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Melt rheological properties of a filled polyethylene

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MELT RHEOLOGICAL PROPERTIES
OF A FILLED POLYETHYLENE

BY

GEORGE L. LEVY

A THESIS

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ABSTRACT

A procedure was developed to convert shear stress at various melt temperatures into a computed shear stress at a constant temperature in an isothermal system.

The isothermal shear stress was first analyzed at an equilibrium condition before time induced stress reduction for

1) the temperature dependency of shear stress
2) non-newtonian flow behavior
3) a relationship between the independent variables of shear rate, filler concentration and temperature, and shear stress.

A statistical analysis was performed on the data to find an empirical relationship between shear stress and the independent variables, at any time, under stress, for unfilled and filled high density polyethylene.

Calculation of the flow behavior index indicated 1) as the polymer concentration is decreased in the polymer-filler melt, the behavior is increasingly non-ideal. 2) the flow behavior index of a filler-polymer melt decreases with increase in temperature, whereas the flow behavior index for virgin polyethylene increases with temperature.

Second order equations relating all variables to shear stress explains 84 to 97% of the variability of shear stress and the contribution of each variable to shear stress.

Time does not significantly change the effect of temperature, the largest contributor to reduction in shear stress.

A procedure has been developed, to predict the shear stress of more than one molecular weight high density virgin polyethylene.

APPROVAL OF THESIS

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BY

GEORGE L. LEVY

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED:

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I INTRODUCTION

For quite some time, and especially more recently, plastic fabricators have been attempting to fill polymers with materials such as carbon black,clay,$CaCO_3$ and asbestos without the assistance of rheological melt flow data on the filled system.

The most commonly given reason for using a filler is to extend the resin in an attempt to reduce material costs. There are, however, many other reasons for adding fillers. They are used to impart opacity, to increase the hiding power of color pigments, to increase the heat distortion temperature, to increase the hardness and stiffness of the polymer, lower thermal shrinkage and improve electrical properties.

However, changing the physical properties of the polymer by filler loading also changes the processing characteristics of the mixture.

It is known that not only the type but amount of filler has an appreciable effect on processing properties. When intimately mixed with the polymer, the filler will change the apparent viscosity of the mixture in the melt state as a function of temperature, concentration of filler, shear rate, and total shear(shear rate multiplied by time under shear). A polymer loses most of its natural lubricating properties when filled to a certain point. At this point, the filler is not being distributed uniformly in the polymer, creating excessive torques or an excessive heat rise in the polymer, and reducing polymer viscosity. The change in polymer viscosity, due to the factors of temperature, shear rate and time and filler concentration can be measured experimentally and can be used to help understand and predict extrusion and molding operating conditions and final physical properties of the molded product.

Except forthe work that was done by Ryan[3], very little is available concerning the rheological melt properties of polyolefins. There is no data available on the flow properties of filled polymer melts.

It is believed that this report first presents rheological data for a filled polymer melt and a discussion of the potential utility of a particular type of rheological instrument to measure melt flow behavior. This may pave the way to a method of evaluating the melt properties of thermoplastics filled with inert or reinforcing materials.

Rheological Instruments

C.W. Brabender Instruments, Inc., Hackensack, N.J. manufactures a Plasticorder to measure the changes in shear stress as a function of shear rate and temperature. The shear rate ranges on the Plasticorder are similar to those encountered in Banbury mixing but fall on the low end of the extrusion range.

The instrument was used in this work because of its versatility in not only measuring the shear stress as a function of shear rate and temperature at a constant shear rate, but also stress as a function of time under a constant shear rate.

For unfilled polymer melts, other devices such as the melt indexer, CIL unit and Westover capillary rheometer, to mention a few, would have been adequate. However for filled sustems, loading, mixing, and time dependency cannot be readily handled and analyzed with these as with the Brabender Plasticorder.

One of the main concerns with the Plasticorder is that under a shearing force, the melt temperature of the polymer rises as a function of time. However one of the objectives of this experiment was to neutralize this effect and estimate an isothermal system response.

Objectives

The general objective of the program was to obtain rheological information on an unfilled and corresponding filled polymer system, as a function of shear rate, temperature, mixing time, and filler concentration

To accomplish this, the following objectives were established:

1. To determine if isothermal conditions can be computed and to find the method by which shear stress values can be corrected to a constant system temperature.

2. To calculate a flow index to describe the non-ideal behavior before time-induced polymer degradation.

3. To determine the temperature dependency of shear stress by the Arrhenius relationship.

4. To find a relationship between the independent variables and shear stress, eliminating the variable, time. This will be referred to as the zero time condition, or the condition before degradation of polymer.

5. To find a relationship between the independent variables and shear stress at any time, t .

6. To find a relationship between the independent variables and shear stress for unfilled polymer at zero time and any time, t, and test the equation with data in the literature.

7. To assess the significance and contributions of each variable on shear stress.

8. To reduce the data to a meaningful interpretation for commercial processing operations.

9. To determine the usefulness of the Brabender Plasticorder for rheological investigations.

II THEORY OF THERMOPLASTIC MELT FLOW

The degree of departure from Newtonian behavior may be obtained quantitatively from a logarithmic shear stress-shear rate plot, defined by the equation:

$$\log \tau = \log (\eta \, du/dr) \qquad (1)$$

where;

τ = shear stress (F/A) in lb/ft

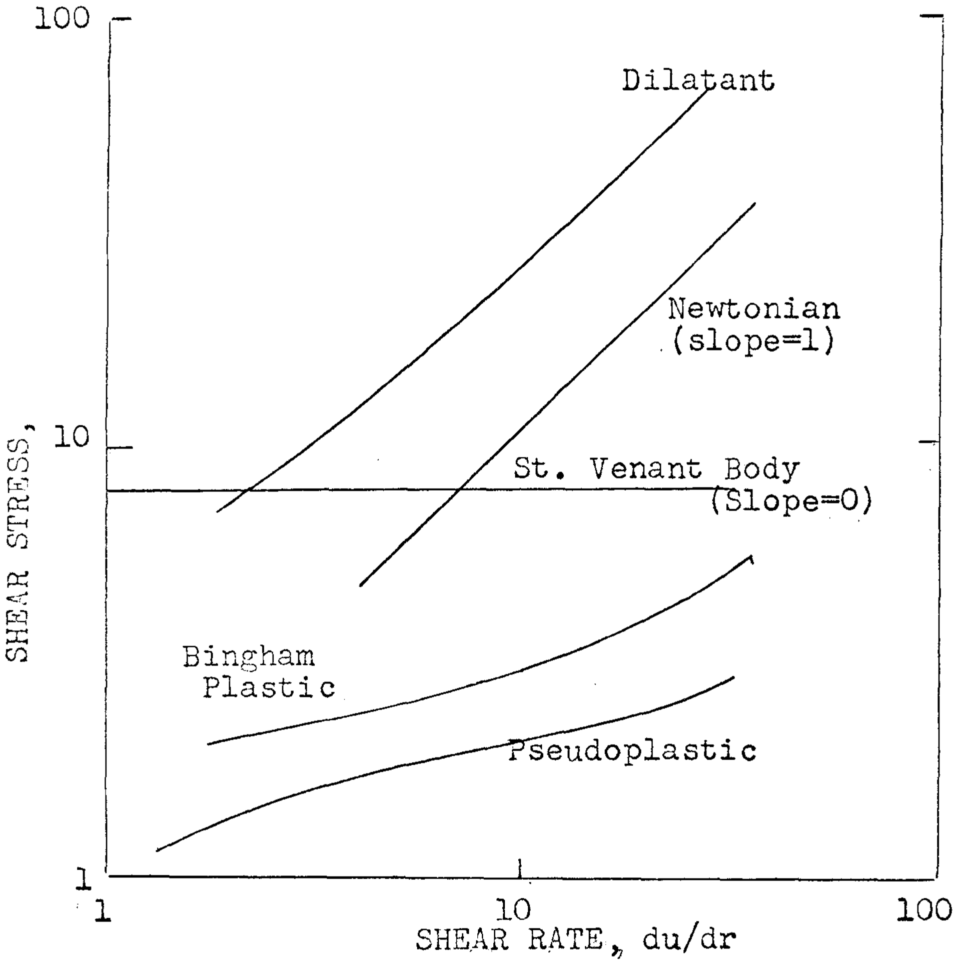
η = Newtonian viscosity, lb sec/in^2

du/dr = shear rate in sec^{-1}

Curves in figure I indicate the various effects of shear rate on shear stress defined by equation (1).

For a Newtonian material, the plot of log τ vs log du/dr is a straight line with a slope, n, equal to 1. For pseudo-plastic and Bingham plastic non-Newtonians, the slopes of the log curves fall between zero and unity. Polyethylene is a pseudoplastic material and falls in this range. Fillers, however, will alter the polyethylene curve. The shear rate-shear stress curves of polyethylene show Newtonian behavior only at high and low shear rates[1]. The effect of a filler on the slope of the shear stress-shear rate curve can be maximized in the non-Newtonian area.

FIGURE I



SHEAR STRESS VS SHEAR RATE OF VARIOUS FLUIDS

The non-Newtonian behavior of polymer melts and solutions in steady flow or shear is directly attributable to the following two characteristics of the molecular structure of these materials;[1]

1) The asymmetric shape (great length as compared to the radial dimensions) of the molecules themselves results in an orientation of the particles when a velocity gradient is imposed on the polymer molecules.

As a result of this orientation, the molecules become progressively more perfectly aligned as the velocity or shear rate of the fluid is increased. Complete orientation will be achieved only when the rate of orientation by this flow mechanism becomes sufficiently great to offset the disrupting effect of random molecular (Brownian) motion. At extremely low shear rates, the balance would be in favor of the disrupting forces, no alignment would occur and the material would behave as a Newtonian fluid. Conversely at extremely high shear rates, further changes in shear rates could not affect the degree of orientation appreciably, and the material would again approach Newtonian behavior.

While the above argument shows clearly why asymmetric particles become aligned during flow, it does not indicate whether or not the alignment alone would be sufficient cause for non-Newtonian behavior at intermediate shear rates, as depicted by the pseudo-plastic curves of Fig.1. To determine this, one must consider the underlying causes of viscosity in a fluid, i.e., the mechanisms by which momentum is transferred from the fast- to the slow-moving elements of fluid.

For all molecules, increases in temperature would tend to make complete alignment more difficult because of the greatly increased Brownian motion of the molecules; hence the differences between the Newtonian viscosities at low and high shear rates would be less, and the inception of non-Newtonian behavior would be delayed to still higher shear rates. Both of these effects would tend to decrease the rate of change of viscosity with shear rate - i.e., the flow-behavior index increases or the degree of non-Newtonian behavior (pseudoplasticity) decreases with increases in temperature.

(2) The size of the flowing elements--if they are groups of molecules rather than single particles--would be decreased progressively by increases in shear stress or shear rate. The restoring tendencies in this case are due to intermolecular forces; the effects of shear rate and temperature on particle size are similar to those on alignment, hence the same type of Newtonian-pseudoplastic-Newtonian behavior is

again observed as one moves progressively from low to high shearing rates. The rheological literature has generally assumed that where alignment of molecules is possible it is the more important factor in determining flow behavior, relegating the importance of size of flow elements to situations in which the polymer molecules are nearly equi-dimensional and to slurries of solids in liquids. No direct observation of the true relative importance of the two mechanisms seems to have been made.

In the works of Philippoff and his associates[4], the best available viscometric data can be found over a wide range of shear rates. Their data show that the viscosity of the solution increasesand non-Newtonian behavior of the pseudo-plastic type(flow behavior index less than unity) may occur. As predicted by the theory of the preceding paragraphs, the solution behavior becomes Newtonian at both extremes of low and high shear rate. As the concentration of the polymer solution is increased, the fluid becomes increasingly non-Newtonian at any intermediate shear rate, and the range of shear rates within which non-Newtonian behavior occurs progressively increases.

In view of the earlier theory that the flow behavior depends on the size and alignment of the effective flowing particles, it would be expected that non-Newtonian tendencies would be suppressed by increases in temperature--since the more rapid molecular motion at higher temperatures would redisperse any aligned particles more rapidly. Higher temperatures would also tend to decrease the size of flow units even in the virtual absence of shear--simply by virtue of the desolvating action of increased Brownian motion. Therefore, the shearing stresses would have only a marginal role in effecting further decreases in particle size, hence in promoting non-Newtonian behavior.

From experimental work, Philippoff and Gaskins[4] have concluded that within the non-Newtonian flow region, the flow behavior index increases slightly with increases in temperature. Table V in the text summarizes this effect.

In addition, Philippoff and Gaskins, et al[4], used the Arrhenius equation;

$$\eta = Ae^{E/RT} \quad \text{or} \qquad (2)$$

$$\frac{d\ln\eta}{d(1/T)} = E/R \qquad (3)$$

to express apparent viscosity as a function of the reciprocal of the temperature.

where: A = constant

E = energy of activation for viscous flow

R = universal gas constant

T = absolute temperature

η = apparent viscosity

III EXPERIMENTAL PROCEDURE

Materials

The polymer used in this study was a high density (0.960) polyethylene with a melt index of 0.7 gms./10 min., manufactured by the Celanese Plastics Company. The material was in commercial, pelleted form. The melt flow index was determined at 190°C on a melt index extrusion device according to ASTM test D1238.

