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# Experimental Investigation on Rheological Characterization of ecovio® F Film C2203biopolymer Melts

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**Abstract:** ***The rheological behavior and properties of polymers fluid are significantly concerned with their internal structure therefore it's has been experimentally and numerically investigated for many of industry applications. This article of research studies the characterization of (ecovio® F Film C2203) biopolymer due to their characteristics and importance in different fields of health and environment. Two type of rheometers instruments have been used at different temperatures range (140 - 220 ˚C) to describe the rheological properties of the (ecovio® F Film C2203) biopolymer melts with various investigating mechanisms. The results were compared with the linear results of oscillatory measurements and non-linear results of steady-state method which provide the storage and the loss modulus of the (ecovio® F Film C2203) melting, and given the model of Cox-Merz. Likewise, in the measuring of a viscosity for the (ecovio® F Film C2203) at the higher shear rate, particularly at the excess temperature, one of the master problems was in the using of a capillary rheometer, because of the long chains of a molecule which led to the high viscosity.***

**Keywords:** ecovio® F Film C2203 biopolymert, thermo-rheological properties

## 1. Introduction

Polymer is a chemical compound or mixture generated by polymerization process that consist a repeating structural units [1].Biopolymer or bio macromolecule is a polymer that formed by organism, like RNA, DNA, proteins, cellulose, and starch[2]. Biopolymers are usually not similar to industrial polymers, and can now easily distinguish between the two types. The structure is the main difference between these two types. The polymers are structurally simpler and have random structures, while the other possess vital infrastructure and well-defined (Biopolymers, 2016). Biopolymers are biodegradable into water and carbon dioxide by the action of microorganisms, heat, and moisture, thus used as fertilizer "Environmental friendly"[3]. The ecovio® F film C2203is the film product able to biodegradable, and that containing the renewable resources. The main compounds of that biodegradable products are "ecoflex® F Blend co-polyester" and (PLA) polylactic acid. For this reason the (PLA) content ecovio® F Film C2203 consisting of 32% of the renewable energy resources. The ecovio® F Film C2203 having the properties similar to low-density polyethylene (LDPE), this biopolymer shows the following characteristics compared with (LDPE):

Semi-crystalline structure, translucent, medium stiffness, high strength, the water vapors transmission rate is high but controllable (WVTR), and the thermo stability is good up to 230 ˚C[4]. The biopolymers are characterized by non-Newtonian fluid and behave as the viscoelastic fluid, because of its ability, to behave between both viscous and elastic response of one sample in the same experiment[5]. Most studies of rheological characterization for biopolymer are concentrated on the dynamic viscoelastic and viscosity function properties with molten biopolymer. So that this article is very important in the molten plastic industries[5].To explain the viscoelastic behavior of (Ecovio F film C2203), we realized that the rheology suggestion three various measuring methods, elongation flow, steady state, and small amplitude oscillatory shear[6] and [5]. The dynamic rheological measurements (oscillation method) is the most common deformation method to investigate the linear behavior of viscoelastic[5].This can be used to find the stability of material, give a clear significance of the sample behavior, and strength. Even though the elastically or viscous behavior predominant over the specific range of frequency. While its confirmed on sinusoidal strain or stress at variable frequency (ω) and the response must be follow the sinusoidal wave [7], that it was performed on the popular rheometer, also it offered rise to storage modulus, in stage with a deformity, and other parts losses modulus. Thus, these moduli are named as elastic modulus (G') and viscose or loss modulus (G"). The angle (δ) of deformation can be defined as a ratio of loss modulus to storage modulus;

$$\tan\delta = \frac{G''}{G'} \quad \ldots(1)$$

It can be explained the damping behavior of biopolymer sample[8] and [9]. Cox-Merz is the familiar relationship which has been used in the relating between complex viscosities that measured by linear oscillatory experiments to the shear viscosity as a function of shear rate[9] and [10]. The rule of Cox-Merz is a correlation that has certain experimentally to the various types of polymers and biopolymers. Superimposition of shear rate depending on the study shear viscosity, which is $\eta(\dot{\gamma})$, also the frequency depending on complex viscosity, which is $\eta^*(\omega)$; equivalents amounts of shear rate and frequency were reported firstly by the Cox-Merz (1958):

$$\eta^*(\omega) = \eta(\omega)\big|_{\omega} = \dot{\gamma} \text{ When } \omega = \dot{\gamma}$$

[11]… (2)

In this research, the thermo-rheological characterization of shear viscosity for "ecovio® F Film C2203" biopolymer melts have been studied at different range of temperature (140 ˚C to 220˚C), and shear rate (0.001 $s^{-1}$-1000 $s^{-1}$), respectively. The results compared with steady viscosity (η) and dynamic viscosity (η*) using the Cox-Merz rule. Likewise, the results obtained for the higher shear rates (G' and G″) using the capillary rheometer were compared with the Cox-Merz rule also.

