RHEOLOGICAL CHARACTERIZATION OF SHORT FIBER COMPOSITE

André Braghini, andrebraghini@yahoo.com
Mônica F. Naccache, mnaccache@puc-rio.br
Dept. Mechanical Eng, Pontifícia Universidade Católica-RJ 22453-900, Brazil

Abstract. *The use of rigid short fiber polymer reinforced composites has continued to show substantial growth due to desirable cost and performance characteristics, especially in relation to mechanical properties. Specifically, the Wollastonite fiber is ideally suited to many different types of industrial applications, such as ceramics, construction products, metallurgy, plastics, friction materials paintings, coating and other end-use aplications. Its vast array of applications suggests potential usage in various fields of work, but there is not much data available in the literature. In this work, a study of shear and extensional viscosities of composite materials containing Wollastonite fibers is performed using the Paar Physica and the CaBER*^{TM} *rheometers. Two suspensions containing the same fiber, in a Newtonian polybutene/kerosene and in a viscoelastic fluid are investigated. The results obtained show that both types of suspensions exhibit similar viscosities when subjected to shear flows. However, when exposed to extensional flows, clearly an increase of the filament break up time is observed, due to an increase of the extensional viscosity. In addition to the rheological characterization, a flow visualization in a contraction geometry is being performed, in order to correlate the fiber orientation with the pressure drop and extensional viscosity.*

Keywords: *rheology characterization, viscoelastic fluids, extensional viscosity*

1. INTRODUCTION

Plastics are increasingly replacing conventional materials, mainly due to their low production costs and their lower density. Fibers and other fillers are added to plastics to improve their mechanical properties and hence their competitiveness with metallic materials. Short fiber filled thermoplastics represent a major class of growing importance since conventional equipment (extruder and injection machines) can be used to produce final parts using this kind of materials. The mechanical properties of the produced parts depend strongly on the process itself, on the rheological properties of the filled polymer and on the orientation of fibers during processing.

Since the kinematics in most types of flow process presents elongational characteristics, the study of the rheological properties under elongational flow have been acknowledge to be of great importance in an array of processes, such as film processing, thermoforming and blow-molding of fiber reinforced polymers. During processing, fibers move and rotate with the flow of the polymer matrix, which inevitably changes their orientation state and affects the properties of the composite material. The orientation state of the finished composite is of crucial importance to the designer who expects optimum performance from a short-fiber reinforced polymer composite. Therefore, when modeling these flows, the aim is to predict the final pattern of flow-induced orientation, and then determine the green strength and stiffness (Takaaki et al. 1990).

With the current developments in the composite industry, the intensity of theoretical and experimental studies on fiber-reinforced operations has increased considerably. The growth in the use of composites also arose due to greater awareness of the product performance and increased competition in the global market for lighter components. Among all materials, composites have the potential to replace steel and aluminum, and often with better performance. The replacement of steel components for composite materials can result in 60-80% reduction in weight of the component, and a reduction between 20 and 50% in weight is expected in the replacement of aluminum parts. Because of these advances, nowadays, composite materials are the leading choice for many engineering applications. However, the lack for high-volume production methods limits the widespread use of composite materials. Currently, Wollastonite versatility and unique properties make it a mineral that is ideally suited to many different types of industrial applications. Earlier studies (Shah, 1991; Choate et al., 1978) have shown that acicular wollastonite can be used as coreinforcer in short fiber composites. Use of wollastonite in high fraction will reduce the cost of composite and improve tensile strength, impact properties and dimensional stability (Singh, 2003). High aspect ratio (< 15) of wollastonite is retained by appropriate milling thus its greater surface area better intercepts stress propagation (Ahmed et al., 1990; Verbeek et al., 2003).

The main goal of this work is to report shear and elongational properties of short wollastonite fiber reinforced fluids, using a Newtonian matrix and a viscoelastic one. Moreover, a flow visualization through an abrupt axysimmetric contraction is being performed in order to obtain the fiber orientation in a typical extrusion process. Shear viscosity is obtained using a rotational rheometer whereas the elongational viscosity is determined using a capillary breakup elongational rheometer.