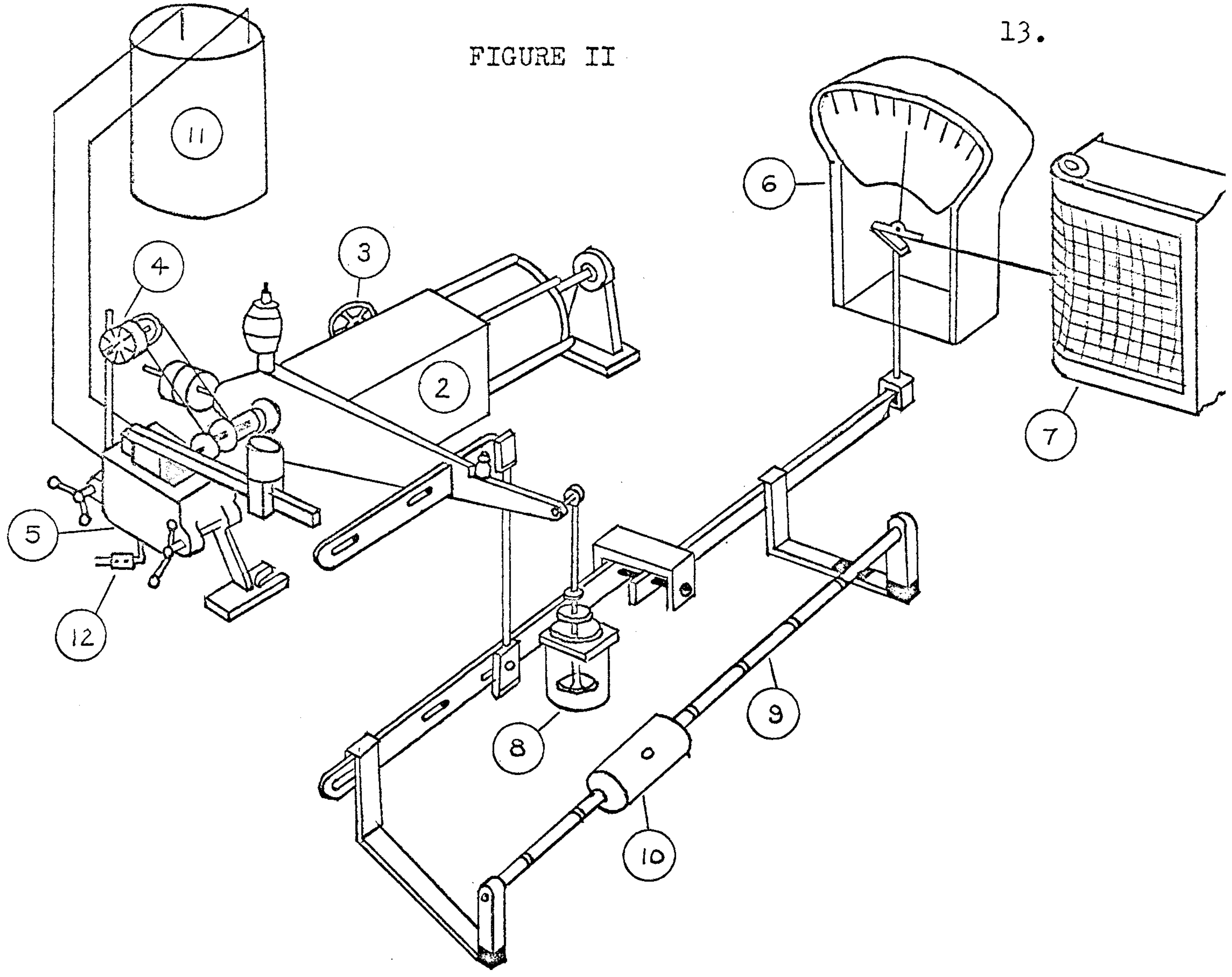
The filler investigated was an uncoated precipitated clay with a specific gravity of 2.65 and an average particle size of 3 microns.

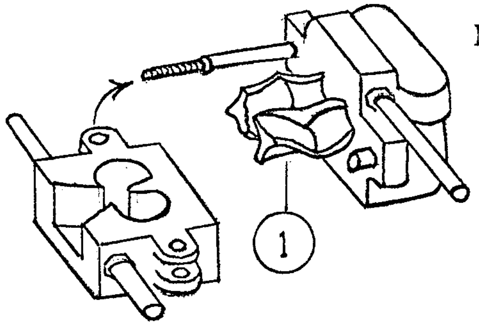
Equipment

The Brabender Plasticorder is shown in Figure II.

1. The rotors 1 are driven by a dynamometer 2 . The speed or shear rate is set by a hand wheel 3 measured by a tachometer located at 4 . The dynamometer rotates in a direction opposite to the rotors when the measuring head 5 contains test material. The torque, measured by the dynamometer is transmitted to an indicator scale 6 and strip recorder 7 through a system of levers. An oil dash pot 8 is used to damp the movement of a lever system.

FIGURE II





BRABENDER PLASTICORDER

2. The arm 9 is used to transpose the sensitivity range without changing sensitivity setting through weight 10 which slides on arm 9 . The full scale range can vary from 1,ooo to 5,000 meter-grams force ,according to the position of the weight.

3. The two shearing rollers 1 are shown at the bottom of Figure II.One rotor rotates at 3/2 the rate of the other. RPM , based on the fast roller,can be varied from 0 to 200.

4. Silicone oil is heated in a thermostatically controlled pressure circulator bath 11 and is pumped through insulated lines and through the measuring head. Both the removable and stationary heads are heated.

5. Stock temperature of the melt is measured at 12 by an iron-constantan thermocouple and is recorded on a strip chart temperature recorder.

Test Procedure

The following test procedure was used in obtaining shear stress data:

1. The oil bath was turned on and set by a thermometer to a desired temperature. Some temperature drop was experienced between the bath and jacket but could be controlled by the jacket temperature.

2. Initial trial runs determined the proper torque scale. Because of high torques, the 5,000 meter-gram scale was used.

3. A simple chute type loading device was used to channel all materials into the mixing head.

4. Polyethylene pellets were loaded into a milling head within one minute. Subsequently, desired amounts of filler were loaded within one minute after the polymer for a total loading time of two minutes.

5. Stock temperatures were recorded by the strip recorder with an error estimated to be 1 % of full scale or 0.5°C. Torque and temperature readings were taken every five minutes from the continuous torque-temperature sheets. A typical torque chart is shown in Figure III.

Mixture weights were calculated from the specific gravity of the filler and the melt density of polyethylene as follows:

$$\frac{\text{Wt \% filler}}{\text{sp.gravity of filler}} + \frac{\text{Wt \% polymer}}{\text{melt density polymer}} = \frac{100\%}{\text{sp. grav.of mixture}}$$

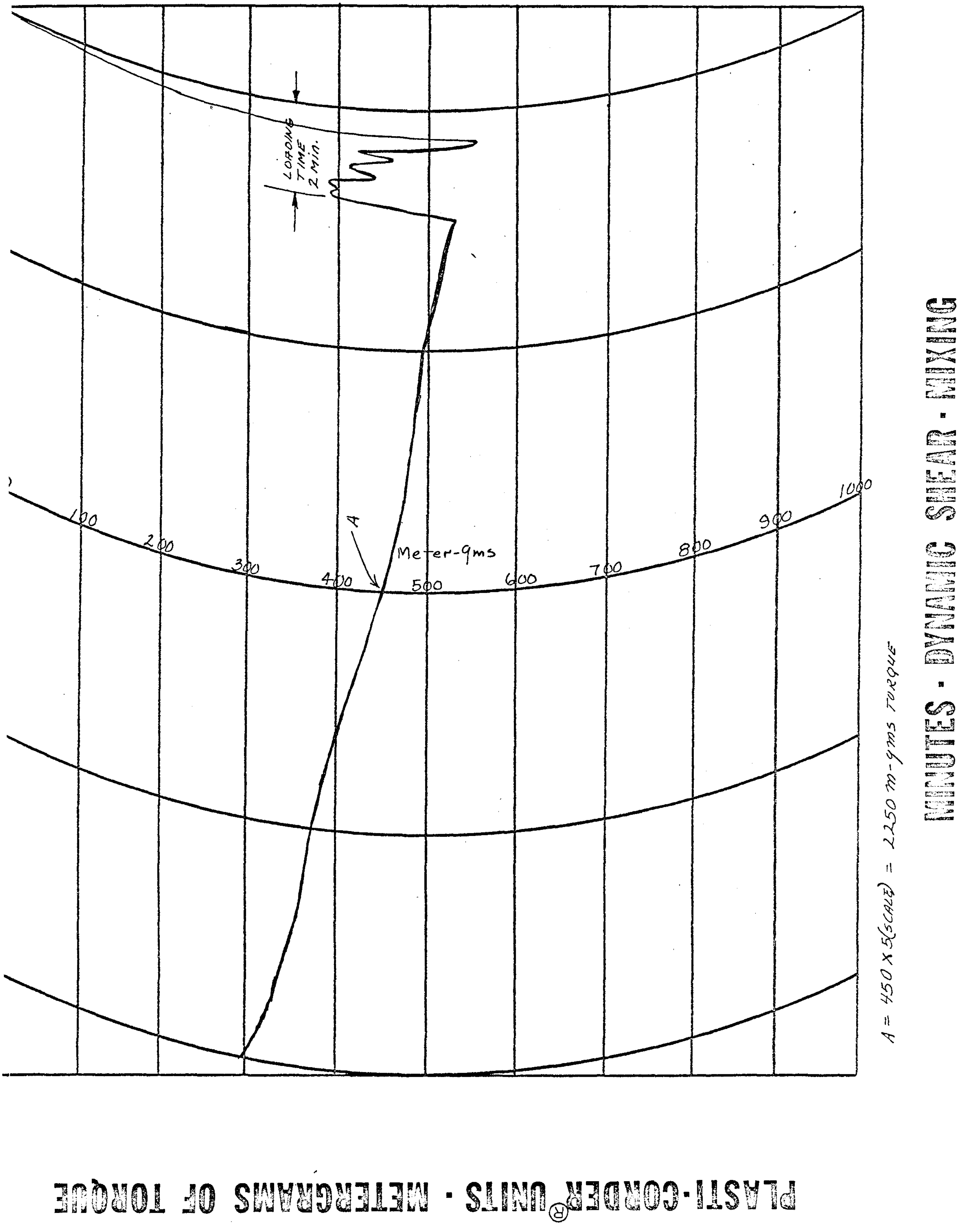
where: specific gravity of clay = 2.65

and : melt density of polythene = 0.584

After the specific gravity of the mixture was calculated for a particular filler-polymer weight % combination, the total charge to the milling head was then computed as follows:

$$\text{Specific gravity} \times \text{volume of milling head} = \text{total weight of mixture}$$

where : the volume of the milling head is 60 cc of water.



A = 450 x 5(SCALE) = 2250 m-gms TORQUE

FIGURE III

The total weight multiplied by the weight % of each component in the mixture determined the weight in grams of each component to be added to the milling head.

Mixture charges are listed in Table I.

Shear stress data was collected at the following levels of parameters:

1) Jacket temperature set at 177°, 199°, and 219°C.
2) Shear rates set at 50, 85, and 120 rpm.
3) Concentration of filler- 0 to 70 % in 10 % increments.

Seventy-two experimental runs were made, producing a total of 288 experimental data points.

TABLE I

MILLING HEAD WEIGHT CHARGES

Wt % Clay	Grams Clay	Grams Polyethylene
0	-	35.0
10	3.85	34.3
20	8.30	32.2
30	13.50	31.5
40	20.50	31.0
50	28.50	28.5
60	39.50	26.3
70	53.70	23.0

IV. DISCUSSION OF EXPERIMENTAL RESULTS

Objectives

The analysis of the data was two-fold. First, material at zero time (Case I), was considered. Time zero was defined as the point at which very little viscosity degradation occurs due to the filler, shear thinning, and time under load. It is at this equilibrium condition that the melt characteristics may be properly analyzed without the fear of a rate of degradation.

Case II, the effect of stress time on the apparent decrease in viscosity, was then studied.

Calculation of Isothermal Shear Stress

It is difficult to obtain an isothermal flow curve in which the torques corresponding to various mixing rates are plotted against these rates, since, at each mixing rate, a different equilibrium temperature is achieved within the test material, even though the temperature of the mixer walls is controlled by the oil circulating from the thermostat.

Through a rather complex set of experiments in which the average temperature of the mix is held constant by adjusting the thermostat for each mixing rate. according to heat-generation and heat flow calculations, it may be possible to obtain a isothermal flow curve from the mixing head of the Plasticorder.

However, an experiment of this nature, as mentioned, would be extremely difficult to control and would be quite lengthy to perform.

A procedure was developed to convert shear stresses at various melt temperatures into an equivalent shear stress at one constant system temperature by using theoretical relationships and making various assumptions.

The following methods and assumptions were used in converting Brabender shear stress data into final isothermal shear stresses.

Case I Figure IV shows a typical melt temperature-time plot of virgin polyethylene corresponding to the torque-time plot of figure III.

Within the zero to three minute period (A to B in Figure IV), the polymer is being melted into a homogeneous mass. The temperature of the mixture rises to an equilibrium temperature at B and remains constant from B to C.