## 2. Methodology

The methodology consisted of five steps:
Step 1: Collection of materials and "ecovio® F Film C2203" granular biopolymer samples,
Step 2 Determine the melting rheological properties of the "ecovio® F Film C2203" granular biopolymer samples using two types of mechanical rheometer
Step 3: determine the relations of viscosity and shear rate with temperature,
Step 4: Discuses the results of melting rheological properties of the "ecovio® F Film C2203"

## 3. Materials and Methods

Two types of mechanical rheometer as shown in Figures (2-4), were used to determine the melting rheological properties of the "ecovio® F Film C2203" granular biopolymer samples. The rheological properties measurements by using (AR-G2) Rotational Rheometer is plate to plate configuration as illustrated Figure 2and Figure 3a, this device is commonly used for viscoelastic material measuring[12]. Whereas, the steady viscosity was obtained at various shear rate in the range of 0.0001/s to 1/s as illustrated in Figure 5. Where the oscillatory technique that used to rheological tests by utilizing the same device of rheometer. While the dynamics characterization such as the angle of phase (δ) as a function of angular frequency (ω) rad/s, "storage modulus" (G') Pa, and "losses modulus" (G") Pa measured as shown Figure 6. The features of rheological behavior have been measured in temperature range between (140˚C-220˚C) and all these measurements have been conducted in the existence of nitrogen gas to prevent samples oxidation. The flow characteristic and deformation in large scale of ecovio® F Film C2203 biopolymer melts using of the Cox-Merz rule was extended gradually from low to high shear rate for measuring range as shown in Figures 5. Capillary rheometer (RG20–Göttfert) as shown Figure 4 was used for the comparison of shear rates values, also the capillary rheometer used for determining the high shear rate viscosities in the range between 10/ s-1000/s. All these measurements were replicated to ensure the exemplary sample. It's important to use high pressure in the capillary rheometer that will be used for measuring viscosities at high shear rates the Figure 5 show the measurements principle. This fluid was compressed with the system of piston cylinder through the capillary tube. The elastic and viscous behavior of ecovio® F Film C2203 Melts for various temperatures and their relations to the viscosity at steady state condition by the Cox -Merz Rule have been experimentally determined.

