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RHEOLOGY OF CONCENTRATED SUSPENSIONS
OF FIBERS IN TUBE FLOW: II.
AN EXPLORATORY STUDY

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II. AN EXPLORATORY STUDY

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FOREWORD

The research reported herein was conducted by the staff of Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 87, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites".

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Rheology of Concentrated Suspensions of Fiber in Tube Flow:

II. An Exploratory Study

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Abstract

The viscosities of concentrated suspensions of glass fibers in high viscosity silicone oil were measured with a capillary viscometer using 1/4" and 1/8" diameter capillaries. The suspensions were mixed by a variety of techniques; the majority were mixed with an extruder. Suspension fiber length distributions and rheological properties were highly dependent on mixing technique.

The viscosity of the suspensions was strongly dependent on fiber length distribution--a few percent of relatively long fibers in the distribution doubled or tripled the suspension viscosity. Special attention was paid to wall effects which complicate the interpretation of suspension viscosity data. Yield stresses, squeeze-through, the capillary entrance exclusion were observed; their magnitudes increased with fiber length and depended strongly on fiber length distribution. The variety of concentrated fiber suspension behavior reported in the literature is consistent with our observation that small differences in fiber length can cause large differences in suspension rheology.

Rheology of Concentrated Suspensions of Fiber in Tube Flow:

II. An Exploratory Study

I. INTRODUCTION

This series of papers (1,2) presents the results of an experimental study of the rheology of concentrated fiber suspensions in capillary flow. Part I of the series contains a literature review of experimental shear viscosity measurements on concentrated fiber suspensions. The present paper i) summarizes that review and briefly discusses wall effects which complicate experimental suspension rheology, ii) describes the experimental techniques used to mix our suspensions and to measure their viscosities, and iii) concludes with some observations on the rheology of concentrated fiber suspensions. Although the observations reported in this paper are quantitative, they are of such diverse nature that the useful results are really only qualitative. The diverse nature of the observations arises from the fact that suspension properties depend strongly on fiber length distribution and the fiber lengths produced during mixing proved difficult to control. Part III of this series (2) presents some quantitative results obtained from suspensions in which the fiber length distribution was kept constant.

Model systems of concentrated suspensions of glass fibers in high viscosity silicone oil were studied. Shear stress-apparent shear rate data were measured with a 1/4" and a 1/8" diameter capillary viscometer over an apparent shear rate range of 0.26 to 5500 sec⁻¹. Special attention was given to the influence of wall effects on these measurements. In the interest of simplicity, normal forces and elastic effects were not studied.

II. PREVIOUS WORK ON CONCENTRATED FIBER SUSPENSIONS

The experimental literature on the rheology of concentrated suspensions of fibers in tube flow has been reviewed elsewhere.(1) To summarize that review: i) there are only about a half dozen studies of shear flow of concentrated suspensions of fibers, ii) each of these studies evaluated different materials under different flow parameters and iii) such a variety of flow behavior was observed that generalizations about flow are hard to draw. Some suspension viscosities were Newtonian, some showed power-law behavior, some suspensions exhibited yield stresses, and some flow curves showed unusual curvature and points of inflection. The recent series of papers which have appeared in the literature discussing the rheology of suspensions of aligned fibers in elongational flow are not reviewed here because of the differences in behavior expected between elongational and tube flow. Theories of the behavior of concentrated fiber suspensions are discussed in the third paper in this series (2).

Viscosity is a material function only for homogeneous, isotropic materials and concentrated fiber suspensions may not behave as such. The measured viscosity of fiber suspensions may depend on both flow geometry and fiber size because of fiber orientation effects and because of fiber interaction with the wall of the measuring instrument (3-5). The following classification of fiber-wall interactions, although not rigorous or mutually exclusive, is useful for our discussion.

Mechanical exclusion (6,7) occurs because the center of a particle in a suspension cannot approach the wall of the viscometer any closer than the effective size of the particle. Hydrodynamic interaction (8-11) arises

from the fact that the velocity profile around a particle near the wall is altered by the presence of the wall. Concentration defect--a lower concentration of particles in the capillary than in the viscometer barrel --arises from radial migration of particles in tube flow (6,7,12-15). Entrance exclusion, in which some of the particles in the barrel are precluded from entering the capillary, also causes a concentration defect (16-19).

Since the interpretation of capillary viscometer data depends on the existence and magnitude of these wall effects, we review what is known about them for concentrated fiber suspensions. Radial migration has not been observed in concentrated fiber suspensions (16-19), perhaps because of the high viscosity of the suspending media used in these studies. Entrance exclusion has been observed, and the effect is usually catastrophic in that most of the fibers mat up at the entrance and pure resin is squeezed through them (17-19)--this phenomenon is appropriately called "squeeze-through". Concentration defects and entrance exclusion may be directly detected experimentally by particle concentration measurements.

