
Extensional Flow of Engineering Plastics with Glass Fibers

By Allen H. Wagner, Dilhan M. Kalyon, Rahmi Yazici, and Thomas J. Fiske

Highly Filled Materials Institute
Stevens Institute of Technology
Hoboken , NJ USA

INTRODUCTION

Blow molding, fiber spinning, thermoforming, and film blowing are all commercial polymer forming operations with strong extensional flow fields. The earlier work in uniaxial extensional flow behavior of polymers is reviewed by Dealy [1, 2] and Petrie [3]. Earlier techniques involved immersion of the annealed specimens into a density-matched oil and application of either a constant first normal stress difference [4-6] or constant strain rate [7-9]. This technique has several limitations including the flashpoint of the oil and the need to match the density of the polymer. Typically the total strain imposed on the sample was limited to 2-3. In 1969 Meissner [10-12] introduced a rotary clamp rheometer which allowed much higher strains to be obtained ($\epsilon > 6$). Meissner refined his design further by replacing the oil bath with a fritted stage which supported the polymer on a bed of inert gas [13] thereby allowing much denser polymers with higher melting or glass transition temperatures to be tested.

Various material functions of glass-fiber filled polymer melts were studied by Laun [14] and Chan et al. [15]. Li et. al. examined the effect of rubber particle concentration on elongational flow behavior of ABS [16] while Utracki reported the flow behavior of filled PE and PP melts containing fillers [17].

The purpose of this present study was to characterize the uniaxial extensional flow behavior of an engineering plastic resin as a function of the orientation distribution of its fiber content.

EXPERIMENTAL

Extensional Rheometer

A prototype Meissner-type uniaxial extensional rheometer (Fig. 1) was used. The rheometer consists of an electrically heated chamber, rotary clamping devices, fritted-metal gas-bed polymer support, and a data acquisition system. Each wall of the chamber contains an independently controlled resistive heater and an RTD sensor to measure temperature. The RTD signal is processed by an Anafaze 8LS PID controller capable of maintaining the chamber isothermal to within ± 0.1 oC. Two rotary clamping systems consisting of four brass caterpillar-type belts and two independently controlled DC motors (Fig. 2) are used to impose a constant strain rate. One of the rotary clamps is suspended from two leaf springs which ensure a parallel displacement of the clamp. The suspended rotary clamp is coupled to a linear variable displacement transducer (LVDT), via a non-ferromagnetic connecting rod. The deflection is used to measure the pulling force. The other rotary system is fixed to the chamber. The molten polymer specimen is supported at both ends by the clamps, while the middle section is supported on an inert-gas bed which is diffused by the fritted metal plate, as shown in Fig. 2. The LVDT signal is sensitive to electromagnetic interference (EMI) and requires filtering and amplification through a Daytronic 3530 conditioner. The conditioner is controlled by a computer which also collects, stores and processes the data with custom developed software. The deformation of the specimen is videotaped through the chamber-window on the top and the true strain rate of the specimen is determined by image analysis. A commercial version of this apparatus is available from Rheometric Scientific of Piscatinny, New Jersey.

Rectangular specimens of uniform cross section are used upon annealing. When the specimen with an initial length L_0 is extended to a length L_f , the true or Hencky strain, ε , is defined as:

$$\varepsilon = \int_{L_0}^{L_f} \frac{dL}{L} = \ln\left(\frac{L_f}{L_0}\right) \quad (1)$$

The time derivative of the Hencky strain under these kinematics is a constant i.e., $\dot{\varepsilon}$. The solution of this relationship with the initial condition of $L(t=0) = L_0$ yields [1, 3, 13]

$$L(t) = L_0 \exp(\dot{\varepsilon}t) \quad (2)$$

The stress growth coefficient is defined as in Eq. 3:

$$\eta^+(t) = \frac{\sigma(t)}{\dot{\varepsilon}} \quad (3)$$

Where $\sigma(t)$ is the first normal stress difference growth function and is defined in Eq. 4

$$\sigma(t) = \frac{F(t)}{A(t)} = \frac{F(t)}{A_0 \exp(-\dot{\varepsilon}t)} \quad (4)$$

Applying the equation of continuity $L(t)A(t) = L_0A_0$ and Equation 2 yields Eq. 5

$$A(t) = A_0 \exp(-\dot{\varepsilon}t) \quad (5)$$

The relationship between the sample puller speed and Hencky strain rate is given in Eq. 6

$$\dot{\varepsilon} = \frac{\pi d}{60} \Omega \quad (6)$$

where Ω is motor speed in revolutions per minute and d is the drive wheel diameter.