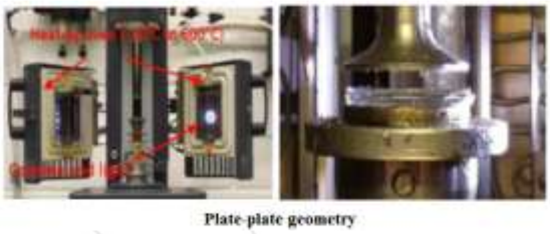



**Figure 2:** AR-G2 rotational rheometer with the plate-plate configuration

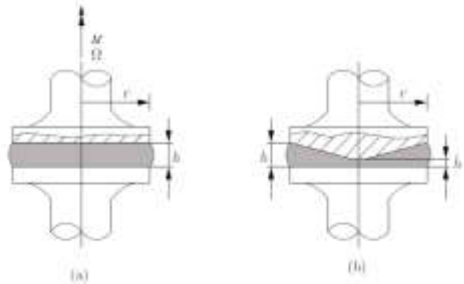


**Figure 3:** (a) plate-plate (b) cone- plate configuration


**Figure 4:** High- pressure capillary rheometer

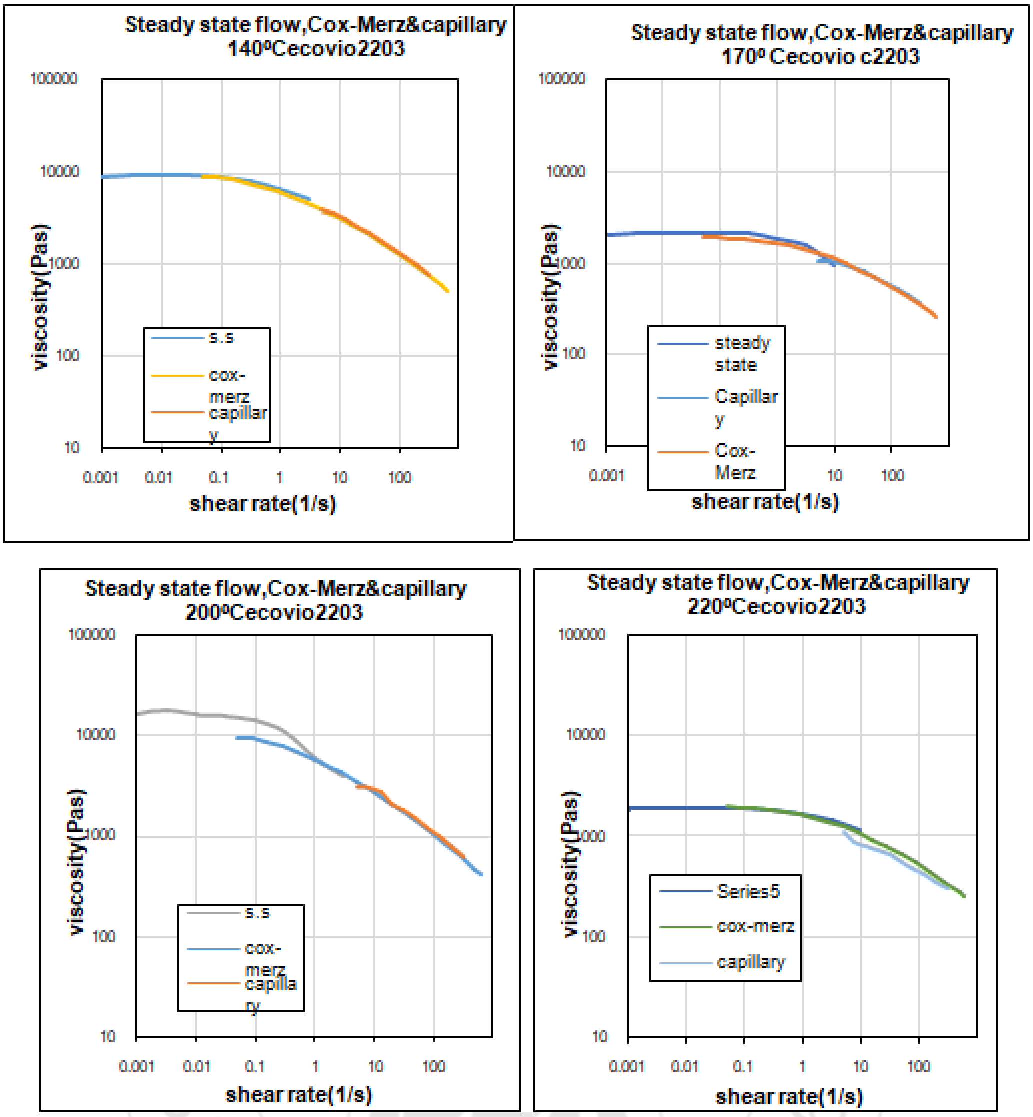
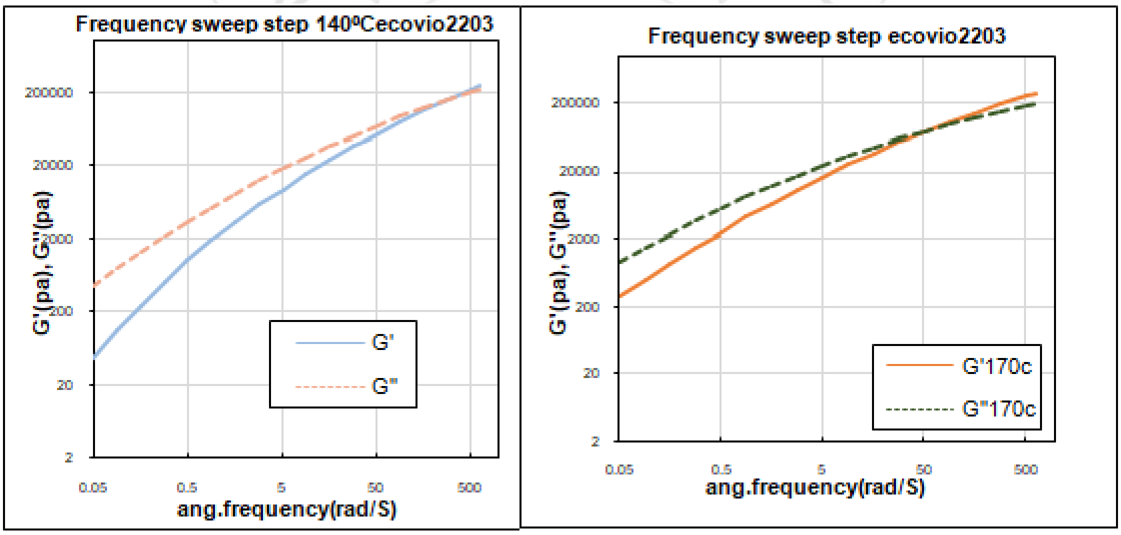
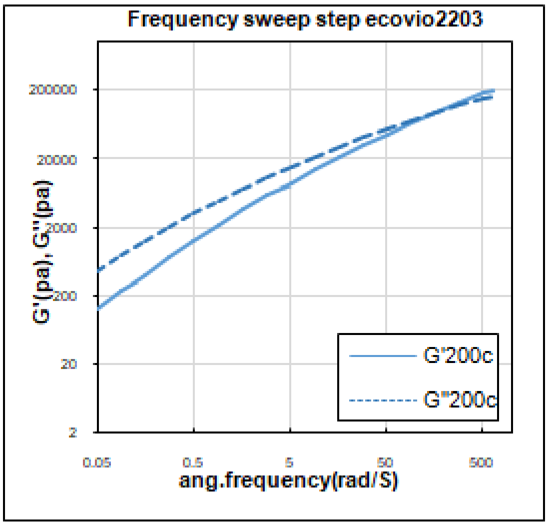



