FLOW PROCESSES IN SHORT FIBER COMPOSITES: A FIBER-FIBER INTERACTION STUDY

S.E. Barbosa and J.M. Kenny
Institute of Chemical Technologies- University of Perugia
Loc. Pentima Bassa, 21 - 05100 Terni - Italy

ABSTRACT

In this work an experimental analysis of the flow reversibility of concentrated fiber-polymer model systems is presented. The interpretation of the experimental results allows a critical analysis of the different theoretical approaches that have been mainly reported in the literature regarding the flow behavior of short fiber-polymer melt systems. In fact, neither the slender body approach for concentrated suspensions nor the slender ellipsoid approximation for dilute suspensions is fully verified by the results reported here. The validity of each theory is discussed as a function of the deformation ranges applied in the different experimental tests. The approach presented here improves the understanding of these complex systems and can be used as a basis of new models developed as a combination of both approaches with the final objective of their integration in mathematical models of the processing technologies of short fiber composites.

INTRODUCTION

There is currently great interest in the flow of concentrated suspensions of fibers in Newtonian solvents and polymers, because these composites can provide lightweight, strong substitutes for metals in many manufacturing operations. Design of feasible manufacturing processes for these composites depends in part on the ability to account properly for the interrelation between local fiber orientation and concentration and the macroscopically observable rheological properties. Currently satisfactory fiber configuration designs are arrived at by trial and error procedures which can be quite costly. In addition to these important practical problems, understanding the interaction between fiber motion and bulk properties in concentrated suspensions is part of the general fundamental problem of learning how to relate microstructure and bulk behavior in non-Newtonian fluids.

The first thing of consider is the definition of concentration limits. If a suspension of n rigid, cylindrical (length L and diameter D) fibers per unit volume is consider: It is clear that for the suspension to be non-dilute in the sense that a fiber cannot rotate freely without encountering other fibers, we must require $n > 1/L^3$. On the other hand, if the spacing between fibers becomes of order D, then the fiber motion is so restricted that the suspension ceases to be a fluid, and instead behaves as a solid [1-2]. It has been shown [3] that for a given fiber weight or volume fraction the spacing between fibers depends on the fiber aspect ratio (L/D) and on the fiber orientation distribution. Then, there is a more useful parameter to describe fiber suspensions: nL^3. This quantity expresses the number of fibers in the domain swept out by a fiber rotating about its minor axis. Its relation with the volume fraction ϕ_V is given by:

$$nL^3 = \phi_v \left(\frac{L}{D}\right)^2 \frac{4}{\pi} \tag{1}$$

In terms of nL^3 the limits for a semiconcentrated suspension are:

$1 < nL^3 < L/D$ for a random fibers orientation system (2)
$1 < nL^3 < (L/D)^2$ for an aligned fibers orientation system (3)

In response to the issues raised above a variety of theories have developed a rheological equation of state to describe suspensions behavior of fibers in Newtonian solvents undergoing homogeneous flows. Principal approaches doing for dilute regimes are those made by Okagawa et al.[4], using Jeffery's equation of motion and the energy dissipation argument to calculate the shear and normal stresses in a dilute fiber suspension. They found that for a monodisperse collision-free suspension, these rheological properties exhibit undamped oscillations. However in the case of polydisperse suspensions, collision-free or monodisperse suspensions with two-body-interactions, the oscillations are damped and the properties reach steady state values. They claimed that fiber-fiber interactions are present even in very dilute suspensions; and in shear flow, the strongest interaction in produced by fibers oriented perpendicular to the flow direction acting on fibers lying in the plane of shear.

Lee and Springer [5] have introduced the concept of two-body interactions into Jeffery's equation of motion. Using an empirical relation for the probability of collision they have shown how the interaction between fibers dampens out the oscillations in the fiber orientation distribution. Leal and Hinch [6] have studied the effect of Brownian motion on the behavior of infinitely dilute fiber suspensions. They found that even with a very weak Brownian motion, the suspension will reach a steady state distribution which is not a function of the initial distribution. The orientation state of the suspension is now determined by a competition between the random Brownian rotation and the alignment induced by the bulk deformation.