Combining the preceding equations yields the uniaxial extensional stress growth function (also referred to as uniaxial extensional viscosity):

$$\eta^+(t) = \frac{F(t) \exp\left(\frac{\pi d}{60} \Omega t\right)}{A_0 \left(\frac{\pi d}{60}\right) \Omega} \quad (7)$$

The tensile force, $F(t)$, is determined from the measured displacement of the suspended rotary clamp system through the LVDT transducer. The cross-sectional area, $A(t)$, changes according to Equation 5, where A_0 is the initial cross-sectional area.

Experimental Procedures

Samples suitable for elongational rheology must be free of residual stresses, have a uniform cross-section and be free of voids and air bubbles. The samples were prepared utilizing a custom designed vacuum compression mold used in conjunction with a 25 ton Dake Corp. model 27-774 Press. The mold was cylindrical with a 136.5 mm outer diameter and a 4.75 mm wall thickness, with a total height of 117.5 mm. The mold was equipped with two Chromalox USA (model DB054102) 500 Watt heater bands

around the circumference of the mold and two Chromalox USA (model CIR 1042) 200 Watt cartridge heaters in the mold base. The temperature was controlled by a Fenwal Model 550 PI controller. Each cavity was designed to produce one rectangular test specimen with dimensions of 2.5 x 8 x 620 mm.

The vacuum compression mold was preheated to 250 oC and a pre weighed quantity of resin was charged into the cavity and vacuum was applied. After five minutes, 16.8 MPa of pressure was applied. The mold was allowed to cool by free convection and under pressure.

The rheometer was heated to the desired test temperature while a constant inert gas flow rate was maintained. The LVDT signal was set to zero, the data acquisition program and the rotary clamp motors were started and data were collected until sample failure. The deformation of the specimen was video taped. Analysis of the width versus time data yielded the true strain rate experienced by the sample as shown in Fig. 3.

The specimens were stretched to predetermined Hencky strains, and quenched (without allowing them to relax) to freeze-in the orientation distributions of the glass fibers.

Microradiography and Fiber Orientation Distribution

In this study, contact microradiography was employed to study the microstructural features of the elongated samples. Cooled samples with frozen-in fiber orientation were reduced in thickness to 0.1 to 0.25 mm by grinding with progressively finer grit sizes of bonded abrasive paper, concluding with a polishing operation. For contact microradiography, relatively soft x-ray white radiation was used. A GE GA5 x-ray unit with a copper target at 15 kV and 1 mA excitation was employed. [18-20].

The images of the microradiographs were digitized and further processed using Adobe Photoshop and Scan Maker software. Orientation distributions of individual fibers with respect to reference axes were characterized employing the digitized images using NIH Image/ppc processing software.

The orientation function (J) of the fibers were determined, following Stein [21], and Yaguchi et al., [22]. The fiber orientation function (J) for two dimensional distribution is given by:

$$J = 2 \int_{-\pi/2}^{\pi/2} \cos^2 \theta \ q(\theta) \ d(\theta) - 1 \quad (8)$$

where θ is the fiber orientation angle and $q(\theta)$ is the distribution of the fiber orientation angles. The orientation function J varies such that: J = 0, for random orientation; J = +1, for unidirectional orientation in x direction ($\theta = 0$); and J = - 1 for unidirectional orientation in y direction ($\theta = \pi / 2$).

In this study, discrete θ values were obtained for each fiber in the microradiographs and the orientation function was determined by numerical integration. The accuracy of the NIH-Image based image analysis tools and the subsequent calculations in determining J values were tested using computer simulated fiber distributions prepared elsewhere [22]. These control measurements were within 2% of the simulated J values.

Materials

The filled polyamide 6 resin is a chain extended, multi-branched polyamide nylon 6 containing 12% by weight chopped glass fibers and carbon black. The pyrolysis of the pellets revealed glass fibers 10 μ in diameter and 500 μ long. This glass-filled commercial nylon resin was supplied by AlliedSignal Inc. Typical properties of this material are listed in Table 1.

