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ECX AND PEX RHEOLOGY

G. T. West

DEVELOPMENT DIVISION

OCTOBER - DECEMBER 1975
(FINAL REPORT)

Normal Process Development
Endeavor No. 103

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INTRODUCTION

The objectives of this project are:

1. To evaluate the capillary rheometer as a device to qualitatively measure the extrusion properties of extrusion cast and paste explosives.

2. To study and determine means to distinguish and characterize the rheological properties of different lots of ECX and PEX.

3. To apply results from (1) and (2) to production loading operations involving ECX and PEX.

ABSTRACT

The second objective (to study and determine means to distinguish and characterize rheological properties) of this project has been accomplished.

Testing procedures were finalized, and general knowledge of the rheometer itself was gained.

Three batches of 85/15 (weight percent) RDX/Sylgard were tested in the Instron Capillary Rheometer. Each lot was statistically distinguishable from the other two lots. One lot exhibited a significantly lower apparent viscosity than the other two lots, which were statistically different from each other, but which were in fairly close agreement.

DISCUSSION

PROCEDURES

The shear rate range which was most likely to allow resolution of apparent viscosity and shear stress differences in 85/15 weight percent RDX/Sylgard was determined and reported in a previous report(*1*). This shear rate range was obtained using the 1.27 mm diameter, 50.937 mm long capillary at the three lowest crosshead speeds (85, 212 and 423 microns per second). This yielded shear rates of 0.03, 0.075, and 0.15 sec^{-1}, respectively. The longer capillary (50.9 versus 25.4 mm) was selected to facilitate faster cleaning after each test.

Since the forces measured by the load cell were relatively small (10 - 700 newtons), it was important to determine the force required to move the plunger in an air-wetted barrel. This force is not very reproducible and is strongly dependent upon the condition of the Teflon O-rings on the plunger. "Zero" forces ranged between 13 and 53 newtons. The force was measured at the beginning of the day and this "zero" force was subtracted from the load measured during the tests for that day. If the "zero" force was outside the range noted above, the Teflon O-rings on the plunger were replaced.

According to the Instron manual the slide lock at the load cell-plunger interface should not be used because it might result in erroneous force measurements. Tests were run with and without activating the slide lock. Those without the lock engaged were "smoother" (± 1 minor paper division, which was approximately ± 1 newton). Those with the lock engaged varied as much as ± 5 newtons. The plunger was marked so that the same orientation would be used for all the tests.

In order to minimize entrapped air, the barrel was always loaded with the test explosive with the plunger in place. Loading the HE pushed the plunger up, and the capillary was inserted and locked in place with the clamping nut. It was very rare that any signs of air bubbles were noticed (two tests out of 24 were rerun because the problem was suspected).

Ideally the tests should be conducted only at the crosshead speed which would produce the desired shear rate. However, the speeds used were quite slow as noted above, so a procedure needed to be devised to help accelerate an already time-consuming test. A test was run in the ideal manner, and another test was conducted using the "final" (see below) procedure. The "final" or practical procedure resulted in measured forces about 10% lower than those measured in the "ideal" procedure. However, the practical procedure required some 30 minutes, while the ideal procedure required more than 2 hours. Since it is likely that some curing occurred during the ideal procedure, it was concluded that the practical procedure would probably not result in significantly different forces.

The procedure selected consisted in lowering the crosshead at a higher speed until contact between the load cell and the plunger was imminent and then conducting the test at the desired crosshead speed. The "final" or practical procedure was different in that the crosshead speed was "stepped down" from the maximum speed to the desired speed without "shock loading" the HE. Each speed was decreased when an increase in load was noted.

A test was considered completed (in other words, the load was "stabilized") when the load varied no more than ± 1 minor paper division. Of course, this varied with the different amplifier sensitivity settings, which were always adjusted so as to yield a deflection at or greater than half the paper width. This criterion was determined in a completely arbitrary manner.

After each test, dry wadded tissue paper was forced through the barrel until the barrel appeared clean. If a different HE batch was to be tested, the barrel was flushed with methyl alcohol. The latter was also done at the end of each day. The capillary was cleaned after each test using alcohol flushing and a cleaning rod.

All tests were randomized according to material and shear rate, and were conducted at room temperature (24 ± 3 C).

TEST OF MATERIALS "A" AND "B"

A known "bad" batch and a known "good" batch of 85/15 (weight percent) RDX/Sylgard were selected for testing to determine the reproducibility of apparent viscosity and shear stress measurements within batches, and to determine the ability of the rheometer to distinguish between the batches. A factorial design with two variables (batch and shear rate) was used at two and three levels (respectively), and six replicates were performed. For simplicity, the batches were designated "A" (4211322B-01) and "B" (4240-322B-01). Formulation and chemical analysis data are available in previous reports(*2*).

Table I contains the raw data and optimized averages with 95% confidence intervals at each shear rate. Values were rejected if they fell outside the range of ± 3 standard deviations (unbiased) of the mean of the set without the suspect point.

The data were submitted to a computer program entitled "Analysis of Variance for Factorial Design." The material, the shear rate and the interaction of material with shear rate were all significant at or above the 0.002 level when the input variable was the apparent viscosity. Only the material was significant at or above the 0.002 level when the input variable was shear stress; the other two factors (shear rate and its interaction with material) were not significant at the 0.20 level. The "bad" batch was statistically distinguishable from the "good" batch, and it exhibited significantly lower apparent viscosity and shear stress at a given shear rate.

Since these materials were formulated in the July-August 1974 era, and the testing occurred during June-July 1975, there was concern that some degree of curing might have occurred. This might have been misleading to the rheometer, especially if one batch had cured more than the other. They had both been stored in the same freezer at -15 C.