Brownian motion is, perhaps, the only difference between suspensions of macro and micro-particles. When we refer to fiber suspensions in this work, it is understood that the particle dimensions are of the order of a millimeter or larger. Except in cases of extremely high temperature or very low viscosity solvents it is clear that Brownian motion is not present in the suspensions. However, theories developed for suspensions of rod-like molecules may be useful to understand fiber suspension behavior.

The landmark paper in the rheology of non-Brownian suspensions is that of Batchelor [7], who derived a general constitutive equation for any concentration of suspension of particles immersed in a Newtonian liquid. The general theory can accommodate a non-uniform distribution of arbitrarily shaped and deformable particles in a force-free system. External couples are allowed. Macroscopic quantities are given as volume averages of the microscopic variables. The bulk stress is obtained by a volume average of the local stresses. In general, the use of this method to estimate the rheological properties of a non-dilute suspension is extremely difficult because the motion of each particle must be determined as well as the solvent flow between the particles. For a dilute suspension in a simple steady shear flow, Jeffery [8] has shown that the particles will rotate in an orbit. Batchelor makes use of this result to determine the shear stress for a dilute suspension. For a concentrated suspension, the instantaneous orientation of each particle is in general unknown. However, in the case of a pure straining flow, the steady state orientation is such that all the particles will be aligned in the direction of the streamlines. With the configuration of the particles known, Batchelor [9] is able to calculate the stress field for a concentrated suspension of elongated particles in this class of flow fields.

Dinh and Armstrong [10] have developed a rheological equation of state for a semi-concentrated suspension of rigid fibers in homogeneous flows, using as a starting point Batchelor's equation for the stress tensor. The Dinh and Armstrong constitutive equation is the only systematic theory which includes fiber-fiber interaction and describe the suspension rheological behavior in the semi-concentrated regime for Newtonian solvents. One of the important aspects of this equation is the relation between the fiber structure and the rheological properties which is used to predict how structure reorganization due to flow will induce transient behavior in the suspension. However, it predicts that there are not a fiber contribution to the viscosity if all fibers are perpendicular or parallel to flow lines because the consideration of infinite aspect ratio. Shaqfeh and Fredrickson [11] working with the slender body approximation describe the transfer of linear moment for suspensions in semiconcentrate regime. The found that initial orientation distribution introduce a small difference in suspensions material parameter. They not describe the evolution of fiber orientations with the time.

A different but related area in theoretical studies is particle orientation. This subject, concerning the motion of particles in a viscous medium, has been a continuing topic of interest in fluid mechanics. Folgar and Tucker [12] have studied the fiber orientation distribution in a semi-concentrated suspension in a Newtonian fluid. They introduced fiber-fiber interaction in Jeffery's equation of motion, through a dispersion term which is structured like a Brownian motion force. In other words, they claim that effect of having fiber-fiber interaction is equivalent to having a suspension in which the Brownian motion is important. The interaction effect is governed by an adjustable parameter, C_I, called interaction parameter which has to be found by fitting the model with experimental data. The main features of this theory in shear flow are: The fiber orientation distribution is not a function of the shear rate. A steady state distribution is obtained for a strain bigger than 10. This distribution is not a delta function around the flow direction and it broadens as the interaction parameter increases. The interaction eliminates the reversibility of the distribution with the shear direction which is described by the Dinh and Armstrong model.

THEORY

Start up of simple shear flow: In general, the stress tensor for the theories summarized above can be written in the form[13]:

$$\tau_{ij} = \eta_s \dot{\gamma}_{ij} + \eta_s \phi_v \left(A \dot{\gamma}_{kl} a_{ijkl} + B\left[\dot{\gamma}_{ik} a_{kj} + a_{ik} \dot{\gamma}_{kj} \right] + C \dot{\gamma}_{ij} + 2 F a_{ij} D_r \right) \qquad (4)$$

where:

$\dot{\gamma}$ is the deformation rate tensor

ηs is the solvent viscosity

a_{ij} and a_{ijkl} are the respective components of a second and forth order orientation tensors, obtains computing all possible combinations of the vector orientation p (= sinθ cosϕ δ 1+ sinθ sinϕ δ2+ cosθ δ3, in spherical coordinates, see Fig. 1)

D_r is the rotary diffusivity due to Brownian motion, following Tucker et al [12] approximation it could be write as: $C_I \dot{\gamma}$

A, B, C and F are material constants that take into account the difference between the models.

