Drag Reducing Polymers in Vascular System: Viscosity Measurement and Polymers Types and Concentrations

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Abstract. Toms (1949) discovered that if a very small amount of drag reducing polymers (DRP) are added in the flow, approximately 10 ppm by weight or less, a substancial reduction in pressure drop at a given flow rate resulted. Then, since 1948, the phenomenon of drag reduction have been studied by many researchers with the objective of understand the drag reduction mechanism. In the last decades, the drag reducing polymers have been applied in vascular system for different pathologies, such as: atherosclerotics plaques, diabetes, hypertension among others. For analysis of this phenomena it is necessary to know the polymer viscosity and also the type and concentration of these polymers. In this study, the measurement is done with different concentrations. The polymers used is polyacrylamide, with concentrations in the range of 5 to 100 ppm. The Ostwald and Couette viscosimeter were used for the measurement of the polymeric solutions viscosity and also to verify the Newtonian fluid conditions of these polimeric solutions . The defined polymeric solutions will be used to simulate, in vitro, drag reduction in blood flow through stenosed large arteries.

Keywords:viscosity, polymer, drag reduction.

1. Introduction

The drag reduction (DR) phenomenon have been extensively studied through the addition of additives, such as high molecular weight polymers (Toms 1949, Lumley 1969, Gyr and Bewersdorff 1995). The study of the drag reduction mechanism is important because it has several applications in engineering, for example, a low concentration of a polymer in turbulent flow, can promote a drag reduction of 50%, in some cases. The drag reduction have been observed with another additives anisotropic and surfactants. These additives that shows drag reduction can be divided in three groups: polymes, surfactants and fibres. A detailed description phenomenon is given by Gyr and Bewersdorff (1995).

The substances cited above act in the turbulent regions of the fluid. These regions show different eddies scales which are related with the Reynolds numbers. As higher are the Reynolds numbers, greater will be the distance between the smallest scale and the biggest scale of the eddies. Although the polymers are primarily active on the smallest length scales, they are able to influence the macroscopic scales of the flow by which the drag is determined.

Drag reduction polymers are normally added in turbulent flow, but in the literature there are works showing applications in laminar flows. In this type of flow, in disturbed laminar flow, such as pulsatile flow in straight and spiral pipes or Couette flow with Taylor vortices (Driels and Ayyash, 1976; Keller and Mackley, 1975) drag reduction polymers act in the flow reducing hydrodinamic resistance.

In the last decades, there were an important growth of the number of applications of drag reduction polymers. Applications in vascular systems through verification the drag reduction in the blood flow have been used. The nanomolar concentrations of these polymers injected intravenously caused an increase in aortic and arterial blood flow and a decrease in both blood pressure and peripheral vascular resistance, with no effect on blood viscosity or blood vessel tone (Coleman *et al*., 1987). Polymer when inserted intravenously shows a significant increase in collateral blood flow in rabbits (Gannushkina *et al*, 1981) and the number of capillaries in normal and diabetic rats (Golub *et al*, 1987). Chronic intravenous injections of DRPs diminished the development of atherosclerosis in several atherogenic animal models (Faruqui et al, 1987; Sawchuk et al., 1999).

Another application of these polymers is that they have been used to diminish mechanical damage to blood cells when the blood is in contact with circulatory assist devices. Kameneva *et al*. (2003) shows the polyethylene glycol (PEG) as a potential erythrocyte protective agent against mechanically induced cellular trauma. The PEG concentration as low as 0.1% reduces hemolysis by more than 40% , compared with the same concentration of Dextran in suspension medium.

In the present work, the measurement of viscosity were done with two types of viscosimeter: viscosimeter of Ostwald and viscosimeter of Couette. The viscometer of Ostwald provides absolute values of viscosity. Analysis of the shear stress in function of the shear rate curve, obtained by Couette viscosimeter, allows to classify the fluid as Newtonian or non-Newtonian. These measures of viscosity were done for differents concentrations of polymer.

