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Experimental Determination of the Elastic and Viscous Behavior of Polycarbonate Melts at Different Temperatures and Their Relationship to the Steady State Viscosity via the Cox-Merz Rule

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Abstract

Rheological instrument is one of the basic analytical measurements for diagnosing the properties of polymers fluids to be used in any industry. In this research polycarbonate was chosen because of its importance in many areas and possesses several distinct properties.

Two kinds of rheometers devices were used at different range of temperatures from 220 ˚C-300 ˚C to characterize the rheological technique of melted polycarbonate (Makrolon 2805) by a combination of different investigating techniques. We compared the results of the linear (oscillatory) method with the non-linear (steady-state) method; the former method provided the storage and the loss modulus of melted polycarbonate, and presented the Cox-Merz model as well. One of the major problems in measuring the viscosity of polycarbonate at high shear rates, especially at the extremes of temperatures, was that during the use of the capillary rheometer, long molecule chains led to high viscosity.

Keywords: Rheology, Rheology dynamic property, Cox-Merz rule, Complex Modulus, Polycarbonate Polymer melt, thermo-rheological modeling, Oscillatory Measurements, Rotational rheometer, High-pressure capillary rheometer.

Introduction

Polycarbonate (Pc) Makrolon®, one of the important polymers, is used in many areas due to having a lot of good specifications. The generic name for polyester contains the repeating carbonate group. There is a wide spectrum of polycarbonates, especially from phenol. Figure1 shows the structure of the repeating unit of polycarbonate [1].

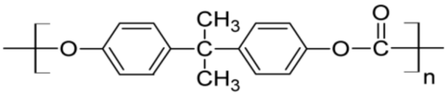

Fig. 1:The stracture of polycarbonate molecule

Polymers fit into a broad class of complex fluid and are characterized by the term non-Newtonian phenomena, e.g. high viscoelastic behavior, because of their ability to vigorously determine both the elastic and viscous response of a sample in one experiment [2]. Techniques for measuring rheological properties especially flow properties were well covered by many scientists [3]. Most rheological studies for polymers concentrated on the viscosity function and dynamic viscoelastic properties, which can be measured continuously as the material undergoes temperature-induced changes from solid to liquid and vice versa because both molten and solid states are extremely important to sectors of plastics industry [2].

The main advantages of polycarbonate are transparency, dimensional stability, flame resistance, high heat distortion temperature, and it is a transparent amorphous polymer which exhibits outstanding physical properties such as impact resistance (almost unbreakable), heat resistance up to 125˚C and excellent clarity [4]. For this reason, polycarbonate is often used to replace glass or metal in demanding applications.

Therefore, it is an important and widely used engineering thermoplastic. However, PC exhibits high notch sensitivity, and it is susceptible to crazing or cracking on exposure to various solvents. To clarify the visco-elastic properties of Pc melt, we know that the rheology offers three different measurements methods, steady state, small amplitude oscillatory shear (saos) and elongation flow [5]. Oscillation technique (dynamic rheological testing) is a popular deformation mode for investigating linear viscoelastic behavior [6]. It may be used to determine the strength and stability of a material, and it gives clear indication of the behavior of the sample, whether viscous or elastically dominated over a given frequency range. It applies a sinusoidal stress or strain at changing frequency ω; the induced response must follow a sine wave [7], which is performed on common rheometer, as well as it gives rise to modulus G', in phase with the deformation, and another part G″, out phase. These two moduli are therefore called the elastic modulus G' and the loss or viscose modulus G" because the latter is related to viscous dissipation of the fluid.

The angle δ contains this deformation through the ratio of the loss modulus to the storage modulus:

$$\tan \delta = G''/G' \qquad \ldots(1)$$

And it represents the damping properties of the sample [8, 9].

The well-known relationship of Cox-Merz has long been used to advantage in relating the complex viscosity measured in linear oscillatory testing to the steady shear viscosity as a function of shear rate [10, 11] .The Cox-Merz rule is an empirical correlation that has been confirmed experimentally for several synthetic polymers. The superimposition of the shear rate dependence of steady shear viscosity, that is $\eta\ (\dot{\gamma})$, and of frequency dependence of the complex viscosity, that is $\eta^*(\omega)$; equal values of frequency and shear rate were first reported by Cox-Merz (1958):

$$\eta^*(\omega) = \eta\ (\omega)\ |_{\omega=\dot{\gamma}} \text{when } \omega= \dot{\gamma}\ [12]\ldots(2)$$

The objectives of this research were to investigate thermal rheological of shear viscosity of Pc (Makrolon) in a temperatures region of 220 ˚C -300 ˚C and a shear rate of 0.001 s^{-1} to 1000 s^{-1}; to compare the steady viscosity η to the dynamic η* by applying Cox-Merz rule values of G, G″ were obtained by using capillary rheometer with high shear rate and compared with Cox-Merz rule.