It is worth mentioning that the development of experiments to measure the extensional elongational viscosity, has been a challenge for more than 30 years (Dealy, 1971; and Winter, 1979). Some techniques can reproduce the kinematics required for the pure extensional elongational flow (T.Sridhar, 1985; Meissner, 1985) but are unable to reproduce the extreme conditions found in typical applications processing. As a result, the development of indirect methods to determine extensional elongational viscosity, such as convergent flow (Binding, 1988; Cogswell, 1972; Cogswell, 1986; Cogswell, 1969) and stagnation flow devices (Fuler, 1987; McGlashan, 1999) are often used.

1.1 Wollastonite Fiber

Wollastonite is a naturally occurring calcium inosilicate mineral that has the chemical formula $CaOSiO_2$ and is formed by approximately equal proportions of CaO and SiO_2. In some cases, wollastonite may contain small amounts of iron, magnesium, and manganese substituting for calcium. The mineral is named after William Hyde Wollaston (1766-1822), a noted English chemist and mineralogist.

Wollastonite production was been intense in several parts of the world. In Brazil, The Technical Research Institute of Sao Paulo (IPT) began accepting bids for mineral rights to a wollastonite deposit located near Itaoca. The deposit consists of two ore bodies. One ore body contains 800.000 tons of fine-grained skarn that comprises 48% wollastonite, 23% garnet, 8% diopside, and 21% plagioclase and other minerals. The other contains 50.000 tons of ore that comprises more than 60% wollastonite, 13% garnet, and 9% diopside, as well as various amounts of calcite, feldspar, and vesuvianite (Industrial Minerals,1996c).

The transverse dimension of an individual particle of wollastonite fiber can vary from about $5\mu m$ to $100\mu m$ and the longitudinal one can range between $50\mu m$ and $200\mu m$. Due to little uniformity in size are usually sold in strips of measures as necessary for use. The physical and mechanical properties of wollastonite NYAD 325 of Nyco Minerals can be found in the table below, as well as its chemical composition:

Table 1. Typical Properties of the Wollastonite NYAD 325.

PROPERTY	VALUE
Morphology	Acicular
Aspect Ratio	20:1 to 3:1
Particle Size	products vary from 10 Mesh to 1250 Mesh
Loose Bulk Density, kg/m3 (lbs./cu.ft.)	products vary from 220 to 1360 (14 to 85)
Tapped Bulk Density, kg/m3 (lbs./cu.ft.)	products vary from 420 to 1440 (26 to 90)
Specific Gravity of Solids	2.87-3.09
pH (10% slurry)	8-10
Molecular Formula	$CaSiO_3$ or alternatively $CaOSiO_2$
Color	Brilliant white to cream
Melting Point (°C)	1540
Water Solubility (g/100cc)	0.0095

Table 2 presents a comparison of some characteristics of wollastonite and short glass fiber for a reinforced Reaction Injection Molding (RRIM), which is a process often seen in automotive applications. The option of using wollastonite instead of short glass fiber, is due to the availability and ease of acquisition within the academic environment. In the present work, the wollastonite fiber is added to a Newtonian matrix and to a viscoelastic matrix. Fig. 1 shows the pure wollastonite fiber and the suspension of wollastonite fiber in the viscoelastic fluid.

Table 2. Comparison between the fiberglass and Wollastonite for a RRIM process.

Product	Features	Benefits
Milled Glass Fibers	Short fiber lenghts Wide variety of grades	Best physical properties Spedific application advantage
Woolastonite	Natural mineral Short fibers with narrow diameter Needle-like shape	Improved cost savings vs. some glass options Improved flow properties Improved mechanical strengths vs. other minerals

2. RHEOLOGICAL CHARACTERIZATION

2.1 Theoretical Approach

Filament stretching extensional rheometers (FiSER) had their origins with the work of Matta and Tytus (1990). The proposed apparatus consists on a falling cylinder sample between two end plates, with the upper plate held fixed. The