Both batches were tested for cure progress using previously reported procedures(*3*). Durometer readings and percentage of extracted dimethylpolysiloxane (DMPS) indicated that some chemical cure had occurred in both batches (12% - 13% DMPS extracted) but that there was no significant difference between the batches. It was concluded, therefore, that the rheometer test results and differences observed were valid. There was some concern, however, that these results might not compare with a "fresh" batch. It was decided to obtain such a fresh batch (5210-322B-01), designated "C" and test it.

Table I. Materials A & B Test Results

Material	Shear Rate (sec^{-1})	Shear Stress (KPa)	Average Shear Stress + L_{95} (KPa)	Apparent Viscosity (KPa-sec)	Average Apparent Viscosity ± L_{95} (KPa-sec)
A	0.030	3.76		126	
	0.030	2.69		89.7	
	0.030	3.25		108	
	0.030	4.71		157	
	0.030	0.755*		25.2*	
	0.030	3.02		101	
	0.030		3.49 ± 0.98		116 ± 32.7
B	0.030	32.7		1090	
	0.030	39.5		1320	
	0.030	37.6		1250	
	0.030	32.5		1080	
	0.030	34.2		1150	
	0.030	31.9		1060	
	0.030		34.7 ± 3.26		1160 ± 110
A	0.075	5.19		69.3	
	0.075	4.25		56.7	
	0.075	2.78		37.1	
	0.075	10.7*		143 *	
	0.075	2.30		30.7	
	0.075	2.81		37.5	
	0.075		3.47 ± 1.50		46.3 ± 20.1
B	0.075	39.2		523	
	0.075	43.9		586	
	0.075	35.7		476	
	0.075	34.7		463	
	0.075	36.1		482	
	0.075	40.4		538	
	0.075		38.3 ± 3.67		511 ± 53.6
A	0.15	5.35		35.7	
	0.15	5.88		39.2	
	0.15	2.69		17.9	
	0.15	9.77*		65.1*	
	0.15	3.99		26.6	
	0.15	5.82		38.8	
	0.15		4.75 ± 1.71		31.6 ± 11.4
B	0.15	10.1*		67.3*	
	0.15	43.6		291	
	0.15	38.7		258	
	0.15	41.5		276	
	0.15	39.0		260	
	0.15	41.3		275	
	0.15		40.8 ± 2.50		272 ± 16.7

*Rejected Values

Table II. Material C Test Results

Shear Rate (sec^{-1})	Shear Stress (KPa)	Average Shear Stress $\pm L_{95}$ (KPa)	Apparent Viscosity (KPa-sec)	Average Apparent Viscosity $\pm L_{95}$ (KPa-sec)
0.030	49.2*		1640*	
0.030	53.7		1790	
0.030	55.8		1860	
0.030	53.8		1790	
0.030	58.1		1940	
0.030	55.8		1860	
0.030		55.4 ± 2.25		1850 ± 77.3
0.075	59.8		798	
0.075	58.7		783	
0.075	56.7		756	
0.075	61.7		823	
0.075	56.6		754	
0.075	58.6		781	
0.075		58.7 ± 4.28		782 ± 30.0
0.15	58.7		392	
0.15	55.2		368	
0.15	61.3		409	
0.15	57.4		383	
0.15	42.5*		284*	
0.15	63.2		421	
0.15		59.2 ± 3.93		395 ± 26.0
0.300	36.2*		120*	
0.300	51.2		171	
0.300	57.6		192	
0.300	46.8		156	
0.300	53.0		177	
0.300	52.0		173	
0.300		52.1 ± 4.81		174 ± 16.1

**Rejected Values*

TEST OF MATERIAL C

Tests were conducted on material C in essentially the same manner as materials A and B. The shear rates used were 0.03, 0.075, 0.15 and 0.30 sec^{-1}. The additional shear rate was selected to provide another set of data. The tests were randomized according to shear rate; again six replicates were done and the testing was completed in a two week period (mid-October).

Results of the rheometer tests on material C are summarized in Table II. The same criteria were used to reject questionable data points.

Samples of batch C were also tested for cure in the same manner as A and B. The DMPS extracted (15%) indicated that no significant chemical cure had occurred.

DATA SUMMARY

Rectangular and logarithmic plots of the raw shear stress data are shown in Figs. 1 and 2. A general examination of these plots shows several suspect data points (circled) which were subsequently tested in the manner described above. Although these points were included in the analysis of variance calculations described below, they were rejected when averages were computed. The data for material C at the highest shear rate were not included in the analysis of variance.

As described above, all the data was submitted to the "Analysis of Variance for Factorial Design" computer program. A variance ratio (F) test was then performed on the results. Data are shown in Table III, with F-ratios at various significance levels shown in Table IV.

Table III. F-Ratio Tests of Significance for Shear Stress

Source of Variation	F-Ratio
Material Batch	418.1
Shear Rate	1.541
Interaction Between Material Batch and Shear Rate	0.214

The first two variation sources each had 2 degrees of freedom in the numerator with 45 degrees of freedom in the denominator, while the interaction term had 4 in the numerator with 45 in the denominator.