Less is known about mechanical exclusion and hydrodynamic interaction. Theories for these effects have been developed only for dilute suspensions in creeping flow. (5,8-11) The theories predict that the measured viscosity of a suspension will decrease with decreasing instrument/particle size ratio. One experimental study of suspensions of spheres (14,15) indicates this conclusion is not valid for concentrated suspensions. Very little experimental evidence is available for suspensions of fibers. Attanasio, et. al. (20) compared the viscosity of dilute suspensions of

rigid rods in creeping flow as measured in both capillary and Couette viscometers and found the viscosities equivalent for instrument/fiber length ratios greater than three. This is a remarkably low number in view of the fact that, as a measure of the characteristic size, fiber length is too large. Karnis, et. al. (21) observed that the characteristic dimension of a fiber lay somewhere between its length and diameter. Stankoi, et. al. (16) found the viscosity of concentrated fiber suspensions to be independent of capillary diameter over the relatively small range they measured: 0.35 to 0.47 inches. These results suggest that wall effects in concentrated fiber suspensions may not be large, but insufficient data is available for this to be a firm conclusion. The ultimate result of wall effects is that the data presented in this paper may be valid only for the geometry in which it was measured.

III. MATERIALS AND MIXING STUDIES

Suspensions of glass fibers in glycerine were tried initially but viscometry was impossible because of the prevalence of squeeze-through. Glass fibers in silicone oil proved more tractable as a model system. The important physical properties of these materials are given in Table I and Figure 1. The sizing on the fibers was removed by heating to 400C for sixteen hours. The oil and fibers were then mixed by a variety of techniques in an attempt to meet the following goals: reproducible suspension viscosity, minimum fiber breakage, good fiber dispersion, and minimum air entrapment. None of the techniques was successful because of the inherent incompatibility of the goals. The bulk volume occupied by

Table 1. Physical Properties of the Materials (25 C) (22)

Glass Fibers

Density - 2.54 gm/cm^3

Original Length - $1/8''$ nominal

Diameter - $0.00051''$

Poisson Ratio - 0.20

Youngs Modulus - 10^7 psi

Silicone Oil

Density - 0.98 gm/cm^3

Molecular wt. (M_w) - 10^5

randomly-oriented, high aspect ratio fibers is quite large. For the glass fibers used in this research, the bulk volume of a random dispersion is so large that the volume occupied by fibers is only about one to three percent of the total. As pointed out by Milewski (23), this is clearly the highest fiber concentration possible in a suspension of randomly oriented stiff rods. If higher concentrations are desired, the fibers must either be bent, broken, or aligned. Hence, the goals of good dispersion and minimum fiber breakage are incompatible.

We decided to retain the goal of good dispersion and abandon the goal of minimum fiber breakage. An extruder was chosen as a mixer because of its widespread industrial use for processing fiber reinforced plastics. The extruder used was a 3/4" Brabender Extrusion Rheometer fitted with a piston and cylinder crammer-feeder and operated at 80 rpm at ambient conditions without a die. The mixing procedure was a two step process: flow of the oil into the fibers under its own weight, followed by extruder mixing. When the entire batch of suspension had passed through the extruder once, it was mixed briefly on a Hobart planetary mixer to ensure good bulk homogeneity. Stresses developed in the Hobart were much lower than those in the Brabender.

Extruder mixing met the goals of good dispersion and minimum air entrapment. The goal of reproducible suspension viscosity, however, was difficult to achieve with suspensions which passed through the extruder only once. As described later, the difficulty was due to the occasional presence of a very small fraction of unusually long fibers in the suspension. The long fibers appeared to come from unwetted fiber bundles in the feed

material. A second pass through the extruder was necessary to break down the long fibers to give suspensions with reproducible viscosities.

Fiber length distribution measurements were made by sampling the suspension, photomicrographing the sample, and measuring the fiber images on the photograph. Typical fiber length histograms are shown in Figures 2 and 3. Comparing different histograms is difficult unless the information they contain can be summarized by a few parameters. Fortunately, there is a theory which predicts that for most reasonable breakage processes the fiber lengths should approach a log-normal distribution (24) characterized by only two parameters: a mean and a standard deviation. As noted later, care must be used to determine whether the breakage process has proceeded far enough in each suspension for the log-normal distribution to adequately characterize the fiber length population. Each population was accepted as log-normally distributed if the test values for skewness and kurtosis indicated less than a 5% probability of a Type I error.

As will be shown later, fiber length distribution is a very important parameter in determining the flow properties of a suspension. An exploratory study of mixing parameters indicated that the fiber length distribution in an extruder-mixed suspension was correlated with the fiber concentration and the oil viscosity of the suspension. The separate influences of fiber length, fiber concentration, and oil viscosity on the flow properties of a suspension could not be determined unless the fiber length could be independently controlled during mixing. A factorial-design study (20) indicated the operating parameters of the extruder (screw speed, etc.) afforded little control over the fiber length distribution.

Although completely independent control over fiber length distribution never was achieved, Part III of this series (2) describes a technique by which the same fiber length distribution could be produced in all suspensions.