**Figure 5:** Shear viscosity of ecovio® F Film C2203 measurements at steady state, Cox-Merz and Capillary for different temperatures region (140 ˚C to 220 ˚C)





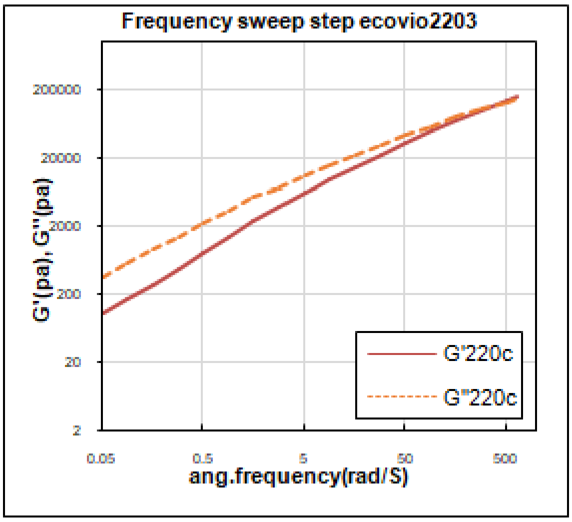




**Figure 6:** Storage and loss modulus of ecovio® F Film C2203, for wide range of frequency and different temperatures region (140 ˚C to 220 ˚C)

## 4. The Theory and the Relations between Parameters

The measurements of the theoretical viscosity and shear rate of the rotational rheometer was gained from a given movement velocity angle Ω with

$$\dot{\gamma} = \frac{\Omega r}{h} \qquad \ldots(3)$$

And the "measured moment" M with the "shear stress" and a given "shear viscosity" which can be calculated by(Al-Baldawi, Ammar et al., 2013).

$$\eta = \frac{2M}{\pi r^3}\dot{\gamma} \qquad \ldots(4)$$

The pressure difference (Δp) between tube inlet and outlet in the case of capillary rheomete was measured by the connection with the "volume flux" $\dot{v}$. To calculate two new parameters by using these quantities the wall shear stress and a weighted flow rate.

$$q = \frac{32}{\pi d^3}\dot{v} \qquad \ldots(5)$$

$$\tau_w = \frac{\Delta p d}{4l} \qquad \ldots(6)$$

The relationship between the "wall shear rate" and the "flow rate" under the steady condition in the tube which resulting from the equation of reads and momentum.