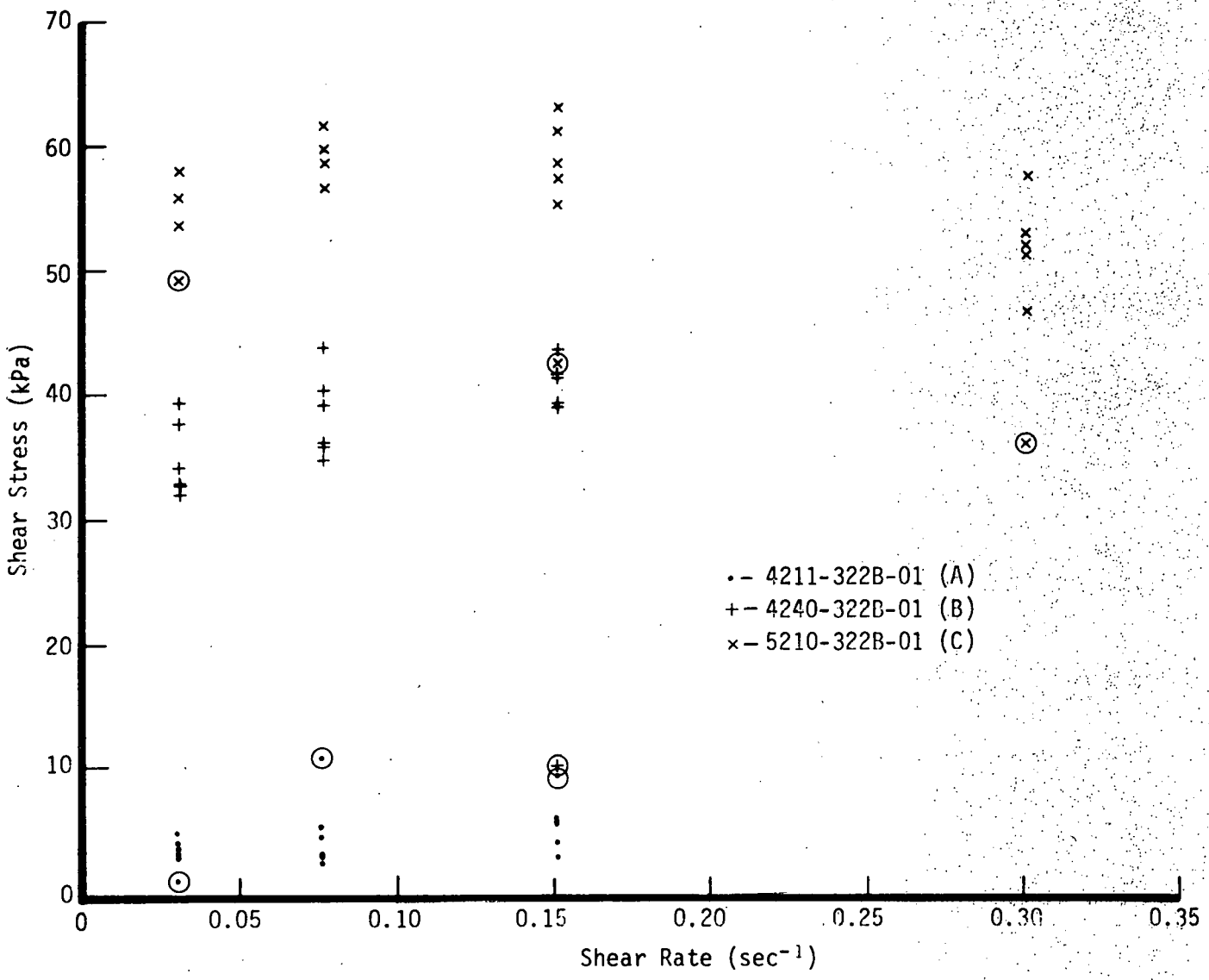

Fig. 1. Shear Stress as a Function of Shear Rate (Rectangular Coordinates)