IV. VISCOMETRY

The capillary viscometer used to measure the suspension viscosities is shown in Figure 4. It is a stainless steel viscometer designed for use on an Instron Universal Testing Machine at ambient conditions. The Instron lowers the viscometer piston at a constant speed while recording the force necessary to push the suspension through the viscometer. Two sets of capillaries with diameters of 1/4" and 1/8" and two conical entrance cones with apex angles of 90° and 180° are available for the viscometer. The length-to-diameter ratios of the capillaries range from 4 to 32. The viscometer has an apparent shear rate range of 0.05 to 5500 sec⁻¹ and a shear stress range of 10³ to 10⁷ dynes/cm². The viscometer has been standardized with fluids of known viscosity and has a measurement accuracy of $\pm 6\%$.

The force necessary to extrude a suspension at a given crosshead speed sometimes fluctuates with time. The fluctuations can be caused by log-jamming of fibers in the capillary entrance. (18,19) We have observed that fluctuations can also be caused by inherent variations in the speed of the Instron crosshead. (20) The fluctuations were visually averaged to obtain a mean force. The shear stress at the wall of the capillary, σ_w , was calculated from the force, F, by means of an end correction analysis:

$$\Delta P = \frac{2\sigma_{\omega}}{R} L + \Delta P_e$$

where $\Delta P = \frac{F - F_{\text{Drag}}}{\pi R_b^2}$, and R_b is the barrel radius, F_{drag} is the

mechanical drag of the piston against the barrel (negligible in our measurements), L and R are the capillary length and radius, and ΔP_e is the "entrance losses". The linearity of the end correction fit was tested statistically and the probable error of σ_{ω} calculated for each set of measurements.

The apparent shear rate at the wall, $\dot{\gamma}_a$, was calculated from the crosshead speed, V , by

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3}$$

where $Q = \pi R_b^2 V$.

Shear stress and apparent shear rate at the wall data are reported because they are essentially pressure-drop and flow-rate data and are thus independent of the fact that the suspensions are not homogeneous. We note again that because of fiber orientation and wall effects, the data cannot be expected a priori to be valid for any flow geometries except those used in the measurements.

The first (top) curve in Figure 5 is a flow curve for a single-pass, extruder-mixed suspension of 30 vol. % fibers in a 600 P oil. The same batch of material was used for the measurements at all shear rates. A measurement at 0.26 sec^{-1} was not possible because squeeze-through

occurred. The squeeze-through was obvious both because pure oil flowed from the capillary and because the force to extrude the suspension increased steadily, never reaching steady state. Figure 6 shows a similar but less drastic force rise observed at the next highest shear rate measured, 1.3 sec^{-1} . Capillary entrance exclusion was suspected as the cause of the force rise, and fiber concentration measurements as reported in Figure 6 confirm the suspicion. These observations indicate that squeeze-through and entrance exclusion are really the same phenomenon and are readily recognizable from the force curves they produce with our viscometer.

The peculiar dip at 130 sec^{-1} in the first flow curve of Figure 5 suggests that the flow properties of the suspension were changing during measurement. To test the validity of the suggestion, the same material was remeasured and the second flow curve of Figure 5 resulted. The second curve is clearly different from the first: the viscosity is lower, squeeze-through and entrance exclusion have disappeared, and a yield stress has appeared. In an effort to obtain a flow curve on a material which was not changing during measurement, the suspension was passed through the extruder a second time and its viscosity remeasured. The third (bottom) curve of Figure 5 resulted. Additional mixing of up to six passes through the extruder did not change the third flow curve. If the second curve is corrected for its yield stress, it superimposes on the third curve.

Figure 5 clearly shows that the rheological behavior of a concentrated fiber suspension depends strongly on mixing. One explanation of this strong dependence is that the fibers in the suspension broke during mixing.

Figures 3 and 4 show histograms of the fiber lengths in the suspensions before and after the viscosity measurements were made. As expected the fibers were longer before the measurements degraded them.

Despite the apparent differences between the two histograms, the means and standard deviations of the distributions are not significantly different. The long fibers in Figure 3 constitute only about 3% by number of the fibers present, and such a small fraction does not shift the mean very much. On the other hand, the test statistics show that the population of Figure 3 is not log-normally distributed, so this comparison really illustrates the difficulties that arise when a population which is not log-normal is treated as if it were.

It is surprising that such a small fraction of long fibers could cause such large changes in suspension properties. To test this conclusion, two batches of suspension were mixed on the extruder, each for a different number of passes. To half of each batch enough oil and 1/8" fibers were added by extruder mixing to maintain the overall concentration at 30 vol.% but to ensure that 5 wt.% of the fibers present were relatively long. Table 2, listing the viscosities of these suspensions along with their controls, confirms that a small fraction of relatively long fibers can double or triple the suspension viscosity.

Table 2. Effect of a small fraction of relatively long fibers on suspension viscosity. Uncertainties are one standard deviation.

Passes Through Extruder	Wt.% of Fibers Present Which are Long	Viscosity (Poise)
2	0	8,900 ± 400
2	5	22,400 ± 400
7	0	5,140 ± 90
7	5	8,900 ± 800

V. OBSERVATIONS AND CONCLUSIONS

Achieving good dispersion with little fiber breakage appears to be inherently impossible with high aspect ratio fibers except at very low fiber concentrations (23). At higher concentrations the fibers break and their lengths approach a distribution determined at least in part by fiber concentration and oil viscosity.