Experimental Work

All the measurements reported were carried out on two kinds of rheometer devices as shown in the Figures 2-4 to determine the melt behavior of granular polycarbonate; the type of polycarbonate used is Makrolon®2805 of the material science Bayer Company. The samples were pre dried at 120 ˚C before analysis for 12 hours to make sure the arrival of humidity is not more than 0.02% residual moisture; that Pc may be adversely affected by water at high melt temperature of greater than 250˚C. Therefore, vigorous drying was important for good reproducibility. The dryer used was TORO-SYSTEMS Dry-Jet Mini made by (GFK) company. Rheological measurements were performed with the Rotational Rheometer (AR-G2), by using the plate-plate geometry as shown in Figure 2 and Figure 3 (a). Thus parallel plates are usually preferred for measuring viscoelastic material functions [13]. Steady viscosities were obtained at different shear rates between 0.0001 s^{-1} and 1 s^{-1} as shown in Figures 5 and 6. Oscillatory mode was used for rheological measurements using the same rheometer above. The dynamic properties i.e. storage modulus, G' [Pa], loss modulus G" [Pa] and phase angle δ as a function of angular frequency ω [rad/s] were measured as show in Figures 7 and 8. The frequency of oscillation was varied from 0.01 to 1000 rad/s. The rheological characteristics were measured at different rate of temperatures from 220-300 ˚C. All tests were conducted under the presence of nitrogen gas to prevent oxidation of the samples. To study the large-scale deformation and flow characteristics of pc by applying the Cox-Merz model, the range of shear rate measurements can be extended from low shear rate to high shear rate as shown in Figures 6 and7.

The other device that was used for the comparison between the values of the shear rate is capillary rheometer (RG20 – Göttfert) shown in Figure 4. Capillary rheometer is used primarily to determine the viscosity at high shear rates from10 to 1000 s^{-1}. All tests were performed in replicate to ensure representative sampling.

In case of the high shear rates of viscosity measurements, the use of the high-pressure capillary rheometer is important. Figures 5and 6 show the principle of the measurements.

The fluid is pressed with a piston-cylinder system through a capillary tube.

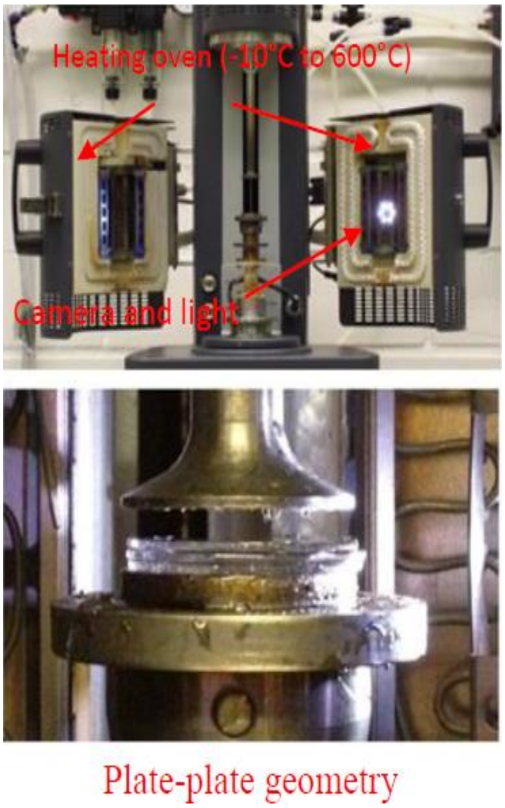

Fig. 2: AR-G2 (TA-Instruments) rotational rheometer with the used plate-plate geometry