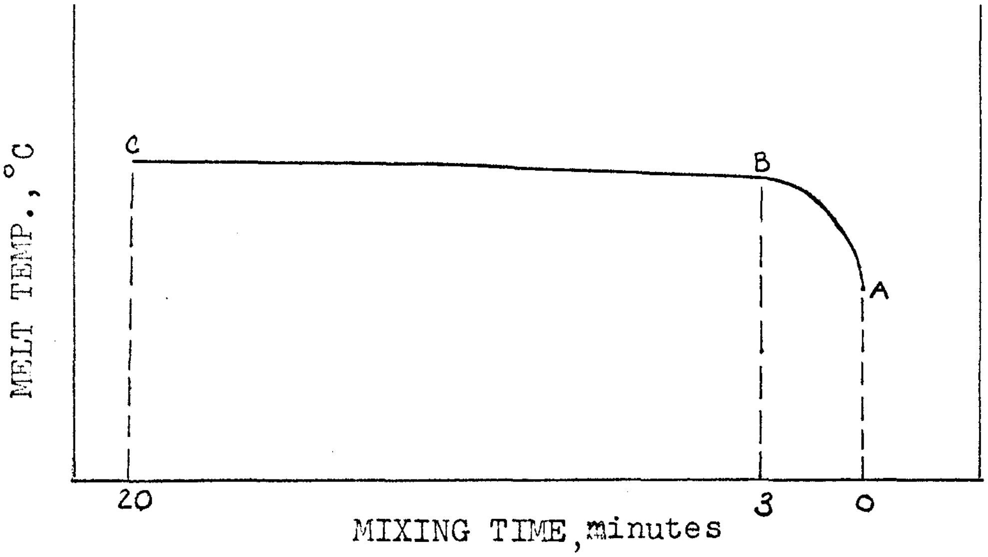
Figure V shows a superimposed curve of the virgin polyethylene temperature-time plot and another temperature-time plot of a filler-polyethylene mix at the same shear rate and jacket temperature setting. Time, t_i is recorded at the intersection of the two curves.

A torque value at time t_i is read on the corresponding torque-time curve for the filler-polyethylene mix. (Fig. III).

The procedure is repeated for each filler concentration at one particular shear rate and jacket temperature setting using the same polyethylene temperature-time plot.

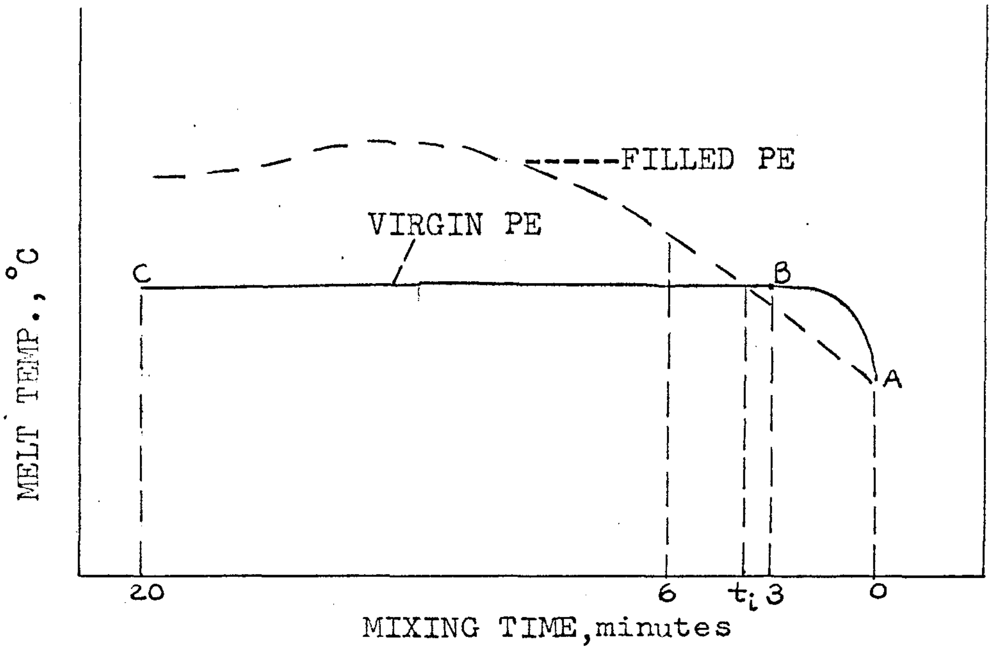
In turn, the same method is employed as described above for a new series of concentrations at a different shear rate and jacket temperature setting, using the equilibrium melt temperature of polyethylene for that series as the,reference temperature.

FIGURE IV



MELT TEMPERATURE-MIXING TIME PLOT, VIRGIN PE

FIGURE V



MELT TEMPERATURE-MIXING TIME PLOT, VIRGIN & FILLED PE

Table II lists the superimposed isothermal shear stress values at zero time for Case I.

Case II In order to evaluate the effect of the variable of shearing time on shear stress, the stress values at all shearing times must be converted to shear stresses at a constant system temperature.

It was assumed that if a plot of logτ versus the reciprocal of absolute melt temperature (Arrhenius relationship), taken from the data in Table II was linear for each shear rate, the curves may be used to predict a shear stress at any melt temperature. This assumption is based on Philippoff's work[4] previously cited.

The relationship between the $\log_{10}$ of τ and $1/T_{abs}$ was found to be linear.

Once the slopes of the lines were determined, the Arrhenius equation was used to convert the torque values at various temperatures and shearing times into a torque at the proposed system temperature.

The entire system was then analyzed for the reduction of shear stress due to shear rate, concentration of filler, melt, temperature, and shearing time.

Table III lists all final isothermal shear stress values used in the analysis.

TABLE III

FINAL SHEAR STRESS DATA (ISOTHERMAL CONDITIONS)

TIME	TEMP.	SHEAR RATE	Wt. % FILLER							
min.	°C	rpm	0	10	20	30	40	50	60	70
0	210	50	1325	1425	1475	1550	1900	2150	2500	2850
		85	1650	1750	1780	1950	2300	2600	2850	3150
		120	2000	2000	2000	2190	2640	2820	3170	3720
	245	50	1030	1210	1260	1320	1630	1910	1	2580
		85	1500	1550	1450	1500	1700	2200	2500	2800
		120	1675	1700	1700	1700	1900	2450	2900	3300
5	210	50	1325	1350	1300	1400	1660	1910	2500	3110
		85	1650	1550	1490	1650	1950	2500	2900	3470
		120	1910	1550	1480	1780	1875	1870	3245	3630
	245	50	1110	1080	1025	1135	1150	1290	2135	2345
		85	1500	1550	1400	1350	1350	1300	1960	2250
		120	1550	1600	1550	1380	1380	1275	1975	2290
10	210	50	1300	1200	1200	1300	1460	1610	2430	3025
		85	1550	1410	1325	1530	1675	1900	2800	3250
		120	2160	1485	1180	1390	1585	1550	3390	3590
	245	50	1100	1035	1040	1050	1025	933	1950	2320
		85	1500	1550	1350	1250	1140	990	1600	2100
		120	1860	1460	1300	1350	1375	1325	2470	2880
15	210	50	1275	1050	1100	1225	1415	1350	2370	2970
		85	1510	1320	1285	1395	1600	1470	2700	2870
		120	2300	1350	1100	1240	1290	1240	2820	3320
	245	50	1130	934	1030	1030	934	800	1740	2190
		85	1500	1550	1350	1200	1000	795	1190	2060
		120	1700	1700	1475	1335	1100	905	1060	2340

Effect of Temperature

Case I - (Zero Time) Figures XXII through XXIX in the Appendix show the effect of temperature on shear stress at 8 concentrations and 3 shear rates. The relationship between the $\log_{10}$ of τ and $1/T$ was found to be linear.

Slope m, defined as the change in $\log \tau/(1/T)$ is plotted against each concentration at three different shear rates in Figure VI in the text.

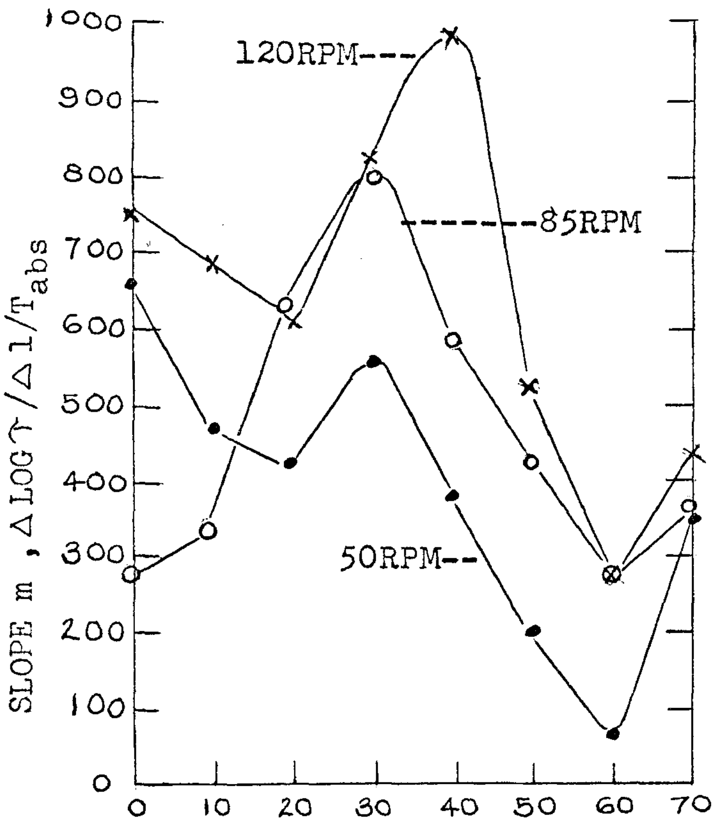
Except for zero concentration, the curves are similar. The higher the rpm, the greater the slope of $\log \tau$ vs $1/T$ at all concentrations. Maxima and minima in the slopes are evident. The maximum decrease in shear stress occurs at the maximum slope. The maximum for 50 and 85 rpm occurs at 30% concentration and for 120 rpm, at 40% concentration. The minimum slope for all three shear rates occurs at a concentration of 60%.

Except for 85 rpm, the slope m does not change radically between 0 to 20% concentration. Another minimum occurs at 20% concentration for 50 and 120 rpm.

After the maximum, the sensitivity of stress to a temperature change decreases significantly to a minimum.

The "grindstone effect" of filler particle on polymer is most evident at the maximum slope. As the concentration increases above the maximum, a thickening or thixotropic

FIGURE VI



SLOPE OF SHEAR STRESS/ RECIPROCAL ABSOLUTE TEMPERATURE AS A FUNCTION OF FILLER CONCENTRATION effect occurs, masking the reduction of polymer viscosity. In the critical area of 30 to 40% concentration, there is not enough polymer to lubricate filler particles. According to Einstein[2], filler particles tend to act as particles in suspension up to a certain point. As the concentration increases above this critical value, some cross linking may occur in the three dimensional network as a result of an adsorptive interaction between the polymer and filler particles. Upon incorporation of filler, the segmental mobility of the polymer strands in contact with the filler surface is restricted and the molecular packing is decreased.

At an extremely high filler concentration (70%), very little polymer is left and a filler-rich mixture results. At this point, the viscosity of the mixture is really a measure of the viscosity of the filler held together by a binding agent.

Case II - (Anytime, shearing t) Since log τ vs 1/T is linear, the Arrhenius relationship may be deduced as:

$$\log \tau = \log \tau_o + m(T_o - T)/(T - T_o) \qquad (4)$$

where τ is the torque at temperature T, τ_o is the original torque at temperature T_o, and m is the slope.

The above equation was used to correct all original torque data taken at various stock temperatures listed in Table XVII in the Appendix.

Figures XXX to XXXV in the Appendix show the changes in torque as a function of time at three different shear rates at two constant temperature levels in an isothermal system.