2. Materials and methods

2.1 Reagents

In this study, the drag reducing polymers used was polyacrylamide 1822S and 1340S with average molecular weight of $1,3 \times 10^6$ Da and $2,0 \times 10^6$ Da (according to Cytec Industries Inc.), respectively.

Initially, the solution was prepared with a concentration of 100 ppm. To reach this concentration it was mixed 50 mg of polymer in 0,5 kg of water. The solution was agitated (magnetic agitator, Fisatom – model. 752) with a nearly constant rotation of 130 rpm during 6 hours to reach the homogeneity. After this procedure, the solution stayed in rest in the workbench during 24 hours before carrying through the measurement of viscosity.

The following polymer concentrations had been prepared from the main concentration solution of 100 ppm: 5, 10, 20, 30, 40, 60, 75 e 100 mg/kg. From the solution of 100 ppm, the dilutions above were obtained of following way:

$$C_i V_i = C_f V_f \qquad (1)$$

where

- C_i – initial concentration;
- V_i – initial volume;
- C_f – final concentration;
- V_f – final volume.

For each dilution preparation it was necessary nearly 10 minutes of solution agitation.

2.2 Viscometer of Ostwald

The viscometer of Ostwald (Fig. 1) is used to measure viscosity of liquids based in the fluency resistence through a capillary. The law of Pouiseuille allows to establish a relationship between the time of fluency and the viscosity of a liquid through a capillary:

$$\mu = \frac{\pi R^4 \Delta P}{8lQ} = \frac{\pi R^4 \Delta P t}{8l \forall} \qquad (2)$$

where R – radius of capillary, ΔP – pressure difference between the extremities of the capillary, l – length of capillary. Q – volumetric flow, $\forall$ – volume of fluid, t – fluency time.
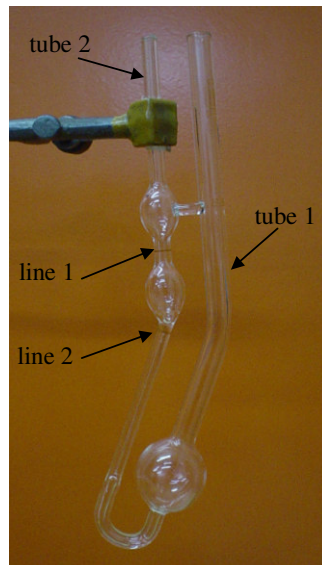

Figure 1. Viscometer of Ostwald.

The viscometer of Ostwald allows to a simple determination of a liquid viscosity coefficient by comparison with a standard liquid (distilled water in this case). According to figure 1, it is measured the liquid transit time from line 1 to line 2, and this interval is compared with the correspondent time interval of the standard liquid.

Equation 2 applied to the liquids of unknown and standard viscosities, allows the determination of the relative viscosity, according to equation 3:

$$\mu_{rel} = \frac{\mu_1}{\mu_2} = \frac{\rho_1}{\rho_2}\frac{t_1}{t_2} \tag{3}$$

where µ, ρ e t are, respectively, absolute viscosity, density and time interval of flow between the line 1 and 2 (Fig. 1). This method gives good results for liquids with average viscosity (water). For liquids of high viscosity (glycerin and oils in general), the method of the speed of the fall of balls through a liquid is better, using, in this case, the viscometer of Höppler (UFSC).

For all measurements, a volume of 8 ml was introduced in the viscometer of Ostwald. The solution was introduced in tube 1 (Figure 1) and it was aspirated through the tube 2 (Figure 1) making the liquid cross the line 1. After that, the time is chronometered for the liquid drain between lines 1 and 2. This procedure was made for all the solutions measurements and for the distilled water.

The density was measured by weighting the empty volumetric balloon, and after that, it was filled with the solution. Thus the difference between the measurements is the mass of the solution. By dividing the mass of the solution by the respective volume it is possible to get the density of the solution. These procedures were repeated for all dilutions.