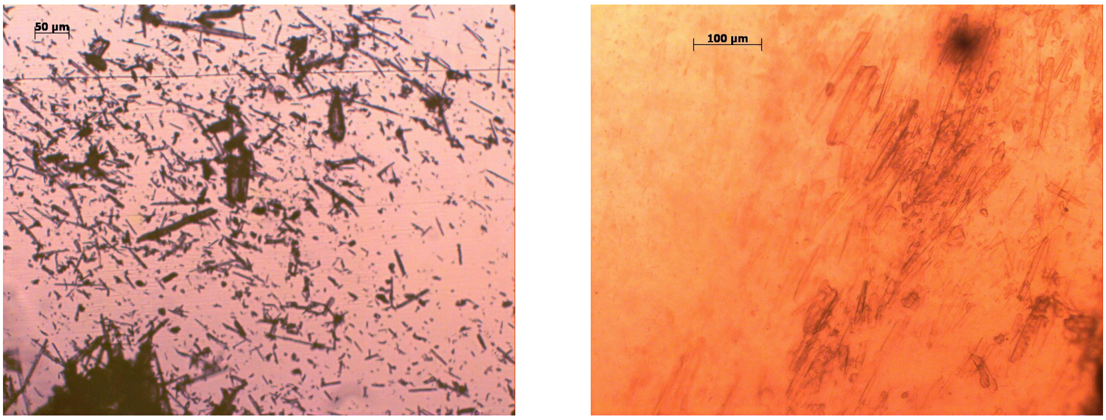

Figure 1. Wollastonite fiber $50\mu m$ (left), Wollastonite fiber in a viscoelastic fluid. (right).

lower region of the sample is attached to the lower plate, which is initially at rest and moves down when the test begins, stretching the adhering sample. In the same year, Bazilevsky et al. (1990) described a liquid filament microrheometer that suggested a simple way of determining the "stickness" of a suspicious unknown material, which is best compared to the quantitative version of the "thumb and forefinger" test (McKinley et al. 2001). The main difference between the filament stretching rheometer and the filament breakup one is that in filament stretching devices, a cylindrical liquid bridge is formed between two rigid end plates, which are then actively stretched apart with an exponentially increasing separation profile. In the filament breakup device, these end plates are rapidly separated and then held at a fixed axial gap, and the subsequent evolution of the mid filament diameter is monitored during the process of necking and breakup (Shelley L. Anna, 2000). A small droplet of a fluid is set between two plates that slowly move apart. The free surface of the droplet takes a characteristic concave shape, and a liquid bridge is formed. As the disks are separated further, the bridge becomes unstable and begins to collapse under the action of capillary forces. As a result, a neck is formed, which, in the case of Newtonian fluids, rapidly thins and finally disintegrates. In the case of polymeric fluids, a filament uniform in diameter may be formed, which thins with time (Fig. 2). The breakup of bridges and filaments is governed by a competition between capillary, inertia, and internal rheological forces, which arise in liquids when they are deformed (Bazilevskii et al. 2001). The relative magnitudes of the gravitational force and surface tension are given by a dimensionless number known as the Bond number, defined as

$$Bo = \frac{\rho g R_0^2}{\sigma} \tag{1}$$

where σ is the surface tension and ρ is the density of the fluid. A Bond number $Bo \ll 1$ states that gravity can be neglected, whereas gravity becomes more important with increasing values of the Bond number.

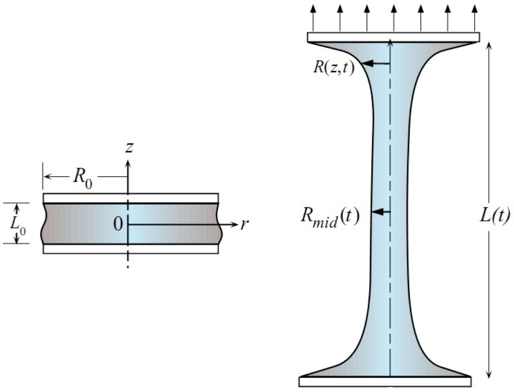

Figure 2. Schematic diagram of a filament stretching extensional rheometer (FiSER).