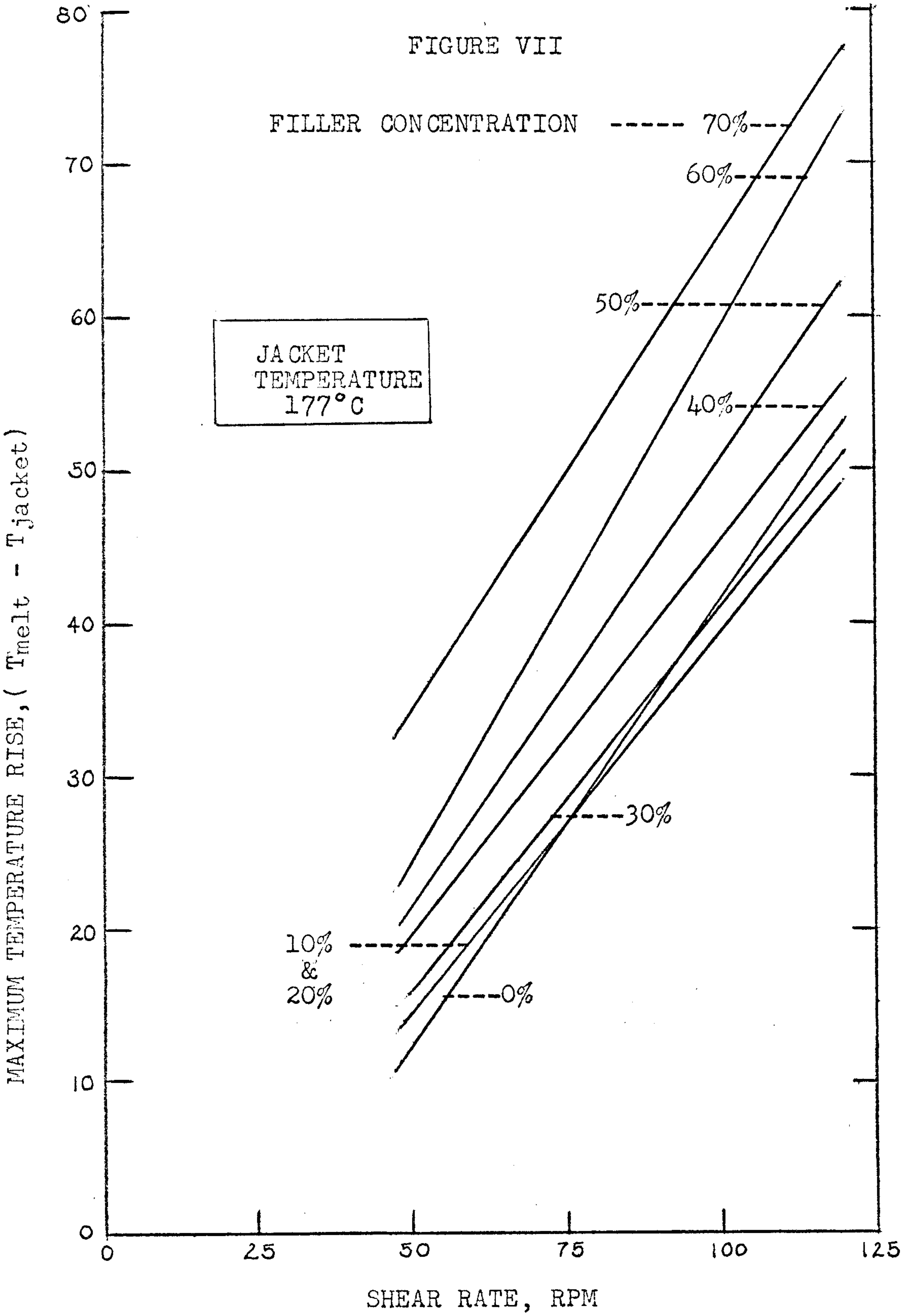
At the lower temperature, (210°C.), torque decreases significantly between 10 and 50% filler, but decreases less rapidly near 60 - 70%. At the higher temperature , 245°C., the 60% filler concentration curve also decreases rapidly. It is assumed that the increasing temperature reduces the polymer viscosity faster than the filler can increase the system viscosity.

The effect of temperature on a commercial processing extruder would indicate that a small change in extruder output would occur up to30% filler by changing the temperature only. A vast change in output would occur around 30 - 40% filler loading. Temperature changes above 50% filler concentration would not significantly affect output. The above represents the sensitivity of flow as a function of temperature. In a sense, it is a measure of the activation energy of non-Newtonian flow.

Temperature Rise in Polymer-Filler Melt Mixture

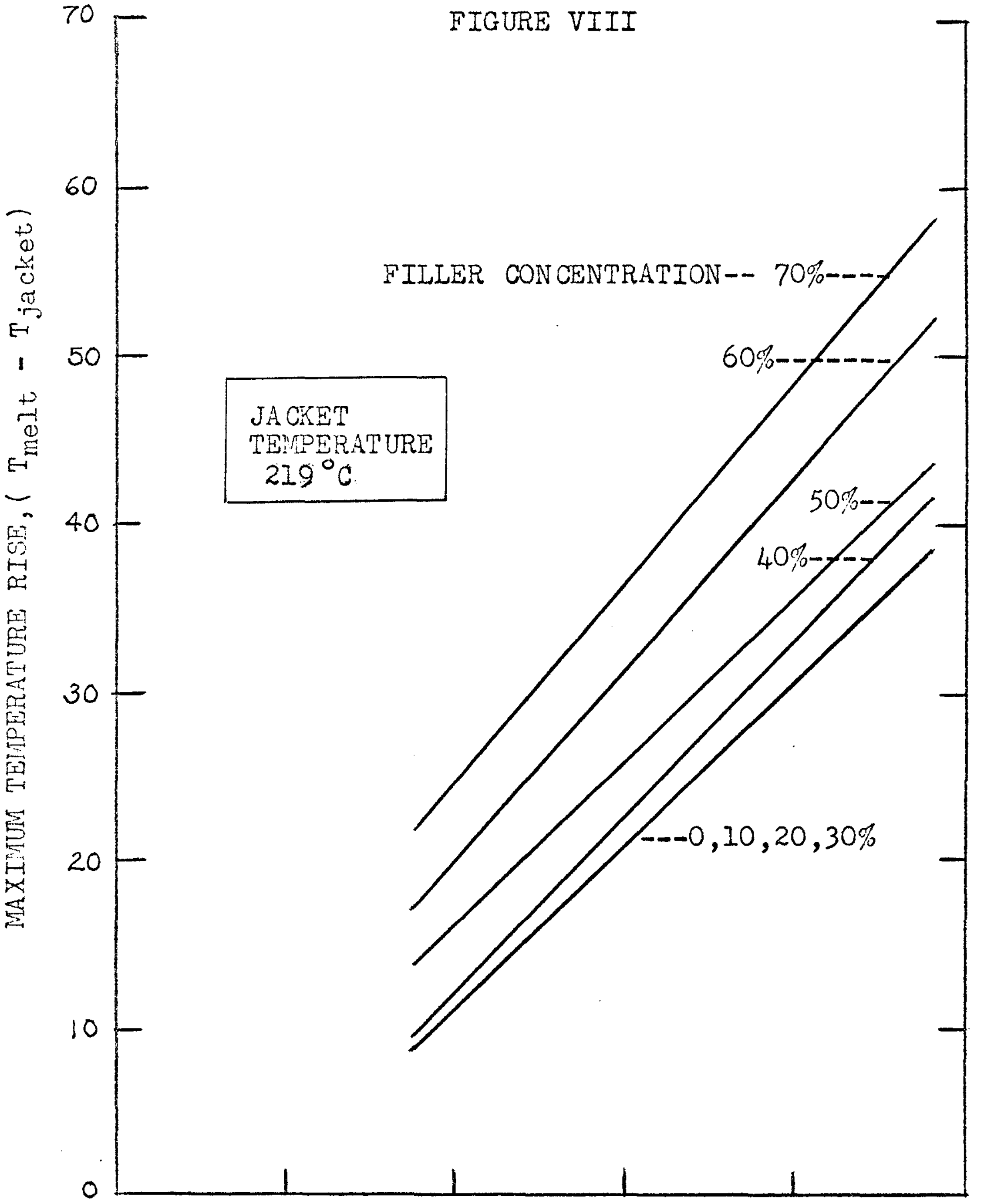
Figures VII and VIII show the maximum temperature rise in the polymer-filler melt as a function of shear rate and filler concentration at two jacket temperatures. The relationship is linear. An average rise of 0.65°C./(rpm) was

FIGURE VII



MAXIMUM TEMPERATURE RISE IN THE POLYMER-FILLER MIXTURE AS A FUNCTION OF SHEAR RATE AT VARIOUS CONCENTRATIONS OF FILLER

FIGURE VIII



MAXIMUM TEMPERATURE RISE IN THE POLYMER-FILLER MIXTURE AS A FUNCTION OF SHEAR RATE AT VARIOUS CONCENTRATIONS OF FILLER calculated for a setting of 177°C. At a jacket setting of 219°C., the rise to the maximum temperature was less. A rate of 0.38 to 0.47°C./RPM was achieved.

The maximum temperatures attained in each run are tabulated in Table IV. It is evident from the table that shear rate has a very significant effect on the rise of melt temperature, compared to the increase due to the setting on the jacket.

TABLE IV

T, MAXIMUM STOCK TEMPERATURE -JACKET TEMP. VERSUS SHEAR RATE AND FILLER CONCENTRATION

Jacket Temperature °C	Shear Rate rpm	Wt. % Filler							
		0	10	20	30	40	50	60	70
177	50	12	14	15	16	19	20	24	33
199	50	12	13	13	14	17	20	24	29
219	50	11	12	12	12	14	16	21	26
177	85	33	33	35	35	39	46	51	60
199	85	29	28	26	29	31	34	44	47
219	85	26	28	28	26	26	31	35	41
177	120	53	49	49	50	55	61	73	75
199	120	46	47	46	46	47	51	61	66
219	120	38	41	41	38	39	43	53	58

Filler Concentration Versus Shear Stress

Figures IX and X indicate the shear stress level as a function of filler concentration at 2 temperatures and 3 shear rates.

The shear stress is not affected at concentrations up to 30%, but does increase significantly above 30% at a constant rate of approximately 32 m-gms per percent concentration at 210°C. and 34 m-gms per percent concentration at 245°C.

It is interesting to note that the break in the slope of shear stress vs. concentration moves towards the lower concentration of filler as the shear rate increases and moves towards the high filler concentration as the melt temperature increases. This indicates that temperature is reducing shear stress while the filler increases shear stress.

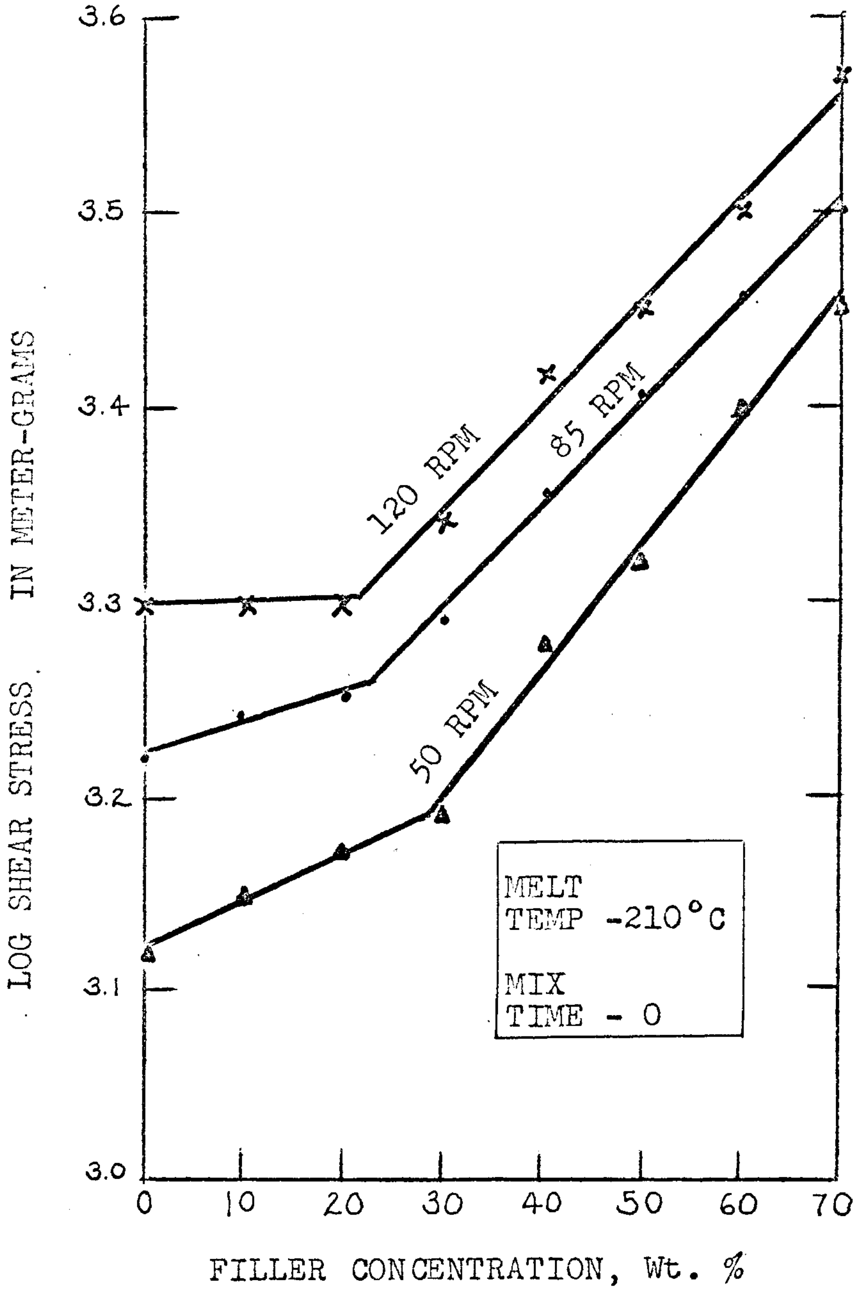
Flow Index

In the power law,

$$\eta = \eta^\circ \left| \frac{\gamma}{\dot{\gamma}_0} \right|^{n-1} = \eta^\circ \left| \frac{\tau}{\tau_0} \right|^{\frac{n-1}{n}} \qquad (5)$$