2.3 Viscometer of Couette

The laminar flow of a liquid in the space between coaxial cylinders is known as "Couette Flow" in honor of Maurice Frédéric Alfred Couette, Professor of Physics at the end of the 19th Century at the French provincial University of Angers (Freshman Organic Chemistry). In this case, the outer cylinder, with a radius R_2 remains stationary. The inner cylinder with a radius R_1 and height h which contains the test fluid is rotated at constant speed (Ω rad/s). It is assumed that the flow of the fluid between the cylinders is steady and laminar and that the end effects are negligible.

Consider a volume of fluid between the inner cylider and an arbitrary radius r. Let ω be the angular velocity of the fluid at this radius r. The torque exerted on the fluid at this radius is

$$T = \tau_r\left(2\pi r h\right)r \tag{4}$$

where τ_t is the shear stress. The torque T measured at the surface of the inner cylinder must be the same as the torque at any arbitrary radius r since the motions is steady. Rewriting in terms of the shear stress we get

$$\tau_r = \frac{T}{2\pi r^2 h} \tag{5}$$

It can be observed from the equation 5 that the shearing stress is inversely proportional to the square of the distance from the axis of rotation. It is interesting to note that by using an annular gap that is small compared to the cylinder radii, the shearing stress on the fluid will be almost constant throughout the volume of the testing fluid.

The tangential velocity of the fluid at the radiu r is

$$v = r\varpi \tag{6}$$

The gradient of velocity will be given by

$$\frac{dv}{dr} = r\frac{d\varpi}{dr} + \varpi \tag{7}$$

In equation 7, the first term represents the rate of shear and the second term represents the radial velocity gradient of rigid body rotation.

For a Newtonian fluid, $\tau_r = \mu\dot{\gamma}$, or

$$\frac{T}{2\pi r^2 h} = \mu r\frac{d\varpi}{dr} \tag{8}$$

where $\dot{\gamma} = r\dfrac{d\varpi}{dr}$

and thus

$$\frac{d\varpi}{dr} = \frac{T}{2\pi h \mu r^3} \tag{9}$$

Integrating the equation 9 with appropriate boundary conditions results in the expression,

$$T = \frac{4\pi \mu h R_1^2 R_2^2 \varpi}{\left(R_2^2 - R_1^2\right)} \tag{10}$$

or $T = C\mu\varpi$ where C is the instrumentation constant.

The measures of viscosity were carried through with a viscometer of the Brookfield, model DVIII, that allowed to vary the rotation of the internal cylinder and to determine the shear stress and the rate shear (Figure 2).

Figure 2. Viscosimeter of Couette

A volumetric value of 16 ml was used from the diluted solution for measurement of viscosity. The speeds of rotations fixed were: 20, 50, 80, 100, 130, 160, 200 and 240 rpm. Each one of these rotations remained constant during a period of 30s.

3. Results

The measurements of viscosity were done for polyacrylamide 1822S and 1340S. For polyacrylamide 1822S the following concentrations were used: 5, 10, 20, 40, 60, 75 and 100 mg/kg and for polyacrylamide 1340S it was used: 60, 75 and 100 mg/kg.

The Table 1 presents the results of viscosity for polyacrylamide 1822S and 1340S for different concentrations using the viscometer of Ostwald.

Table 1. Experimental results of viscosity for poliacrilamide 1822S and 1340S.

Concentrations (mg/kg)	Polymers (Polyacrylamide)[1] (mPa.s)	
	1822S	1340S
5	$0,7609 \pm 0,0666$	---------
10	$0,8136 \pm 0,0699$	---------
20	$0,9522 \pm 0,0788$	---------
40	$1,1520 \pm 0,0921$	---------
60	$1,2478 \pm 0,0986$	$3,1409 \pm 0,2479$
75	$1,3799 \pm 0,1077$	$3,3112 \pm 0,2596$
100	$1,6463 \pm 0,1263$	$5,2486 \pm 0,3964$

[1]: measured at 25°C.