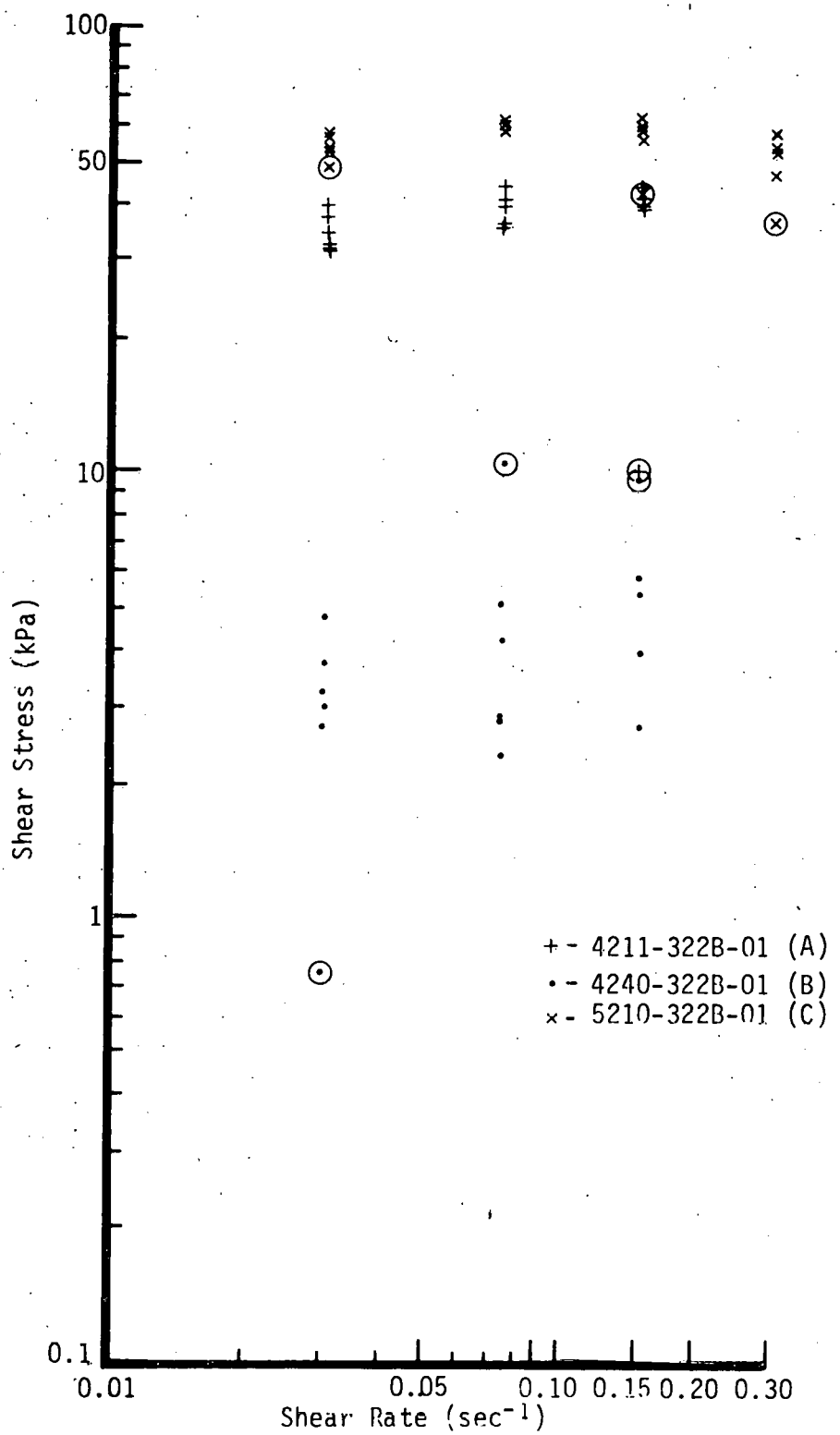

Fig. 2. Shear Stress as a Function of Shear Rate (Logarithmic Coordinates)

Table IV. F-Ratios at Various Significance Levels

Significance Level	F-Ratio (2/45)	F-Ratio (4/45)
0.002	8.087	5.570
0.01	5.977	4.293
0.02	5.113	3.770
0.05	4.010	3.090
0.10	3.203	2.583
0.20	2.423	2.073

As is typical of a pseudoplastic material, the only significant source of shear stress variation is the material batch (above the 0.002 level). The other two variation sources were not significant at or above the 0.20 level. Table V summarizes the overall and the optimized (with suspect data points rejected) average shear stresses, with 95% confidence intervals shown for the optimized averages. Rectangular and logarithmic plots of the optimized averages and 95% confidence limits are shown in Figs. 3 and 4, respectively.

Rectangular and logarithmic plots of the raw apparent viscosity data are shown in Figs. 5 and 6, respectively. These data were also submitted to the variance ratio test with the resulting data summarized in Table VI.

The number of degrees of freedom for each variation source corresponds to those given in Table III.

Consulting Tables IV and VI, all three sources of variation are significant well above the 0.002 level.

Table VII summarizes the averaged apparent viscosity data, with corresponding rectangular and logarithmic plots shown in Figs. 7 and 8, respectively.

The Instron Capillary Rheometer is quite capable of distinguishing between known good and bad batches of 85/15 RDX/Sylgard, when used within the proper shear rate limitations. No attempt will be made to determine ranges of apparent viscosity for good and bad RDX/Sylgard formulations. This work will be done using LX-13/XTX-8003.

CONCLUSIONS

The range of shear rates reported previously as those most likely to produce the best resolution of different apparent viscosities has been affirmed for RDX/Sylgard.

The Instron Capillary Rheometer is capable of distinguishing between good and bad batches of these materials.