Squeeze-through and capillary entrance exclusion are the same phenomenon, differing only in intensity. Initiation of squeeze-through occurs gradually as flow conditions change, rather than abruptly, as in the case of turbulence, for example. Squeeze-through increases with slower flow, longer fibers, and either lower oil viscosity or less compatible fiber oil systems. The fact that squeeze-through occurs at low shear rates means that it is probably not a significant problem for plastics processing.

Suspension viscosity increases as fiber length increases. The nature of the dependence appears to be very complex, being much stronger for longer fibers. This conclusion suggests that treating a fiber length population as log-normally distributed may be inappropriate, because this distribution weighs least heavily the longest and therefore most important fibers.

In summary we can conclude that:

- i) Suspension properties are highly dependent on mixing technique. Suspensions could be reproducibly mixed by passing them through the extruder twice.
- ii) The viscosity of all suspensions, no matter how mixed, could be reproducibly measured with the viscometer (although some suspensions degraded during the measurement). This fact is significant in that

explicit control over fiber orientation in the viscometer barrel was not necessary to achieve reproducible results.

- iii) The standard end correction analysis could be applied to all suspensions measured.
- iv) The variety of concentrated fiber suspension behavior reported in the literature is consistent with our observation that very different suspension behavior can arise from small differences in fiber length distribution.
- v) The existence and magnitude of special suspensions effects, such as yield stress, squeeze-through, and capillary entrance exclusion, are highly dependent on fiber length distribution.

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CAPTIONS FOR FIGURES

1. Viscosity-shear rate dependence of silicone oil. The smooth curves are standard curves supplied by the manufacturer. Data points are for the specific lots used in the research; 0-1/4" capillaries; Δ -1.8" capillaries.
2. Diagram of the capillary viscometer.
3. Histogram of fiber length distribution in a 30 vol.% 600 P suspension before viscosity measurements.
4. Histogram of fiber length distribution in a 30 vol.% 600 P suspension after all viscosity measurements.
5. Effect of degradation and mixing on the flow curves of a 30 vol.% 600 P suspension. Measurements were made consecutively on the same batch of material, starting with the highest shear rate on the top (\square) curve. The suspension was passed through the extruder between the second (Δ) and third (+) flow curves. "Sq" means squeeze-through.
6. Fiber concentration in the capillary and entrance reservoir at the beginning (left) and end (right) of a viscometer run. The force curve shows a gradual rise as the suspension concentration increases.