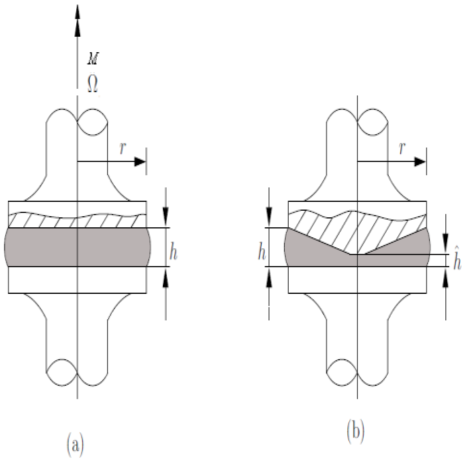

Fig. 3: (a) plate-plate (b) cone- plate system

Fig. 4: Rheograph 20 (RG20 - Göttfert) high- pressure capillary rheometer

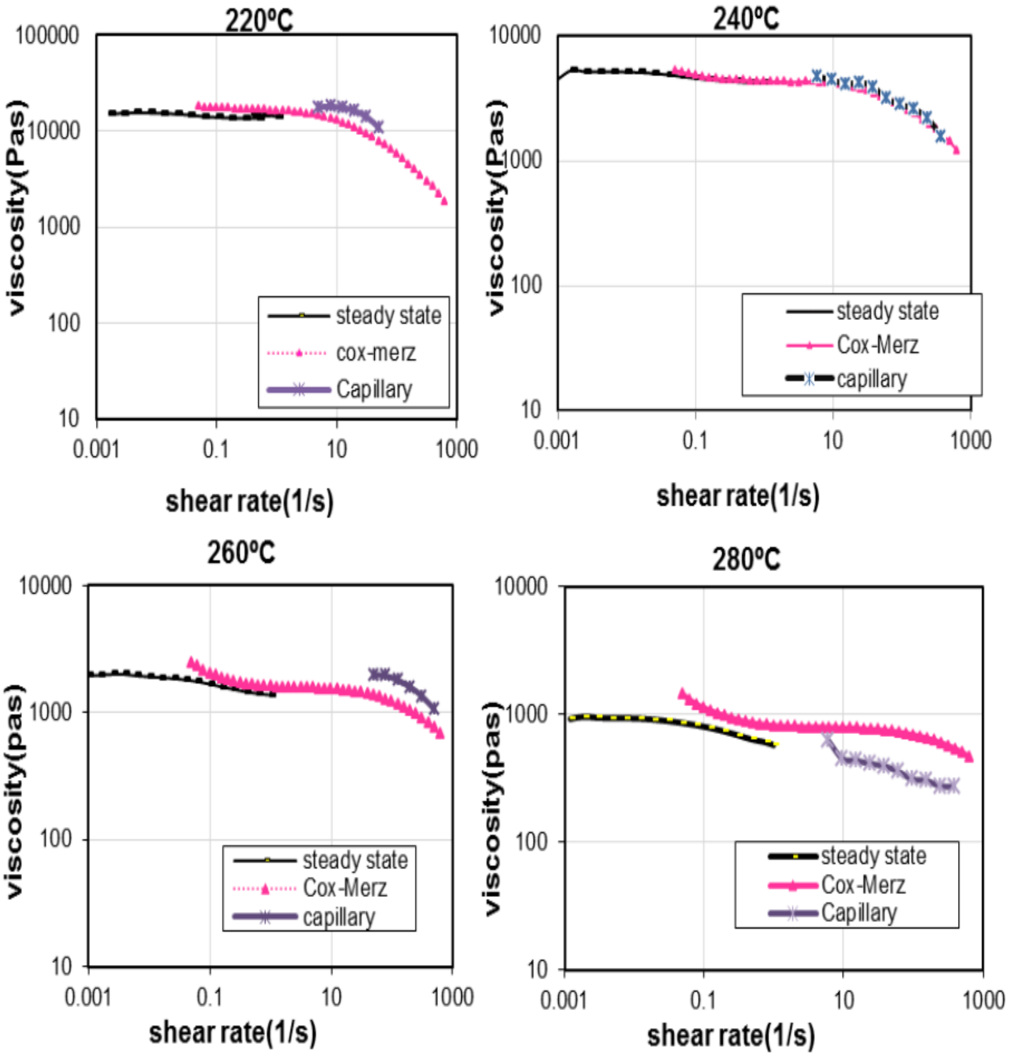

Fig. 5: Measurements of the shear viscosity of Polycarbonate at a temperature region of 220 ˚C to 280 ˚C for Steady state, Cox-Merz and Capillary

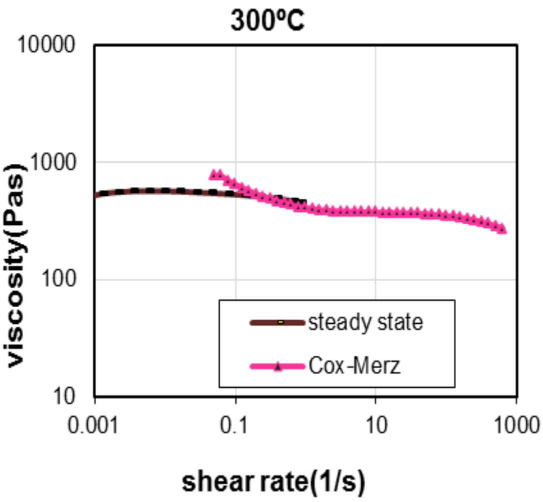

Fig. 6: Measurements of the shear viscosity of Polycarbonate at a temperature 300 ˚C for Steady state and Cox-Merz