For slender ellipsoid approximation (SEA) of revolution in a dilute suspension the coefficients are:

$$A = \frac{r^2}{2[\ln(2r) - 1.5]}$$

$$B = \frac{6\ln(2r) - 11}{r^2}$$

$$C = 2 \tag{5}$$

$$F = \frac{r^2}{[\ln(2r) - 0.5]}$$

Some approximations consider slender body theories (SBT)are the following, notice that B=C=0 in all of the cases:

$$A = \frac{8r^2}{3\ln(r)} \quad \text{Batchelor -Evans} \tag{6}$$

$$A = \frac{(L/D)^2}{3\ln(2h/D)} \quad \text{Dinh-Armstrong} \tag{7}$$

$$A = \frac{16r^2}{3\ln(1/\phi_v)}\left[1 - \frac{\ln\ln(1/\phi_v)}{\ln(1/\phi_v)} + \frac{C_c}{\ln(1/\phi_v)}\right] \quad \text{Shackfeh -Fredricson} \tag{8}$$

where r is the ratio between the major and the minor axes of the ellipsoid, and *h* the distance characteristic between fibers that is a function of fiber orientation [14]

If Equation (4) is used to calculate the fiber contribution to suspension viscosity in the start up of simple shear flow (vx= $\dot{\gamma}$ y), considering slender body approximation , becomes:

$$\frac{\eta}{\eta_s} - 1 = \phi_v\left(Aa_{ijkl}\right) \tag{9}$$

And if the SEA is taking into account, considering Tucker approximation to the diffusion term [12], Equation (4) becomes:

$$\frac{\eta}{\eta_s} - 1 = \phi_v\left(Aa_{ijkl} + C + 2Fa_{ij}C_I\right) \tag{10}$$

Note that the terms in B are null because $\dot{\gamma}$ik=$\dot{\gamma}$ki =0 in the flow consider. If initially all fibers are perpendicular to the flow direction, ($\theta = \pi/2$, $\phi = \pi/2$), the initial fiber orientation distribution could be consider a delta function [15], then the orientation tensors could be calculated as:

$$a_{ij} = sin^2\theta \ \cos\phi \ sin\phi \tag{11}$$

$$a_{ijkl} = sin^4\theta \ \cos^2\phi \ sin^2\phi \tag{12}$$

Considering this equations and replacing in Equations (9) and (10) resp. The predicts equations for fiber contribution to suspension viscosity are:

$$\frac{\eta}{\eta_s} - 1 = \phi_v\left(A(sin^4\theta\cos^2\phi \ sin^2\phi)\right) \quad \text{(SBT)} \tag{13}$$

$$\frac{\eta}{\eta_s} - 1 = \phi_v\left(A(sin^4\theta\cos^2\phi \ sin^2\phi) + C + 2F\,C_I \ sin^2\theta \ \cos\phi \, sin\phi\right) \quad \text{(SEA)} \tag{14}$$

Using the shear flow equations of movement to calculate the variation of orientation angles with the deformation in the first case and Jeffery equation of motion [15] in the second case the results obtained are shown in Figure 2. In this figure, the values are normalized with its maximum value to evaluate the form of the curves. Note that in the SBT, this curve is only a function of the fiber movement (angles θ and φ) but in the SEA depends also on the concentration interaction coefficient and aspect ratio of the fibers. The form of this curves is similar for small deformations. They increase with the deformation to a maximum at deformation near 1, after this point they decrease but the form in this part is different: SEA predicts a greater contribution of fibers to the viscosity than SBT. Moreover, SBT erroneously predicts that when fibers are perpendicular or parallel to the flux they do not contribute to the suspension viscosity. In the second approach (SEA), a finite and very small zero strain viscosity, as a function of the concentration and the aspect ratio, is predicted.