Figure 2 shows a scheme of a filament stretching rheometer. On the right side of Fig. 2, it can be observed that the radius of the thin fluid column is almost uniform in the central region. This is true for a strongly strain-hardening fluid, such as a dilute polymer solution. As a result, it is shown that the midpoint radius of the filament evolves according to the following equations (Entov and Hinch, 1997) :

$$\frac{R_{mid}}{R_0} = \frac{\sigma}{6\mu R_0}(t_c - t) \text{ for a Newtonian fluid} \tag{2}$$

and

$$\frac{R_{mid}}{R_0} = \left(\frac{GR_0}{\sigma}\right)^{1/3} exp\left(\frac{-t}{3\lambda}\right) \text{ for a viscoelastic fluid} \tag{3}$$

where t_c is the critical time to breakup for a Newtonian fluid of viscosity μ, whilst G is the elastic modulus of the viscoelastic fluid and λ is the relaxation time.

At time $t = 0$, the upper plate is set into motion and the resulting midpoint radius of the filament $R_{mid}(t)$ and tensile force $F_z(t)$ exerted by the elongating column are measured. The endplate velocity profile $\dot{L}_p(t)$ is chosen such that the midpoint of the fluid filament decreases exponentially with a constant stretching rate $\dot{\epsilon_0}$ given by

$$\dot{\epsilon_0} = -\frac{2}{R_{mid}}\frac{dR_{mid}}{dt} \tag{4}$$

Selection of this velocity profile is difficult, due to the no-slip pinning condition imposed by the rigid endplates. The total Hencky strain experienced by the fluid elements at the midplane of a filament stretching device can be directly computed by integrating (4) to give

$$\epsilon = \int_0^t \dot{\epsilon_0} dt' = ln\left[(R_0/R_{mid}(t))^2\right] \tag{5}$$

2.2 Test Fluids

2.2.1 The Newtonian Fluid

The Newtonian fluid consists of a kerosene-polybutene solution, from Polibutenos S.A.. The surface tension, density and viscosity at 25^oC were measured at the Laboratory of Fluids Characterization (LCF) of the Department of Mechanical Engineering, PUC-Rio. The surface tension was measured at 25^oC with a tensiometer from LAUDA, and is equal to 33.2 mN/m. The density at the same temperature was also measured, and is equal to 876.5 kg/m^3. The kerosene, used to dissolve the PIB, was obtained from Vetec Química Fina, having at 20^oC a density of 810 kg/m^3 and a viscosity of 0.002187 Pa.s.

2.2.2 The Viscoelastic Fluid

A polymer solution was prepared with the aim of obtaining an elastic fluid with constant shear viscosity, similar to that prepared and characterized by Nguyen and Sridhar (1990). These fluids are called Boger fluids, and were first described by Boger (1979).The key feature of a Boger fluid is the nearly constant shear viscosity. In a polymer solution, the polymer chains are loosely coiled, usually entangled and randomly oriented. Shearing tends to stretch the chains, which straightens out segments of the chain and aligns them in the direction of shear, an orientation that minimizes resistance to shearing. The stretching and alignment increase with shear rate, thus a polymer solution is always shear thinning. However, if the solution is sufficiently dilute, the viscosity contribution by the polymer is only a fraction of the total viscosity, then the decrease in shear viscosity with shear rate can be acceptably small, so that the fluid effectively has a constant shear viscosity (James 2009). This class of fluids is important because they enable elastic effects, which can be clearly separated from viscous effects in an experiment. The fluid investigated here consists of a solution of 0.24% of polyisobutylene, 6.98% of kerosene and 92.78% of polibutene in accordance with the solution presented by Nguyen. Unfortunately, there wasn't enough data available for the PIB, hence properties were obtained from the literature from Quinzani et al. (1990).

2.3 Rheological Measurements

Prior to the rheological testings, eight fluid solutions were prepared. Four of them were polybutene and kerosene solutions with 0.0, 0.1, 0.5 and 1.0 wt% of wollastonite fiber and the remaining four were the viscoelastic (Boger fluids with 0.0, 0.1, 0.5 and 1.0 wt% of wollastonite fiber.

