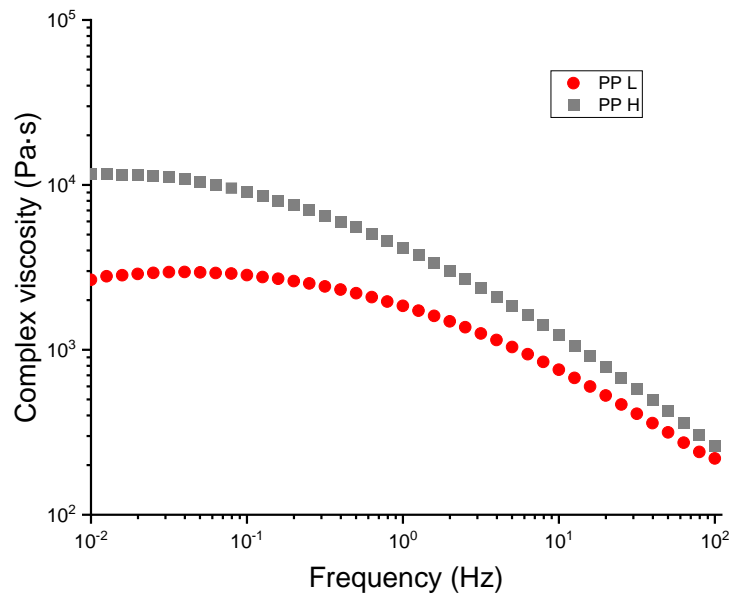

Fig. 22: Frequency sweep of both PP, G' and G''.

In both cases, the typical viscoelastic behaviour of a linear polymer melt in the end-flow region is shown [41]. Thus, a solid-like behaviour at high frequencies, where G'>G", and a liquid-like behaviour at low frequencies, with G">G', can be observed. It is also noted that the crossover point (G'=G") of PP H is shifted to lower frequencies in PP L. This behaviour is related to the difference in molecular weight and the density or kind of entanglements: the higher molecular weight, the longer the relaxation time.

From the same experiment it is possible to obtain another parameter that is also considered important, the complex viscosity. In Fig. 23 results corresponding to the complex viscosity, at 190ºC, are represented for both PP.

Fig. 23: Frequency sweep of both PP, complex viscosity.

In both cases, the viscosity acquires a constant value at low frequencies (Newtonian viscosity), which decreases with increasing frequency. This is a pseudo-plastic behaviour with shear thinning (Fig. 5), typical of linear polymer melts [17]. Comparing both, PP H having higher molecular weight makes the number of entanglements increase. With more entanglements, more force will be needed to disentangle and therefore the viscosity is higher.

Once the oscillatory tests had been carried out and the viscoelastic spectra of both PPs at 190ºC had been analysed, flow tests were carried out. In these tests, the shear viscosity has been determined as the shear rate increases in the range between 0,1 and 100 s^{-1}. Then, in order to verify the thermorheologically simple behaviour, the shear viscosity and shear stress results were compared with the ones obtained in the frequency sweep. The comparison for both PP are shown in Fig. 24 and Fig. 25.
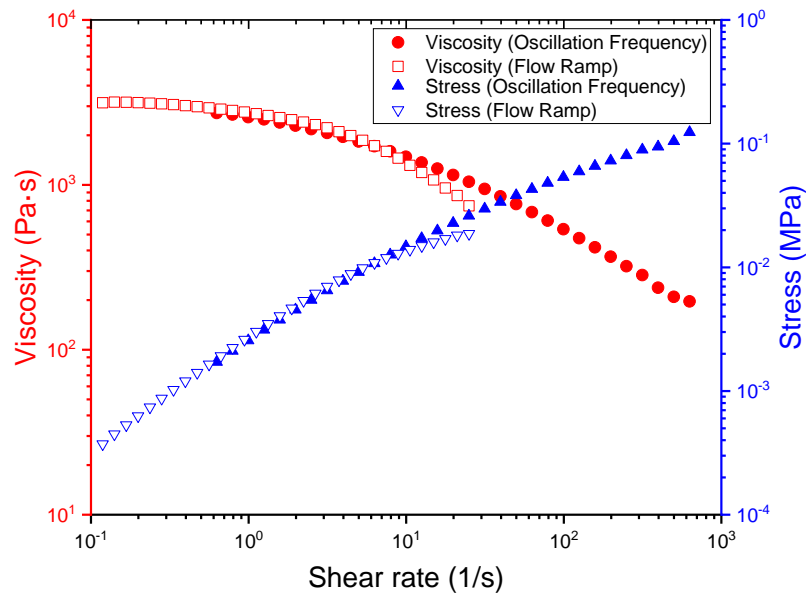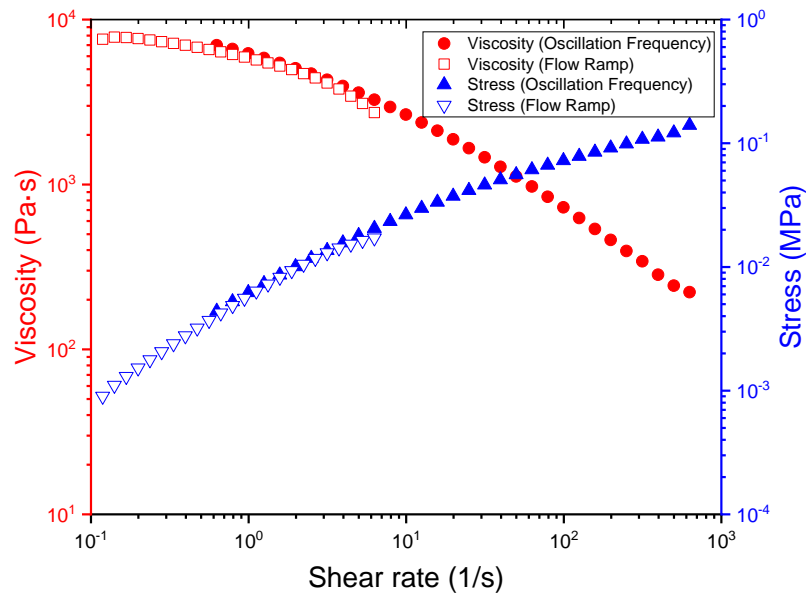
Fig. 24: PP L Cox-Merz Relationship.

Fig. 25: PP H Cox-Merz Relationship.

The viscosity values, shear viscosity and complex viscosity, of both measurements were represented in the left axis and the ones of the stress in the right axis. Looking at the graphs, there are overlaps of both shear stress and viscosity in a shear rate range between more or less from 1 to 10 s^{-1}. This means that the oscillation and the flow have the same effect in the structure of the materials during those shear rates. This overlap indicates that PP fulfils the Cox-Merz rule, demonstrating that they are thermorheologically simple materials.

Once the rheological properties of PP have been analysed, the rheological properties of the selected PLLA will be analysed. Initially, a testing protocol similar to the one carried out for PP will be applied. In this case, the diameter of the plates was increased from 12 to 25 mm, the gap from 0,4 to 0,9 mm and N_2 atmosphere was used to avoid degradation. As previously, the strain sweep was performed in order to determinate the linear viscoelastic region and choose an amplitude for the frequency test. Then, the frequency sweep was carried out in order to analyse the viscoelastic spectra. Fig. 26 shows the results obtained by the mentioned measurements.
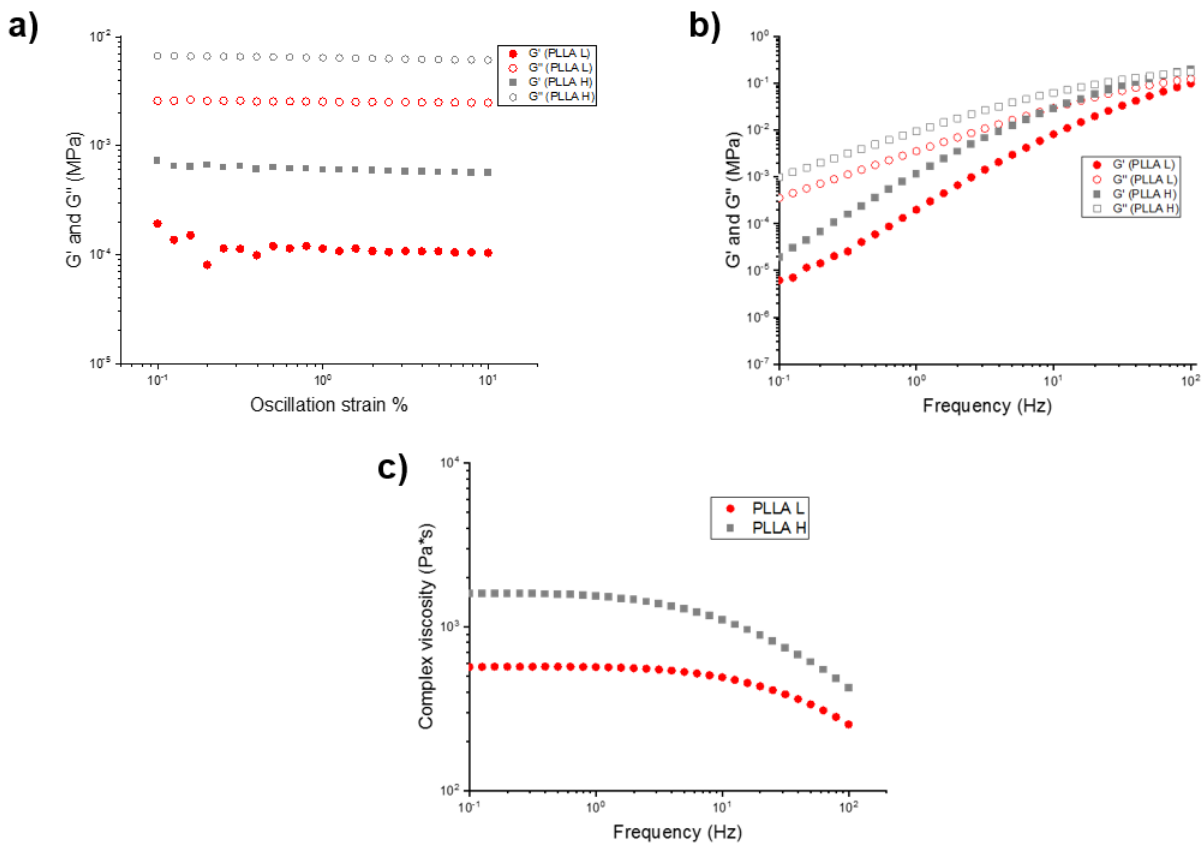
Fig. 26: Rheological protocol in PLLA: a) Strain Sweep b) *Oscillation Frequency sweep c) Complex viscosity vs frequency. All tests have been made at T= 185°C under inert atmosphere.