$$q = \frac{4}{\tau_w}\int_0^{\tau_w} \tau^2 \dot{\gamma}(\tau) d\tau \qquad \ldots(7)$$

Integration by parts leads to the real shear rate at the wall

$$\dot{\gamma}w = \dot{\gamma}\left(\frac{d}{2}\right) = \frac{1}{4}\left[3 + \frac{d(\log q)}{d(\log \tau_w)}\right]q \qquad \ldots(8)$$

the shear viscosity can be calculated by the following equation

$$\eta = \frac{\tau w}{\dot{\gamma} w} \qquad \ldots(9)$$

This relation is termed as “Rabinowitsch-Weissenberg-correction” (Al-Baldawi, Ammar et al., 2013).And for a more accurate description of the behavior for viscous material which is carried out with mechanical dynamic analysis [14]. The sinusor (oscillating) uterine tests are often used to describe the dependence on the frequency of melting polymer. The mathematical model for the oscillation test can be illustrated as follow:

$$\gamma = \gamma \circ \sin \omega t \qquad \ldots(10)$$

$$\sigma = \sigma \circ \sin(\omega t + \delta) \qquad \ldots(11)$$

Hereby, equation10 represents, the stress function, where the γ and $\gamma_0$ in $s^{-1}$ represents the strain and strain capacity respectively, and the ω is the angular frequency (2πF) and F is the frequency. It’s clearly noted that all the rheological measurements use ω in [rad / S]. Equation 11 represents the function of stress, where σ and $\sigma_0$ is the "stress" and "breadth of stress" respectively, and the angle δ that results in this stress delayed by the angle of phase [15]. From Figure 7, the state of two waves of frequency ω, at one phase and 90° out-of-phase for the strain is clearly explained by Equation 12:

$$\sigma = \sigma' + \sigma'' = \sigma'' \circ \sin \omega t + \sigma'' \cos \omega t \qquad \ldots(12)$$

Where σ 'and σ" respectively illustrate the stress which consist of phase-in and phase-out. G′ and G″ modulogy can also know dynamic by the relationship between strain and stress:

$$G' = \frac{\sigma \circ'}{\dot{\gamma} \circ}$$

Which is called elastic or in-phase modulus… (13)

$$G'' = \frac{\sigma \circ''}{\dot{\gamma} \circ}$$

Which is called viscous, loss or out-phase modulus… (14)

By applying the model of Maxwell, the first order differential equation with its solution which gives the shear stress is explained by equation 15:

$$\sigma = (\omega\tau\cos\omega t - \sin\omega t) \quad \ldots (15)$$

G' is written as:

$$G' = \frac{\eta\omega^2\tau}{1+\omega^2\tau^2} \quad \ldots (16)$$

By placing sin [ωτ] =0, if the portion of in-phase is used and G″ is written as:

$$G'' = \frac{\eta\omega}{1+\omega^2\tau^2} \quad \ldots (17)$$

By putting cosωτ =0, if the stress out –phase is applied.
Where τ in the equations of 15, 16 &17 is called time of the relaxation s.
By deriving the strain in equation 3; shear rate was computed, which is lead to the "dynamic viscosity" η.

$$\dot{\gamma} = \frac{dy}{dt} = \gamma\circ\omega\cos\omega t \quad \ldots (18)$$

We defined the viscosity is the function of the shear stress to the shear rate ratio, as we notice in the below relationships which can be gained [16]:

$$\eta' = \frac{\sigma\circ'}{\dot{\gamma}\circ} = \frac{G\circ''}{\omega} \quad \ldots (19)$$

$$\eta'' = \frac{\sigma\circ'}{\dot{\gamma}\circ} = \frac{G\circ'}{\omega} \quad \ldots (20)$$

Where η′ is the "dynamic viscosity", η″ is regarding to the "dynamic rigidity" through G′. In equation 21 the complex modulus and the overall Magnitude of the complex viscosity was defined [5] and [7]:

$$|\eta *| = (\eta'^2 + \eta''^2)^{1/2} = [(\frac{G''}{\omega})^2 + (\frac{G'}{\omega})^2] = [\frac{|G *|}{\omega}] \quad \ldots (21)$$