RESULTS AND DISCUSSION

Uniaxial Extensional Stress Growth Function

Figure 4 shows the typical uniaxial extensional stress growth versus time behavior of the glass-filled polyamide 6 at 240°C and at the constant Hencky strain rates of 0.055, 0.33 and 0.60 s⁻¹. In this strain rate range, the glass-filled nylon 6 resin did not

exhibit any significant strain hardening. The Lodge model was tested (employing relaxation spectrum data best-fitted from small-amplitude oscillatory shear flow) and as could be expected failed to fit the behavior of the glass filled polyamide. The presence of the glass fibers obviously is a complicating factor not accounted in viscoelastic constitutive equations based on unfilled macromolecules.

Fiber Orientation

A series of eight glass filled nylon samples were elongated or "pulled" with the rheometer under constant and controlled Hencky strain rate conditions. Each specimen was pulled at a strain rate of 0.055 s⁻¹ up to total Hencky strains of 0, 0.275, 0.55, 0.825, 1.1, 1.65, 2.2, and 2.75.

The radiographs of selected specimens are shown in Fig. 5. In Fig. 5a, almost randomly distributed domains of fiber orientation can be identified in the initial polymer specimen which was heated and cooled without any strain imposed. These domains of fiber orientation are the legacy of the individual, randomly distributed pellets used to compression mold the elongational test specimens. After elongation of the sample to a strain of 0.275 the individual domains of fiber orientation can still be identified. However, the orientation of each domain is no longer random. Fiber domains not parallel to the principal axis of extension are being rotated and aligned along the stretch direction.

The transition of fiber orientation from totally random to completely aligned in the stretch direction occurs with increasing Hencky strain as shown in the sample with a total strain of 0.55 (Fig. 5b). The alignment is greatest near the two outside surfaces and at the center with a transition region located between surface and center. Increasing the strain to 0.825 and 1.10 (see Fig. 5c) yields samples where most fibers are oriented to various degrees along the principle axis of extension. Samples strained to 1.65, 2.20 and 2.75 exhibited almost perfect orientation of the fibers along the principle elongational axis without any discernible micro-domains or inhomogeneities in fiber orientation, as shown in Fig. 5d.

The typical fiber orientation distributions of the resin samples subject to various Hencky strains are shown in Fig. 6 and in Table 2. The relationship between the applied Hencky strain, ϵ , and the fiber orientation distribution approximates a power-law relationship: $J = J_0 + 0.4 \epsilon^{0.5}$, where $J_0 = 0.16$ is the orientation distribution function value of the as-molded sample prior to onset of deformation. The experimental data of J versus ϵ and the fitted power-law curve are shown in Fig. 7.

Fig. 7 indicates that the slope of fiber orientation function, J , versus Hencky strain behavior changes around a Hencky strain of about 0.8. It is interesting to note that at a total strain of 0.8 the extensional viscosity values of specimens stretched at all the strain rates i.e., 0.055, 0.33 and 0.6 s⁻¹ are similar i.e., around 4 x 10⁴ Pa-s. This observation coupled with the observation that all samples extended at the three different strain rates fail at similar values of uniaxial extensional viscosity suggest that the extensional flow behavior of filled polymers is governed by the orientation distribution of the fibers. This is consistent with constitutive equations available for fiber filled polymers [23].

CONCLUSIONS

The uniaxial extensional viscosity of the glass filled resin did not exhibit any strain hardening characteristics. The stress growth depends on the orientation distribution of the fibers. After a Hencky strain of 2, the initial random orientation distribution of the glass fibers in the polyamide resin is replaced with all fibers oriented along the stress field. The extensional stress growth function is dependent on the Hencky strain and the resulting orientation distribution of the fibers.

ACKNOWLEDGMENTS

The authors would like to acknowledge the contributions of Messrs. Thomas J. Krolick and Daniel S. Leydon of AlliedSignal Corporation for supplying the resin and processing guidance. The funding and input of AlliedSignal Inc. and Mobil Chemical Company (Dr. P. Shirodkar and Dr. P. Tong) are gratefully acknowledged. The image analysis was carried out by Ms. Esra Küçükpinar of HFMI.