2.3.1 Shear Rheology

The shear viscosity of the fluids and fibers suspensions have been measured using a rotational rheometer Physica MCR 301, from Anton Paar. The parallel-plate geometry was used instead of the cone-and-plate geometry to avoid wall effects. According to Bibbo et al. (1985), wall effects are not significant only when the gap between the parallel plates is much greater than the fiber length, a condition that the cone-and-plate geometry cannot guarantee. The disadvantage of the parallel-plate geometry is that the shear rate is non-homogeneous and varies linearly with the radial position. For all measurements a 1.0 mm gap was used. The value of the gap-to-fiber length ratio was much larger than 10:1, which has been suggested as the minimum value to prevent wall effects on measurements (Blakeney 1966 and Attanasio et al. 1972). All experiments were carried out at 25^oC, using a Peltier device. The variation of the temperature was considered negligible ($\pm 0.1^oC$).

2.3.2 Capillary Thinning Experiments

The capillary thinning experiments reported here were carried out using a filament rheometer CaBER (Thermo Electron, Karlsruhe, Germany) using circular end plates with a diameter of D_p = 4mm. An approximately cylindrical liquid bridge of height h_0 was formed between the two end plates. Set-up employed a step strain to separate the plates from their initial distance h_0, reaching their final separation h_f in 140 ms. The midplane diameter evolution was followed using a laser micrometer (inside CaBER) and a camera recording at 30 frames/s (self-built apparatus). The aspect ratio increases from an initial value $\Lambda_0 = h_0/D_p$ to a final aspect ratio $\Lambda_f = h_f/D_p$. In the present experiments the values of Λ_0 and Λ_f were 1.0 and 4.98 respectively, to minimize the perturbation effects of gravitational forces and fluid inertia, and thus keep the height h_0 of the sample on the order of or below the capillary length l_{cap},

$$h_0 \leqslant l_{cap} = \sqrt{\frac{\sigma}{\rho g}} \tag{6}$$

where σ is the surface tension and ρ is the fluid density.

3. RESULTS

3.1 Steady-shear results

The effect of shear rate on viscosity, at 25^oC, for polybutene with kerosene (PB-k, Newtonian fluid) and Boger fluid with different concentrations of wollastonite fiber, is shown in Fig. 3. The values of viscosity at low shear rates are an indication of the consistency with the Newtonian behavior for the Boger fluid and the polybutene-kerosene solution, despite having different concentrations of wollastonite fiber. In all Boger fluid solutions, a slightly shear-thinning behavior was observed, due to modifications in the macromolecular organization of the solution as the shear rate changes. With increasing shear rate, the disruption predominates over formation of new entanglements, molecules align in the direction of flow, and the viscosity decreases. The results obtained show that only a slight increase in the shear viscosity occurs with the addition of fibers.

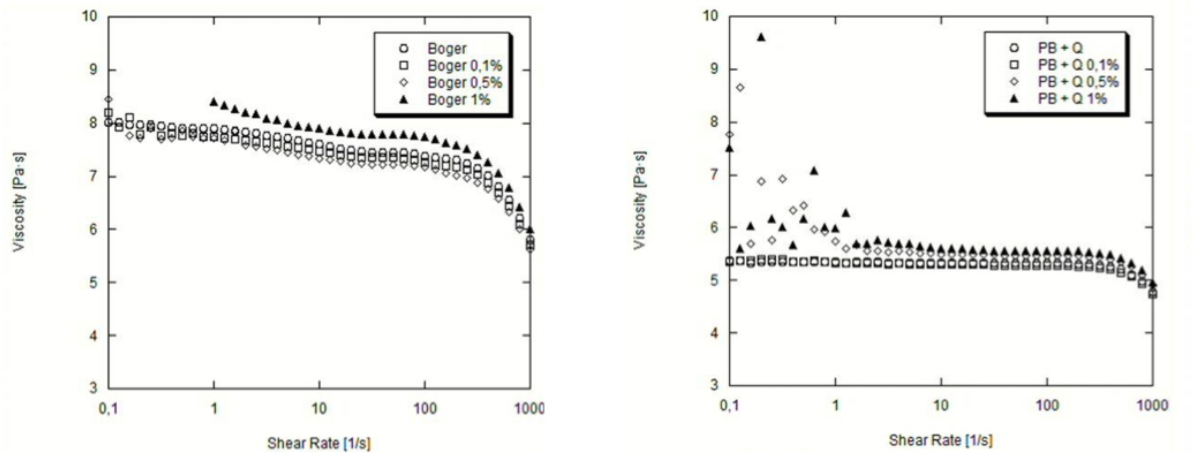

Figure 3. Comparison of the shear viscosity for the Boger (left) and PB-kerosene (right) solutions with different concentrations of wollastonite fiber.