Reversibility Study: The reversibility study has been performed by changing the direction of shearing in start-up of shear flow. The suspension with an initial align fiber orientation distribution is sheared from its resting state up to a maximum strain γ_m, and then the direction of shear is changed. When the shear direction is changed during the experiment the total shear strain is given by the equation

$$\gamma(t) = \int_0^t \dot{\gamma}_{xy} t' dt' \tag{11}$$

If this procedure is done with our predict equations, results shown in Figure. 3 is obtained. The start up of the flow (points 1-2) reproduce Figure. 2. When the direction of shearing is inverted, the two approach turns to the same curve, but when deformation is grathee than the value of start, SBT predict a mirror effects, moreover SEA predicts a peak but with minor intensity. All approaches predict this peaks at deformations one, positive or negative. If the flux is reversed once again (5-6), SEA predicts a first peak similar to the first one (1-2) and a second small. On the other hand, SEA predict that when the direction of shearing is change, the viscosity of first new point (ex: change to point 4 to 5) is major of the last one. This is verify for all the changes except por the first one (2-3). The cause of this variation could be justify by the strains doing to the fibers. When the direction of shear change, the strains on the fibers change to extension to compression one. And this change of strain state is reflect in a increment of fiber contribution to the viscosity.

Notice that the form of reversibility state curves in the SEA are very sensible to the variation of interaction coefficient. The better description of the reality is obtained for a C_I aprox 0.3. For $C_I = 0$, the second peak is quasi equal to the first one, but the 3-4 curves not superposed 5-6 ones. When $C_I \approx 0.05$ the instabilities in the model are verify, and when the coefficient tends to infinite, a total reversible behavior like SBT is obtained.

EXPERIMENTAL

Model Suspensions: Nylon monofilament has been used as the material for the fibers. Silicone oils (PDMS) has been selected as Newtonian suspending fluid. These liquid shows a constant viscosity (30 Pa.s) over the range of shear rates tested. There are several assumptions that the fiber suspensions have to obey in order to be considered as a model suspension. These assumptions are common in all theoretical modeling, and they are also required for better and easier data interpretation. They are: The inertia in the shear flow experiment can be neglected, Brownian motion is not present in the suspension, The fibers are neutrally buoyant, The fibers are rigid, The initial fiber orientation distribution is perfectly aligned. All these assumption have been check to be valid for the suspensions used in these experiments.

Apparatus: Parallel plate was the geometry used to perform the shear flow experiments. The rheometer is a Rheometrics Mechanical Spectrometer (Model RMS-610) with sensitive transducer (Model T-100) has been used to measure the torques. We have developed a cup and plate assembly, that can be mounted on the Mechanical Spectrometer. The cup is made of Lucite to permit flow visualization of fiber orientation in shear flows. The cup base and the surface of upper plate are metalled to became the plates of a condenser. With this assembly, a suspension can be prepared inside the cup, bubbles can be removed by vacuum and also align orientation can be obtain there. Consequently, potential orientation changes developed during sample transfer from the mixing container to the viscometer and bubble inclusion in the suspension are avoided, and the suspension has a close controlled aligned fiber orientation distribution.

Sample preparation: Homogeneous fiber concentration and aligned fiber orientation distribution are the purpose of the sample preparation technique. Bubbles, something that is usually avoided, can produce a suspension with random fiber orientation distribution. The technique works as follows: The fibers and solvent are mixed by hand using a glass spatula trying to generate as many bubbles as possible. At the end of this step, we have a homogeneous emulsion of fibers, solvent and air. The suspension is then placed under vacuum and a random suspension is obtain. The reason why this technique produces suspensions with fiber orientation close to random is that the bubbles are homogeneously distributed in the system and in a very large amount. The sample is performed into the rheometer and is placed under and strong electric field (15000 V) for 10 minutes, time necessary to orient all fibers in the electric field direction. After this, a field is taking out and the sample has with all of theoretical requirements.

RESULTS AND DISCUSSION

The transient contribution of the fibers to the suspension viscosity as a function of the total shear strain applied to the suspension is shown in Figure 4 for a suspension with nL^3 =20 and L/D=33.3. The theoretical predictions and the data have been normalized with its maximum value. Theories describe well the variation of the viscosity with the strain; however they fail in the value of zero strain because predicts or zero or very small values and in spite of SEA predict a non zero contribution for great strains, this prediction is minor than the real value. This observation is expect because this theory is done for dilute suspensions. In effect the prediction is better for suspensions with small concentrations. SBT describes better the suspensions with long fibers, as expect. Notice that the values of C_I used are similar for all predictions, but there are not a value that adjust our experimental results. In this way we are working now.