$\tan\delta = \frac{G''}{G'} = \frac{\sigma''}{\sigma'} = \frac{\eta'}{\eta''}$ Is called a "loss factor", or "the relation between the viscoelastic moduli"; i.e. the rate between viscous and elastic η*, G* which can be defined in the oscillatory measurements as we notice in the below equations:

$$\eta* = \eta' + i\,\eta'' \quad \ldots (22)$$

$$G* = G' + iG'' \quad \ldots (23)$$

Where $i=\sqrt{-1}$

The Cox-Merz rule can be used to expand the shear rate tests from low to high shear rate. The Cox-Merz tests generated a correlation between the linear amount and the nonlinear amount of the oscillatory shear tests as observed in the following equations [17] and [18]

$$|\eta *(\omega)| = (\eta'^2 + \eta''^2)^{1/2} = \eta(\dot{\gamma}) \,|\, \dot{\gamma} = \omega \quad \ldots (24)$$

We can duplicate Equation 20:

$$|\eta *(\omega)| = [\eta'^2(\omega) + (\frac{G'}{\omega})^2]^{1/2} \quad \ldots (25)$$

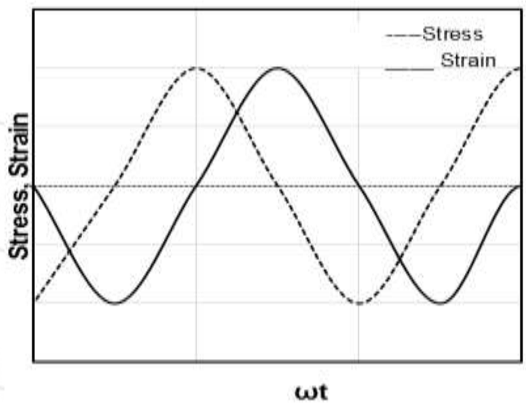



**Figure 7:** Sinusoidal forms of stress and strain characteristics for a viscoelastic material

## 5. Modeling Approaches

Carreau-Yasuda model (as explained in Equation 26) as a suggested analytical model for experimental data, in this work of thin-film shear behavior was found to be suitable analytical model.

$$\eta(\gamma) = \frac{\eta(\gamma)}{(1+(\lambda*\eta)^n))^m} \quad \ldots (26)$$

Where λ is the time constant (s), n and m are dimensionless exponents to adjust the transition of the viscosity into the non-linear.

As shown in Figure 10 and Table 1, the modeling approaches for isothermal and non-isothermal processes can be used to provide a close representation of the measurements.