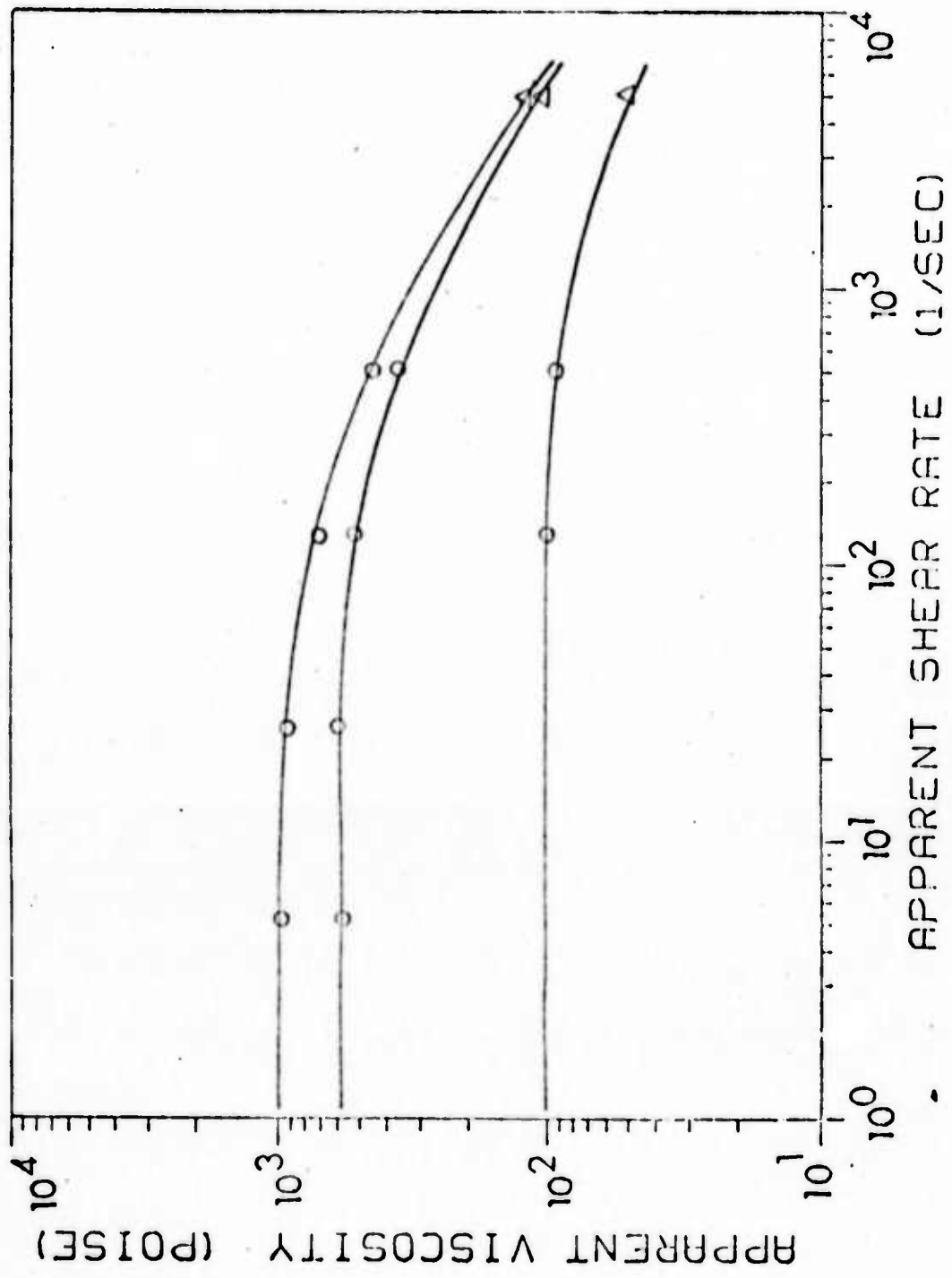
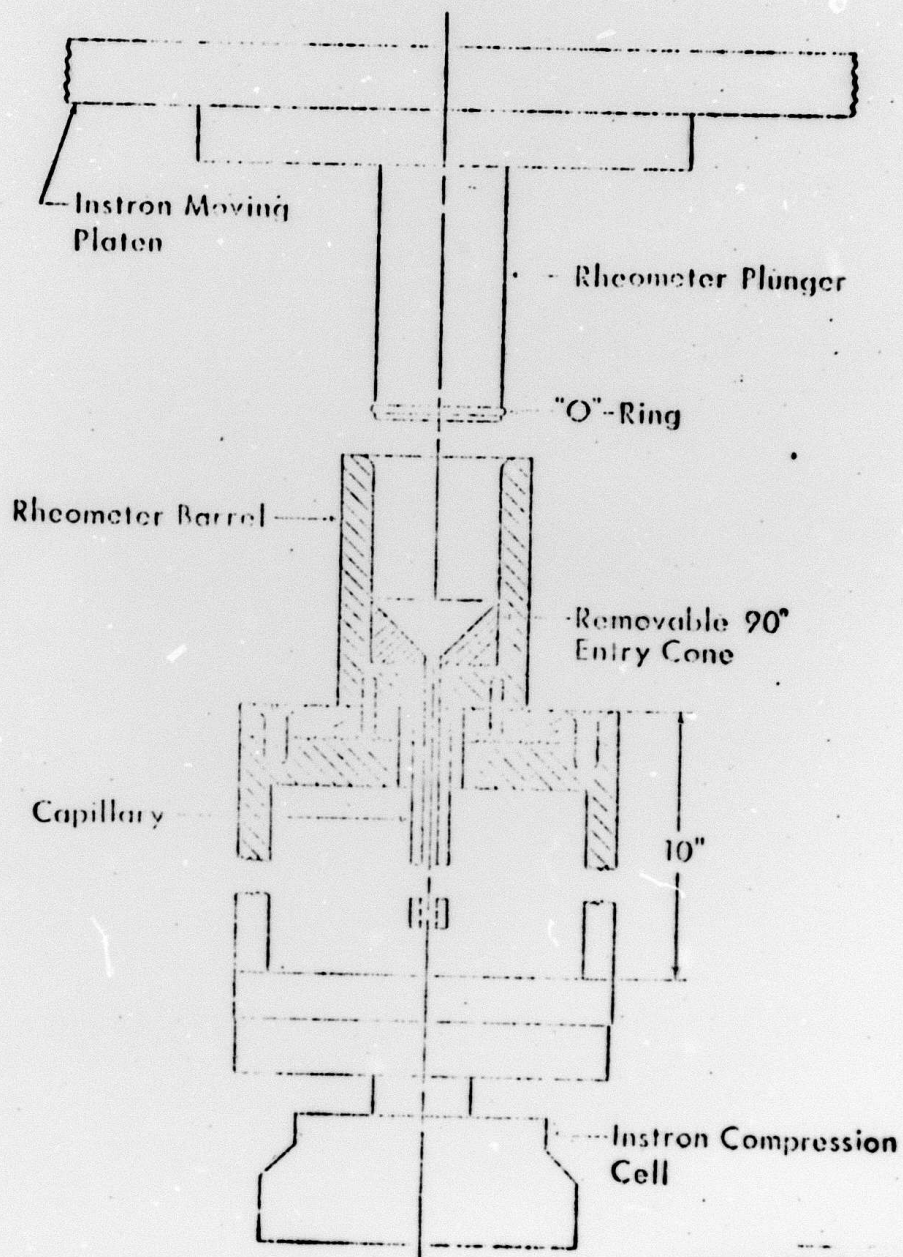