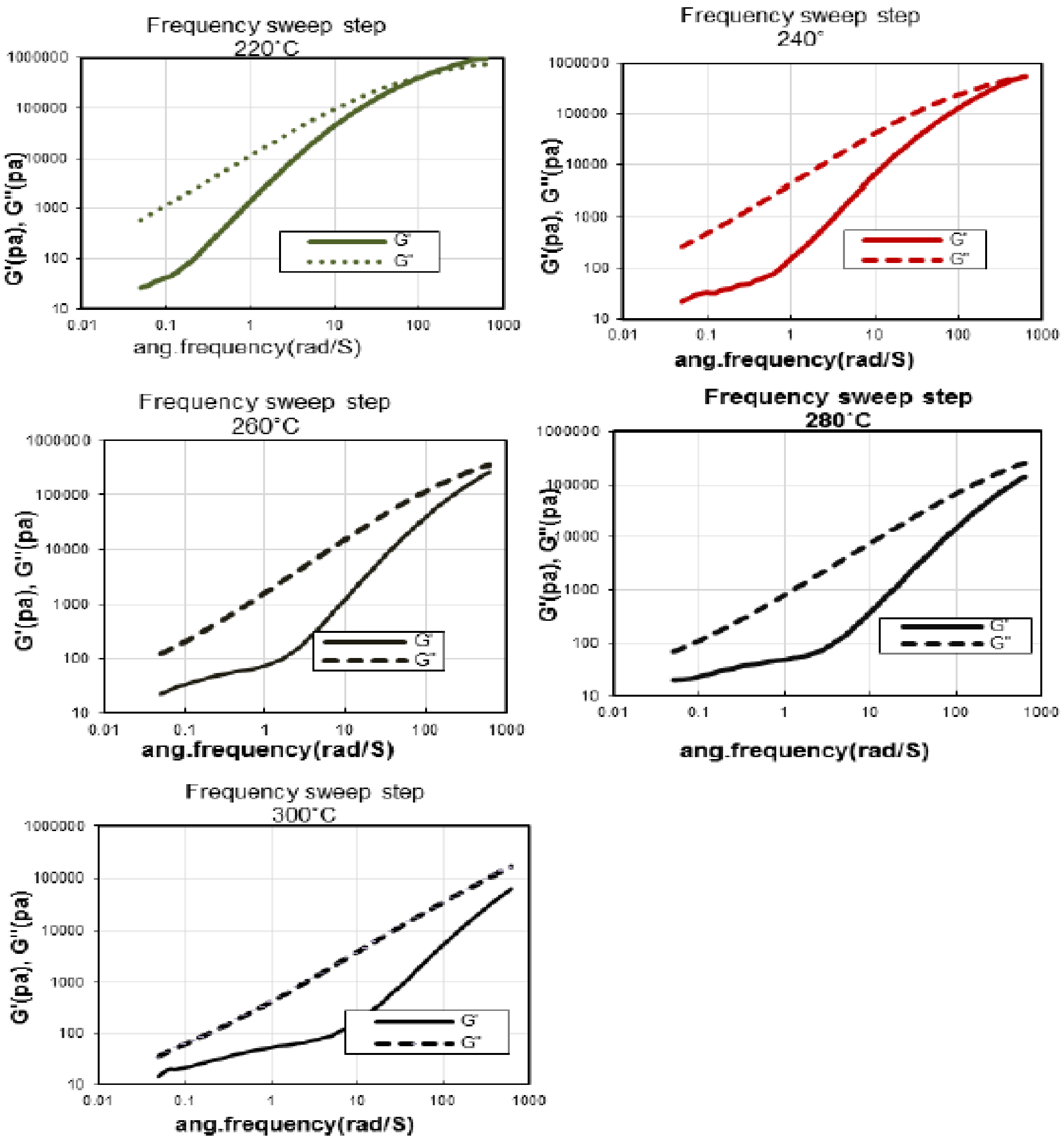

Fig. 7: Srorage and loss modulus for a wide range of frequency, from 220 ˚C to 330 ˚C

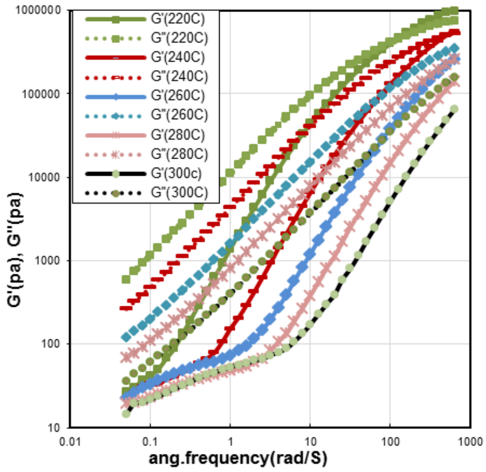

Fig. 8: Srorage and loss modulus for a wide range of frequency, from 220 ˚C to 300 ˚C