    Figure 3 presents the results of viscosity varying with shear rate, using Couette viscosimeter. More trustful results are obtained, in the range of lower shear rate, for high concentration polymeric solutions. The explanation for this can be associated with the range of application of the measurement device. The beginning of the band of measurement of the device is 1 mPa.s and the viscosity of the distilled water and of low concentrations polymers is next to this value, thus the viscometer does not supply a real measurement. For higher viscosities the results are more trustful and for concentrations of 30 ppm or more, the results present a trend to a constant value of viscosity. To a precise determination of this value, would be necessary to increase the rotation of the viscometer above to 250 rpm, which is the end of scale of the device used in this research, but the fluid behavior is obtained through this technique without more complications. Figure 4 presents the relationship between the shear stress and shear rate, and the results show a Newtonian behavior for lower concentrations (until 10 ppm) for polyacrylamide 1822S. For higher concentrations (30, 60, 75 and 100ppm), the Newtonian behavior is not reached. In the range of shear rate between 0 and 30 s^{-1}, the fluid behavior probably can be considered as Bingham plastic (who first coined the term rheology) where there is no flow up to a stress of τ_0 and flows thereafter; the stress τ_0 is called the yield stress (Figure 5).
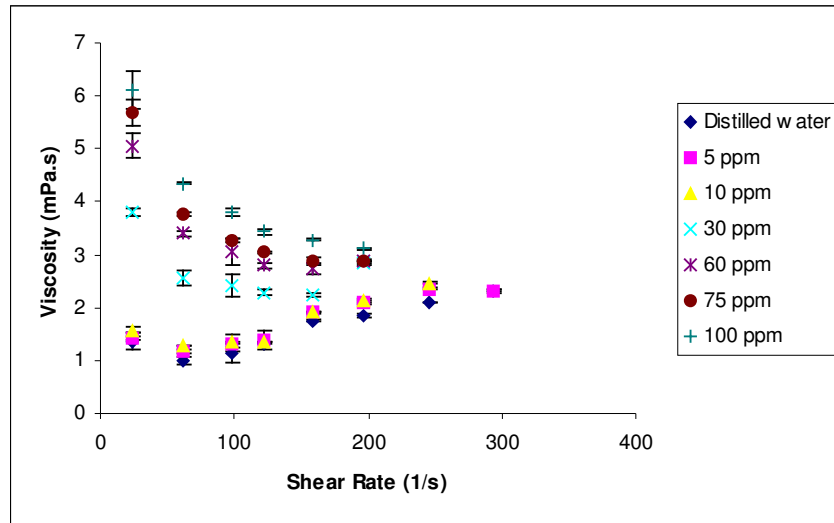

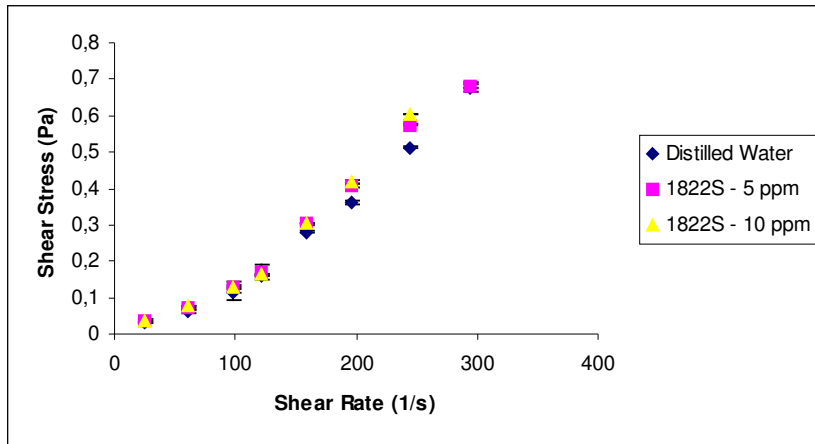Figure 3. Poliacrilamide 1822S - viscosity versus shear rate.