Figure 1



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Figure 2

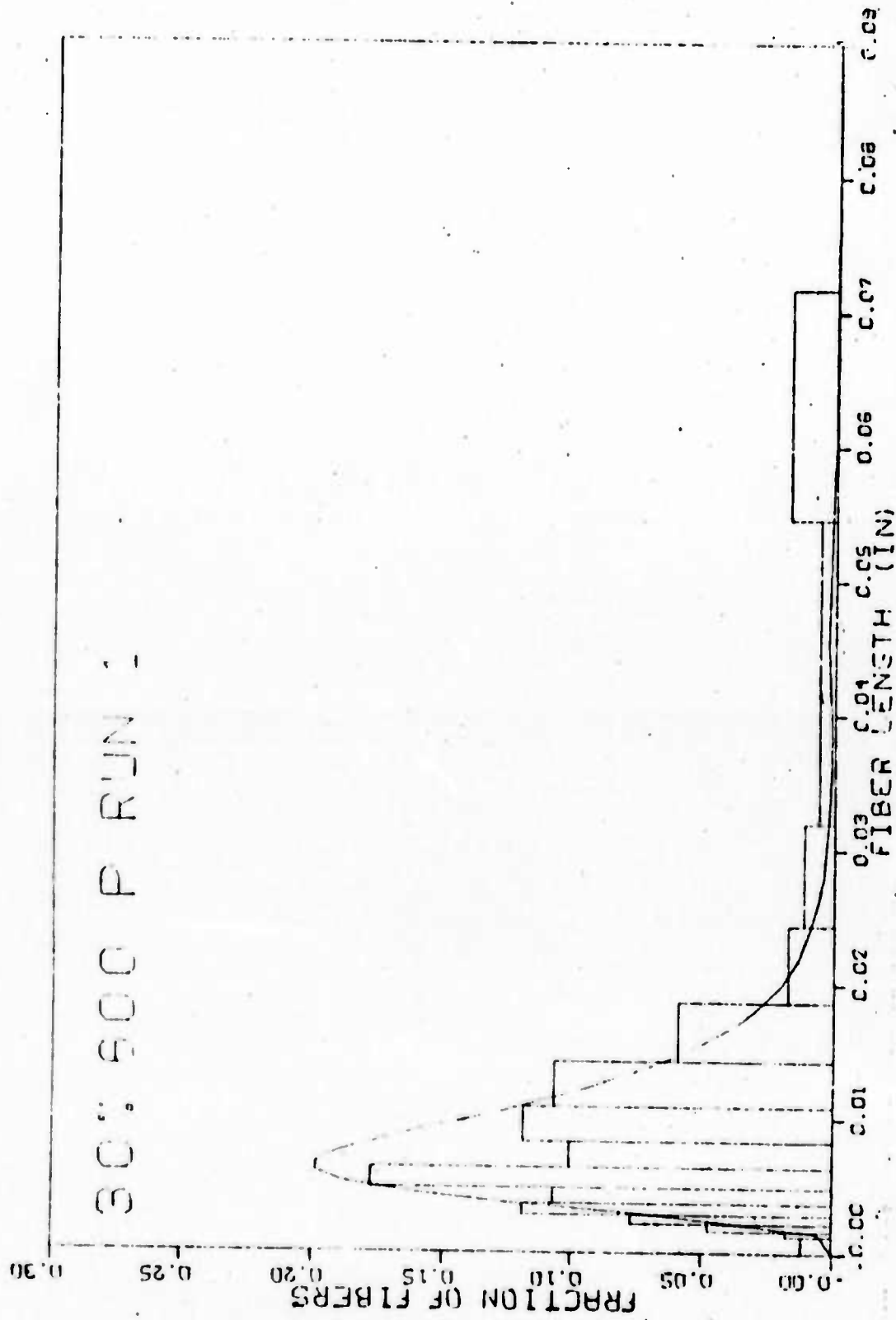


Figure 3

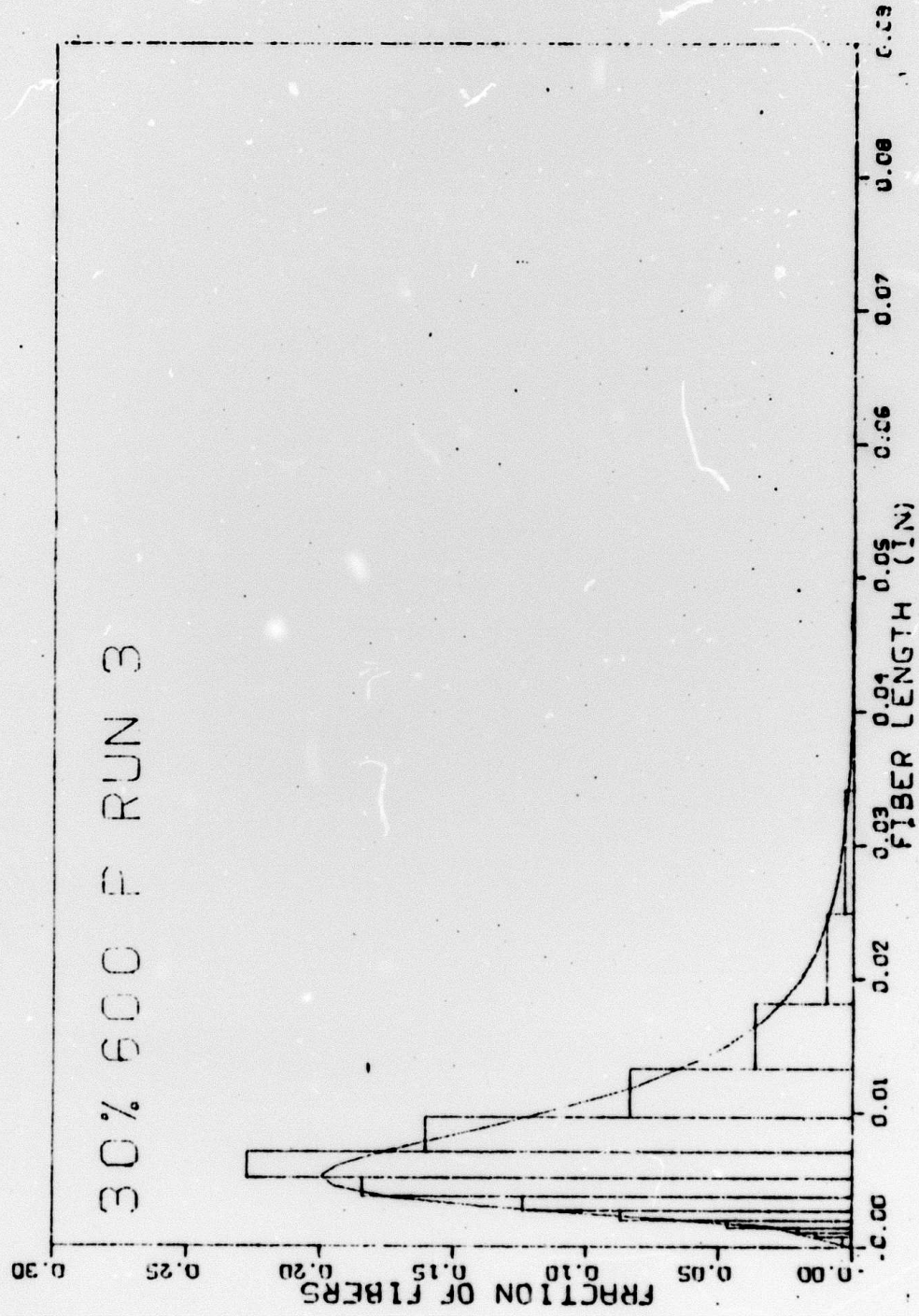


Figure 4.