Theory and the Relationship between the Parameters

The theoretical measurements of the shear rate and viscosity for rotational rheometer is obtained from the given angle movement velocity Ω with

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

And the measured moment M with the shear stress τ and the given shear viscosity can be calculated with [15]

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

In case of capillary rheometer, the difference of the pressure Δp between inlet and outlet of the tube is measured in connection with the volume flux $\dot{V}$. These quantities are used to calculate two new variables, a weighted flow rate and the wall shear stress

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

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

The correlation between the flow rate and the wall shear rate under stationary condition in a tube results from the balance of momentum and reads

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

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

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

Afterwards the shear viscosity is calculated by

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} \qquad \ldots(9)$$

This relation is called Rabinowitsch-Weissenberg-correction [15].

The most accurate characterization of viscoelastic behavior is achieved with dynamic mechanical analysis [16]. Sinusoidal or (oscillatory) rheometry is often commonly used to characterize the frequency dependence of polymer melts. The mathematical application of the oscillatory test is as follows:

$$\gamma = \gamma_0 \sin\omega t \qquad \ldots(10)$$

$$\sigma = \sigma_0 \sin(\omega t + \delta) \qquad \ldots(11)$$

Equation 10 represents the strain function, where γ and γ_0 in[s^{-1}] are the strain and the strain amplitude respectively, ω is the angular frequency which is equal to $2\pi f$ and f is the frequency. It need to be mentioned that all rheological measurements used ω in [rad/s]. Equation 11 represents the stress function, where σ and σ_0 are the stress and the stress amplitude respectively, and δ is the angle which the resultant stress will be delayed time by the phase angle δ [20]. Figure 9 shows the Sinusoidal of two waves of frequency ω, with one in phase with the strain and one 90^0out-of-phase; Equation 12 clarifie this state:

$$\sigma=\sigma'+\sigma''=\sigma''_0\sin\omega t+\sigma_0''\cos\omega t \qquad \ldots(12)$$

Where σ' and σ" represent the stress that consists of in-phase and out-phase, respectively.
From the relationship between stress and strain, the dynamic moduli G′ and G″ can be defined:

$G'=\frac{\sigma_0'}{\dot{\gamma}_0}$is called elastic or in-phase modulus …(13)

$G''=\frac{\sigma_0''}{\dot{\gamma}_0}$ is called viscous, loss, or out-phase modulus …(14)

By using the Maxwell Model, a first order linear differential equation with a solution gives the shear stress as in Equation 15:

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

If the part of the stress in-phase is applied by putting sin [ωτ] =0, G' is written as:

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

And if the stress out –phase, by setting cosωτ=0, G″is written as:

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

Where τ in Equations 15, 16 and 17 is so-called relaxation time (s).
To compute the shear rate $\dot{\gamma}$, by the derivative of the strain in Equation3, this leads to the dynamic viscosity η.

$$\dot{\gamma}=\frac{d\gamma}{dt}=\gamma_0\omega\cos\omega t \qquad \ldots(18)$$

We know the viscosity is a function of the ratio of the stress to the shear rate as shown in the following relationship which can be obtained [17]:

$$\eta'=\frac{\sigma_0'}{\dot{\gamma}_0}=\frac{G_0''}{\omega} \qquad \ldots(19)$$

$$\eta''=\frac{\sigma_0'}{\dot{\gamma}_0}=\frac{G_0'}{\omega} \qquad \ldots(20)$$

Where η′ is dynamic viscosity, η″ is related to the dynamic rigidity through G′. The overall Magnitude of the complex viscosity and complex modulus are defined as in Equation 21 [6, 7]:

$$|\eta^*|=(\eta'^2+\eta''^2)^{½}=[(\frac{G''}{\omega})^2+(\frac{G'}{\omega})^2]=\frac{|G*|}{\omega} \qquad \ldots(21)$$

$\tan\delta=\frac{G''}{G'}=\frac{\sigma''}{\sigma'}=\frac{\eta'}{\eta''}$ is called the loss factor, or the relation between the viscoelastic moduli; i.e. the ratio between viscous and elastic
η*, G* can be defined in oscillatory test as shown in the following equations:

$$\eta^*=\eta'+i\eta'' \qquad \ldots(22)$$

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

Where $i=\sqrt{-1}$

To extend the shear rate measurements from very low shear rate to high shear rate, Cox-Merz rule can be applied. The empirical Cox-Merz rule created a link between linear and nonlinear quantities from amplitude oscillatory shear experiments as in the following equations [10, 18]:

$$|\eta^*(\omega)|=[\eta'^2(\omega)+\eta''^2(\omega)]^{½=}\eta(\dot{\gamma})|\dot{\gamma}=\omega \qquad \ldots(24)$$