Figure 5 shows the experimental result for a suspension with L/D=50 and nL^3 =20. The suspension with an align initial fiber orientation distribution is sheared from its resting state up to a maximum strain γ_m=6, and then the direction of shear is reversed. The results shows that the curves are reversible but there is a shift in the values of maxima and minimum. Moreover, the "second" peak is minor than the first one as predict SEA. There is a not a similar shift in the curves 3-4 and 5-6.

Figure 6 shows experimental results of the fiber contribution of the suspension viscosity for reversibility studies in suspensions with L/D=33.3 and nL^3 =20 to different values of maximum strain applied. The γ_m used were 4, 6, 8, 10 ,12 and 15. The principal observations to do are: that when the maximum strain increases, the shift of the peak in the strain axis and the magnitude of the first and second peak increases. In fact when γ_m=4, the first and second peak are very similar in magnitude and symmetric to the strain axis, but when γ_m=20 the second peak is not significative, the shift in the strain axis is bigger and the broadness increases. Summarizing, in this picture is possible to observe how the "reversibility" is a function of the final strain applied.

CONCLUSIONS

There are not a theory that describe very well the rheological properties in the start up of short fiber suspensions. The slender body approach is very interesting because it is simpler and does not require any adjustable parameter, but its predictions fail for zero and infinite strain, and its suspension behavior description is good for fibers of long aspect ratio. On the other hand, the slender ellipsoid approach does a better description of suspensions behavior if the concentration is small, but there is an interaction coefficient to adjust empirically.

The slender ellipsoid reproduces better the reversibility behavior than the slender body approach. However, the model ability is strongly dependent of the interaction coefficient. As a general conclusion it is evident that more efforts are needed in this modeling field, including the development of combined models between both approaches studied.

REFERENCES

1. Doi M. and Edwars S.F., *J. Chem Soc. Faraday Trans 2,* **74**, 560. (1978a)
2. Doi M. and Edwars S.F., *J. Chem. Soc. Faraday Trans.,* 2, **74**, 918. (1978b)
3. Doi M. and Kuzuu N., *J. Polym. Sci.(Phys.)*, **18**, 409. (1980)
4. Okagawa A., Cox R.G. and Mason S.G., *J. Colloid and Interface Sci.,* **45**(2), 303. (1973)
5. Lee W.I. and Springer G.S., *J. Reinforced Plast. Compos.*, **1**,.279. (1982)
6. Leal L.G. and Hinch E.J., *Rheol. Acta,* **12**, 127. (1973)
7. Batchelor G.K., *J. Fluid Mech.*, **44**(3), p. 419. (1970)
8. Jeffery G.B., *Pro. Roy. Soc.,* **102**, 161. (1922)
9. Batchelor G.K., *J. Fluid. Mech.,* **46**,. 813. (1971)
10. Dinh S.M. and Armstrong R.C., *J. Rheol.,* **28**(3), 207. (1984)
11. Shaqfeh E.S. and Frederickson G.H., *Phis. Fluids A,* **2**, 7. (1990)
12. Folgar F.P. and Tucker C.L., *J. Reinf. Plast. Compos.,* **3**, 98. (1984)
13. Tucker C and Advani S.*Flow and Rheology in Polymer Composites Manufacturing. Composites Materials Series.*Advani S Editor, 465, Elsevier, 1994
14. Barbosa S "Rheology and Processing of Short Fiber Composites" PhD Thesis, Univ. Nac. Sur, Bahia Blanca Argentina. 1992
15. Barbosa S and Bibbo M.*"Fiber Motion and Rheology of Suspensions with Uniform Fiber Orientation"* Submitted to J. Polym Sci