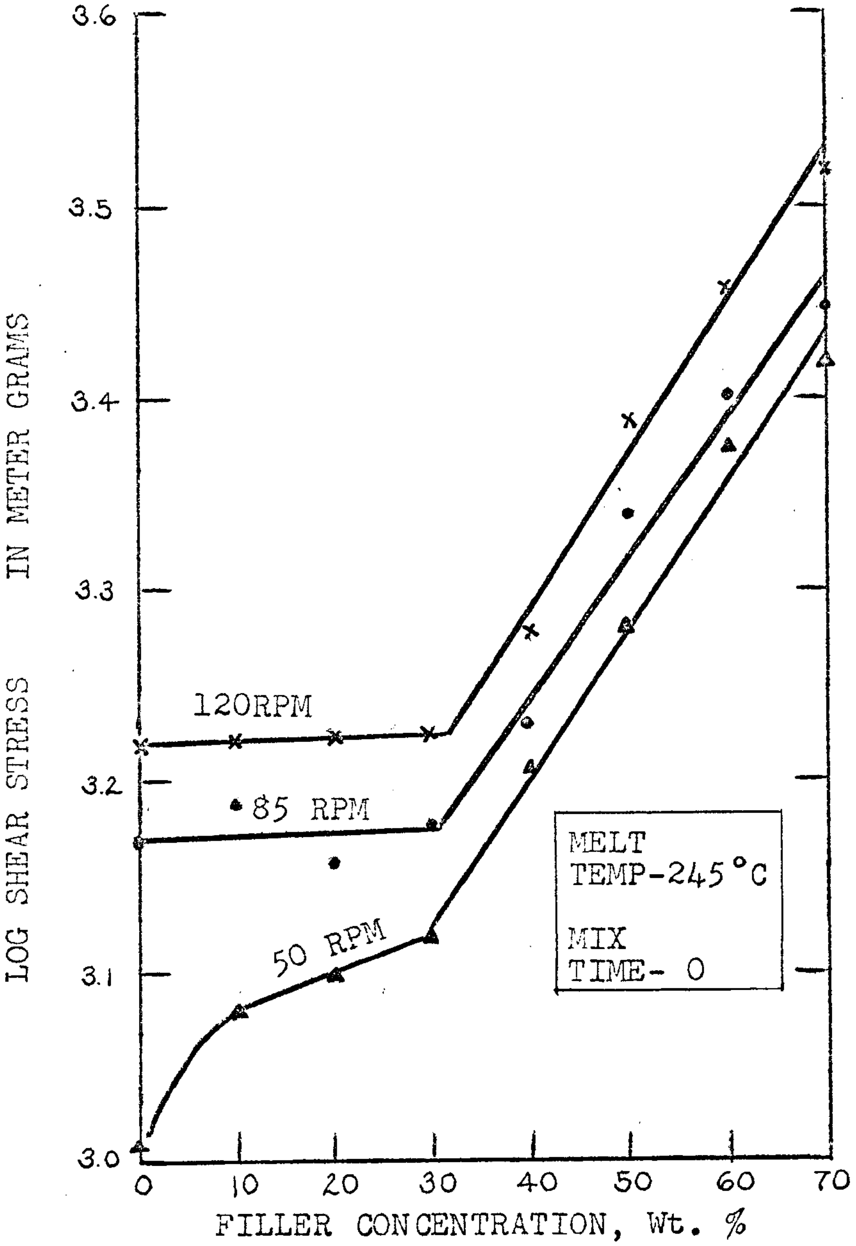
, $\dot{\gamma}_0$ and τ_0 represent values of shear rate and shear stress in a chosen state and η° is the non-Newtonian viscosity of the fluid in this state. The parameter, n, is the flow index of the fluid. When n is less than unity, the viscosity of the fluid decreases with increasing shear rate. Therefore, the power law describes the behavior of a pseudoplastic fluid when n<1 and a dilatant fluid when n>1. According to Mc Kelvey[3], the flow index may be considered to be a true physical property of the fluid.

FIGURE IX



SHEAR STRESS AS A FUNCTION OF CONCENTRATION OF FILLER AT VARIOUS SHEAR RATES (CASE I)

FIGURE X



SHEAR STRESS AS A FUNCTION OF
CONCENTRATION OF FILLER AT VARIOUS
SHEAR RATES (CASE I)

The degree of departure from Newtonian behavior may be obtained from a logarithmic shear stress-shear rate plot according to the following equation[2]:

$$\log \tau = \log (\eta\, du/dr) \qquad (6)$$

$$\log \tau = \log \frac{du}{dr} + \log \eta \qquad (7)$$

Log du/dr vs log τ of all concentrations at three temperatures are represented in Figures XI and XII.

The curves converge as the concentration of filler increases at the lower shear rate, indicating that the difference in shear stress is not as great at the lower shear rates as at the higher shear rates.

For virgin polyethylene, a flow index of approximately 0.5 has been established in the literature [1], corresponding to the value obtained for polyethylene in this experiment*.

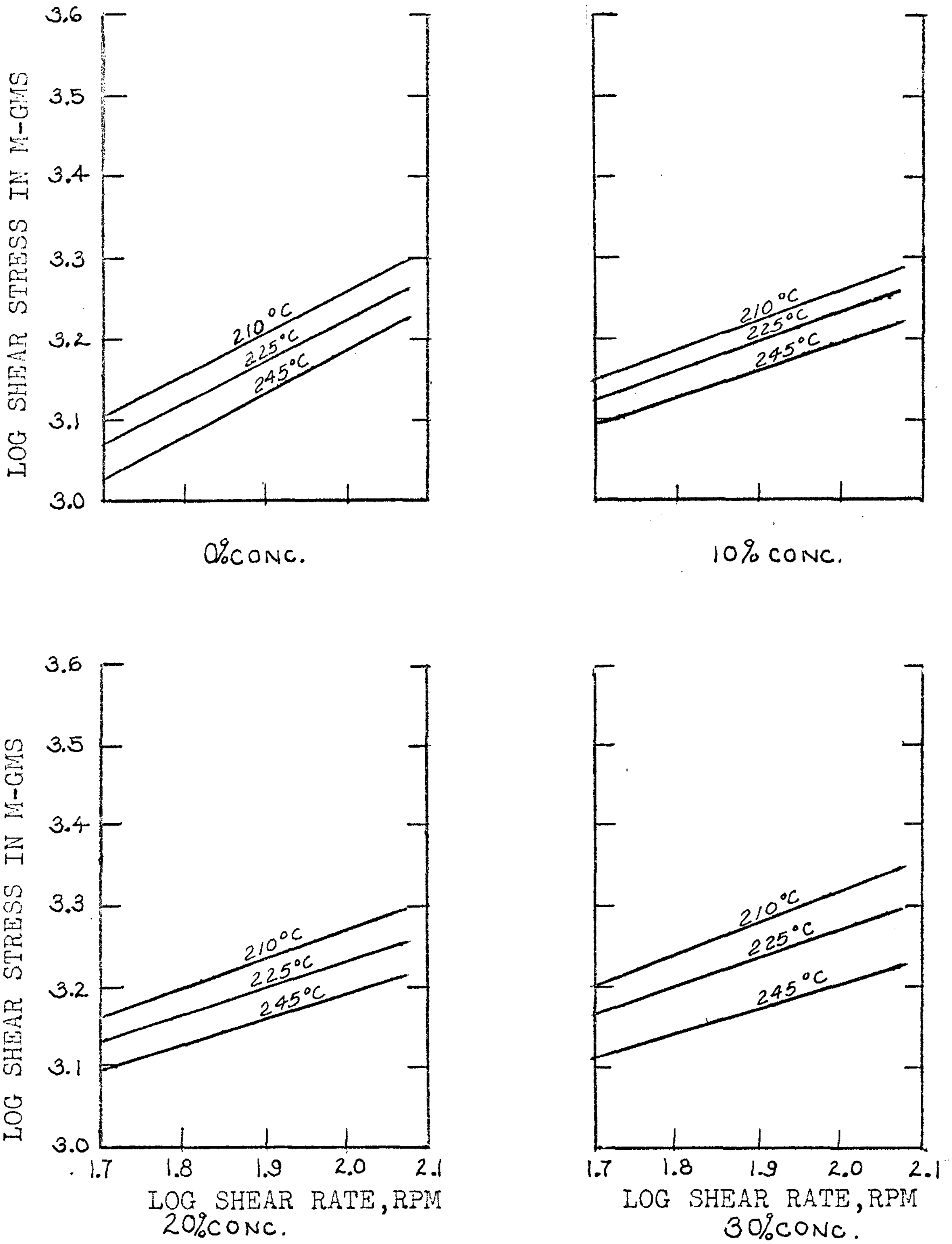
The flow indices at each concentration for three temperatures have been summarized and plotted in Figure XIII.

As the filler concentration increases in the system, the rate of change of shear stress with shear rate (or the non-Newtonian flow index, n), decreases. This is due to the effect of increasing and decreasing factors of shear stress.

The decrease in polymer shear stress by chain scission and shear thinning is opposed by (1) the thickening effect of the filler as its concentration increases in the system, (2) polymer cross-linking and (3) loss of the elastic properties of the mixture due to reduction in polymer concentration.

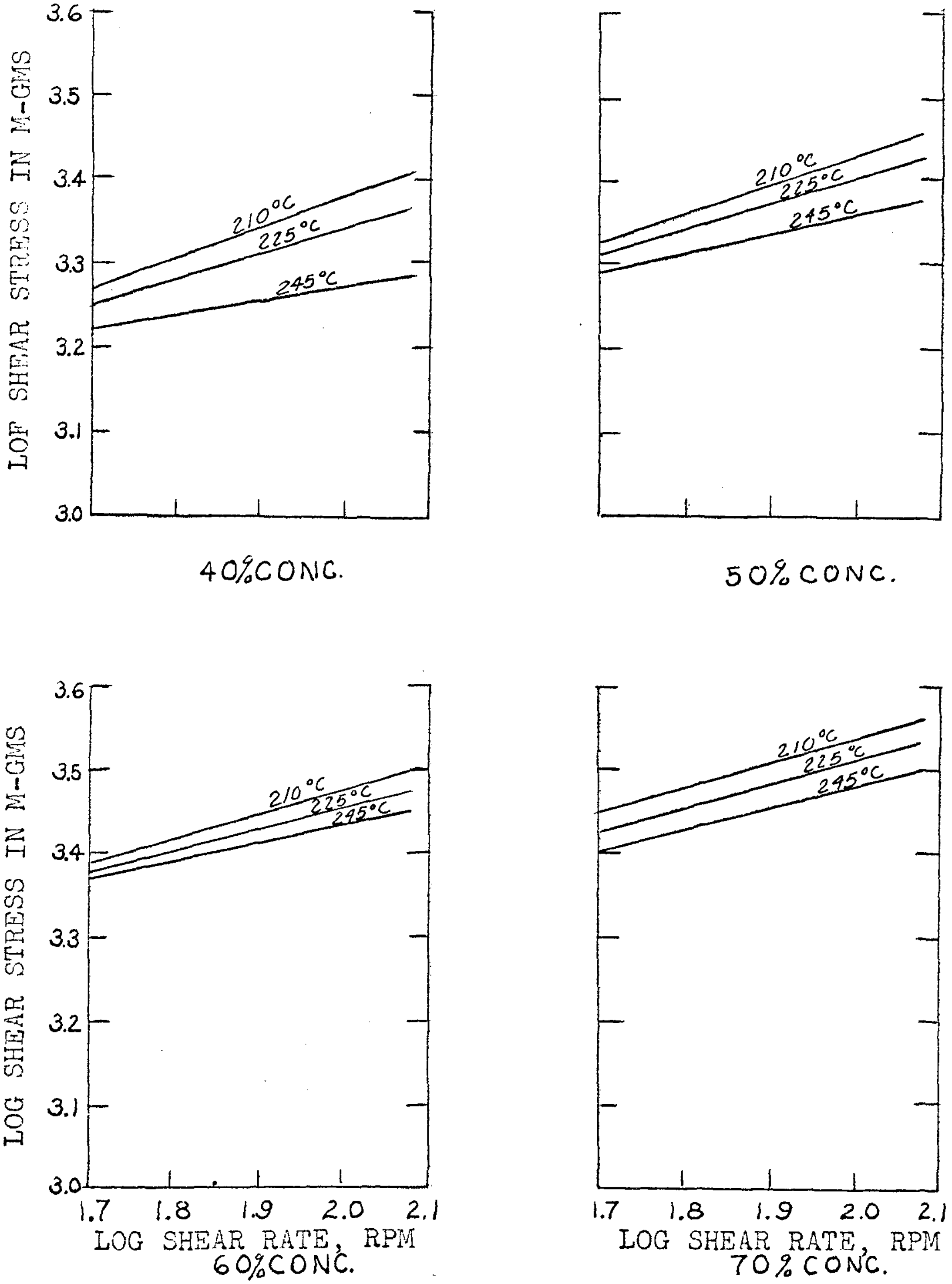
* Figure XIII in the text.