We can repeat Equation 20:

$$|\eta^*(\omega)|=[\eta'^2(\omega)+(\frac{G'}{\omega})^2]^{½} \qquad \ldots(25)$$

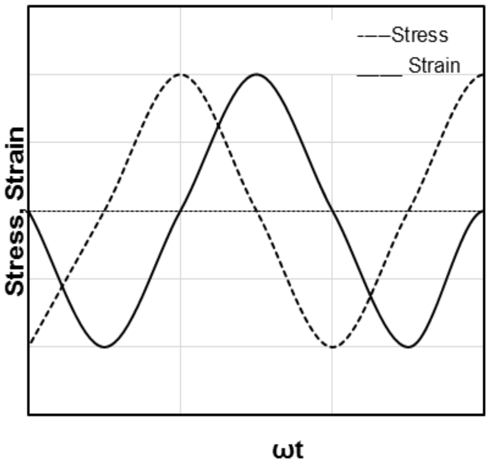

Fig. 9: Sinusoidal forms of stress and strain for a viscoelastic substance

Modeling Approaches

In order to reach a possible analytical approach for the experimental data, Carreau- Yasuda model (as explained by Equation 26) was adapted to model the shear thinning behavior for the proposed polymer in this work.

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

Where λ is the time constant to start the non-linear region in (s), n and m which 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.

Table 1: Parameters of the Carreau-Yasuda model obtained for each temperature step

temperature ˚C	λ	n	M	η_o
220	0.1	0.8	0.6	16350
240	0.05	0.82	0.4	4520
260	0.014	0.7	0.6	1956
280	0.01	0.6	0.6	921.4
300	0.006	0.4	0.55	497.8

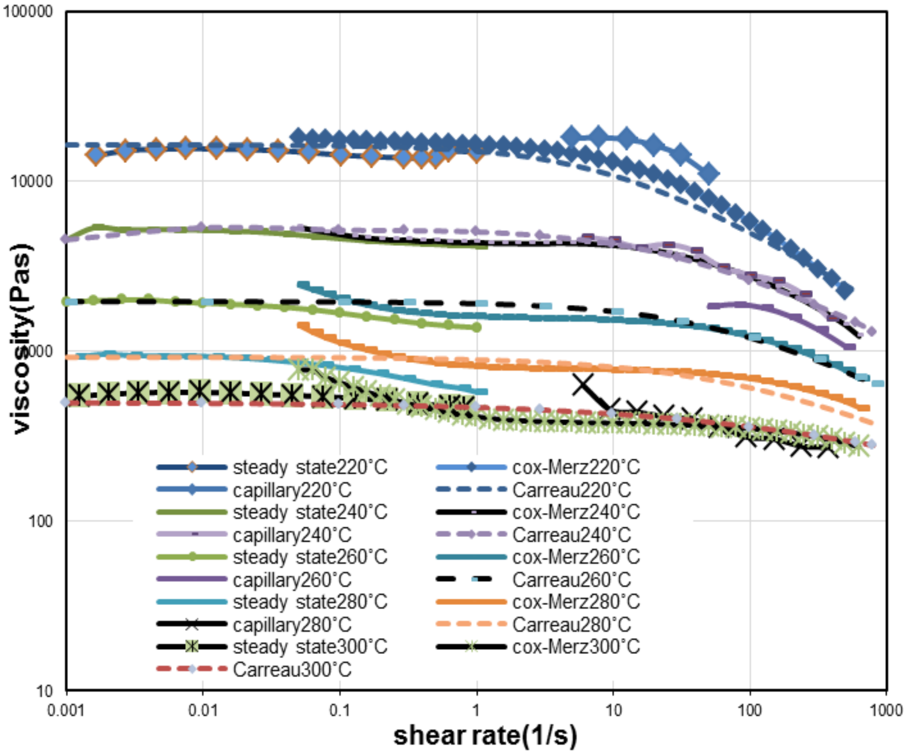

Fig. 10: Averaged experimental results (Symbols) and fitted lines with the Carreau model on each temperature

Discussion and Conclusion

The steady and dynamic state of viscosity for melt polycarbonate (Makrolon 2805) is plotted in the Figures 7 and 8. The stationary shear flow in polymer melt is so important to characterize the rheological technique by using Rotational Rheometer. To quantify the visco-elastic flow behavior of polymer solutions, all measurements were accomplished in a nitrogen atmosphere in order to avoid oxidation processes of the polymer molecules, using 10 L/min volumetric flow rate of nitrogen. Moreover, all the temperatures were used except the high temperature (280, 300 ˚C) and were matched with Cox-Merz rule; we see that the dynamic viscosity is consistently higher than its steady state equivalent as we move away from zero frequency, where they tend to coincide as shown in Figures 5 and 6.