Looking at the strain sweep (Fig. 26a), the linearity of G' and G'' is achieved for both materials at all the strain range. Therefore, the chosen value was 4% strain amplitude for the tests.

On the other hand, as can be seen in Fig. 26b, the moduli evolution for PLLA with the frequency is similar to those in PP, as corresponds to a linear polymer However, in this case, the crossover point (G'=G") is barely visible, with both PLLAs showing fully viscous behaviour over the entire frequency range analysed. The high modulus values of PLLA would also be related to its higher molecular weight and higher entanglement density. Moreover, there is not a crossover point in PLLA L, a frequency higher than 100 Hz should have been used for that.

The behaviour of the complex viscosity is similar to that observed for PP. The only difference is the larger extension of the linear range.

A comparison of the results obtained in flow measurements and those obtained in dynamic measurements is shown below (Fig. 27 and Fig. 28). Thus, it can be seen that the values fit well.
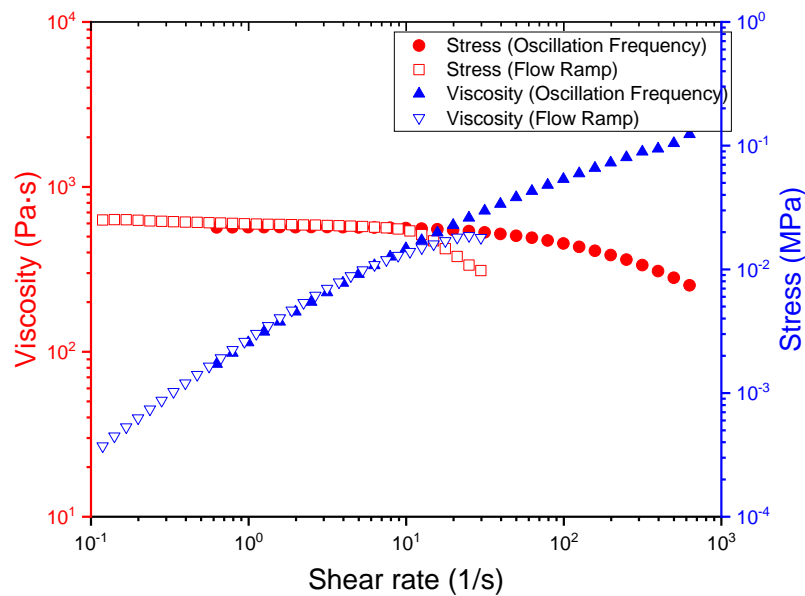

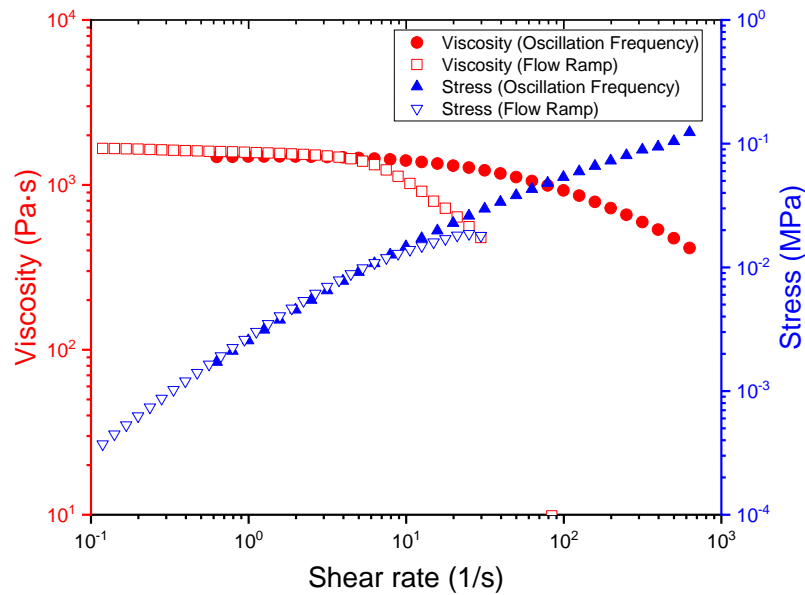**Fig. 27:** PLLA L Cox-Merz relationship.

Fig. 28: PLLA H Cox-Merz relationship.

This time as well, the viscosity and stress were placed in different axis and the change with the shear rate were studied. The overlap was detected from more or less 0,7 to 10 s^{-1}. Consequently, it is confirmed that PLLA is also a thermorheologically simple material. However, it is to mention that, after the end of the overlap, there is a decrease of both parameters. It occurs as a consequence of the break of the material due to the implementation of a high shear rate. That is why shear rates higher than those values cannot be implemented.

4.2.2   Advanced rheology: Superpositions

After performing both continuous flow and linear viscoelastic measurements, the rheological superpositions were carried out. The superpositions were performed with the objective of seeing the change of the viscoelastic spectra during a continuous flow. This way the results should be closer to the ones that suffer the materials in the processing.

4.2.2.1   Parallel superposition

The first experiment was the parallel superposition. The rheological protocol for these cases was the oscillation frequencies with the same parameters as in conventional rheology, but with the addition of shear in the same axis.
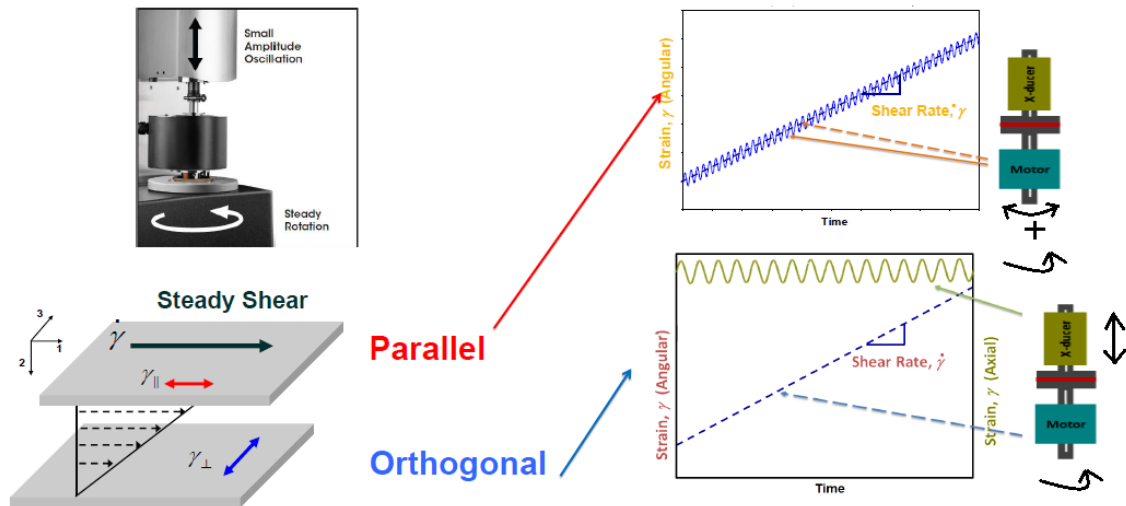
Fig. 29: Parallel and orthogonal superpositions [28].

First, the superposition was performed in PP. To decide the shear rate range, the results of the conventional rheology were analysed. In the case of PP, looking at the maximum overlap value in the Cox-Merz graphs (Fig. 24 and Fig. 25), it could be thought that the maximum shear rate that could be implemented to do the superposition could be about $10\,s^{-1}$. However, after a few tries it was concluded that smaller values, as $0,5\,s^{-1}$ are much better in order to obtain more accurate results The obtained results, both PP L and PP H are represented in Fig. 30 and Fig. 31 respectively.
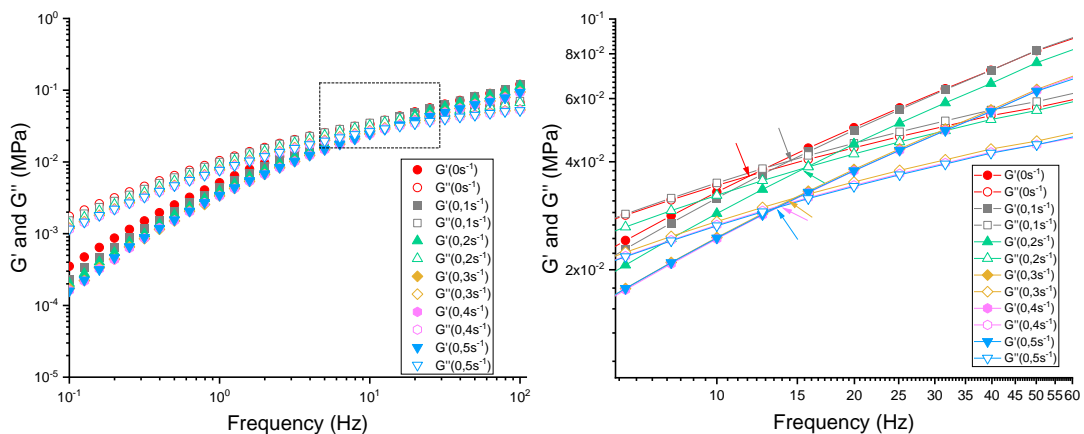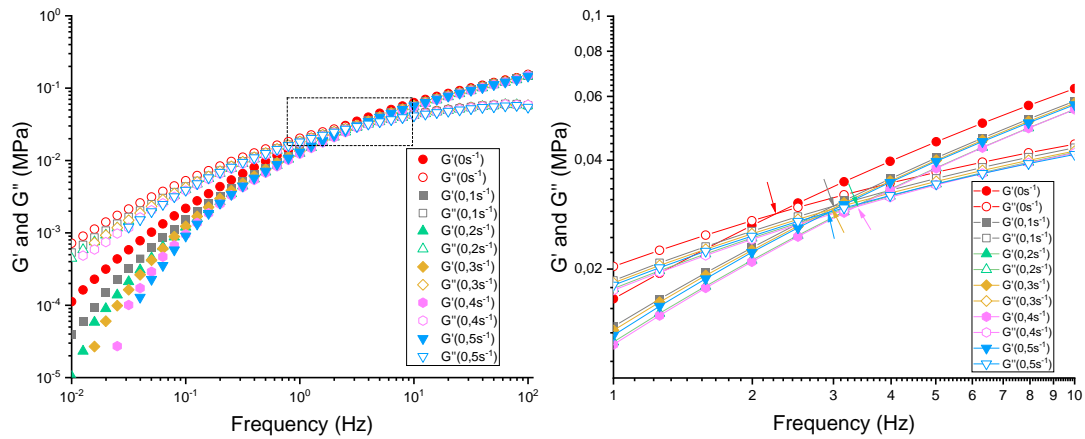