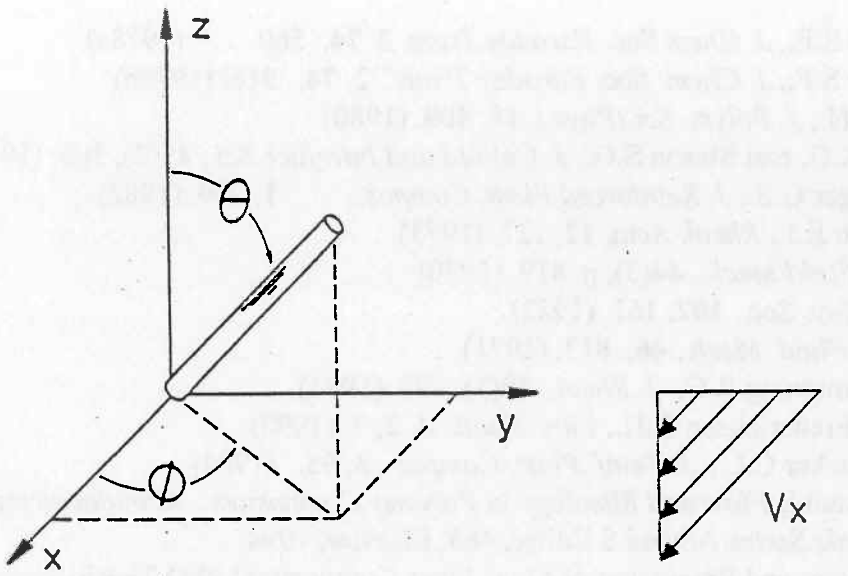

Figure 1: Spherical angles that describe fiber orientation

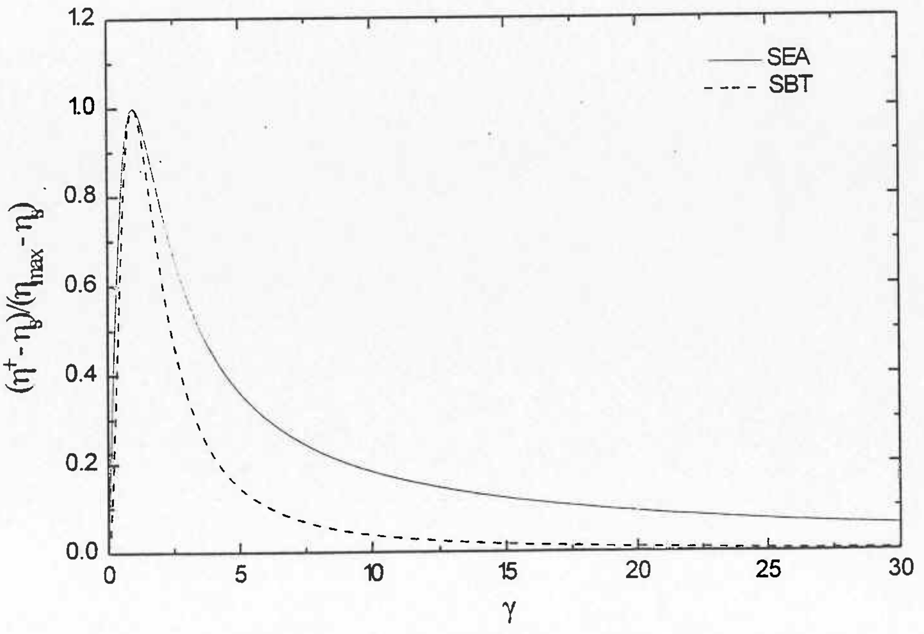

Figure 2: The transient viscosity normalized with its maximum value, as a function of the shear strain. Solid and dots lines are theoretical predictions for SEA and SBT