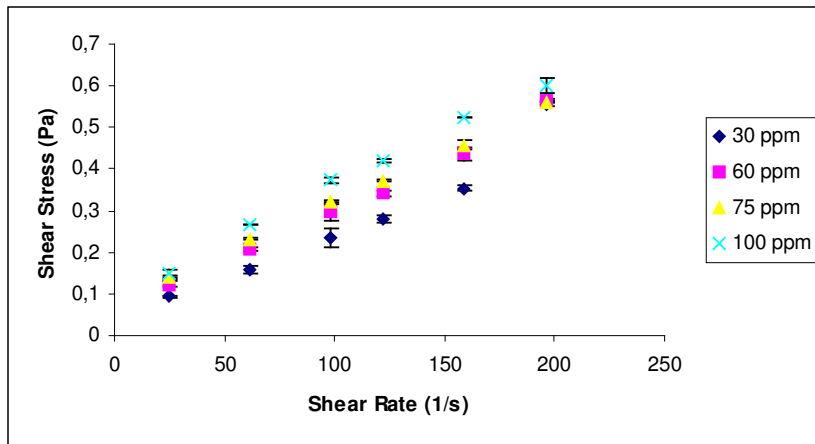Figure 4. Shear stress versus shear rate for lower concentrations of poliacrilamide 1822S.

Figure 5. Shear stress versus shear rate for higher concentrations of poliacrilamide 1822S.

Figure 6 presents the results of viscosity varying with shear rate, using Couette viscosimeter. The results of the polyacrylamide 1340S are similars to that results obtained for polyacrylamide 1822S. The viscosities values of polyacrylamide 1340S are higher that polyacrylamide 1822S, and this occur because the average molecular weight of the polyacrylamide 1340S is higher that 1822S. For the viscosity computation it is necessary to increase the rotation of the viscometer above 250 rpm, which is the end of scale of the device used in this research. Figure 7 presents the relationship between the shear stress and shear rate, and the results show a Newtonian behavior for lower concentrations (until 10 ppm) for polyacrylamide 1340S. For higher concentrations (30, 60, 75 and 100ppm), as was showed in figure 5, the Newtonian behavior is not reached. In the range of the values shear rate between 0 and 30 s^{-1}, the curve shear stress-shear rate can be extrapolated until shear stress axe and the fluid behavior would be considered as Bingham plastic.
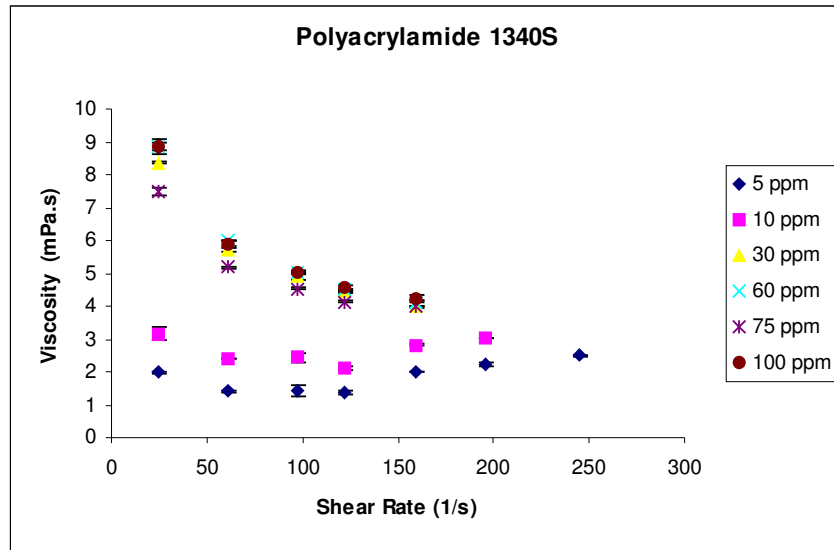
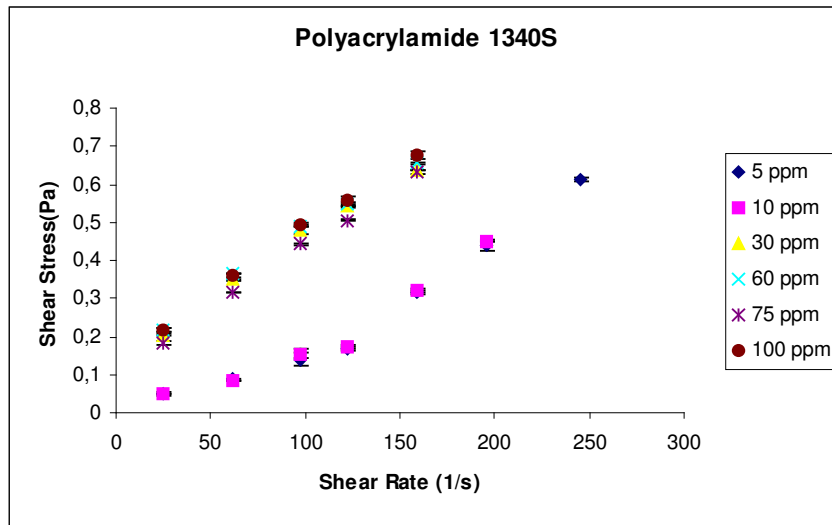Figure 6. Poliacrilamide 1340S - Viscosity versus shear rate.