Fig. 30: Parallel superposition for PP L at 190ºC. Filled symbols correspond to storage moduli and empty symbols correspond to the loss moduli.

Fig. 31: Parallel superposition for PP H at 190ºC. Filled symbols correspond to storage moduli and empty symbols correspond to the loss moduli.

First, without taking into account the differences due to the shear rate, it is to mention that the overall decrease of moduli follows the same behaviour as in Fig. 22. However, when an increasing shear rate is imposed, a decrease in both moduli is observed, especially in the terminal flow region, i.e., in the low frequency region. This is because the viscoelastic behaviour of the material is altered with the application of flow. Looking at the crossover point, enlarged in the left graphs of Fig. 30 and Fig. 31, it can be seen that, in general terms, this crossover points shift to higher frequencies as the superimposed shear rate increases. This behaviour has been previously observed in the work carried out by L. Costello [42]. This behaviour is attributed to the greater mobility of the chains due to the imposed shear flow.

The viscosity values achieved from the same measurement of both PP are in Fig. 32.
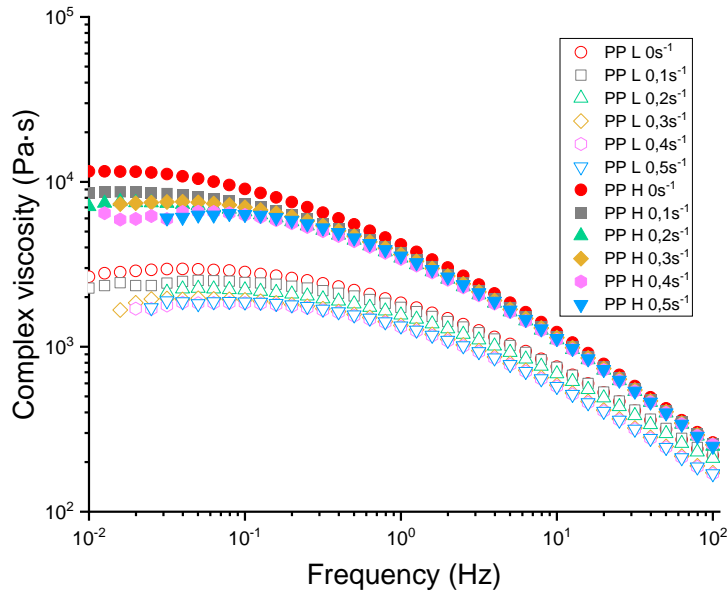
Fig. 32: Parallel superposition for PP at 190ºC. Filled symbols correspond to PP H and empty symbols correspond to PP L.

In both cases, the general behaviour is that observed in conventional tests (Fig. 23), i.e., the complex viscosity decreases with increasing frequency. However, when imposing an extra shear flow, a decrease in viscosity is observed, mainly in the low frequency region (Newtonian viscosity). This decrease is, moreover, more pronounced in the case of PP L.

The specific results of the parallel superposition are in Table 3.

Table 3: Results from parallel superposition for PP.

Sample	Shear rate in continuous flow (s⁻¹)	Crossover frequency (rad/s)	Relaxation time (s)	G_x (Pa)	Newtonian viscosity (Pa·s)
PP L	0	74,4	0,0134	36617	3040
	0,1	90,87	0,0110	40271	2552
	0,2	98,42	0,0101	38536	2393
	0,3	92,58	0,0108	31643	2086
	0,4	88,02	0,0113	30366	1996
	0,5	84,71	0,0118	29741	2044
PP H	0	14,15	0,0706	28468	11976
	0,1	18,81	0,0531	29848	9031
	0,2	21,19	0,0471	30003	7816

	0,3	18,68	0,0535	29276	8056
	0,4	21,04	0,0475	29676	7350
	0,5	18,36	0,0544	28665	7237

In order to have a closer look into the results of Table 3, it was decided to do the comparison of relaxation time and Newtonian viscosity. The relaxation time is considered the time it takes for the recovery of the entanglements after the disentanglements have happened. It represents how easily the material goes from solid to liquid-like behaviour. It is calculated as the inverse of the frequency at the crossover point. The Newtonian viscosity, on the other hand, is the viscosity the polymer will have when the velocity tends to 0. At this point the polymer will be in the entangled state. In other words, this value represents the resistance to flow of the viscoelastic liquid during the processing. So, the lower it is, less inconveniencies will be in the processing. Fig. 33 shows the values of relaxation time when the superimposed flow increases.
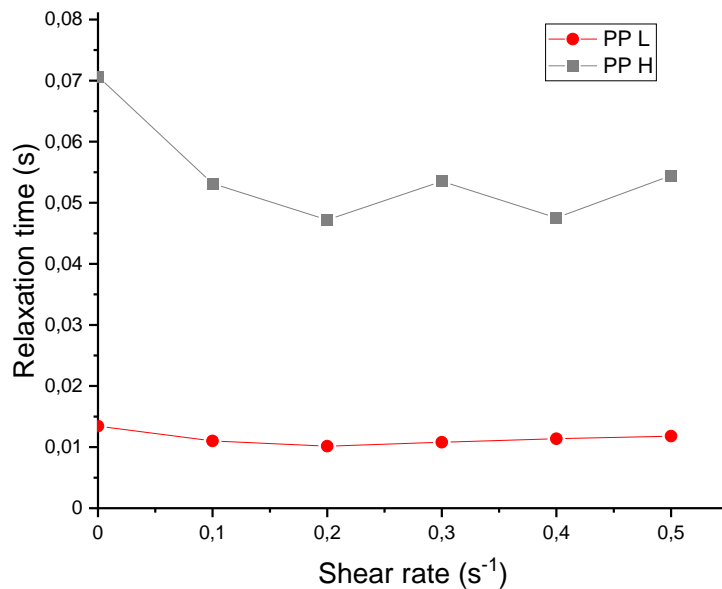
Fig. 33: Relaxation time change of PP with the shear rate in parallel superposition.

As can be seen in the graph, the relaxation time decreases slightly in the case of PP H, while in PP H it remains relatively constant with increasing imposed shear rate. This difference could be related to the higher molecular weight and the greater effect of the shear rate on entanglements. Thus, conventional rheology shows that PP H starts its shear thinning behaviour at lower shear rates than PP L,

so it can be thought that the effect of the superimposed shear rate may be more pronounced.

In Fig. 34, the evolution of the Newtonian viscosity with the increase of the flow rate imposed is represented.
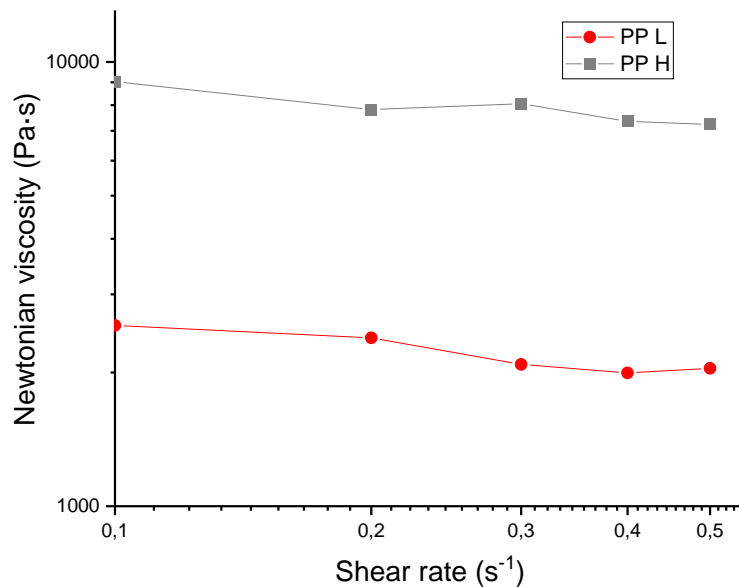

Fig. 34: Newtonian viscosity change of PP with shear rate in parallel superposition.

As can be seen, the effect of the superimposed shear rate in Newtonian behaviour is rather similar. The decrease in Newtonian viscosity is more pronounced in PP H than in PP L. This behaviour is probably due to the difference in molecular weight and the effect on entanglement discussed above.