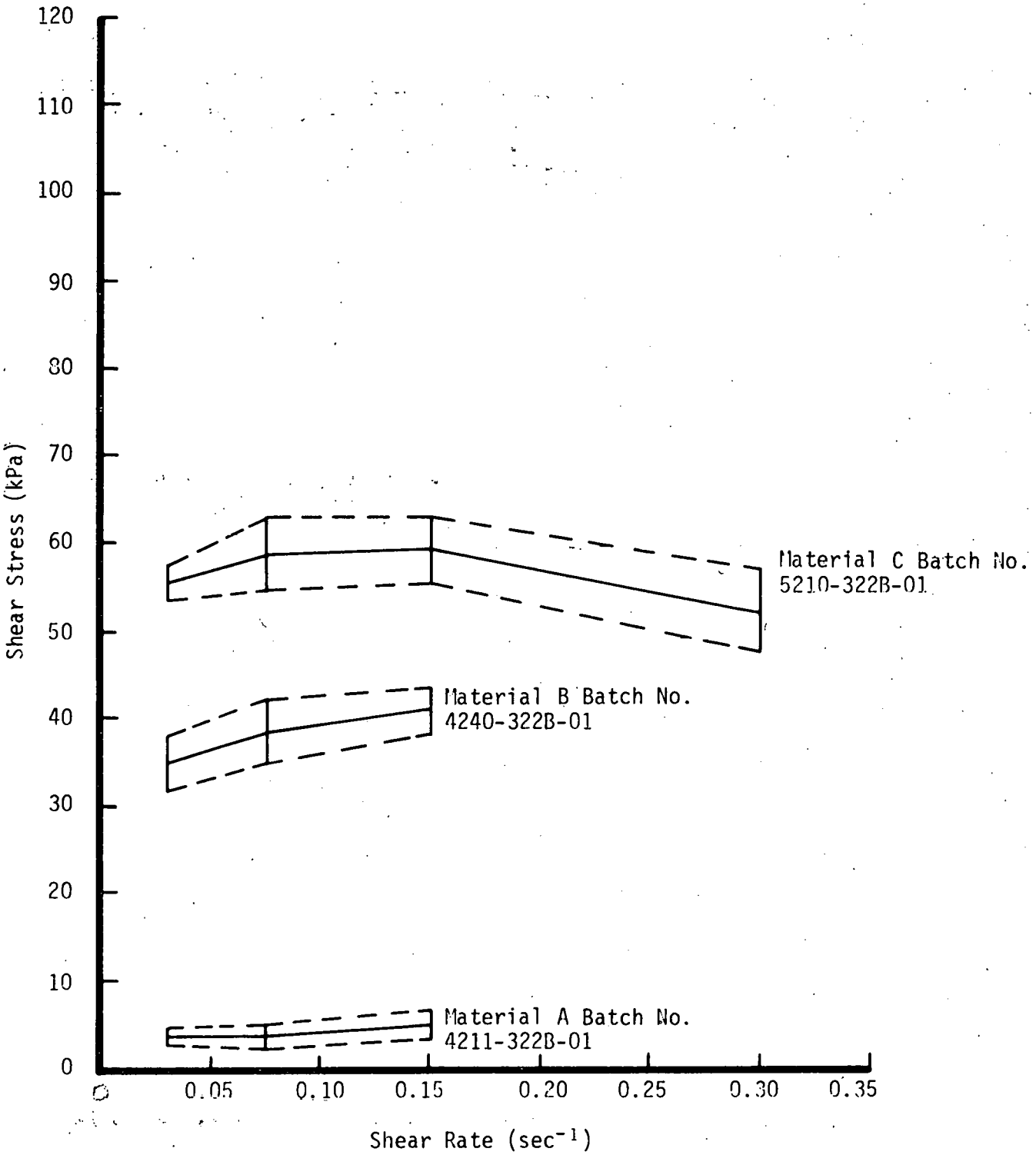

Fig. 3. Average Shear Stress as a Function of Shear Rate (Rectangular Coordinates)

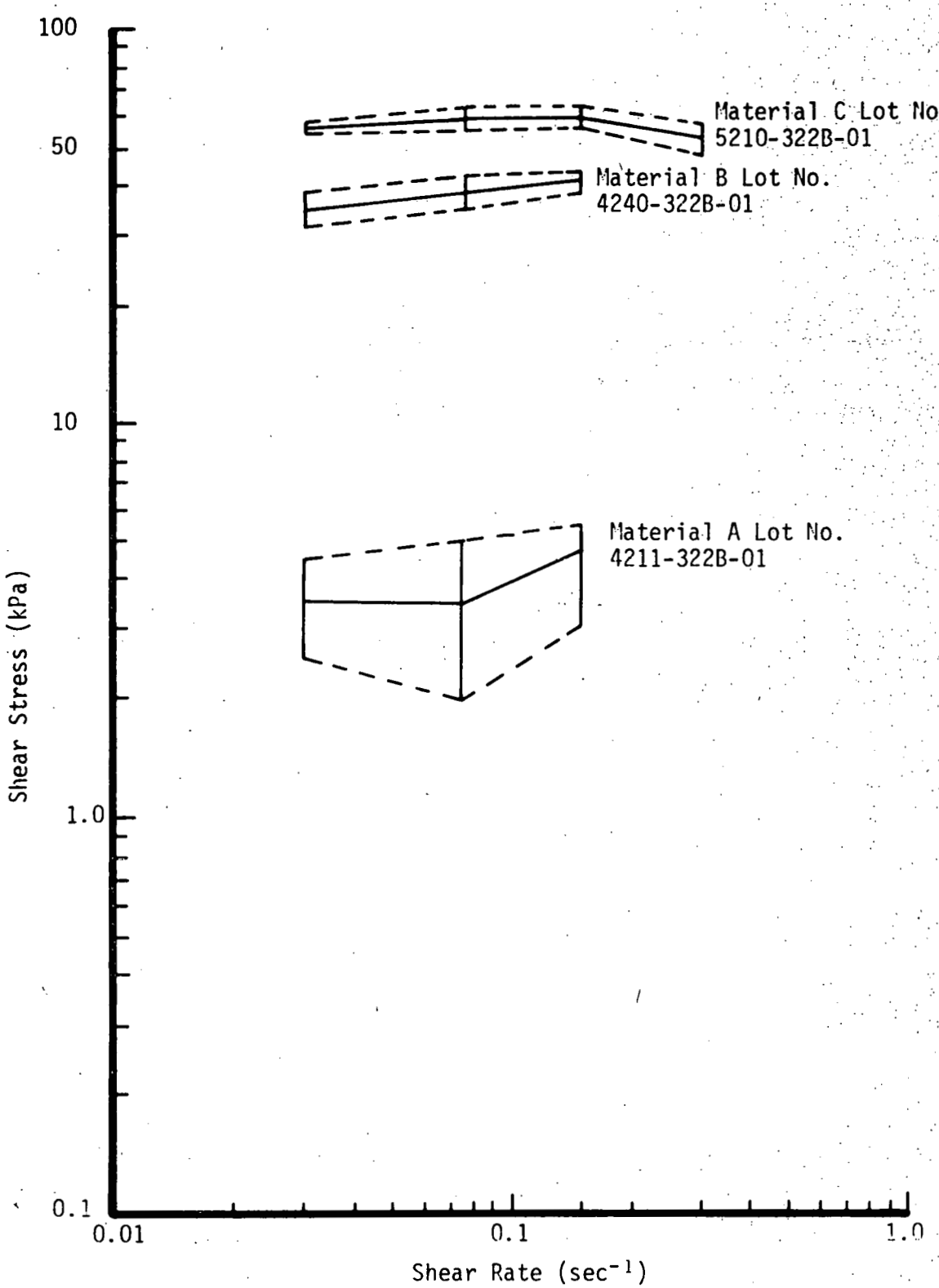

Fig. 4. Average Shear Stress as a Function of Shear Rate (Logarithmic Coordinates)