Figure 7. Shear stress versus rate shear for lower and higer concentrations of poliacrilamide 1340S.

4. Discussion

The values of viscosity obtained from poliacrilamide 1340S and 1822S with Ostwald viscometer and Couette viscometer is different. This difference can be atributed a two factors: (1) the Couette viscometer used in this work have a limitation associated a lowest viscosity (near water viscosity), therefore the absolute values of viscosity are more trustfuls to higher concentrations of polymers; (2) from the results showed above, the Ostwald viscometer only could be used until 10 ppm due this viscometer to be used when the fluid behavior is Newtonian. Therefore, It is necessary more measurements and one adapter which possibilities measurements to low viscosity.

Polymers 1822S and 1340S which were presented in this work, can be simulated in numerical analysis as Newtonian fluid in lower concentratrions (until 10 ppm) and for higher concentrations (30, 60, 75 and 100 ppm), can be simulated as Bingham plastic. But, in the literature, there are stress-rate-of-strain laws that show the fluid behavior through Casson (1959) equation which represent also the fluid behavior for low shear rate

$$\tau^{1/2} = \tau_y^{1/2} + (K\gamma)^{1/2} \Big/ 2 \qquad (11)$$

where τ is the shear stress, τ_y the yield stress, and γ is shear rate, and K is a constant which, can be considered as been Newtonian viscosity obtained when the viscosity-shear rate curve reached the asymptotic. This equation is utilized to represent the blood behavior. It assumes that at low shear rates the particles form aggregates which link into chains; the interactions of these chains are the cause of the yield stress and when this is exceeded the chains break and the viscosity falls until, when all the particles are separate, the asymptotic viscosity is reached. Merrill et al. (1965a, b) found that at shear rates in the range 0.1 to 1.0 s^{-1} the Casson equation fitted very well but that in the further range up to 40 s^{-1} there were appreciable deviations from linearity. From this commentary, one analogy can be done for the poliacrilamide 1822S and 1340S behavior. The stretch of molecular chain not happened until the yield stress is reached. Then, when the molecular chain stretch occur, the viscosity falls until the asymptotic viscosity is reached.