FIGURE XI



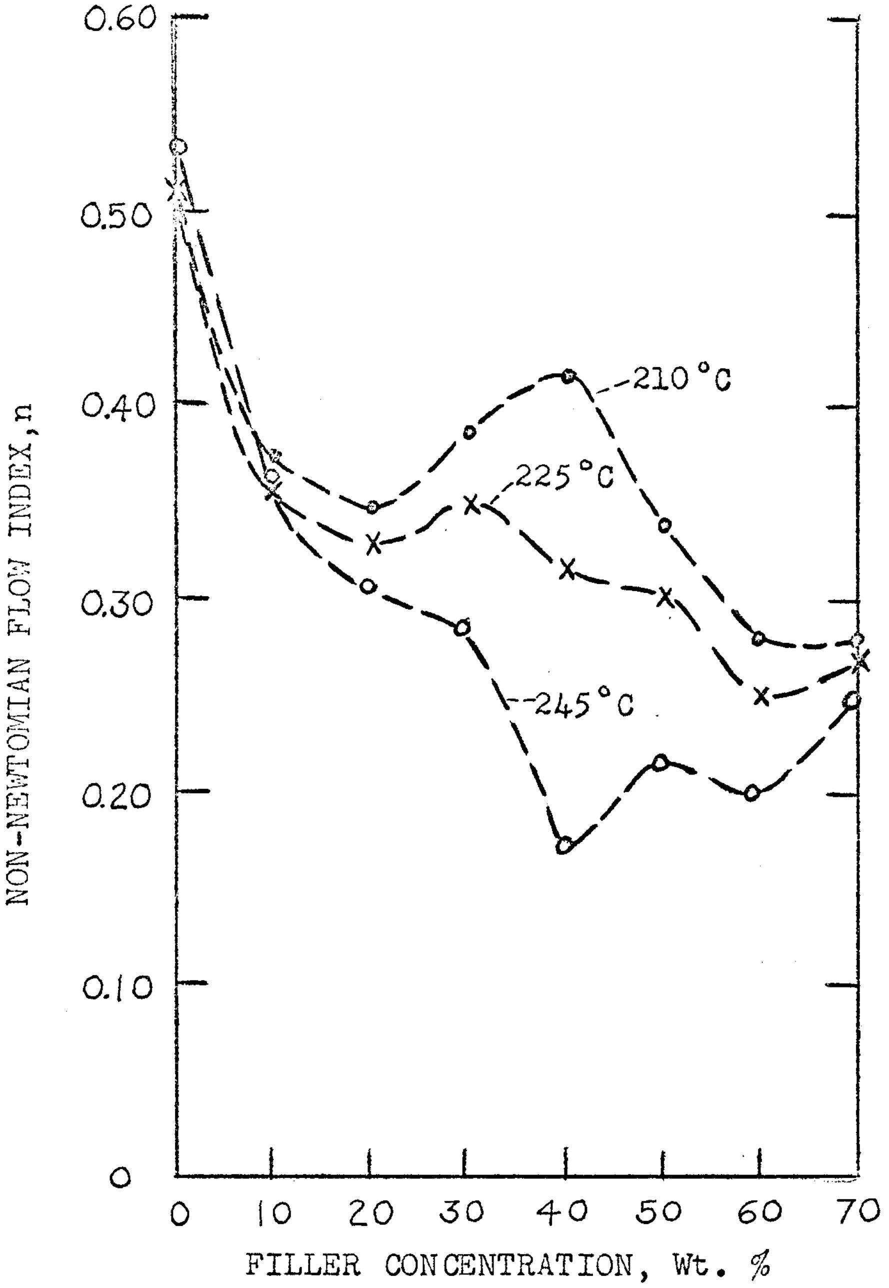
SHEAR STRESS AS A FUNCTION OF SHEAR RATE AT VARIOUS FILLER CONCENTRATIONS AND MELT TEMPERATURES

FIGURE XII



SHEAR STRESS AS A FUNCTION OF SHEAR RATE AT
VARIOUS FILLER CONCENTRATIONS AND
MELT TEMPERATURES

FIGURE XIII



NON-NEWTONIAN FLOW INDEX AS A FUNCTION OF FILLER CONCENTRATION AT VARIOUS MELT TEMPERATURES

Since the rate of change of shear stress with shear rate of the polymer filler mixture decreases, the factors affecting the increase in shear stress must predominate as the concentration of filler increases.

Up to 40% filler concentration, the filler particles are in suspension and do not significantly increase the shear stress level. However, at 40% concentration of filler, there is not sufficient polymer to lubricate filler particles and the maximum reduction in apparent melt viscosity of the polymer will occur. As temperature is increased at 40% filler, the polymer viscosity will be reduced and significant cross-linking will occur, increasing the shear stress of the system and reducing the rate of change of shear stress with shear rate.

Above 40% filler concentration, the mixture is almost entirely made up of filler particles, which are not subject to the same reduction in shear stress as polymer molecules. The shear stress of the system above this concentration is not greatly affected by a shearing force and the rate of change of shear stress with shear rate decreases as the filler concentration increases.

Data of Philippoff and Gaskins[4] show that within the non-Newtonian flow region, the flow behavior index increases slightly with increases in temperature as summarized by the following;

TABLE V

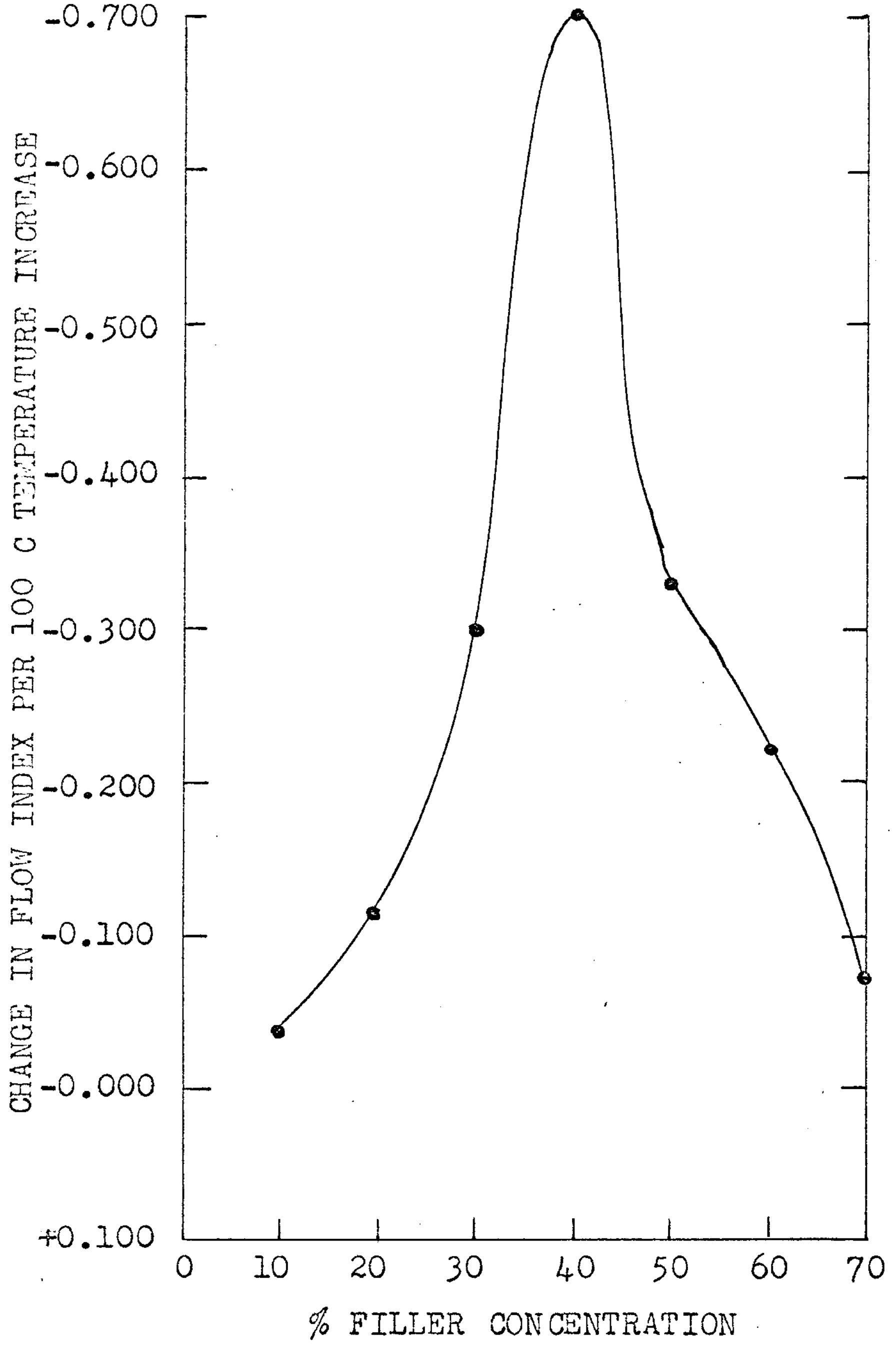
Material	Shear Rate Sec.$^{-1}$	Flow Behavior Index, n	Increase in Flow Behavior Index Per 100°C Temperature Increase
Polyethylene (MI=2.1)	0.01	0.84 @ 108°C and 1.0 @ 230°C	0.13
	100	0.32 @ 108°C and 0.49 @ 230°C	0.14
Polyethylene (MI=2.0)	0.1	0.59 @ 112°C and 0.88 @ 250°C	0.21
	10	0.33 @ 125°C and 0.59 @ 250°C	0.21

This phenomena was also established with virgin polyethylene in this experiment.

Material	Shear Rate Sec^{-1}	Flow Behavior Index, n	Increase in Flow Behavior Index Per 100°C Temperature Increase
Polyethylene (MI=0,7)	45-108	0.513 @ 210°C and 0.538 @ 245°C	0.07

However, Figure XIV indicates the same is not true when polyethylene is filled with clay. The flow index decreases with an increase in temperature.

FIGURE XIV



FILLER CONCENTRATION VERSUS THE CHANGE IN FLOW INDEX PER 100 °C TEMPERATURE INCREASE

V STATISTICAL ANALYSIS OF TEST DATA

As previously explained, zero time was defined as the point at which degradation of the polymer was not severe but at which the filler-polymer mix was essentially uniform in the melt phase. Two separate analyses were performed: one at time zero and the second at any time, t. This can be represented as follows:

Case I time=0, $\tau=f(T,\ ,c)$

Case II time=t, $\tau=f(T,\ ,c,t)$

where T-temperature, γ=shear rate, c=concentration, and t=time.

In both cases, an analysis of variance was performed to determine the level of significance of variables. A regression equation was fitted to both cases to predict shear stress as a function of the three variables at time=0 and as a function of four variables at any time, t.

A response surface was constructed for Case I showing the relationships among the variables at various stress levels.

Analysis of Variance

The mean squares and f ratios have been calculated and are presented in Tables VI and VII in the (Appendix).

For Case I, it can be seen that only the interaction of temperature and shear rate is not a real effect. All other main and interacting effects are significantly independent and have real main effects.

For Case II, temperature-shear rate, time-temperature-shear rate, and time-shear rate-concentration are not significantly independent. All other main and interacting variables have real main effects.

In both cases, the temperature-shear rate interaction does not independently affect shear stress.

From these results, it was evident that a second order model might fit as the regression equation.

Regression Equations - Case I

The main effects are represented by x_1, x_2, and x_3; the interaction of variables by x_1 x_2, x_1 x_3, x_2 x_3, and the quadratic effect by x_2^2 , x_3^2.

The sum of squares attributable to this model of regression is 0.77156. The sum of squares deviation from regression is 0.02252. On a percentage basis then, 97% of the variability can be explained by this model.

The equation is

$$\log y = \hat{y} = b_o + \Sigma b_i x_i + \Sigma b_{ii} x_i^2 + \Sigma b_{ij} x_i x_j \quad (8)$$

where

xi = main effect variable

xi_2 = quadratic effect

$x_i x_j$ = interaction of variables

b_o = intercept on shear stress axis
$\hat{Y} = b_o$ at $T = C = \gamma = 0$

$\hat{y}$ = log of shear stress

b_i, b_{ii}, b_{ij} = regression coefficients for the least square equation

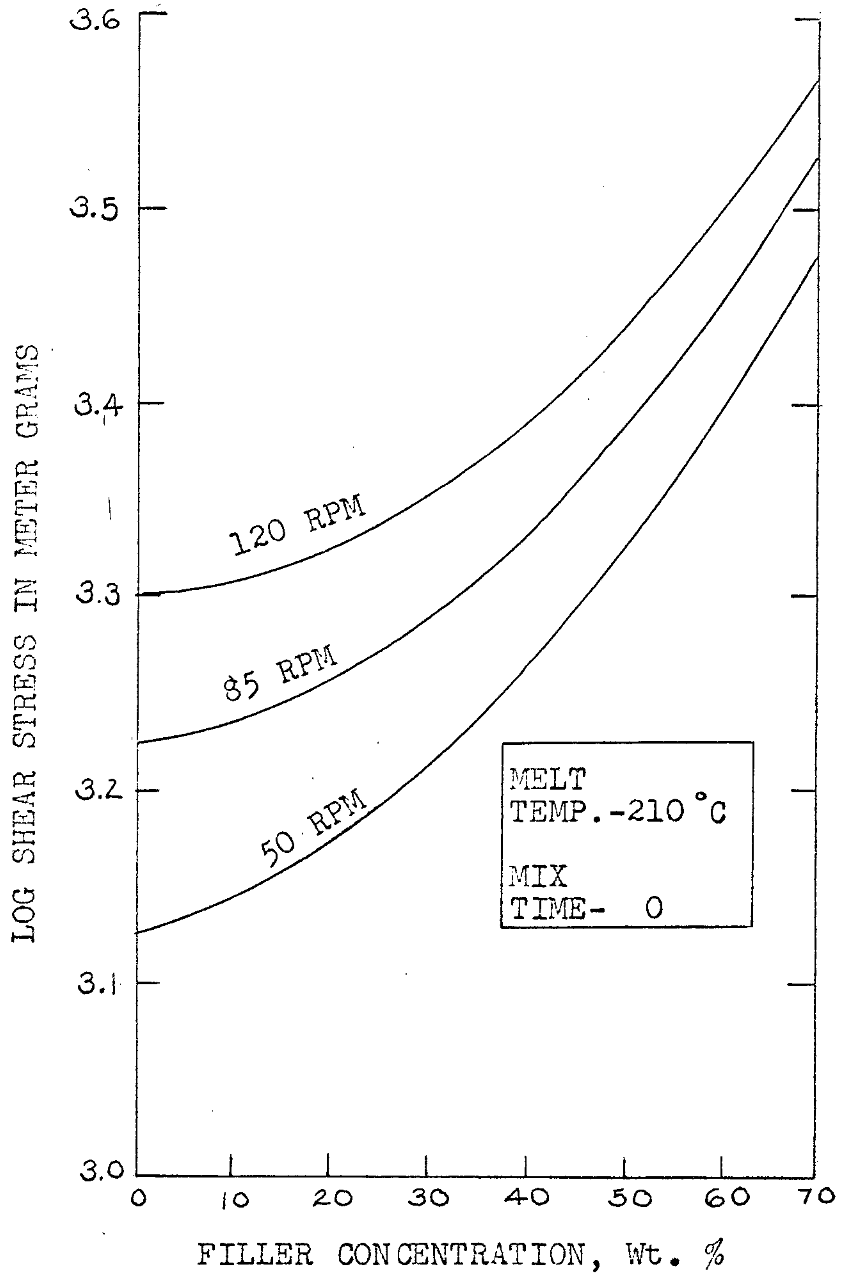
Table VIII is a summary of regression coefficients for equation (8). Table XVIII in the appendix lists the shear stress values calculated by equation (8) compared with the actual observed stresses. Column 3 is the residual or error in each calculation.