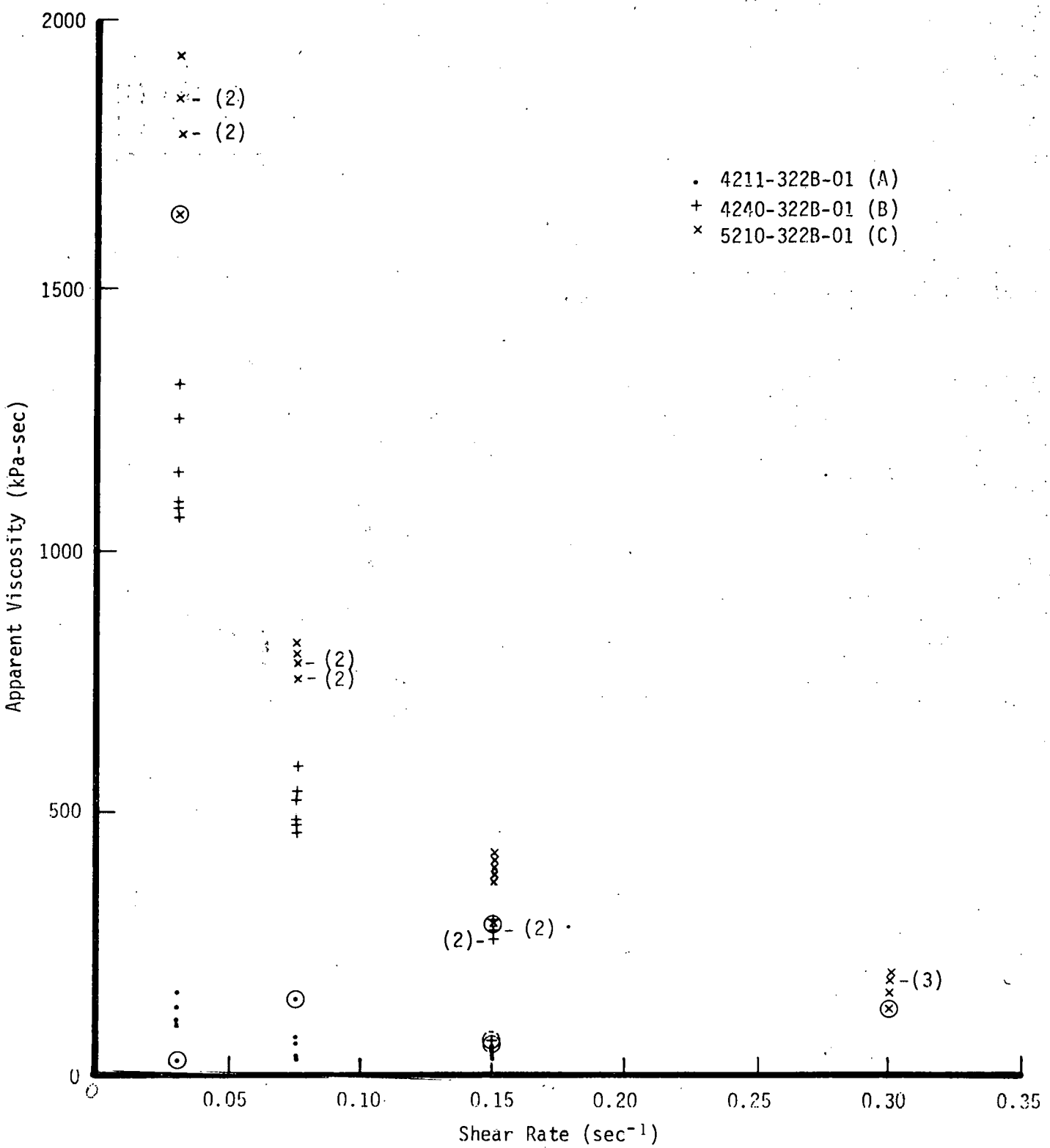

Fig. 5. Apparent Viscosity as a Function of Shear Rate (Rectangular Coordinates)