3.2 Extensional results

The experimental observations in a filament stretching experiment include global evolution in the axial profile of the filament. Fig. 4 shows the filament diameter vs. time profiles for the polybutene-kerosene and Boger fluid solutions with different concentrations of wollastonite fiber, obtained with the CaBER rheometer. The shape of the filament diameter vs. time curve and the time of breakup provide information about the extensional rheological properties of fluids.

It can be observed that the diameter evolution for the PB-k solution has a linear behavior, which is predicted by equation (2). The filament evolution is basically controlled by the balance of capilary, viscous and elastic forces. Viscous

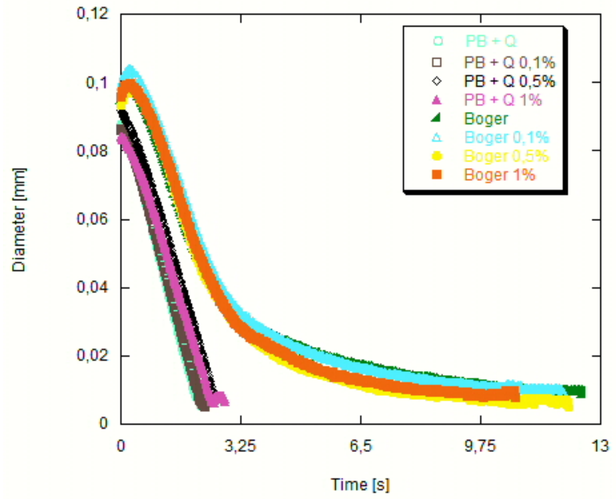

Figure 4. Comparison of filament diameter vs. time profiles for PB-kerosene and Boger solutions for different wollastonite fiber concentrations.

forces tend to stabilize the filament, while capillary ones (surface tension) acts to destabilize it, causing a steep decrease in the filament diameter till the breakup of the filament thread. It can be also noted that the increase of wollastonite concentration has almost no effect in filament breakup time, but for the same concentrations, much higher breakup times were obtained in Boger solutions due to it's high elasticity.

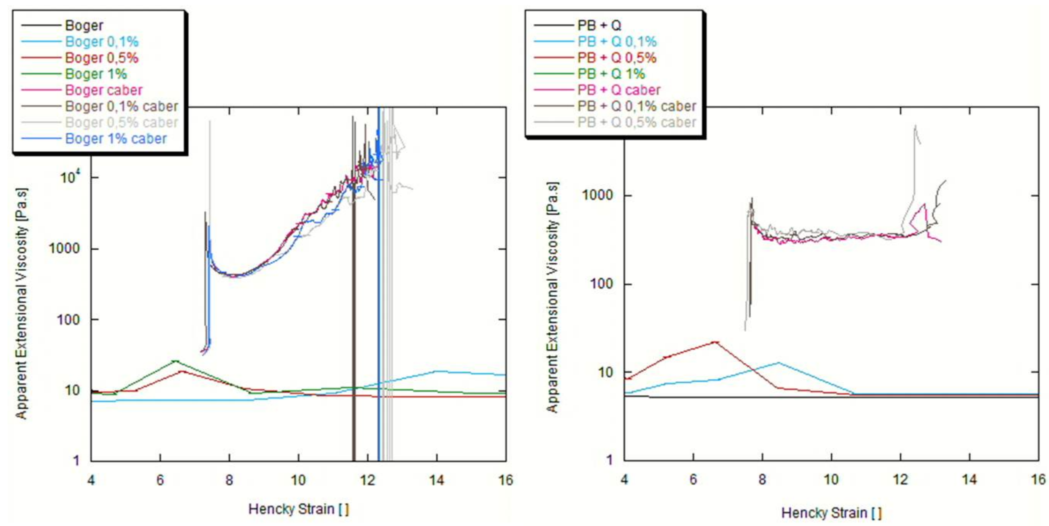

Figure 5. Comparison of shear (lower curves) and apparent extensional viscosity vs hencky strain for Boger solutions (left) and PB-kerosene solutions (right).