Once observed the results of the parallel superposition in PP, the same was done with PLLA. For these materials, after some tries, different shear rates were chosen attending to the viscoelastic and flow spectrum obtained by conventional rheology: In the case of PLLA L 0, 0,5 and $2s^{-1}$, and 0, 0,5, 2, 5 and $10s^{-1}$ for PLLA H.

In Fig. 35 and Fig. 36 the results corresponding to the parallel superposition in both PLLA are presented.
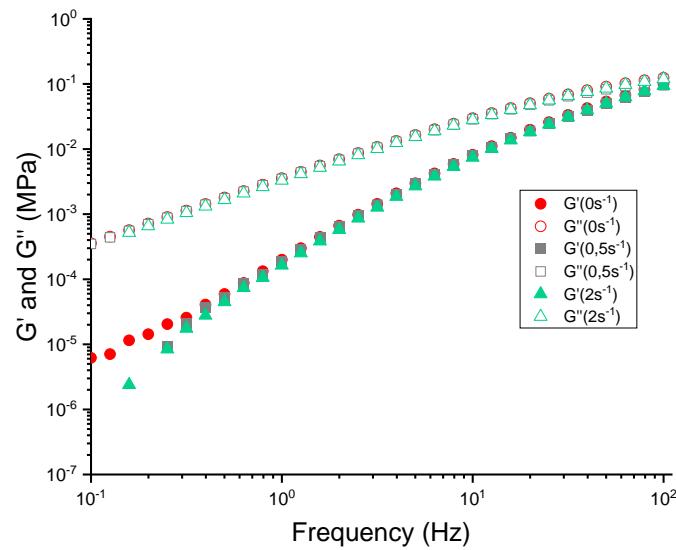
Fig. 35: Parallel superposition for PLLA L at 185ºC. Filled symbols correspond to storage moduli and empty symbols correspond to the loss moduli.
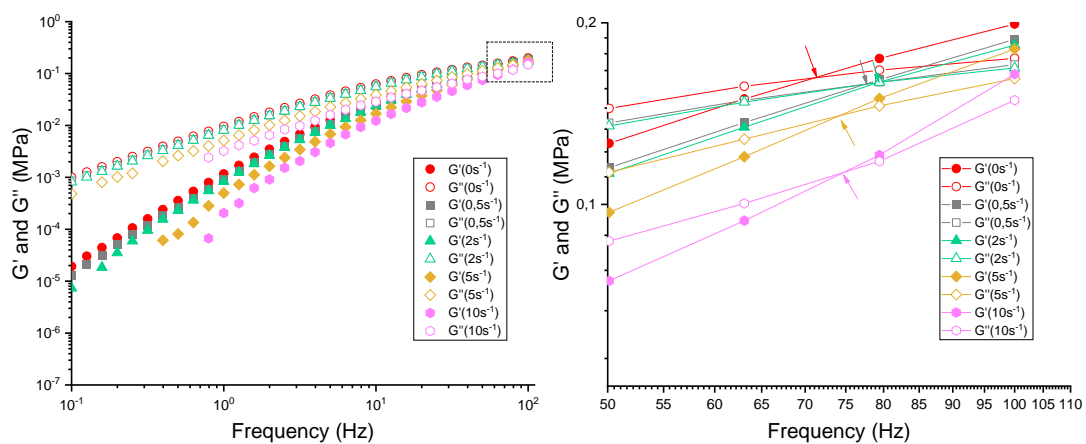
Fig. 36: Parallel superposition for PLLA H at 185ºC. Filled symbols correspond to storage moduli and empty symbols correspond to the loss moduli.

As can be seen, the viscoelastic properties of PLLA L are hardly altered by increasing the shear flow. However, the moduli G' and G'' of PLLA H are significantly altered in the same way as observed for PP H. On the other hand, in the case of PLLA L, a crossover is not detected, it happens in a frequency higher than 100 Hz. Comparing the differences between the materials, it can be seen that the decrease of the moduli is higher in PLLA H, meaning that the effect of the shear rate is higher in there. The cause behind it is that there more entanglements in PLLA H. Applying

the same shear rate in both materials, more disentanglements occur where more entanglements are. So, the difference in PLLA H is bigger than in PLLA L.

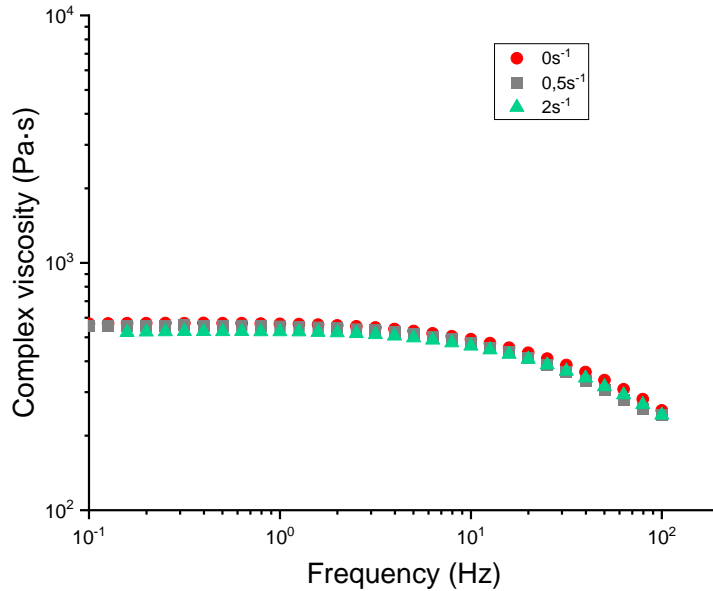The complex viscosity of both, PLLA L and PLLA H is represented in Fig. 37 and Fig. 38 respectively.

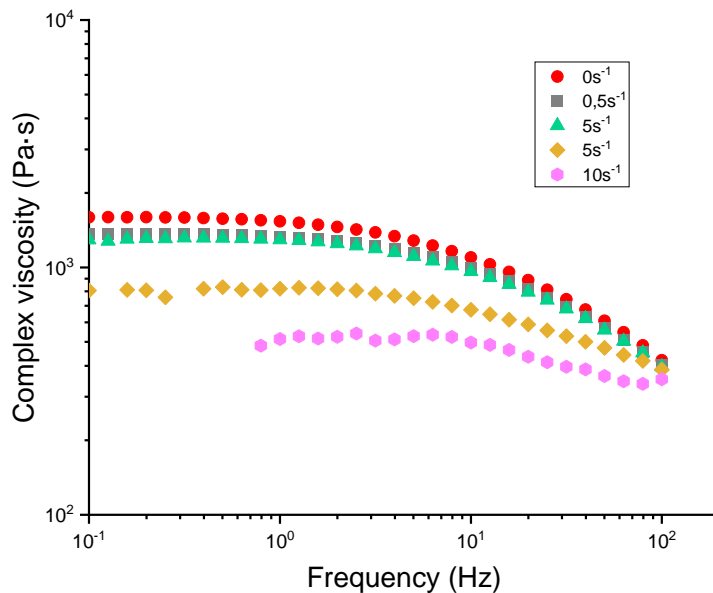**Fig. 37:** Parallel superposition for PLLA L at 185°C, viscosity changes.

Fig. 38: Parallel superposition for PLLA H at 185°C, viscosity changes.

The results for the complex viscosity corroborate the observations made on the evolution of the G' and G'' moduli. Thus, there is hardly any influence of the shear rate in the case of PLLA L, which means that there is hardly any change of the

viscoelastic properties during the flow in the analysed shear rate range. This is probably due to the fact that we are in the linear range. However, the viscoelastic properties of PLLA H are altered, due to its higher molecular weight.

The numerical results corresponding to the parallel superposition of both PLLAs are represented on Table 4.

Table 4: Results from parallel superposition for PLLA.

Sample	Shear rate in continuous flow (s^{-1})	Crossover frequency (rad/s)	Relaxation time (s)	G$_x$ (Pa)	Newtonian viscosity (Pa·s)
PLLA L	0	-	-	-	573
	0,5	-	-	-	559
	2	-	-	-	530
PLLA H	0	448,16	0,00223	162707	1622
	0,1	487,24	0,00205	158324	1388
	0,5	498,02	0,00201	159294	1323
	1	466,36	0,00214	140323	818
	5	469,59	0,00213	113008	519

In this case, it has not been possible to compare the relaxation times as could not be characterized in PLLA L. Nonetheless, Newtonian viscosity evolution was represented in Fig. 39.
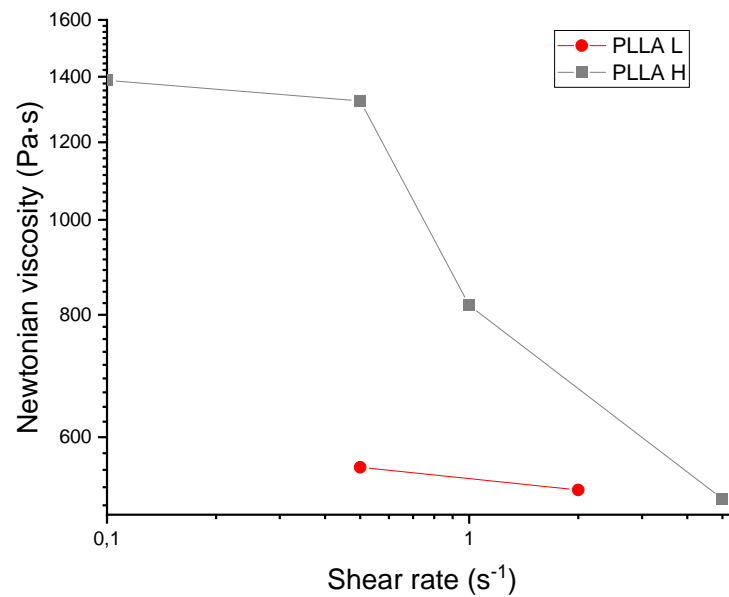
Fig. 39: Newtonian viscosity change of PLLA with shear rate in parallel superposition.