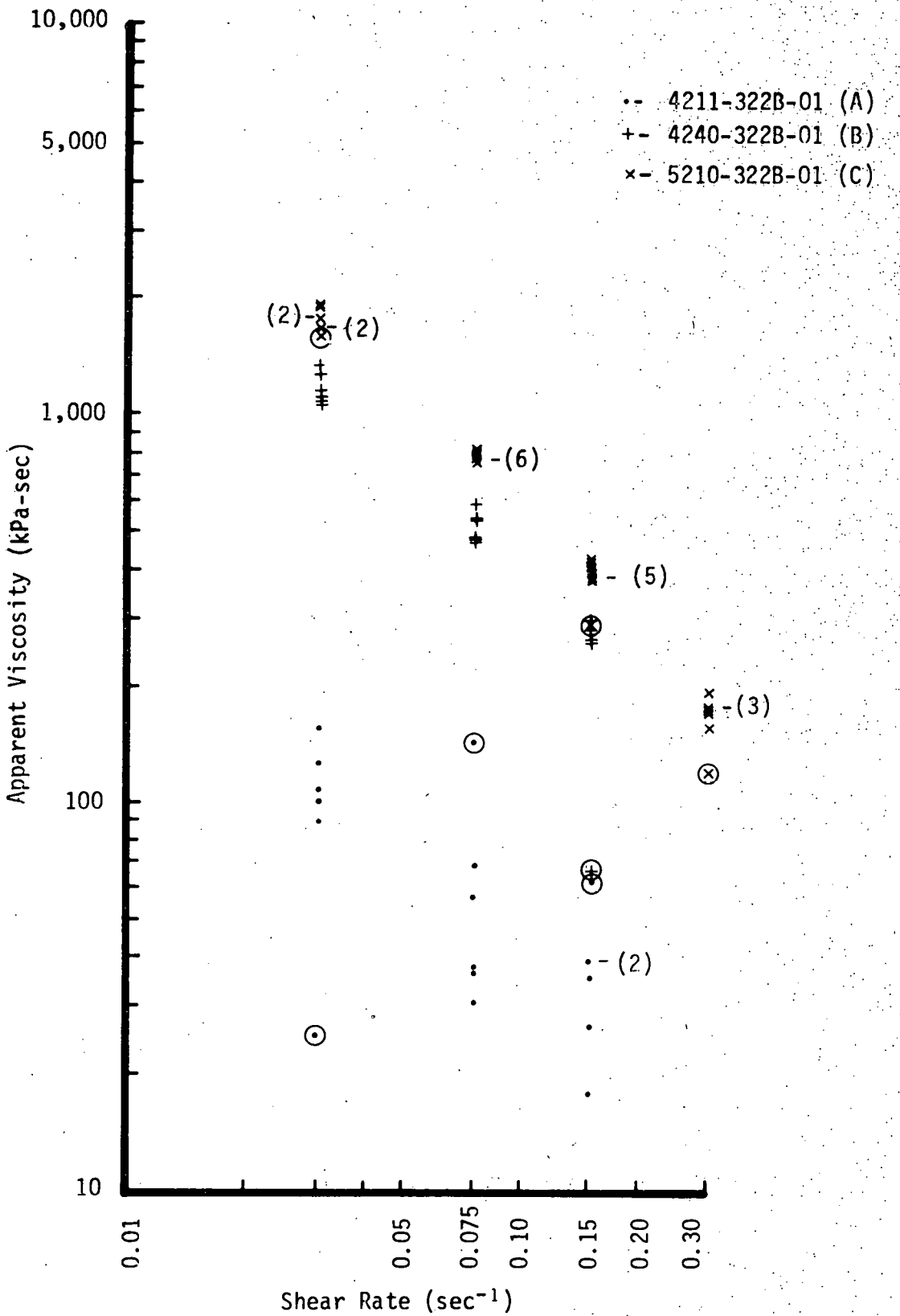

Fig. 6. Apparent Viscosity as a Function of Shear Rate (Logarithmic Coordinates)

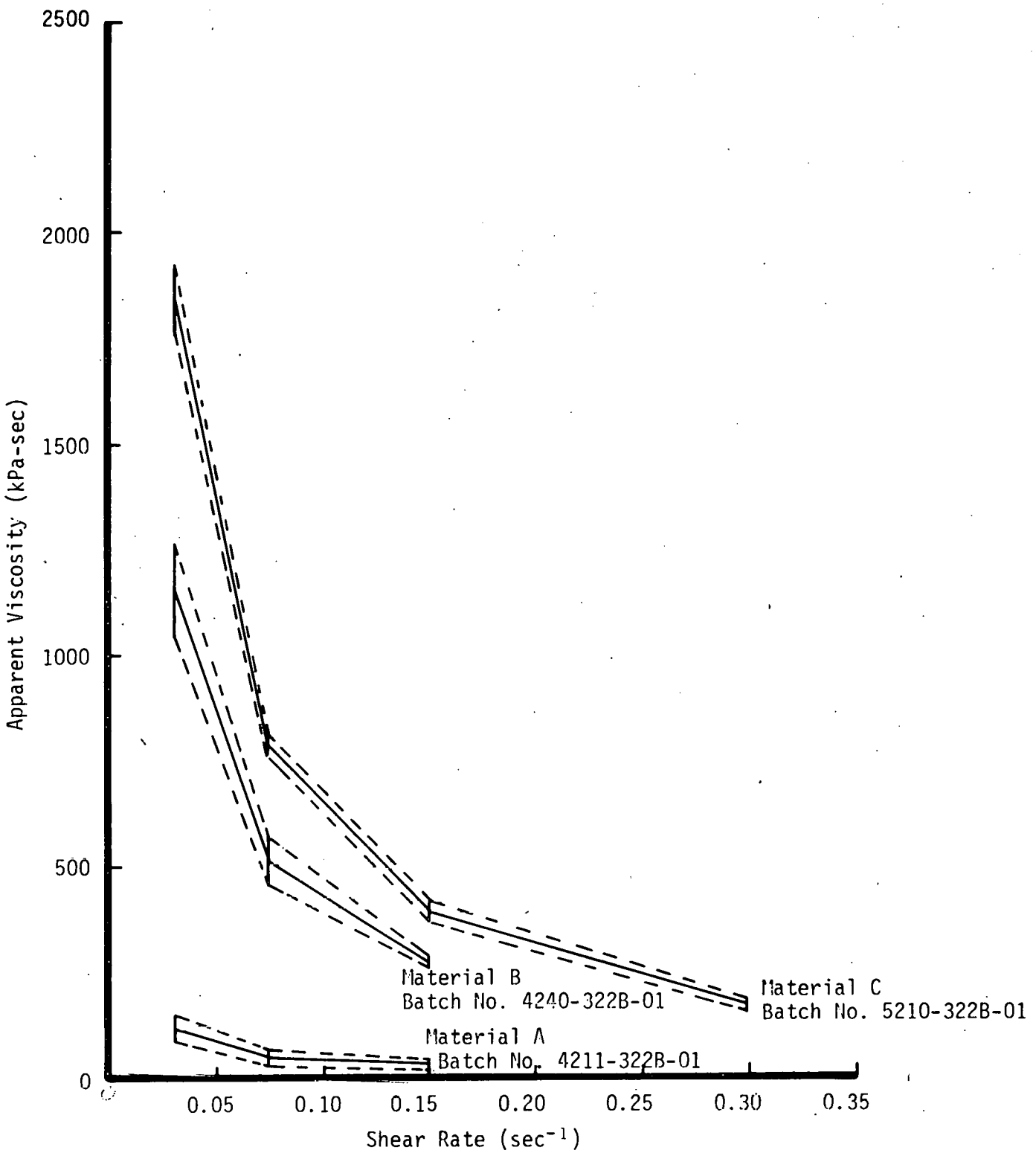

Fig. 7. Average Apparent Viscosity as a Function of Shear Rate (Rectangular Coordinates)