On Fig. 5 we compare the shear viscosity and apparent extensional viscosity for Boger fluids and PB-k solutions for different concentrations of wollastonite fiber, and the same range of Hencky strain. The apparent extensional viscosity for the Newtonian solutions shows a constant behavior as expected, whereas the Boger fluid solutions shows initially the same behavior but the extensional viscosity rapidly increases as the Hencky-strain increases. Moreover the extensional viscosity values are much higher in the viscoelastic solutions, as expected.

4. CONTRACTION FLOW

Flows through sudden contractions are subjected to a complex deformation, with shear and extension dominated regions. Several works have studied contractions flows in order to elucidate the stretching phenomenon under contraction flows, and to estimate the extensional viscosity using these geometries. In lieu of that, a contraction apparatus is being assembled in order to estimate the extensional viscosity, using the Cogswell (1978) and Binding (1988) analysis. Moreover, a flow visualization will be performed to observe the fiber orientation through the contraction in order to correlate it with the extensional viscosity behavior (Fig. 6). The results obtained with this apparatus will be compared to the extensional viscosity results shown in the previous section.

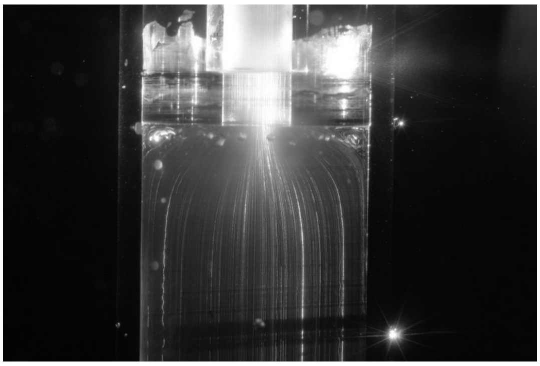

Figure 6. Contraction flow of a newtonian fluid.

5. FINAL REMARKS

The objective of the current research is to get a better understanding of the effects of fiber interactions in the mechanical response of Newtonian and polymer-fiber solutions. To achieve these objectives, an experimental study to obtain the rheological properties of these fluids has been carried out. The extensional viscosity was obtained using the filament stretching CaBER rheometer. The shear viscosity was determined using an Paar Physica rotational rheometer. The shear results obtained from both solutions, the Newtonian and the viscoelastic fluid, with the wollastonite fibers, displayed a similar behavior at low shear rates whereas at higher shear rates shear-thinning was observed in the viscoelastic (Boger) fluid solutions. Extensional viscosity obtained through the evaluation of the diameter of the filament clearly demonstrates that the Newtonian solution portrays a constant value. On the other hand, all Boger (viscoelastic) fluids solutions distinctly exhibit much higher and increasing extensional viscosities. Further studies in understanding the contribution of the fibers on the rheology of the fluids are still being carried out.

6. ACKNOWLEDGEMENTS

The authors would like to thank CNPq, CAPES and Faperj for the financial support.

7. REFERENCES

Ahmed, S., Jones, F.R., 1990, "A Review of Particulate Reinforcement Theories for Polymer Composites", J. Mater. Sci., Vol. 25, pp. 4933-4942.

Attanasio, A., U. Bernini, P. Galloppo, and G. Segre, 1972,"Significance of viscosity measurements in macroscopic suspensions of elongated particles", Trans. Soc. Rheol., Vol. 16, pp. 147-154.

Bazilevskii, A. V., Entov, V. M. and Rozhkov, A. N., 2001, "Breakup of an Oldroyd Liquid Bridge as a Method for Testing the Rheological Properties of Polymer Solutions", Polymer Science, Vol. 43, pp. 716-726.

Bibbo, M., Dinh, S.M. and Armstrong, R.C., 1985, "Shear Flow Properties of Semi-Concentrated Fiber Suspensions", Journal of Rheology, Vol. 29, pp. 905-929.