In addition, the capillary rheometer was carried out at high shear rate and was compared with the Cox-Merz rule. Only at 220 and 240 ˚C, it matched with Cox-Merz. Other temperatures approximated conformity except the temperature 300 ˚C. At 300 ˚C, a problem was observed in shear rate measurement using capillary rheometer, due to the long molecule chains and that led to high viscosity and pressure linearly. supposing that we are another possible nozzle for this kind of polymer at high temperatures. In fact this type is not available in the lab. The modeling approaches for the processes can be used to provide a close representation of the measurements. In fact, it is possible to use the Carreau-Yasuda model for isothermal and non-isothermal processes.

Oscillatory experiments have to be accomplished according to the *Rheological Circle* [16] (see Figure 11). The elastic components of a polymer solution can then directly be correlated with the storage modulus *G'*, whereas the viscous components are represented by the loss modulus *G"*. Furthermore, this device was used to introduce the dynamic oscillatory shear flow which described the response to small amplitude deformation with different temperatures to quantify the viscoelastic flow in addition to its mission to comply with the steady state measurements to extend the shear rate. In oscillatory measurement shown in Figures 7 and 8, we noted that G" is greater than G' in all temperatures used. This means the energy used to deform the material is dissipated viscously and the material behavior is liquid like, and indicates that the viscous component of the modulus is dominant over the elastic counter. But at high angular frequency, G' is greater than G". This phenomenon for a flow behavior of polycarbonate shows which is radically different from many typical polymer. Furthermore, the high frequency limit is about 628; the maximum is achieved by using the Rotational Rheometer (AR-G2). So we can only get values equal to G'with G" in the temperatures 220 and 240 ˚C but at elevated temperatures it is not enough to enter the plateau regime of the storage modulus. This means that the network parameters are not accessible for each temperature without extrapolation as shown in Table 2 and Figure 12 to designate the value of the angular frequency.

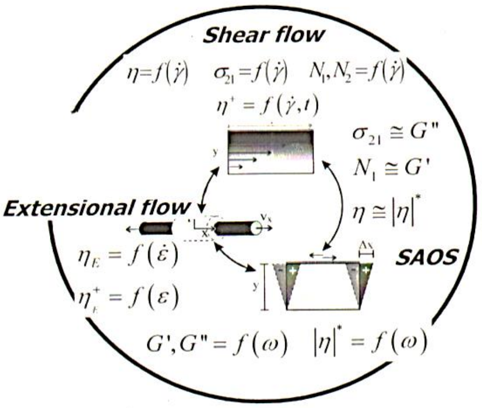

Fig. 11: Rheological cycle [16]

Table 2: The angular frequency at different temperatures with the same values of G`and G``

Temp. ˚C	ω (rad/s)	G`=G″
220	110.161	438269.777
240	506.304	504105.202
260	876.436	643405.797
280	1057.002	703756.66
300	3193.39	869615.603

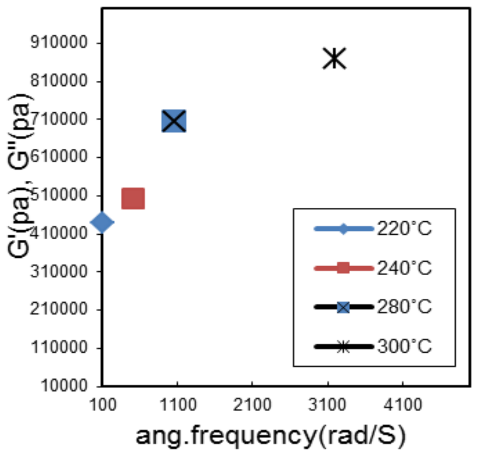

Fig. 12: The angular frequency at different temperatures with the same values of G`and G``

List of Symbols

$\dot{\gamma}, \dot{\gamma}_W$	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)
$\eta, \eta(\dot{\gamma})$	Viscosity and the viscosity function (Pas)
η', η'',	Dynamic viscosity (Pas),dy rigidity(Pas) (pa)
η^*	Complex viscosity(Pas)
M	Measured moment (Nm)
q	Weighted flow rate (s^{-1})
$\dot{V}$	flow rate (volume flux) (m^3/s)
d	Diameter of the tube of the capillary rheometer (m)
τ, τ_W	Shear stress and wall shear stress (N/m^2)
Δp	Pressure gradient (bar)
l	Length of the tube of the capillaryry rheometer (m)
σ, σ_0	stress and stress amplitude (N/m^2)
σ', σ''	Stress of in-phase and out-phase (N/m^2)
G', G''	Elastic and viscous modulus (pa)
G^*	Complex modulus (pa)

References

1- Gert.F.Bumann, Smual Steingiser "*Rheological Measurement on Polycarbonate*", Journal of polymer Science,**Vol** 1, pp.3395-3406, 1963.