The figure 8 show the comparison between the behavior of blood and poliacrilamide 1822S. Viscosity-shear rate curve of blood was obtained from Rand *et al.* (1964).
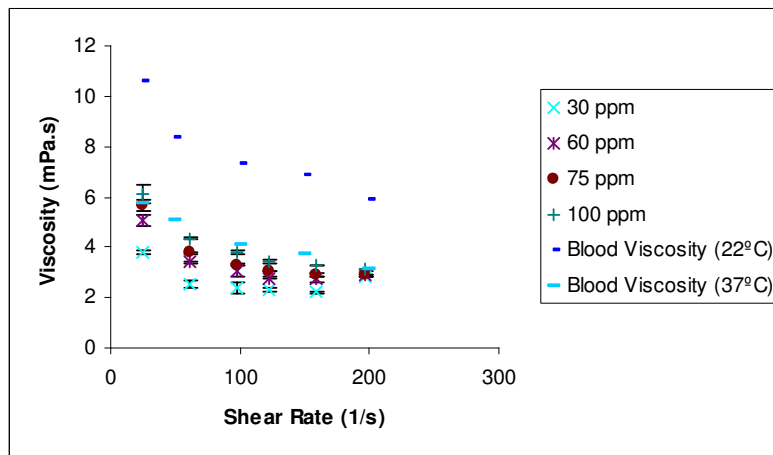

Figure 8. Comparison of the values of viscosity between poliacrilamide 1822S and blood.

What is most significant about these curves is that they are all asymptotic to constant values of the viscosity for large values of shear rate. For blood viscosity (22ºC), the asymptotic value is higher than the others. So, for example, blood with a normal male hematocrit of about 45% has, for values of shear rate ≥ 100 s^{-1} a constant viscosity of about 3-4 mPa.s (3-4 cP) and for poliacrilamide 1822S, in that concentrations (Figure 8), the asymptotic viscosity (3-4 mPa.s) occur for shear rate ≥ 150 s^{-1}. For poliacrilamide 1340S, the value of constant viscosity is higher than that obtained to poliacrilamdie 1822S (4-5 mPa.s).

Figure 9 show Casson plot for whole blood at a hematocrit of 51.7 (temp. 37ºC) (Fung, 1993). In the figure 9 can be observed that around to the origin at low shear rate one curve is formed. The yield stress τ_y given by Merril *et al* (1963) is very small: of the order of 0.05 dyn/cm^2, and is almost independent of the temperature in the range 10-37ºC. τ_y is markedly influenced by the macromolecular compositions of the suspending fluid. A suspension of red cells in saline plus albumin has zero yield stress; a suspension of red cells in plasma containing fibrinogen has a finite yield stress (Fung, 1993). In the figure 5 and 7, for the higher concentrations (30, 60, 75 and 100ppm) that were assumed as been Bingham plastic, but they should be better analysed around the origin where the values of shear rate are small and after that analysis, It will be considered as been Bingham plastic or Casson plastic.
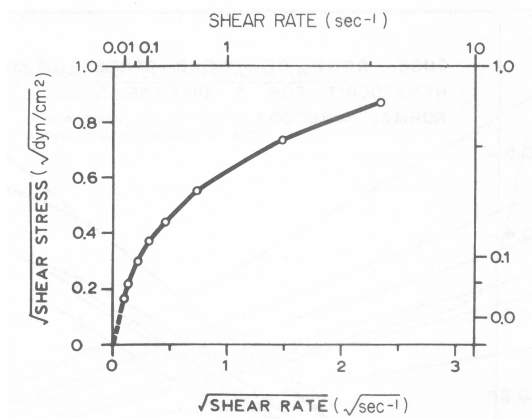
Figure 9. Casson plot for whole blood at a hematocrit of 51.7 (temp. = 37ºC) (Fung, 1993).

4. Conclusions

The values of viscosity of poliacrilamide 1340S are higher than the values of viscosity of poliacrilamide 1822S due the molecular weight.

From the gotten initial results, it is possible to believe that for the lower concentrations (until 10 ppm), the solutions shows a Newtonian behavior and for the higher concentrations (30, 60, 75 and 100 ppm) more measurements should be gone, in the range of shear rate below 30 s^{-1} for concluded whether the behavior these polymers can be considered as been Bingham plastic or Casson plastic.

The poliacrilamide 1340S and 1822S behavior seem the same of blood, therefore they can simulated in physical models as substitute of blood. The polymers choose and polymeric concentrations definition still remain in research. It can be concluded that the polymers tend to a limit of an absolute value when shear rate are above 100 s^{-1}, that dependence of weight molecular, which is compatible with shear rate range that occurs in large arteries.

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