Equation (8) is represented graphically in Figures XV and XVI as a function of concentration at two temperatures.

In order to assess the contribution of each variable on shear stress, the following procedure was used:

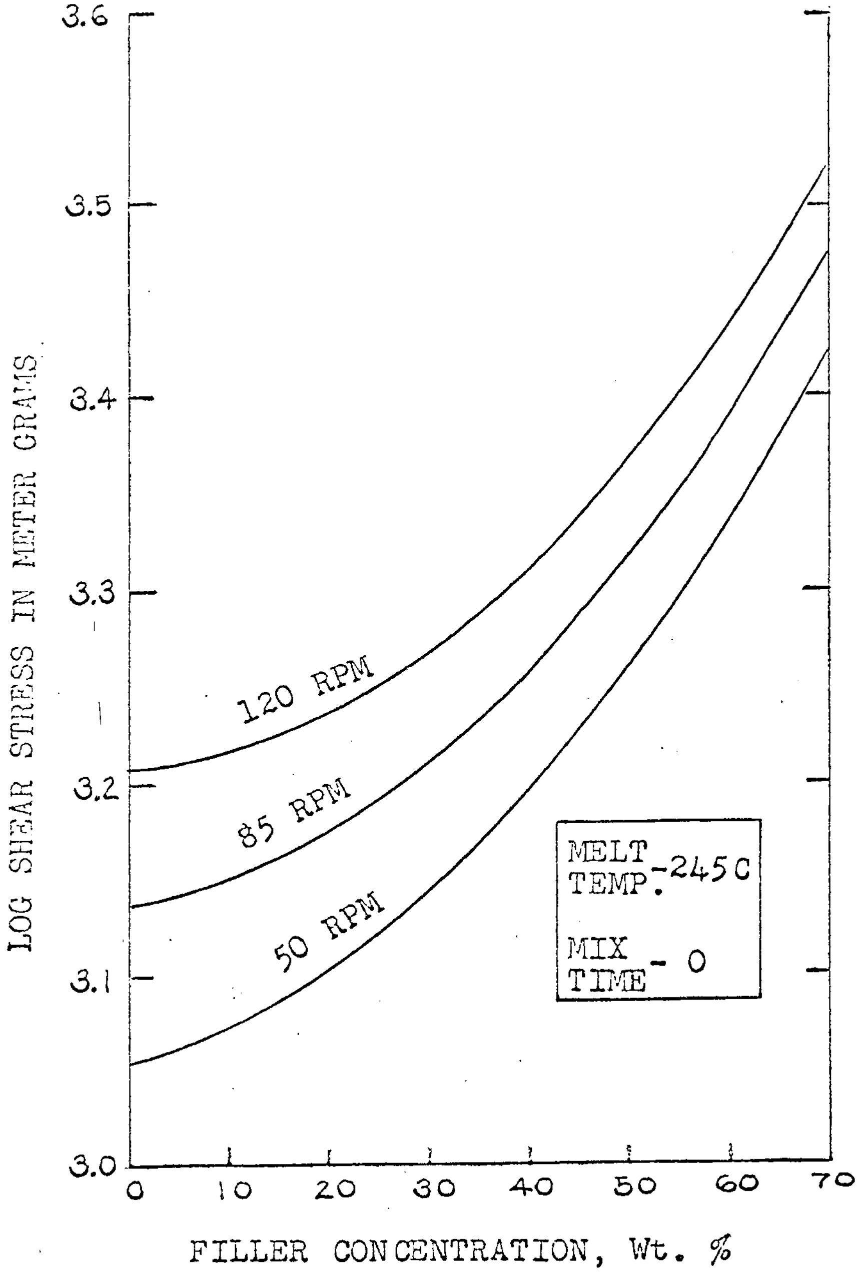
For example, at 245°C., 120 rpm and 70% filler concentration, the calculated y = 3.5078 = 3225 meter-grams, while the y (observed) = 3.5185 = 3300 meter-grams

FIGURE XV



GRAPHICAL PLOT OF EQUATION ,
SHEAR STRESS AS A FUNCTION OF FILLER
CONCENTRATION AT VARIOUS SHEAR RATES

FIGURE XVI



GRAPHICAL PLOT OF EQUATION ,
SHEAR STRESS AS A FUNCTION OF FILLER
CONCENTRATION AT VARIOUS SHEAR RATES

The error associated with the predicted value is 2.26% well within the 97% explained variability. The unexplained variability may be due to errors in weighing, loading, measurement, and materials. An equation for predicting the shear stress of this virgin polyethylene can be made by setting x_3 (concentration) equal to zero.

$$\hat{y} = b_0 + b_1 x_1 + b_2 x_2 + b_{12} x_1 x_2 + b_{22} x_2^2 \qquad (9)$$

All coefficients have the same values as the coefficients in equation (8).

Substituting 50 rpm and 210°C. into equation (9)

$$\hat{y} = 3.370 - 0.405 + 0.245 - 0.063 - 0.0162$$

$$y_{calc.} = 3.1277 = 1342 \text{ meter-grams}$$

$$y_{obs.} = 3.1222 = 1325 \text{ meter-grams}$$

and observing the contribution of each term, it can be said that;

(a) temperature decreases shear stress

(b) shear rate increases shear stress

(c) interaction of shear rate and temperature affect shear stress more significantly than the quadratic effect of shear rate, however much less than the main effects of shear rate and temperature.

Figures XI and XII in the text show the effect of shear rate on shear stress for virgin polyethylene. The temperature effects on shear stress are shown in Figures XXII through XXIX in the appendix.

Testing Equation (9) For Virgin Polyethylene

Although this experiment was intended to analyze the effect of fillers on a particular polymer, the derived equations can be directly applied to unfilled high density polyethylenes of varying molecular weight.

If, for example, it were intended to load a polyethylene with a different molecular weight with a filler, the Brabender curve for virgin polyethylene must be known. An arbitrary set of conditions can be chosen for this curve. Any shear stress number can then be obtained for any set of conditions if the constant, b_o, is re-calculated. To do this quickly without going through a statistical procedure of the type presented in this report, take the temperature corrected shear stress value at zero time and substitute it into equation (9), $\hat{y} = b_o + \sum$ variables, determine the value of the $\sum$variables, and recalculate bo.

Since b_o is the intercept on the log shear stress axis at zero time, b_o can be recalculated for polyethylene of varying molecular weight. The assumption for keeping variables constant is that the reduction of shear stress as a function of time, shear rate, temperature and filler concentration will be similar to that experienced in this experiment.

As a check, data generated by J. Ryan [3] on a high density polyethylene with a higher molecular weight than the one used in this experiment was analyzed.

Ryan generated a value (corrected for differences in stock temperature) of 2050 meter-grams at 5 minutes, 225°C. and 50 rpm.

According to the method outlined in this report, equilibrium conditions at zero time were stress values taken between 3 and 6 minutes. For approximation, Ryan's five minutes will be considered zero time or time at which the polymer is completely melted and homogenous but not degraded.

Using the method outlined above and arbitrarily choosing 50 rpm and 225°C. as the starting point;

(a) log 1250 = 3.370-0.2737

or

1250 = 2345/1.88

(b) inserting Ryan's value of shear stress

$\log 2050 = \log (b_o/1.88)$

$\log 3850 = b_o$

$3.585 = b_o$

(c) calculate shear stress at 25 rpm and 225°C.

$\hat{y} = -1.93 \times 10 (225) + 4.9 \times 10 (25) - 6 \times 10 (225) (25) -6.5 \times 10 (25)^2$

$\hat{y} = 3.235$

τ cal. = 1718 meter-grams

Ryan's observed τ = 1720 meter-grams

(d) at 75 rmp and 225°C.

τcalc=2410 meter-grams

Ryan's observed τ = 2380 meter-grams

Since temperature ($1/T_{abs}$) varies linearly with log shear stress, it would be simple to obtain the shear stress at a particular temperature by referring to Figures XXII through XXIX in the Appendix.

It is quite difficult to say however that this procedure will work for all high density polythenes of varying molecular weights. More Brabender data must be tested in order to prove the method completely.

Because there is no data available for filled polymer systems, the above method cannot be tested further.

Regression Equations - Case II

Eighty-four percent of the variability is explained for Case II, using the second order equation of Case I. Because of the introduction of a fourth variable, time, a greater error is present due to additional interactions. A cubic equation could have been used to explain added variability, however, the second order equation is highly significant for an analysis of this type. Considering 191 degrees of freedom, the calculated F value is quite large.

The four variables:

x_1 = time in minutes

x_2 = temp. in °C.

x_3 = shear rate in RPM

x_4 = concentration of filler in weight percent

are substituted into the general second order regression equation to obtain:

$$(3)\quad \log y = \hat{y} = 3.17 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{11}x_1^2 + b_{33}x_3^2 + b_{44}x_4 + b_{12}x_1x_2 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4 \qquad (10)$$

The regression coefficients for this case are listed in Table IX. in the appendix.

The T test is used to calculate the significance of the variables and their mean contributions in the regression equation.

The main, interacting and quadratic effects must be analyzed separately because each does not contribute equally at every portion of the curve relating all variables.

The following table separates the effects according to the T test and lists the variables in order of magnitude, the larger first. The algebraic sign in front of the effecting variable indicates the net effect on shear stress.

TABLE X (CASE II)

Main Effects	Interactions	Quadratic
+ concentration	-temp - conc	+ concentration
+ shear rate	-shear - conc	- shear rate
- temperature	- time - conc	+ time
+ time	- time - shear	
	- time - temp	
	+ temp - shear	

It is evident that terms involving concentration affect shear stress more significantly than other variable effects. Linearly, concentration, shear rate and time increase shear stress while temperature decreases stress. When variables are interacted, only the combination effect of temperature and shear rate increases shear stress.

A T test was also performed on the regression equation of Case I. Contributions are listed in order of magnitude, the larger first.

TABLE XI

Main Effects	Interactions	Quadratic
- temperature	- shear - conc	+ concentration
+ shear rate	+ temp - conc	- shear rate
- concentration	- temp - shear	

Comparing The Two Cases

Comparing Tables X and XI, time reverses the effects of temperature and concentration, and contributes the least to main effects. Time also changes the negative effect of concentration to a positive effect on shear stress.

Time reverses temperature-concentration and shear-concentration interactions and reverses the sign of temperature-concentration and temperature-shear.

Mixing time in the form of a main and quadratic effect contributes the least to a change in shear stress. The interactions with time are significant.

Further calculations have been made in order to assess the combined effects of all variables involved in the regressions.

The higher the absolute value of the variable, the more effect it has on shear stress. Substituting, for example, 15 minutes, 245°C., 120 rpm, and 70% concentration into equation (10), the following is obtained:

TABLE XII (CASE II)

Main Effects	Interactions	Quadratic
concentration = + 0.697	temp-conc + -0.970	concentration = +0.685
shear rate = + 0.366	shear-conc = -0.223	shear = -0.183
temperature = - 0.262	time-conc = -0.130	time = -0.052
time = + 0.079	time-shear = -0.082	Total = +0.450
Total = +0.880	time-temp = -0.156	
	temp-shear = +0.205	
	Total = -1.356	

Substituting 245°C., 120 rpm, and 70% concentration into equation (8), a similar analysis can be made for Case I.

TABLE XIII (CASE I)

Main Effects	Interactions	Quadratic
temperature -0.473	shear-conc -0.135	concentration +0.245
shear rate +0.487	temp-conc +0.021	shear rate -0.0935
concentration -0.042	temp-shear -0.177	Total = +0.152
Total = -0.028	Total = -0.291	

If the terms containing each variable are summed up, e.g. for concentration, $x_4 + x_{24} + x_{34} + x_{14} + x_4^2 = x_c$ total, the total effect or contribution of the variable on shear stress may be approximated.

TABLE XIV (CASE I)

Variable	Stress Log	Percent of Total Contribution
temperature	-0.629	-71.4
shear rate	+0.166	+18.8
concentration	+0.089	+9.8

	Variable	Stress Log	Percent of Total Contribution
Case II w/o time	temperature	-1.183	-89.5
	shear rate	+0.083	+6.3
	concentration	+0.059	+4.2
Case II w/time	temperature	-1.183	-76
	time	-0.237	-15.2
	shear rate	+0.083	+5.3
	concentration	+0.059	+3.5

Temperature contributes much more to the change in shear stress in both cases. It must be pointed out that interactions are inseparable, and that it would be most difficult to assess the effect of each variable in the interaction. The percent contribution is a relative one and points to a general trend.