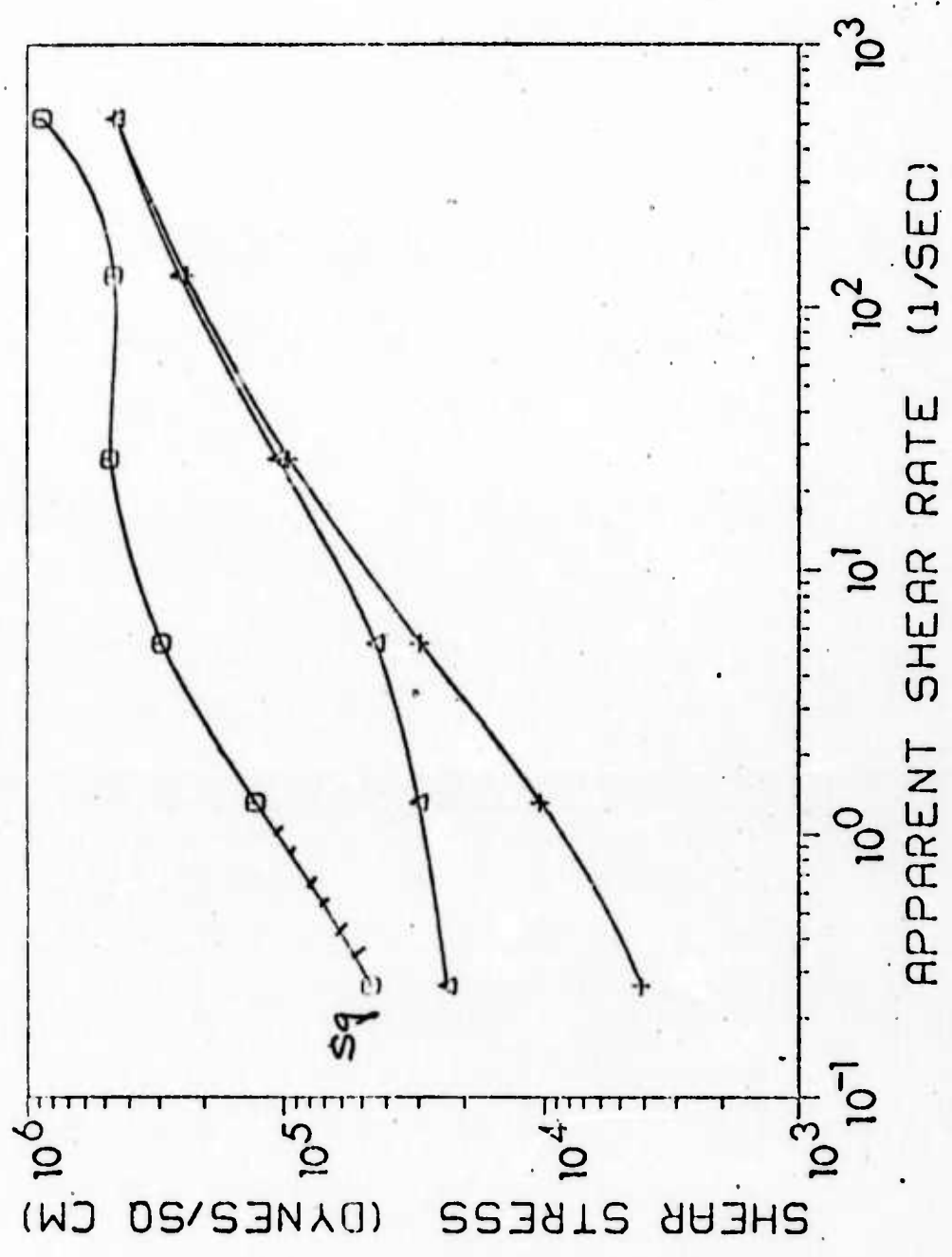
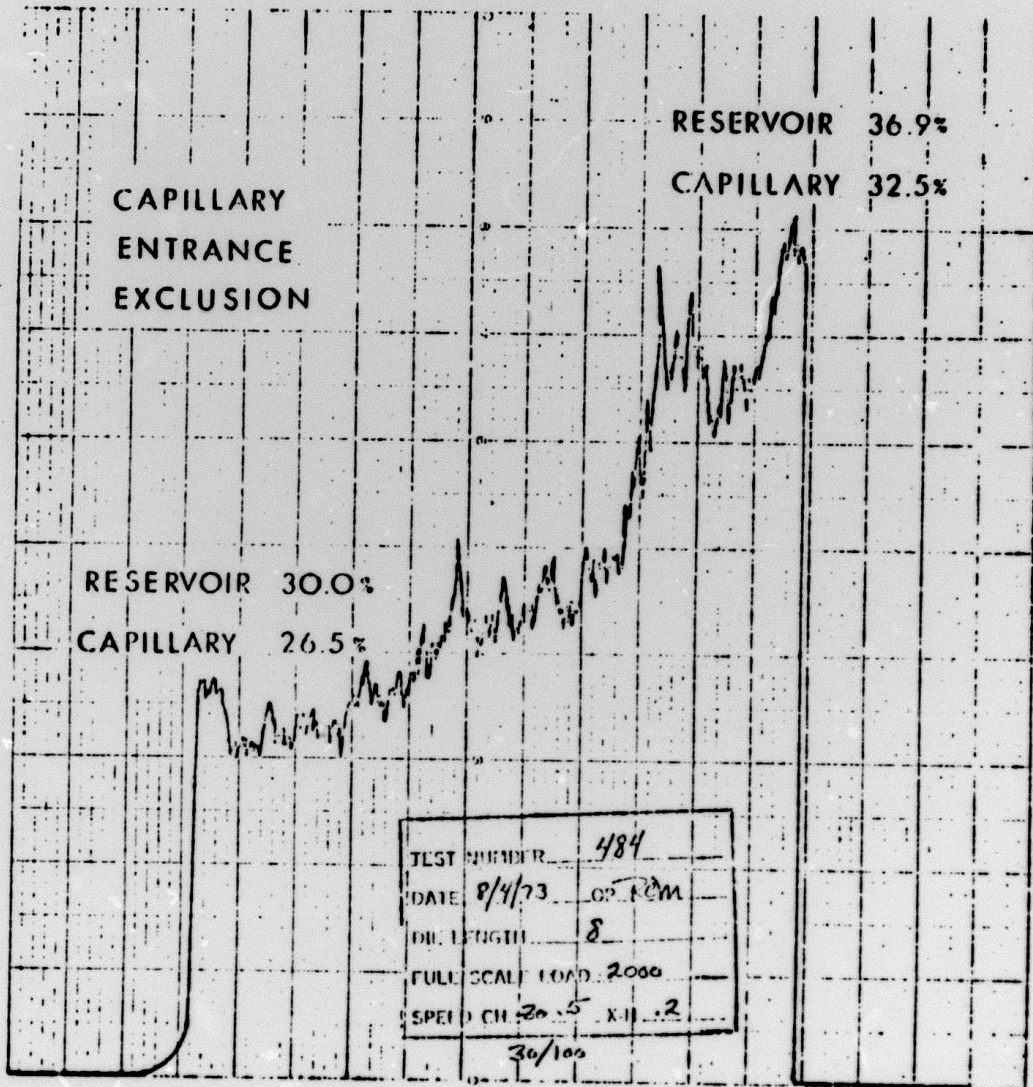


Figure 5



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Figure 6