This graph shows more clearly the effect of the imposition of a flow on the behaviour of the PLLA discussed above. That is, the decrease of the viscosity is much higher in PLLA H than in PLLA L. This decrease indicates that the shear rate has more effect in there.

4.2.2.2 Orthogonal superposition

Due to the oscillation and shear being on top of each other in the parallel superposition, the results can be affected. Consequently, it was decided to perform the orthogonal superposition and compare the results with the parallel ones.

To do correctly, some parameters were changed. The oscillation in the vertical axis is limited by the gap instead of the circumference of the geometry. Accordingly, for PP, the gap was increased to 2mm and the diameter of the plates was reduced from 12 mm to 8 mm. Also, the amplitude of the strain was changed to 2% (still in LVE) after finding errors with the previous one.

First, Frequency Sweep was carried out without shear, to have it as a reference for the superposition. It has to be completed because the orthogonal superposition produces a compression stress.

35

The angular frequency went from 40 to 0,1s⁻¹, and the moduli changes of both PP are represented in Fig. 40.
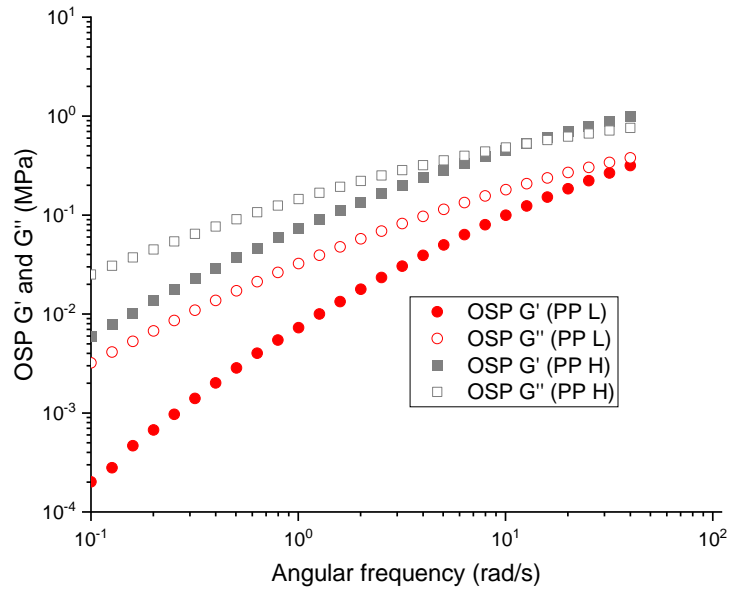
**Fig. 40**: Orthogonal Frequency Rotation of both PP, G′ and G″.

The evolution of G′ and G″ shows the same behaviour as in shear (Fig. 22), with some differences. One of them is the values of both moduli being at much higher values than in shear (10^0 - 10^{-5} MPa vs 10^1 - 10^{-4} MPa). Another one is the shift of the relaxation time to lower frequencies with the molecular weight.

Later on, the orthogonal superposition experiments were performed and the results are shown in Fig. 41 and Fig. 42.
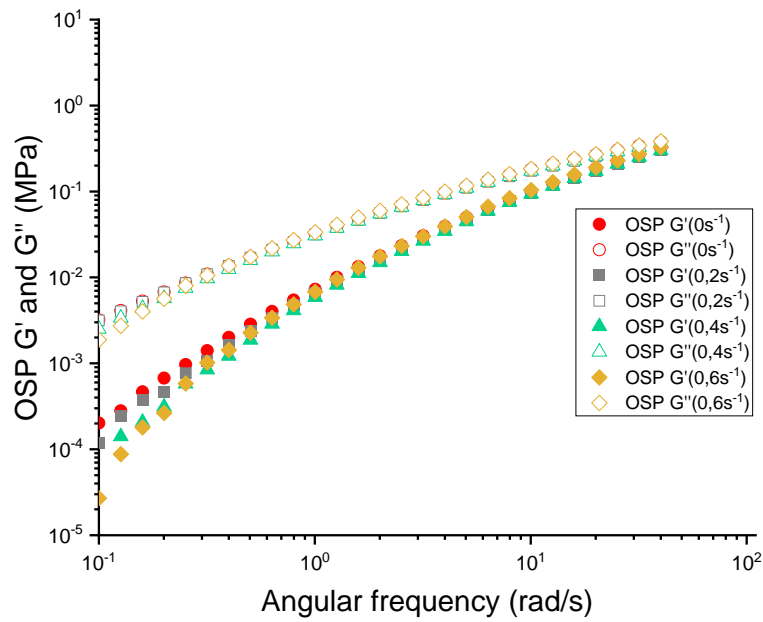
Fig. 41: Orthogonal superposition for PP L at 185°C. Filled symbols correspond to storage moduli and empty symbols correspond to the loss moduli.
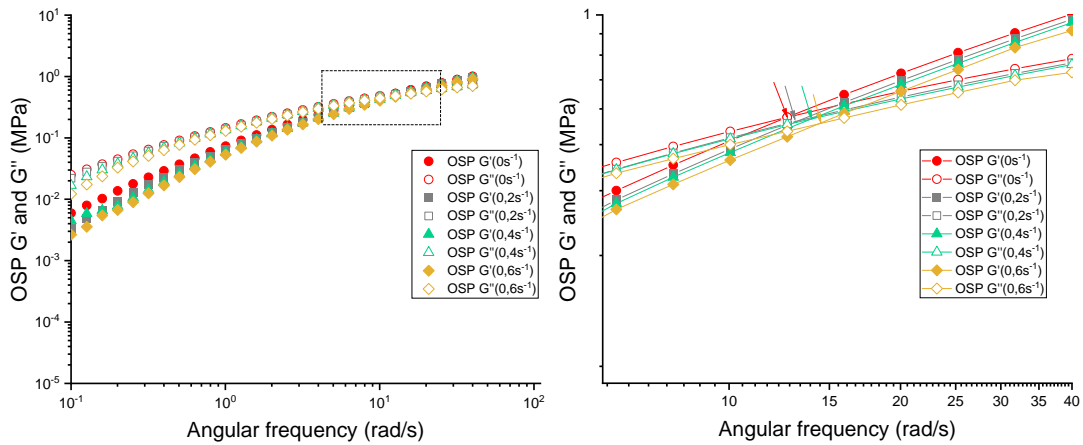
Fig. 42: Orthogonal superposition for PP H at 185°C. Filled symbols correspond to storage moduli and empty symbols correspond to the loss moduli.

In this case, the crossover was not observed in the PP L, but it did in PP H. Doing zoom to observe the progression of the crossover point, this time the linearity was followed: the higher the shear rate the higher the frequency for the crossover. Besides, the effect the shear had in them was checked, being PP H the most affected by it.

Again, the viscosity values of both PP were gained at the same time as the moduli, and they are shown in Fig. 43.
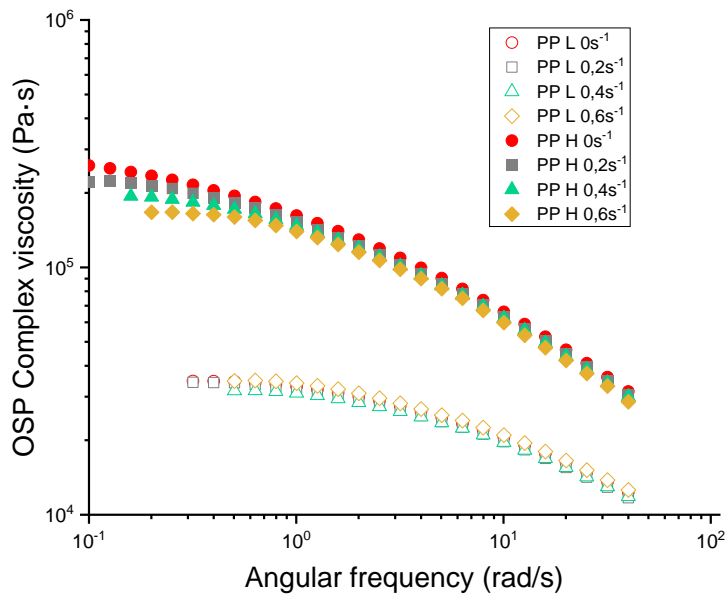
Fig. 43: Orthogonal superposition for both PP, viscosity changes.

It is to point out that, like in the parallel superposition, the effect of the shear rate decreases the viscosity values, mainly in the Newtonian region. In addition, the effect is higher in PP H, decreasing more the complex viscosity values.

The results of the orthogonal superposition are summarized in Table 5. In this case, the crossover was not achieved in PP L, so the relaxation time and G_x values cannot be accessed.

Table 5: Results from orthogonal superposition for PP.