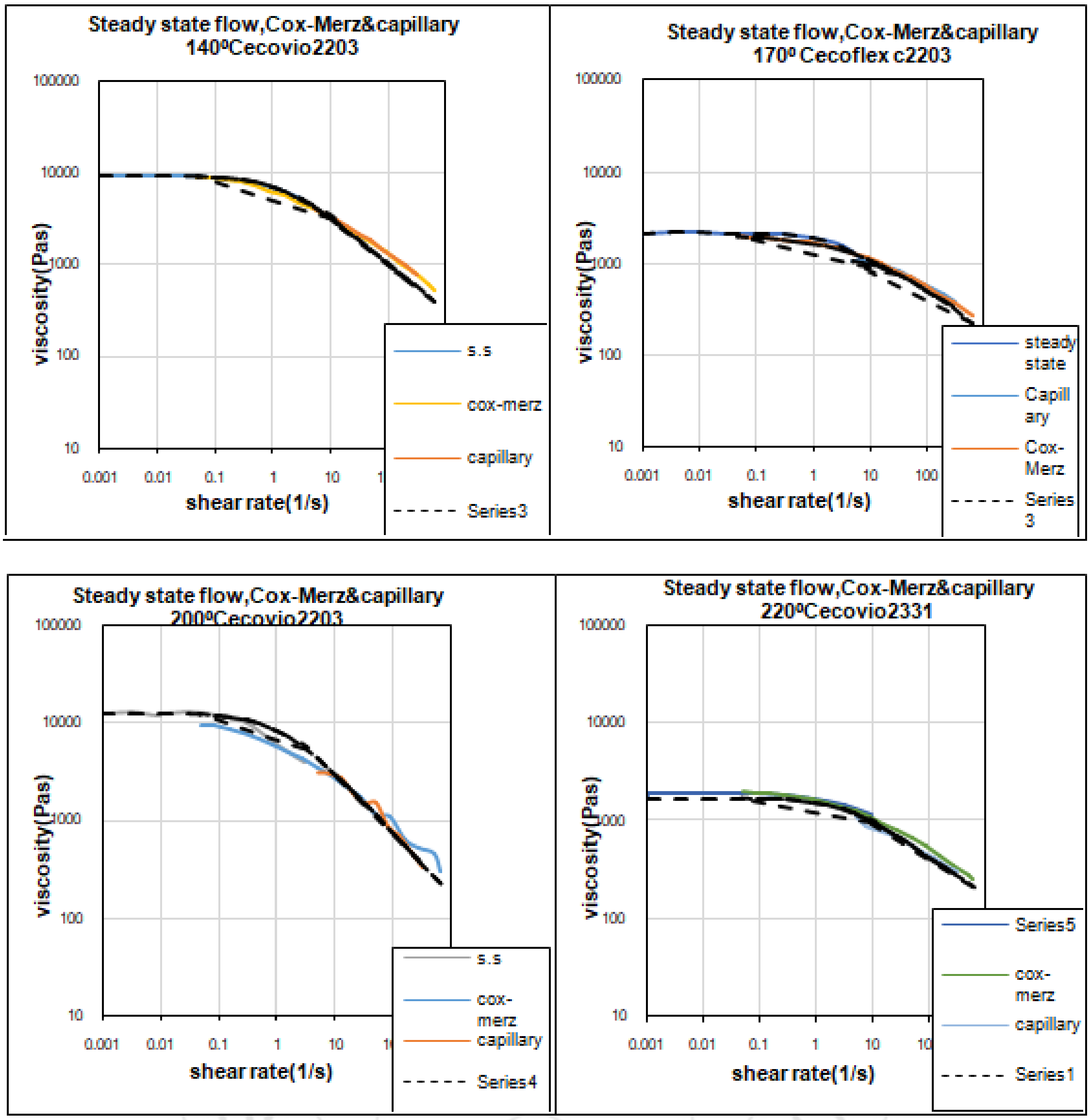



**Figure 8:** The experimental results with Carreau model at different temperatures

**Table 1:** Parameters of the Carreau-Yasuda model at different temperatures

| Temperature °C | $\lambda$ | n | m | $\eta_0$ |
|---|---|---|---|---|
| 140 | 0.71 | 0.86 | 0.6 | 9251 |
| 170 | 0.4 | 0.3 | 0.1 | 2961 |
| 200 | 0.4 | 0.7 | 0.5 | 2712 |
| 220 | 0.5 | 0.85 | 0.4 | 2373 |

## 6. Results and Discussion

The dynamic and static state of the ecovio® F Film C2203 viscosity is drawn in (Figures 5&6). For distinguishing the rheological behavior by using rotational scale the fixed shear flow for melting polymer is important. To estimate the flow behavior of the visco-flexible polymer, all the tests were perfect under nitrogen atmosphere to prevent the molecules of polymer oxidation, by using the volumetric flow rate of 10 l/min of nitrogen. Furthermore, all temperatures were applied in the range between (140 ˚C -220 ˚C) which were suitable for the Cox-Merz base; we notice that the dynamic viscosity is often higher than its equivalent steady state when moving from the zero frequency, where they tend to concur as noticed in Figure 5. Moreover, the capillary rheometer was done at the high shear rate and which was compared with Cox-Merz base. Only at 140, 170 & 220˚C, which coincides with the Cox-Merz. But in the other temperature approximated conformity, because of long molecule chain of the biopolymer, a problem was noticed in the measuring shear rate by using the capillary rheometer which then led to linear pressure and high viscosity. It can also be used as a process model to provide documented representation of these measurements. In fact, the model of Carreau-Yasuda can be used for both isothermal and non-isothermal processes. The Oscillatory tests must be done similar to the rheological Circle [14](as shown in fig. 9). Then can be immediately correlated the elastic components for the solution of the polymer with the "storage modulus" G', while the viscous components which were illustrated by the "loss modulus" G".

In addition, this device was used to obtain a dynamic shear oscillating flow that describes the response to small-scale amplitude deformation at different temperatures so that we can measure the viscosity flow in addition to its work in compliance with stable state measurements to extend the shear rate. In the oscillation test shown in Fig. 6, we note that G" is greater than G' in all the temperature grades used in this tests. From this, we conclude that the energy was used to deform this substance was clearly dissipates viscously and physical behavior is like liquid, and it is indicated here that the viscous component of the coefficient is controlling on the flexible counter. While at the higher angular frequency, G' is more than G". In this phenomenon of the flow behavior for ecovio® F Film C2203 display which is different radically from many polymers. Moreover, the higher frequency limit is around 625; however, the Rotational Rheometer (AR-G2) was used to provide maximum. For this, we can obtain the equal value of G' with G" in all temperature range we used but at higher temperature, it is not adequate to input the plateau regime of the "storage modulus". This is mean that the parameters of a network are not attainable at each temperature unless extrapolation as shown in Table 2 & Figure 9 to assign the angular frequency value.