Binding, D. M., 1988, "An Aproximate Analysis for Contraction and Converging Flows", Journal of Non-Newtonian Fluid Mechanics, Vol. 27, pp. 173-189.

Blakeney, W. R., 1966, "The viscosity of suspensions of straight rigid rods", Journal of Colloid Interface Science, Vol. 22, pp.324-330.

Boger, D. V., 1979, "A Highly Elastic Constant-Viscosity Fluid" Journal of Non-Newtonian Fluid Mechanics, Vol. 3, pp. 87-89.

Choate, W.L., in: H.S. Katz, J.V. Milewski (Eds.), 1978, "Handbook of Fillers and Reinforcement for Plastics", E-Publishing, New York, pp. 405-414.

Cogswell, F. N., 1969, "Tensile Deformations in Molten Polymers", Rheological Acta, Vol. 8, pp. 187-194.

Cogswell, F. N., 1972, "Converging Flow of Polymer Melts in Extrusion Dies", Polymer Eng. and Science, Vol 12, Nž 1, pp. 64-73.

Cogswell, F. N., 1986, "The Rheology of Polymer Melts Under Tension Plastics and Polymers", Vol. 36, pp. 109-111.

Dealy, J. M., 1971, "Extensional flow of non-Newtonian fluids - a review", Polym. Eng. Sci., Vol. 11, pp.433-445.

Fuller, G. G., Cathey, C. A., Hubbard, B. and Zebrowsk, B. E., 1987, "Extensional Viscosity Measurements for Low-Viscosity Fluids Journal of Rheology", Vol. 31, pp. 235-249.

James, D. F., 2009, "Boger Fluids", Annual Review of Fluid Mechanics, Vol. 41, pp. 129-142.

Matta, J. E. and Tytus, R. P., 1990, "Liquid Stretching Using a Falling Cylinder", Journal of Non-Newtonian Fluid Mechanics, Vol. 18, pp.215-229.

McGlashan, S. A., Mackay, M. E., 1999, "Comparison of entry flow techniques for measuring elongation flow properties", Journal of Non-Newtonian Fluid Mechanics, Vol.85, pp. 213-227.

McKinley, G. H. and Yao, O. B., M. Filament Stretching Rheometry and the Extensional Viscosity of Dilute and Concentrated Polymer Solutions, 2001.

Meissner, J., 1985, "Experimental Aspects in polymer melt elongation rheometry", Chem. Eng. Commun., Vol. 33, pp. 159-180.

Nguyen, D. and Sridhar, T., 1990, "Preparation and Some Properties of M1 and its Constituents", Journal of Non-Newtonian Fluid Mechanics, Vol. 35, pp. 93-104.

Quinzani, L. M., McKinley, G. H., Brown, R. A., and Armstrong, R. C., 1990, "Modeling the rheology of polyisobutylene solutions", Journal of Rheology, Vol. 34, pp. 705-748.

Shah, Y.P., and Ankleshwaria, D. P., 1991, in: S. Sivaram (Ed.), Polymer Science Contemporary Themes, Publishing, New Delhi/New York, pp. 965-970.

Shelley L. A. and McKinley, G. H., 2000, "Elasto-capillary Thinning and Breakup of Model Elastic Liquid", Journal of Rheology, Vol. 45, pp. 115-138.

Singh, B., Gupta, M., Verma, A., Polyester moulding compounds of natural fibres and wollastonite, Compos. Part A: Appl. Sci. Manuf., Vol. 34, pp. 1035-1043, 2003.

Takaaki Matsuoka, Jun-Ichi Takabatake, Yoshinori Inoue and Hideroh Takahashi,1990, "Prediction of Fiber Orientation In Injection Molded Parts of Short-Fiber-reinforced Thermoplastics", Polymer Engineering and Science, Vol.30, pp. 957-966.

Verbeek, C. J. R., 2003, Mater. Lett., Vol. 57, pp. 1919-1924.

Winter, H. H., Macosko, C. W., Bennett, K. E., 1979, "Orthogonal stagnation flow, a framework for steady extensional flow experiments", Rheological Acta, Vol. 18, pp. 323-334.

8. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.