REFERENCES

1. J. M. Dealy, *Polym. Eng. Sci.*, 11, 433-445 (1971).

2. J. M. Dealy, *J. Non-Newtonian Fluid Mech.*, 4, 9-21 (1978).
3. C. J. Petrie, "*Elongational Flows*", Pittman Publishing, London (1979).
4. F. N. Cogswell, *Plast. Polym.*, 36, 109-111 (1968).
5. H. M. Laun and H. Münstedt, *Rheol. Acta*, 15, 517-524 (1976).
6. J. M. Dealy, R. Farber, J. Rhi-Sausi and L. Utracki, *Trans. Soc. Rheol.* 20, 455-464 (1976).
7. R. L. Ballman, *Rheol. Acta*, 4, 137-140 (1965).
8. A. Garcia-Rejon, M. Eng. Thesis, McGill University, Montreal, Canada (1976).
9. D. M. Kalyon and D. Czerwonka, *Plast. Rub. Proc. Appl.*, 14, 29-33 (1990).
10. J. Meissner, *Rheol. Acta* 8, 78 (1969).
11. J. Meissner, *Trans. Soc. Rheol.* 16, 405 (1972).
12. J. Meissner, *Polym. Eng. Sci.* 27, 537 (1987).
13. J. Meissner, *Rheol. Acta* 33 (1), 1-21 (1994).
14. H. M. Laun, *Colloid Polym. Sci.* 262, 257-269 (1984).
15. Y. Chan, J. L. White, and Y. Oyanagi, *J. Rheol.* 22 (5) 507-524 (1978).
16. L. Li, T. Masuda, and M. Takahashi, *J. Rheol.* 34 (1) 103-116 (1990).
17. L. Utracki, *Rub. Chem. and Tech.*, 57, 507-522 (1985).
18. R. Yazici, A. Wagner, D. M. Kalyon and S. B. Han, *SPE ANTEC Tech. Papers*, 40, 1172-1174 (1994).
19. A. Wagner, R. Yazici and D. M. Kalyon, "Extrudate Swell Behavior of Glass Fiber Filled Polyamide 6", accepted to appear in *Polymer Composites* (1996).
20. A. Green, Ed., "Radiographic Inspection", *Handbook of Nondestructive Inspection and Quality Control*, ASM, 295 (1990).
21. R. S. Stein, and S. N. Stidham, *J. Appl. Phys.*, 35, 42 (1964).
22. H. Yaguchi, H. Hogo, D. G. Lee and E. G. Kim, *Intern. Polymer Processing*, 10, 3, 262 (1995).
23. S. Dinh and R. Armstrong, *J. Rheo.*, 28, 207 (1984).

Keywords: Extensional Flow, Composite, Nylon, Engineering Plastic

Table 1. Properties of Nylon 6-12% Glass Resin

specific gravity	1.22
------------------	------

tensile yield strength, MPa	117
flexural strength, MPa	166
flexural modulus, MPa	4658
notched Izod impact, J/m	42
heat deflection temp. @246psi, oC	195
melting point, oC	218
melt index	3.5

Table 2. Orientation Distribution Function, J, versus Hencky Strain

strain, ϵ	0.000	0.275	0.550	0.825	1.100	1.650	2.200	2.75
J	0.16	0.36	0.40	0.57	0.61	0.63	0.77	0.84

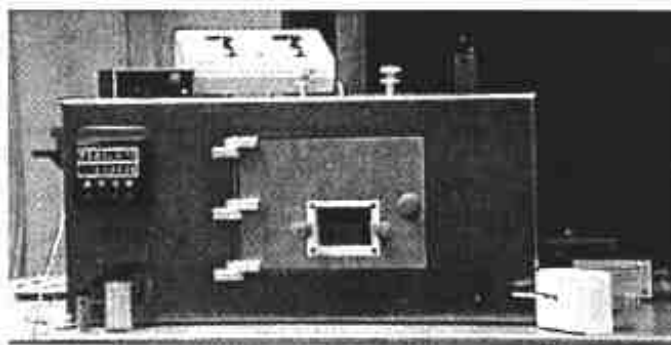


Fig. 1: Elongational Rheometer

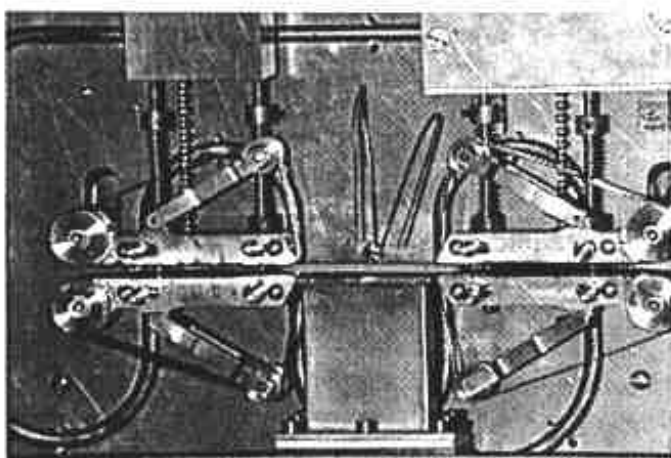


Fig. 2: Rotary Clamping System.