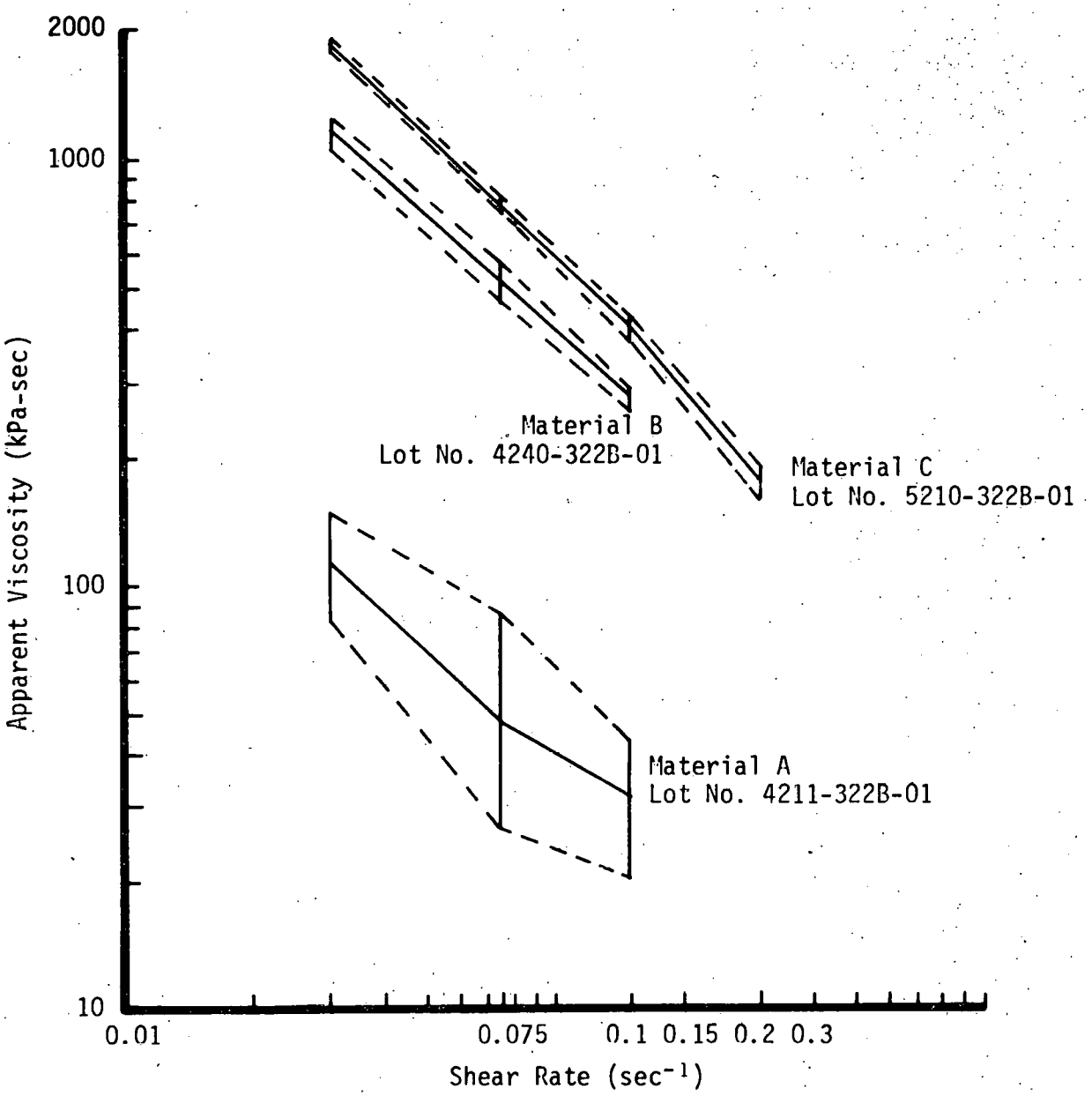

Fig. 8. Average Apparent Viscosity as a Function of Shear Rate (Logarithmic Coordinates)

Table V. Average Shear Stress

Shear Rate (sec^{-1})	Average Shear Stress (kilopascal) Material Batch A Overall	A Optimized ± L_{95}	B Overall	B Optimized ± L_{95}	C Overall	C Optimized ± L_{95}
0.030	3.03	3.49 ± 0.98	34.7	34.7 ± 3.26	54.4	55.4 ± 2.25
0.075	4.67	3.47 ± 1.50	38.3	38.3 ± 3.67	58.7	58.7 ± 4.28
0.150	5.58	4.75 ± 1.71	35.7	40.8 ± 2.50	56.4	59.2 ± 3.93
0.300	← Not Tested			→	49.5	52.1 ± 4.81

Table VI. F-Ratio Significance Tests for Apparent Viscosity

Variation Source	F-Ratio
Material Batch	934.3
Shear Rate	741.6
Interaction Between Material Batch and Shear Rate	183.7

Table VII. Average Apparent Viscosity

Shear Rate (sec^{-1})	Average Apparent Viscosity (kilopascal-seconds) Material Batch A Overall	A Optimized ± L_{95}	B Overall	B Optimized ± L_{95}	C Overall	C Optimized ± L_{95}
0.030	101.0	116 ± 32.7	1160	1160 ± 110	1810	1850 ± 77.3
0.075	62.4	46.3 ± 20.1	511	511 ± 53.6	782	782 ± 30.0
0.150	37.2	31.6 ± 11.4	238	272 ± 16.7	376	395 ± 26.0
0.300	← Not Tested			→	165	174 ± 16.1

FUTURE WORK

This is a final report of rheometer studies on RDX/Sylgard explosives. Further studies, similar to those described in this report, will be conducted with LX-13/XTX-8003.

A factorial experiment designed to determine effects of several process parameters on the end properties of LX-13/XTX-8003 will provide materials for testing on the rheometer.

REFERENCES

1. G. T. West, ECX and PEX Rheology, MHSMP-74-35F (July-September 1974).

2. R. J. Slape, RDX/Sylgard, MHSMP-74-35E (July-September 1974).

3. G. L. Clink, Determination of Degree of Cure of Isothermally Aged RDX/Sylgard, MHSMP-74-9F (January-March 1974).