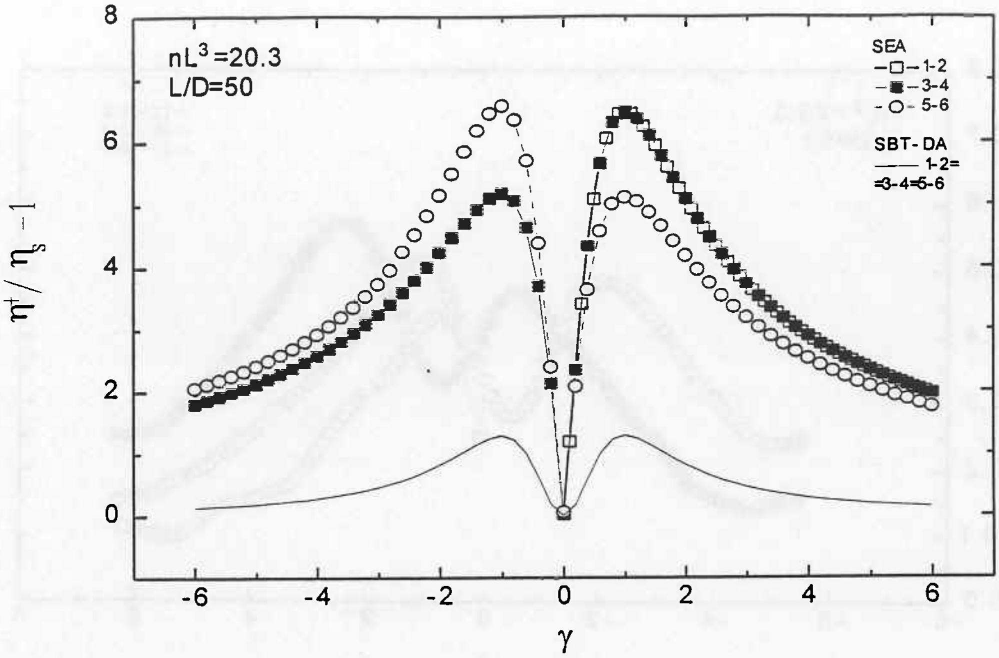

Figure 3: Theoretical predictions of transient normalized viscosity as a function of the shear strain for a reversibility study to a γ_{max}= 6, L/D=50 and nL^3=20.3. Solid line is for SBT and symbols are for SEA.

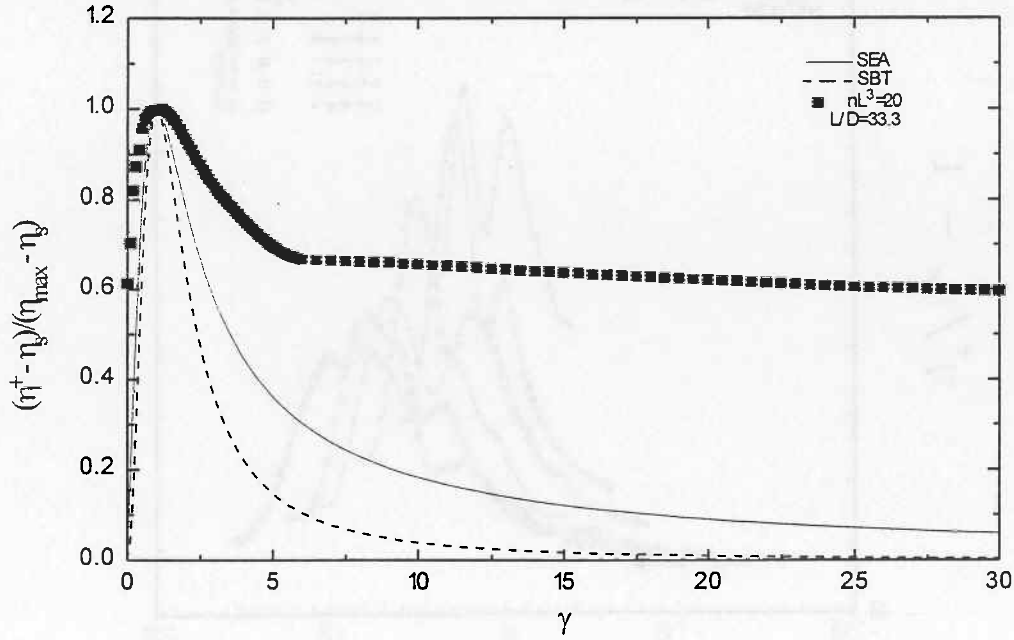

Figure 4: The transient viscosity normalized with its maximum value, as a function of the shear strain. Solid and dots lines are theoretical predictions for SEA and SBT. The squares are the results for a suspension of fibers of L/D=33.3 of length and nL^3=20