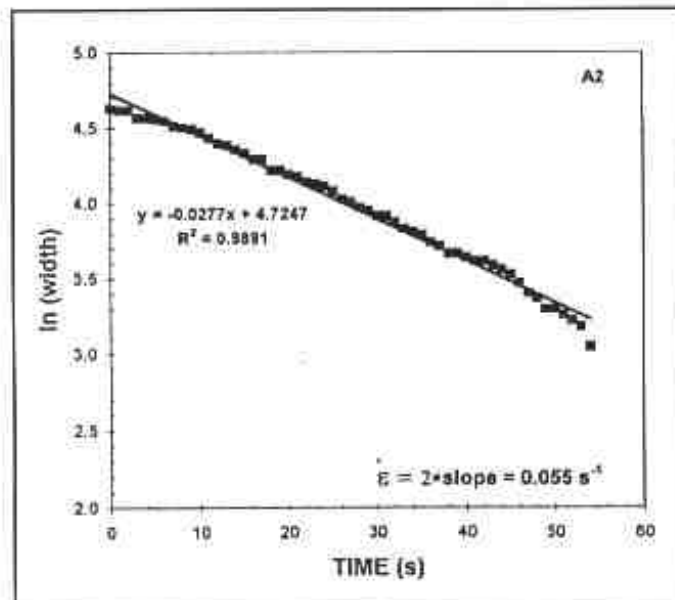


Fig. 3. True Hencky Strain Rate as Measured by Cinematography.