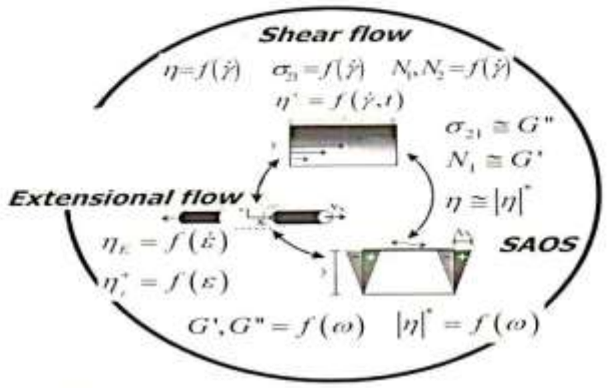



**Figure 9:** Rheological cycle [16]

**Table 2:** The angular frequency at different temperatures for same values of G' and G"

| Temperature ˚C | ω (rad/s) | G`=G″ |
|---|---|---|
| 140 | 158.1 | 121700 |
| 170 | 158.1 | 124500 |
| 200 | 281.2 | 120200 |
| 220 | 500 | 128100 |

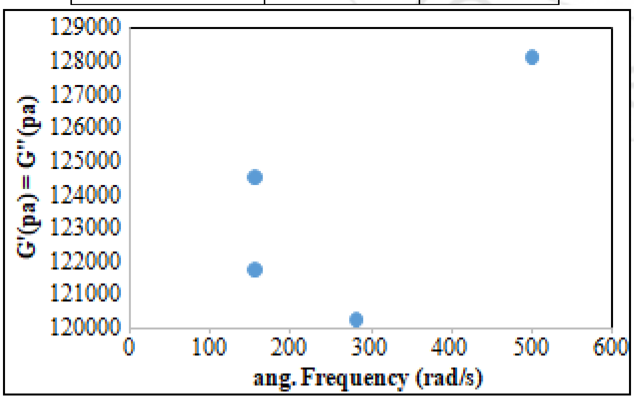



**Figure 10:** The angular frequency at different temperatures with the same values of G`and G″

## 7. Conclusion

The present study showed that all temperatures applied over the range of (140-220) ˚C was suitable for Cox-Merz base and the dynamic viscosity was higher than its equivalent steady state for various frequencies. The results also showed Cox-Merz rule was found to hold excellently for biopolymer at 140, 170 & 220˚C, whereas a slightly different exponent at other temperatures due to long molecule chain formation and difficulty in measuring the shear rate by using the capillary rheometer that which then led to linear pressure and high viscosity. The results also reveal that the energy used to deform the biopolymer was clearly dissipating viscously and physical behavior like liquid which indicated that the viscous component of the coefficient was controlled on the flexible counter at the higher angular frequency, G' is more than G".

## 8. Acknowledgments

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## Nomenclature

$\dot{\gamma}, \gamma_w$ Shear rate ($s^{-1}$)
r The radius of the plate-plate geometry and the sample (m)
Ω Angle velocity of the plate-plate geometry (radius/s)
h Height of the sample (m)
$\eta', \eta''$, Dynamic viscosity (Pas), dynamic rigidity (Pas) (pa)
$\eta *$ Complex viscosity (Pas)
M Measured moment (Nm)
q Weighted flow rate ($s^{-1}$)
$\dot{V}$ Flow rate (volume flux) (m3/s)
d Diameter of the tube of the capillary rheometer (m)
$\tau, \tau_w$ Shear stress and wall shear stress (N/m2)
$\Delta p$ Pressure gradient (bar)
$l$ Length of the tube of the capillary rheometer (m)
$\sigma, \sigma_0$ Stress and stress amplitude (N/m2)
$\sigma', \sigma''$ Stress of in-phase and out-phase (N/m2)
$G', G''$ Elastic and viscous modulus (pa)
$G*$ Complex modulus (pa)

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