2- Bird, R. B., Armstrong, R. C., and Hassager, O., "*Dynamics of polymeric liquids: Fluid Mechanics*", Journal of polymer Science, **Vol** 1, pp.100-101, 1977.

3- M.A.Rao,"*Rheology of Fluid and semisolid Food Principle and applications"*, food Engineering Series, ISBN_13:978_0_387_70929_1, 2007.

4- M. Rahail Parvaiz1, P. A. Mahanwar2, Smita Mohanty1 and Sanjay K. Nayak Morphology, "*Mechanical,Thermal Electrical and Rheological properties of polycarbonate composites Reinforced with surface modified Mica*", Journal of Minerals and Meterials Characterization, **Vol** 9 (11), pp.985-996, 2011.

5- Jan Philip Plog, "*Investigation of visco_elastic Behavior of Water soluble Cellulosic Derivatives in Uniaxial Elongation*", a doctor degree, The Dep. Of Chemistry, The University of Hamburg, Germany, 2005.

6- K.Walters, H.A.Barnes, J.F.Hutton, "*Rheology Series (An Introduction to Rheology)"*, University of Wales, U.K., 1993.

7- Johanna.Aho,"*Rheological characterization of polymer Melts in Shear and Extension: Measurement Reliability and data for practical processing*", thesis for the degree of Doctor of science in Tampere University of Technology, Finland, ISSN1458-8045, 2011.

8- C.Verdier,"*Rheological properties of living materials from cell to Tissues*", Journal of Theoretical Medicines, **Vol** 5 (2), PP.67-91, 2003.

9- Mills and Kokini, "*Comparison of steady shear and dynamic viscoelastic properties of Guar and Karaya Gums*", Journal of Food science, **Vol**. 49, PP.1-4, 1984.

10- Cox-Merz "*Correlation of Dynamic and Steady flow Viscosities*", Journal polymer Sci, **Vol**.28, pp.619-622, 1958.

11- T.S.Al-Hadithi, K.Waters, H.A.Barnes "*The relationship between the linear (Oscillatory) and nonlinear (steady-state) flow properties and colloidal systems*", *Colloid Polym. Sci*., **Vol.** 270, pp.40-46, 1992.

12- David, W.Mead, "*Analytical derivation of Cox_Merz rule using the MLD´´toy´´model for polydisperse linear polymer", Rheo Acta*, **Vol**.50, pp.837-866, 2011.

13- M.Hasan Tareque,*"A study of polycarbonate/poly (butylenes tetra phthalate) compounding in a Twin Screw Extruder*", A thesis, University of Waterloo, Canada, 2009.

14- A.Al-Baldawi, *"Modellierung und Simulation viskoelastischer Polymerschmelzen*", ISBN: 978-3-89958-598-8, Kassel University Press, 2012.

15- A.Al-Baldawi, S.Muallah., **Olaf ünsch**[1], *"Thermo-rheological Investigation and Modeling of the Shear Viscosity of Polypropylene above melting temperature*", Journal of Alkahwrizmi, Iraq ,2013.

16- Stacey, D.Reubush,"*Effects of storage on the linear Viscoelastic Response of Polymer-Modified Asphalt at Intermediate to high Temperatures, Master of science in Civil Engineering*", Virginia polytechnic Institute, 1999.

17- V.Tirtaatmadja,K.C.Tam,and Jenkins, *"Superposition of Oscillations on Steady State Flow as a Technique for Investigation the structure of associative polymer*", Macromolecules, **Vol**. 30(5), pp.1426-1433, 1997.

18- W.M.Kulicka, R.S.Poter,*"Relation between steady shear flow and dynamic rheology*", ISSN 0035-4511, Rheol.Acta., **Vol**.19, pp.601-605, 1980.

19- Pierre,J .Carreau, *"Rheological equations from molecular network theories*", Journal of Rheology, **Vol**.16, pp.99-127, 1972.

20- S.M.Hosseinalipour,A.Tohidi and M.Shokpour ,*"A review of dough rheological models used in numerical applications",* journal of Computational Applied Research in Mechanical Engineering, ISSN: 2228-7922, **Vol**.1 ,No.2, pp.129-147, 2012.