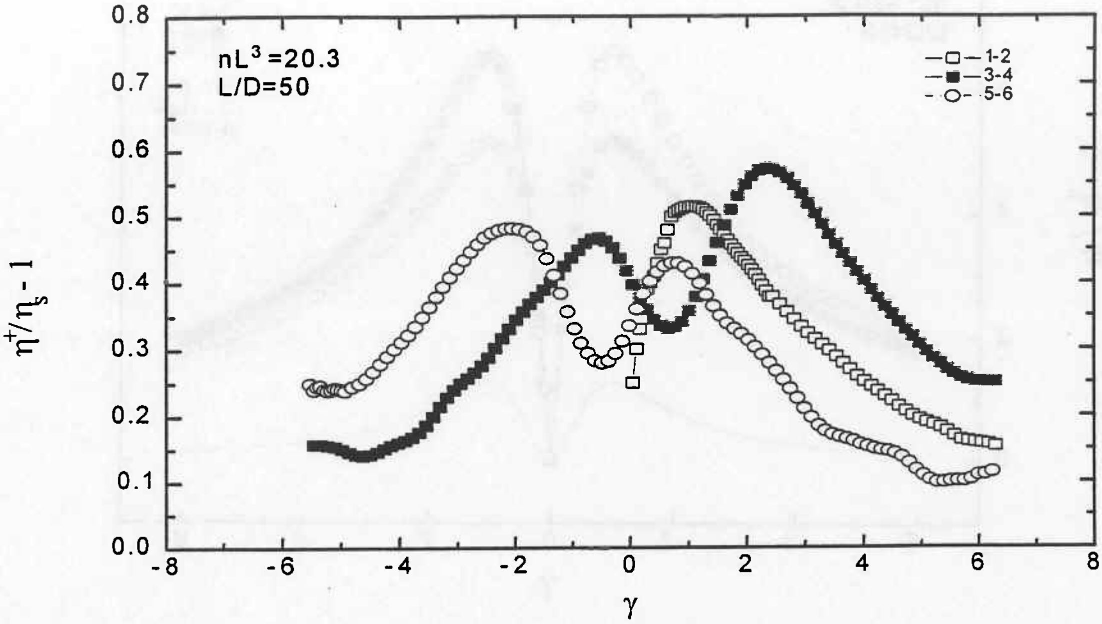

Figure 5: The transient normalized viscosity as a function of the shear strain for a reversibility study to a γ_{max}= 6, L/D=50 and nL^3=20.3

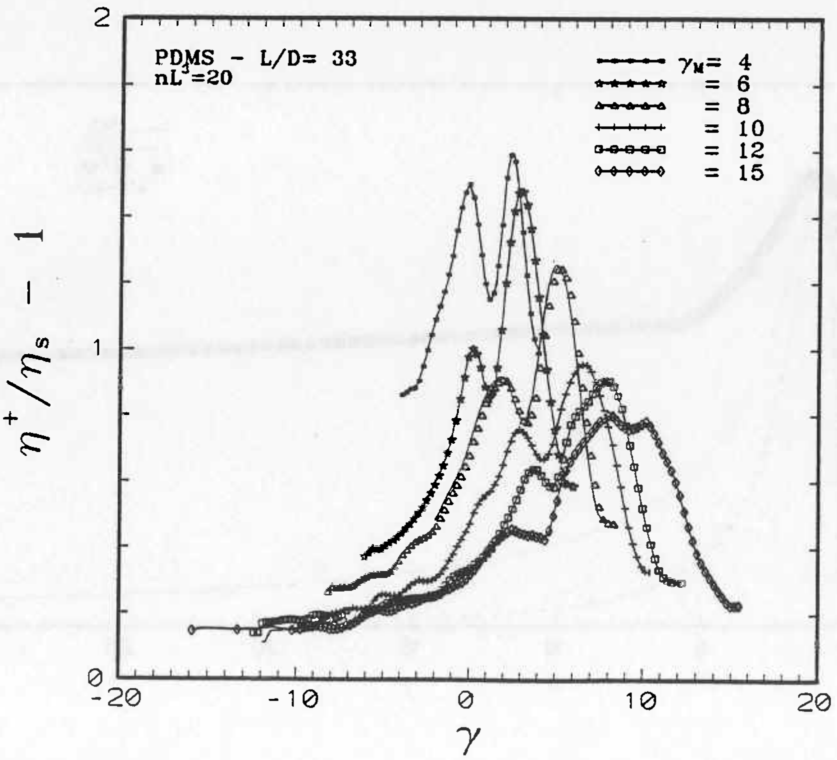

Figure 6: The transient normalized viscosity as a function of the shear strain for a reversibility study of a suspensions of L/D=33.3 and nL^3=20.3 to different values of final strain γ_{max}.