Sample	Shear rate in continuous flow (s⁻¹)	Crossover frequency (rad/s)	Relaxation time (s)	G_x (Pa)	Newtonian viscosity (Pa·s)
PP L	0	-	-	-	36894
	0,2	-	-	-	37077
	0,4	-	-	-	34261
	0,6	-	-	-	37895
PP H	0	12,64	0,0791	527433	322852
	0,2	13,2	0,0757	515644	257095
	0,4	13,94	0,0717	521627	220986
	0,6	14,34	0,0697	505502	183095

Just like in the parallel superposition of PLLA, only the Newtonian viscosity of PP can be compared in the orthogonal superposition, found in Fig. 44.
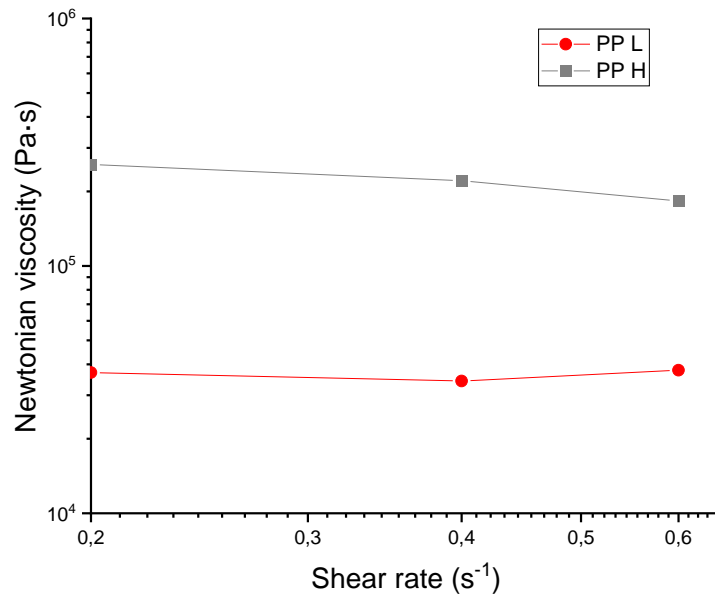

Fig. 44: Newtonian viscosity change of PP with shear rate in orthogonal superposition.

The differences between the materials are similar to the ones of parallel superposition in Fig. 34. The shear rate decreases the values of viscosity and PP H has higher ones due to higher molecular weight.

Having the results and the comparison of PP as a reference, the orthogonal superposition was performed in PLLA. For the orthogonal superposition of PP, the gap was increased to have more space for the oscillation to occur. However, due to lack of material, the gap was not increased in this case and, as countermeasure, the amplitude of the oscillation was decreased to 0,2%. It is still in the LVE region, so the results should be comparable. Thus, the OSP experiments for PLLA are compared in Fig. 45.
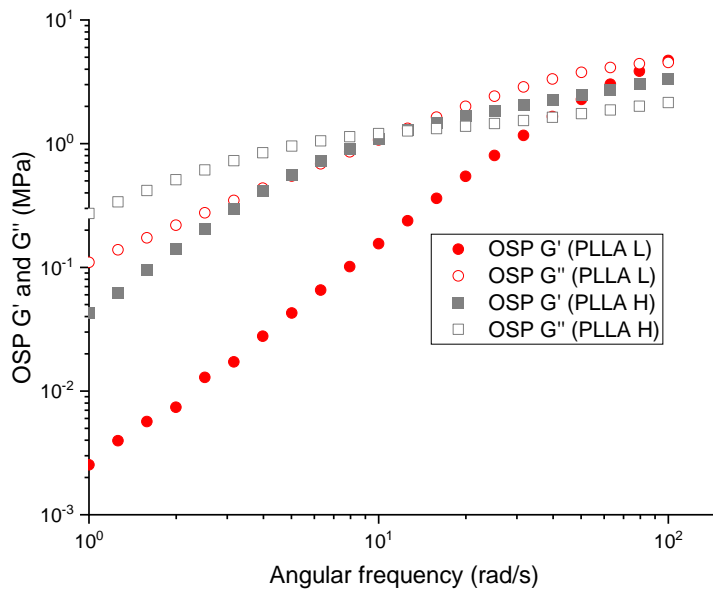
Fig. 45: Orthogonal Frequency Rotation, G′ and G″ of both PLLA.

From this graph, it is apparent that the tendency of the decrease of G′ and G″ happen just like in parallel superposition. The viscoelastic spectrum for PLLA L shows only the terminal region, with a crossover at very high frequencies. In contrast PLLA H show the crossover at lower frequency values.

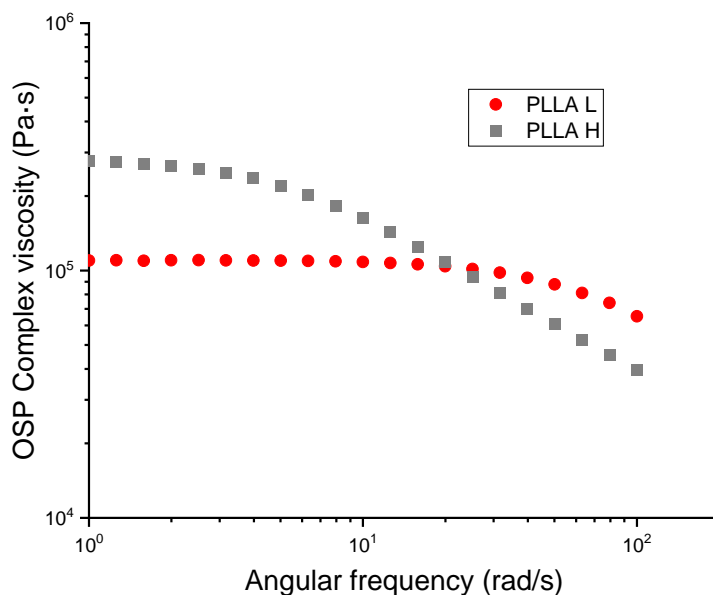Similarly, the viscosity changes from the previous measurement are presented in Fig. 46.

**Fig. 46:** Orthogonal Frequency Rotation, viscosity of both PLLA.

It is evidence here that the materials show a pseudoplastic character as viscosity decreases with the angular frequency. What is interesting in this graph is that, like with G′ and G″, both viscosity values cross. PLLA H ends up with higher viscosity, but still, they should not cross due to the molecular weight difference. This is strong evidence of the degradation of PLLA H.

Turning now to the superposition with the addition of shear, the moduli of both PLLA are compared in Fig. 47 and Fig. 48.
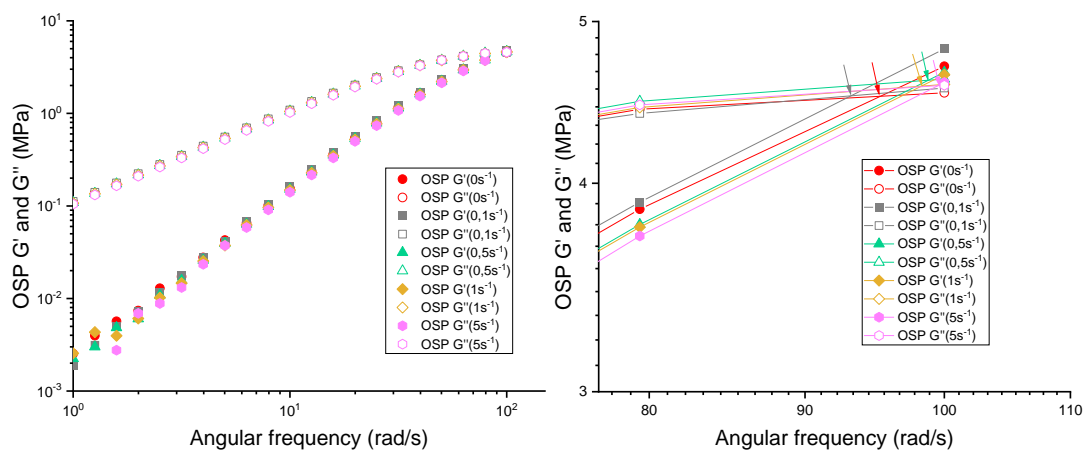
Fig. 47: PLLA L Orthogonal superposition, G′ and G″ changes.
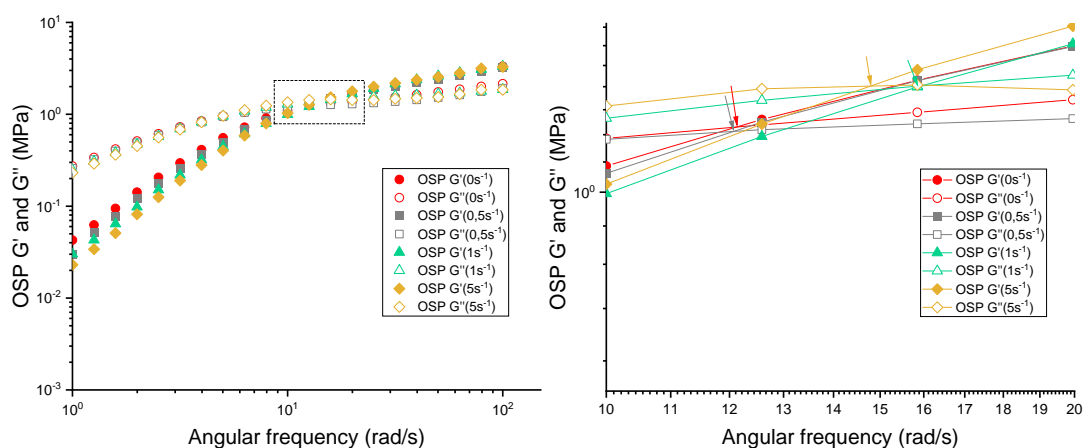
Fig. 48: PLLA H Orthogonal superposition, G′ and G″ changes.

As can be seen from the graphs, the moduli decrease with the shear rate like in the previous ones, and the crossover was detected in both materials. However, unlike what happened in the orthogonal superposition of PP H in Fig. 42, the

linearity of the increase was not followed. This fact can be due to the already mentioned degradation.