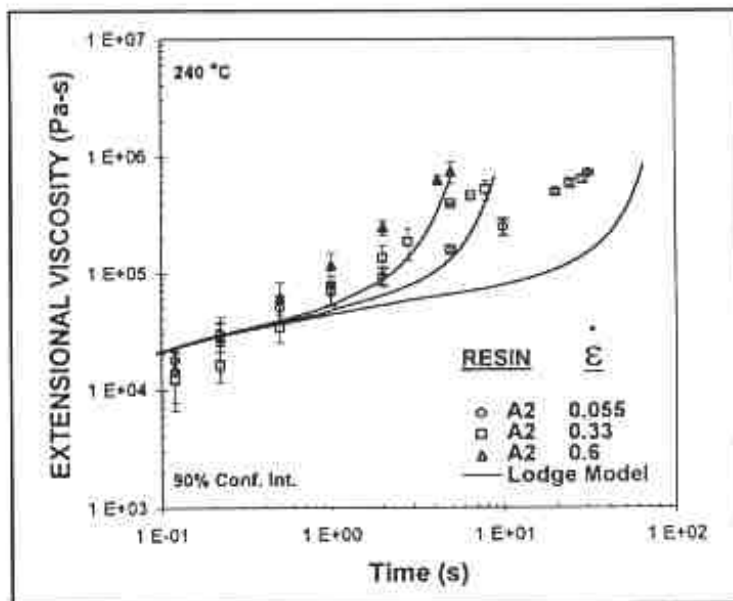


Fig. 4. Extensional Viscosity of Glass Filled Nylon

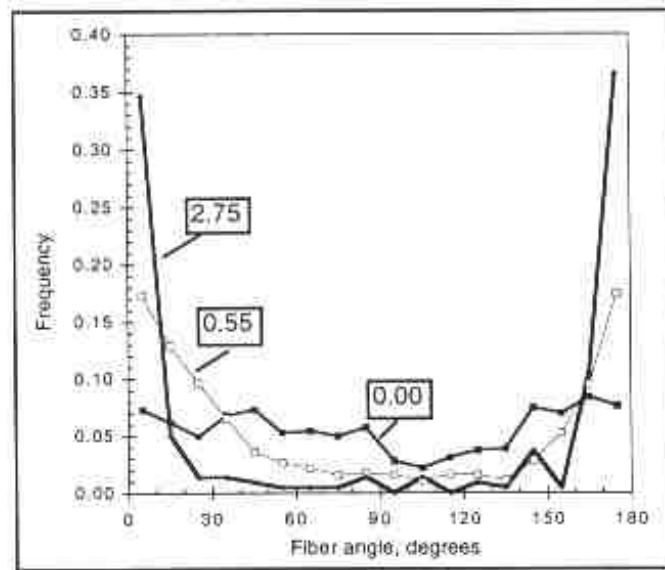
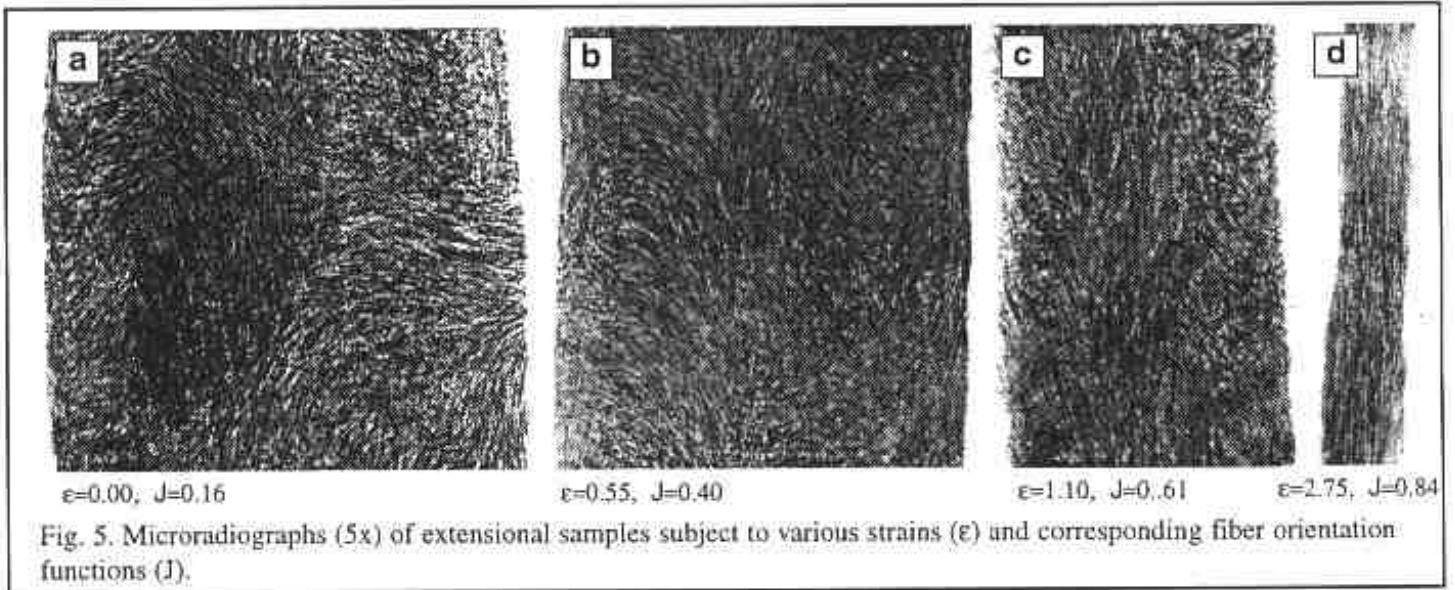


Fig. 6. Fiber distributions for 0, .55, 2.75 strain.

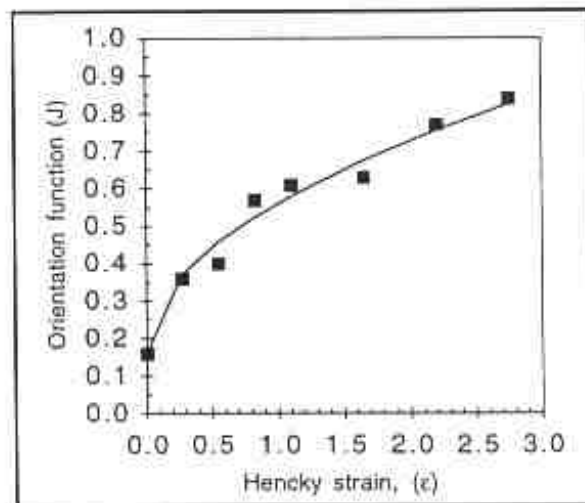


Fig. 7. Variation of fiber orientation function (J) as a function of Hencky strain for Nylon 6-12% glass fiber resin subject to extensional flow.