The complex viscosities were procured with the same measurements, and they are presented in Fig. 49 and Fig. 50.
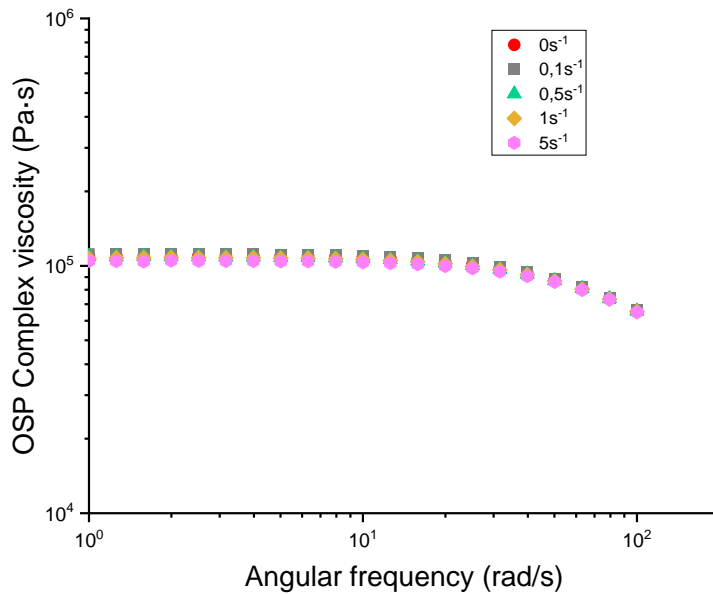
Fig. 49: PLLA L Orthogonal superposition, viscosity changes.

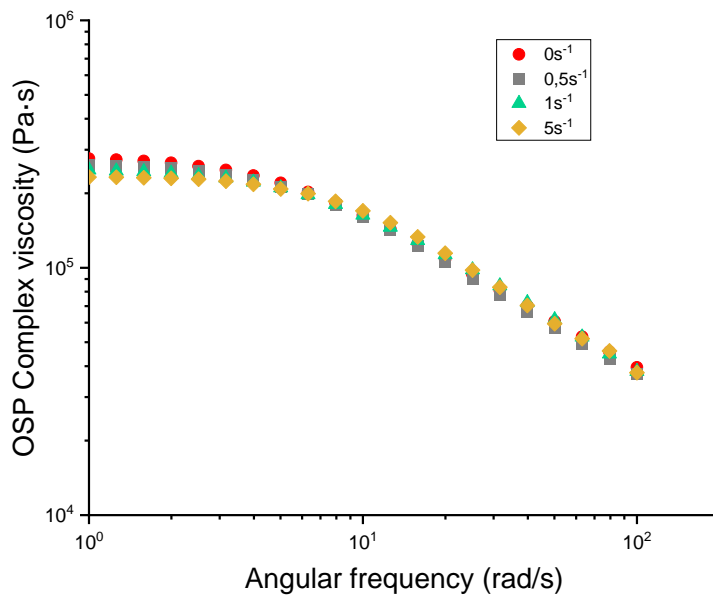**Fig. 50:** PLLA H Orthogonal superposition, viscosity changes.

As it can be seen in the figures, the viscosity of materials is not affected by the application of shear (in contrast to PP results). We can conclude that the shear rate did not have too much effect in both PLLA. The reason of this difference can be related to the molecular weight, that are much higher in the case of PP. It has

been already established with the previous viscosity measurements that with higher molecular weights there are more entanglements, and so, more effect of the shear rate. In this case, as the chain mobility is higher and the shear rate values very low, it is expected that materials are in their entangled situation.

The main results from the orthogonal superposition of PLLA are provided in Table 6.

Table 6: Results from orthogonal superposition for PLLA.

Sample	Shear rate in continuous flow (s⁻¹)	Crossover frequency (rad/s)	Relaxation time (s)	Gx (Pa)	Newtonian viscosity (Pa·s)
PLLA L	0	95,34	0,0105	4521420	110115
	0,1	93,23	0,0107	4519900	111859
	0,5	98,79	0,0101	4611030	109081
	1	98,29	0,0102	4573740	107917
	5	99,52	0,0100	4576340	104750
PLLA H	0	12,09	0,0827	1254690	289131
	0,5	12,04	0,0831	1237160	270137
	1	15,94	0,0627	1449380	257097
	5	14,82	0,0675	1454330	236898

Due to the obtainment of all parameters with PLLA, the comparison of relaxation time and Newtonian viscosity is viable. The relaxation times are compared in Fig. 51.
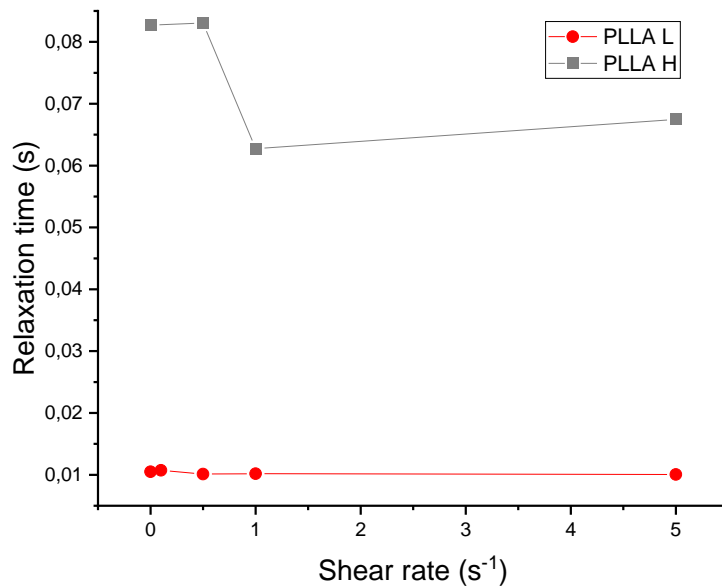
Fig. 51: Relaxation time change of PLLA with shear rate in orthogonal superposition.

In general, it is observed that the relaxation time values of PLLA H are higher than of PLLA L. It is interesting that the effect of the shear rate is much higher in PLLA H as well. However, there are errors regarding those values. There is an increase from $1s^{-1}$ to $5s^{-1}$, where it should have decreased even more.

The Newtonian viscosity of both materials were compared as well, and the comparison is observed in Fig. 52.
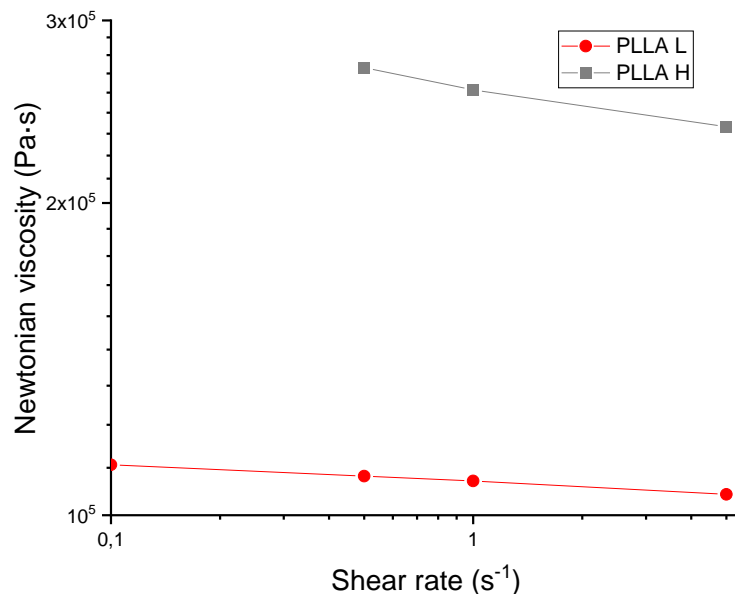
Fig. 52: Newtonian viscosity change of PLLA with shear rate in orthogonal superposition.

As the graph reveals, higher values are in PLLA H due to the molecular weight and there is a significant decrease of the Newtonian viscosity in there compared to PLLA L. However, this effect is much lower than in PP samples.

4.3 Comparison between parallel and orthogonal superposition.

With both superpositions the obtainment of relaxation time and Newtonian viscosity has been possible in PP H. So, the comparison of them can be set to see the relation between the explores superposition techniques. First, the relaxation time was performed in Fig. 53.
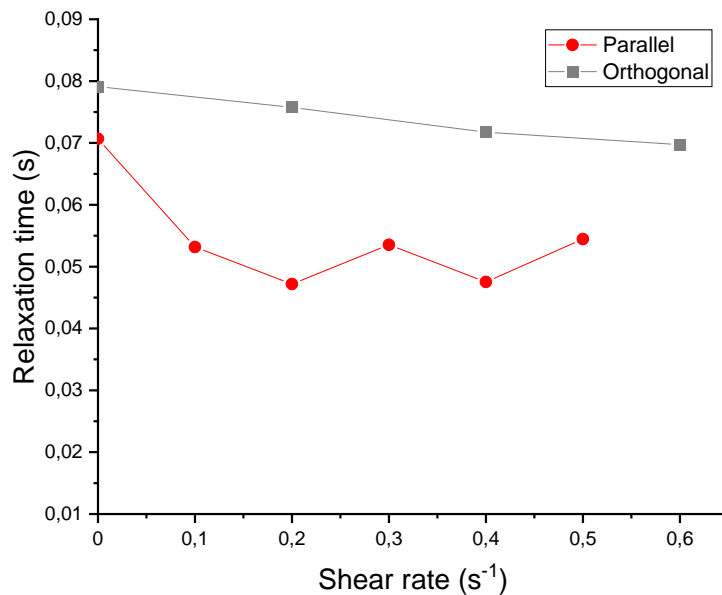

Fig. 53: Relaxation time difference of PP H with parallel and orthogonal superposition.

As shown in the graph, in both cases the relaxation times are decreased. However, there is a main difference between them: Using the orthogonal superposition irregularities are not identified, it always goes down in a linear way with the increase of shear rate. The conclusion of it is that the orthogonal superposition gives cleaner information about the materials, while in the parallel superposition the flow and the oscillation can have influence in each other because they are in the same axis.

The Newtonian viscosity of PP H in both superpositions were compared in Fig. 54.
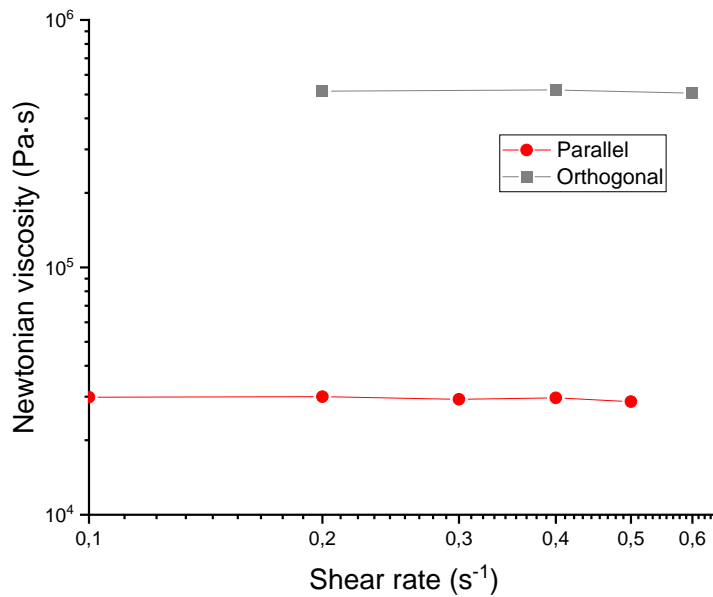
Fig. 54: Newtonian viscosity difference of PP H with parallel and orthogonal superposition.

With the Newtonian viscosity, the differences between them are similar to the modulus, being much higher in the orthogonal. However, in this case, they remain quite constant, meaning that the shear does not have much effect comparing to the relaxation time.

The results of the superpositions in PLLA show that the comparison of the relaxation time and Newtonian viscosity is possible for PLLA H. The relaxation times are presented in Fig. 55.
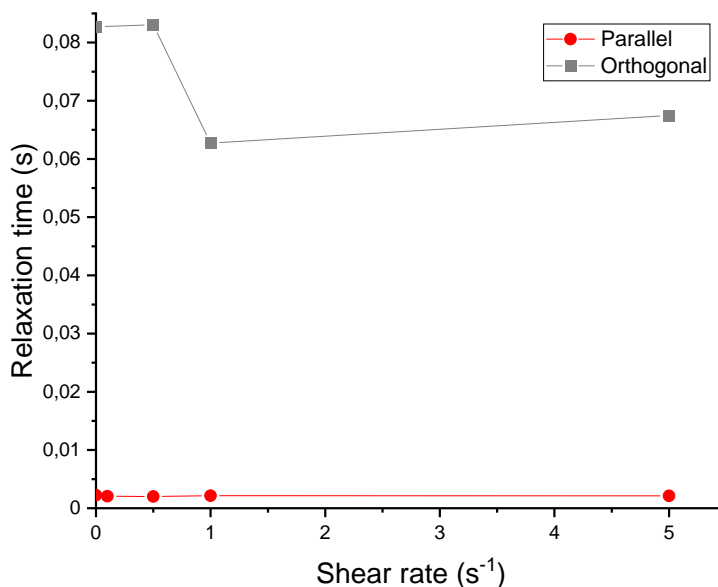
Fig. 55: Relaxation time difference of PLLA H with parallel and orthogonal superposition.

From this graph we can see that the difference between them is too large that the change in the parallel superposition cannot be distinguished. However, it was already observed in Fig. 33 that it goes decreasing with the shear rate, just like in orthogonal superposition. The results are quit irregular, they do not follow the linearity.

As mentioned before, the Newtonian viscosities of PLLA H were comparable as well, and they are shown in Fig. 56.
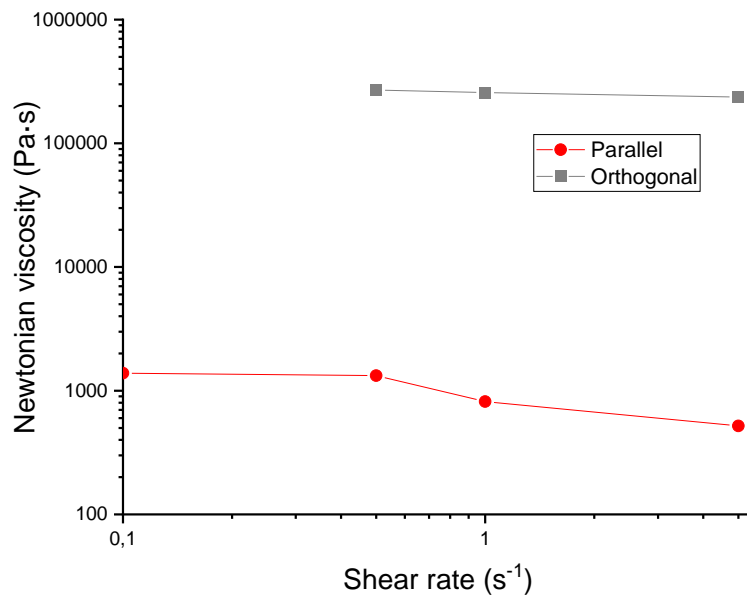
Fig. 56: Newtonian viscosity difference of PLLA H with parallel and orthogonal superposition.

The most striking result to emerge from the graph is that the superposition makes the viscosities at completely different levels. It is up to the point that the values of the parallel seem constant. This is refuted looking at those values in

Fig. 39. Nevertheless, the evolution of them is different, being more linear in the orthogonal superposition. This finding corroborates the reached conclusion in PP H, that the shear and oscillation affect each other in the parallel superposition making the results more irregular.

Finally, it was decided to compare the complex viscosities of PP H in parallel and orthogonal superposition, in order to see the effect of the shear not just in the end, but throughout all the frequency range.
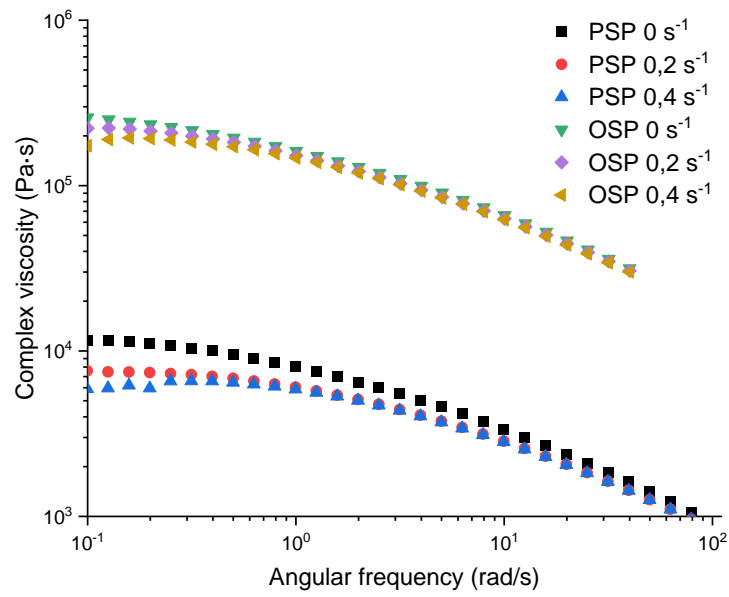
Fig. 57: Complex viscosity difference of PP H with parallel and orthogonal superposition.

The results of Fig. 57 indicate that the viscosity decreased with the simultaneous addition of an oscillation and continuous flow. It is interesting to note that the decrease was more substantial in the parallel superposition. This finding suggests that, as explained in the previous comparisons, the shear and oscillation in the same direction are summed and, as a result, the difference increases.

5. Conclusions

The conclusions based on the results are:

1. The parallel and orthogonal superpositions are useful for the measuring simultaneously the viscoelasticity and the flow properties of material. This information can give a closer look to the real properties of the materials during the processing.

2. The shear moves the crossover point to higher frequencies, decreasing the relaxation time. It also decreases the Newtonian viscosity. Even though a compression was applied instead of shear in the orthogonal superposition, the obtained trends are similar.

3. The maximum shear rates that were possible to apply without breaking the materials have been very low. The maximum value has been of 10 s^{-1} with the parallel superposition of PLLA H. However, the measurements were stopped early due to the break of it, so the measurements are far from manufacturing conditions (for example, polymer extrusion conditions).

4. The low shear rates are not high enough to disentangle polymer chains. This made the materials quite isotropic and the changes observed with the superpositions were not as high as expected.

5. Overall, the results were not very clear and some errors were seen. Sometimes the values were almost the same even though different shears were implemented, even going to contradictory values.

6. Even though the measurements of PLLA were performed under inert atmosphere, the degradation of the material happened, making the comparison between them quite meaningless.

Conclusiones

Las conclusiones basadas en los resultados son:

1. Las superposiciones paralelas y ortogonales son útiles para medir simultáneamente la viscoelasticidad y las propiedades de flujo del material. Esta información puede dar una visión más cercana a las propiedades reales de los materiales durante el procesado.

2. El cizallamiento desplaza el punto de cruce a frecuencias más altas, disminuyendo el tiempo de relajación. También disminuye la viscosidad newtoniana. Aunque en la superposición ortogonal se aplicó una compresión en lugar de un cizallamiento, las tendencias obtenidas son similares.

3. Las velocidades máximas de cizallamiento que fueron posibles de aplicar sin romper los materiales han sido muy bajas. El valor máximo ha sido de $10 \, s^{-1}$ con la superposición paralela de PLLA H. Sin embargo, las mediciones se detuvieron pronto debido a la rotura del mismo, por lo que las mediciones se alejan de las condiciones de fabricación (por ejemplo, las condiciones de extrusión del polímero).

4. Las bajas velocidades de cizallamiento no son lo suficientemente altas como para desenmarañar las cadenas de polímeros. Esto hizo los materiales fueran bastante isotrópicos y que los cambios observados con las superposiciones no fueran tan altas como se esperaba.

5. En general, los resultados no fueron muy claros y se observaron algunos errores. A veces los valores eran casi los mismos, aunque se aplicaran diferentes cizallas, llegando incluso a valores contradictorios.

6. Aunque las mediciones de PLLA se realizaron en atmósfera inerte, la degradación del material se produjo, haciendo que la comparación entre ellas carezca bastante de sentido.

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