Time, in Case II reduces the effect of shear rate and concentration and increases the effect of temperature on shear stress. Concentration, on the other hand, is the least contributing variable in both cases.

At the lower energy levels (50 rpm, 210°C., 10% concentration), interaction and the quadratic term contribute very little to a change in shear stress.

TABLE XV (CASE I)

temperature	-71.8%
shear rate	+25.6
concentration	+ 2.6

Temperature has the same relative effect on shear stress at both energy levels (Table XIV versus Table XV). However, shear rate seems to increase the shear stress to a greater degree at low energy conditions.

If the following conditions (120 rpm, 70% concentration, 150°C.) were substituted into equation (8), the effect of an extremely low temperature on shear stress may be evaluated and compared to 120 rpm, 70% concentration and 245°C.

TABLE XVI

(120 rpm, 70% concentration, 150°C.)

temperature	-45.6%
shear rate	+44.8
concentration	+ 9.6

Even at this extremely low temperature, temperature significantly contributes to a change in shear stress. If shear rate and concentration were reduced, the effect of temperature would increase significantly.

Relation Among Variables

Figure XVII is a response surface constructed for Case I.

1. Concentration vs. shear rate (210°C. and constant shear stress).

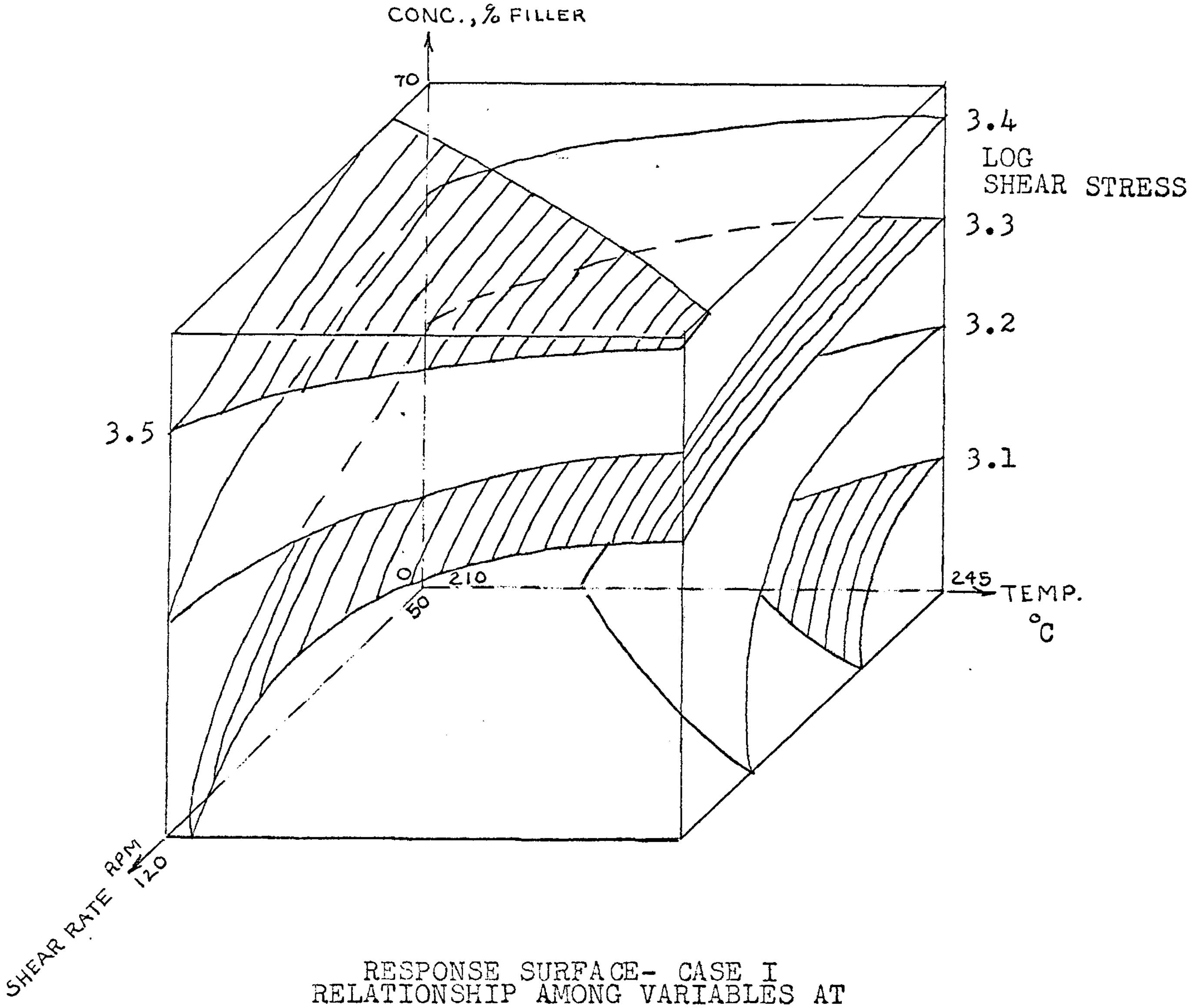
As filler concentration increases, shear rate decreases at all viscosities. As the shear stress level increases, the relationship between shear rate and concentration is more linear. The slope between concentration and shear rate becomes steeper at high levels of shear stress.

2. Concentration vs. shear rate at (245°C. and constant shear stress).

Explanations are the same as for 210°C., except the shear stress levels are lower.

3. Temperature vs. shear rate (0 to 70% filler concentration).

FIGURE XVII



RESPONSE SURFACE- CASE I
RELATIONSHIP AMONG VARIABLES AT
VARIOUS SHEAR STRESS LEVELS

Viscosity levels are dependent upon all variables. At zero concentration, the shear stress levels above log 3.2 could not be obtained, therefore the relationship between temperature and shear rate in the absence of filler can only be evaluated between log 3.1 and log 3.2 shear stress. As the concentration level increases, so does the shear stress level.

It can be generally said that as the temperature increases, shear rate increases. The slope of temperature vs. shear rate is linear. There are no significant changes in slope as the shear stress level changes.

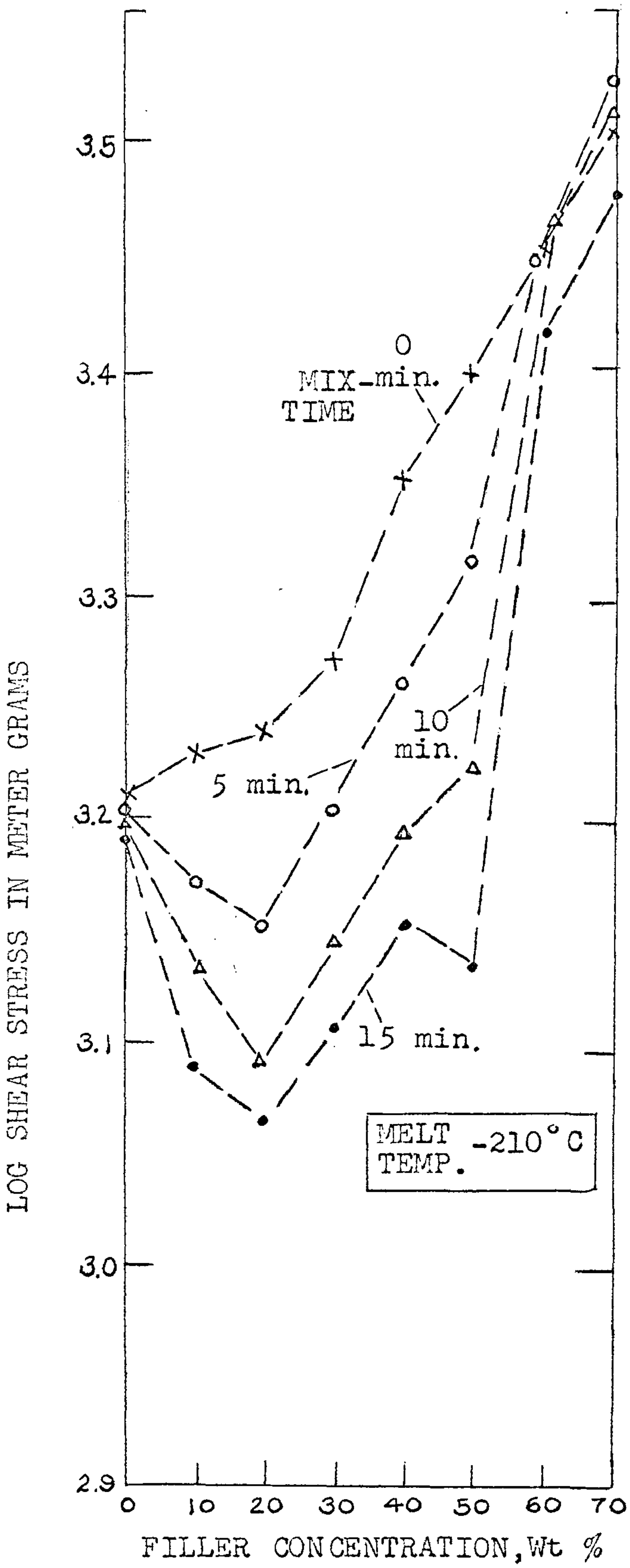
4. Temperature versus concentration (50, 85, and 120 rpm).

At 50 rpm, concentration increases as the temperature increases. At the lowest shear stress level, concentration seems to increase faster than temperature. At the higher stress levels, the relationship is more linear.

At 85 and 120 rpm, concentration increases much faster than temperature at the low temperatures and becomes linear at higher temperatures. At the higher stress levels, the relationship between concentration is linear.

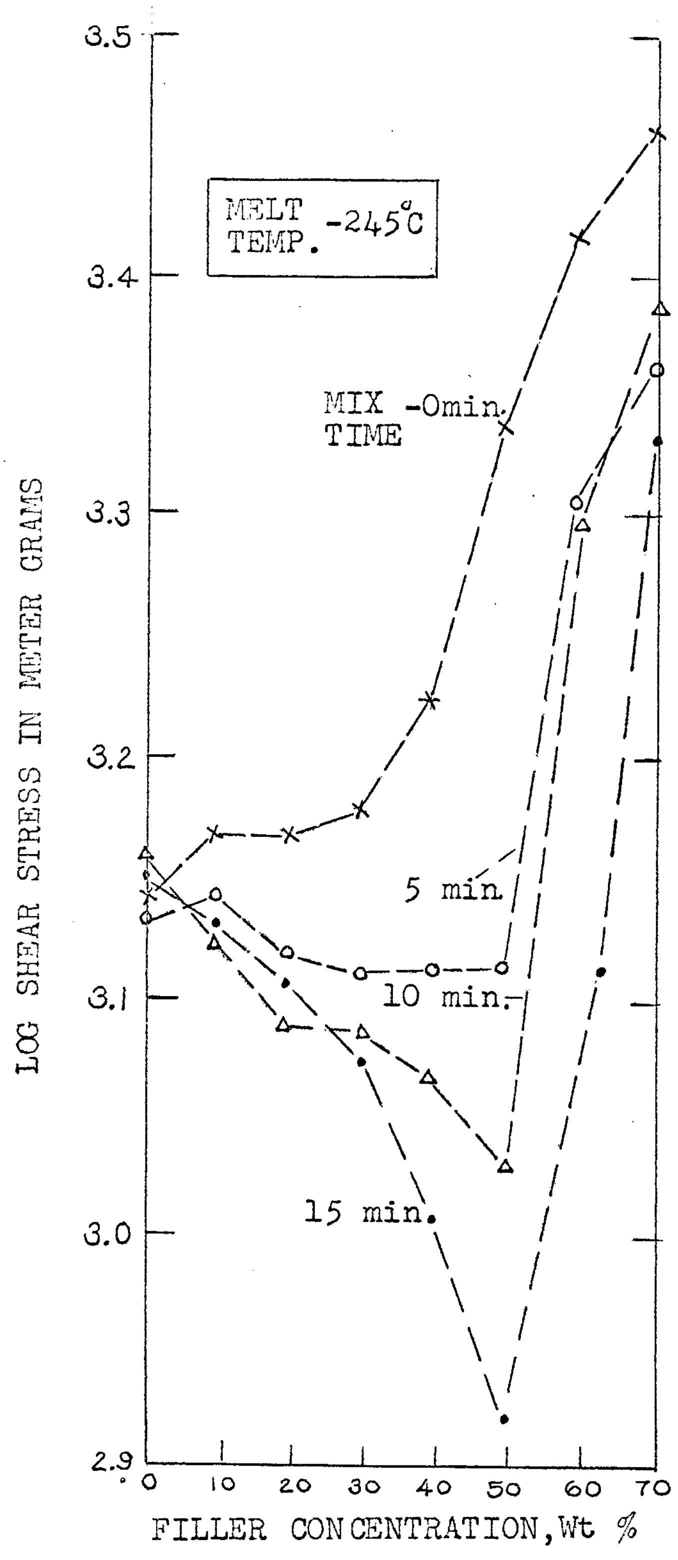
The results of Case II are presented graphically in Figures XVIII, XIX, XX, and XXI. Figures XXVIII and XXIX show the effect of concentration on log τ at various times, averaged over the range of shear rates for two temperature

FIGUREXVIII



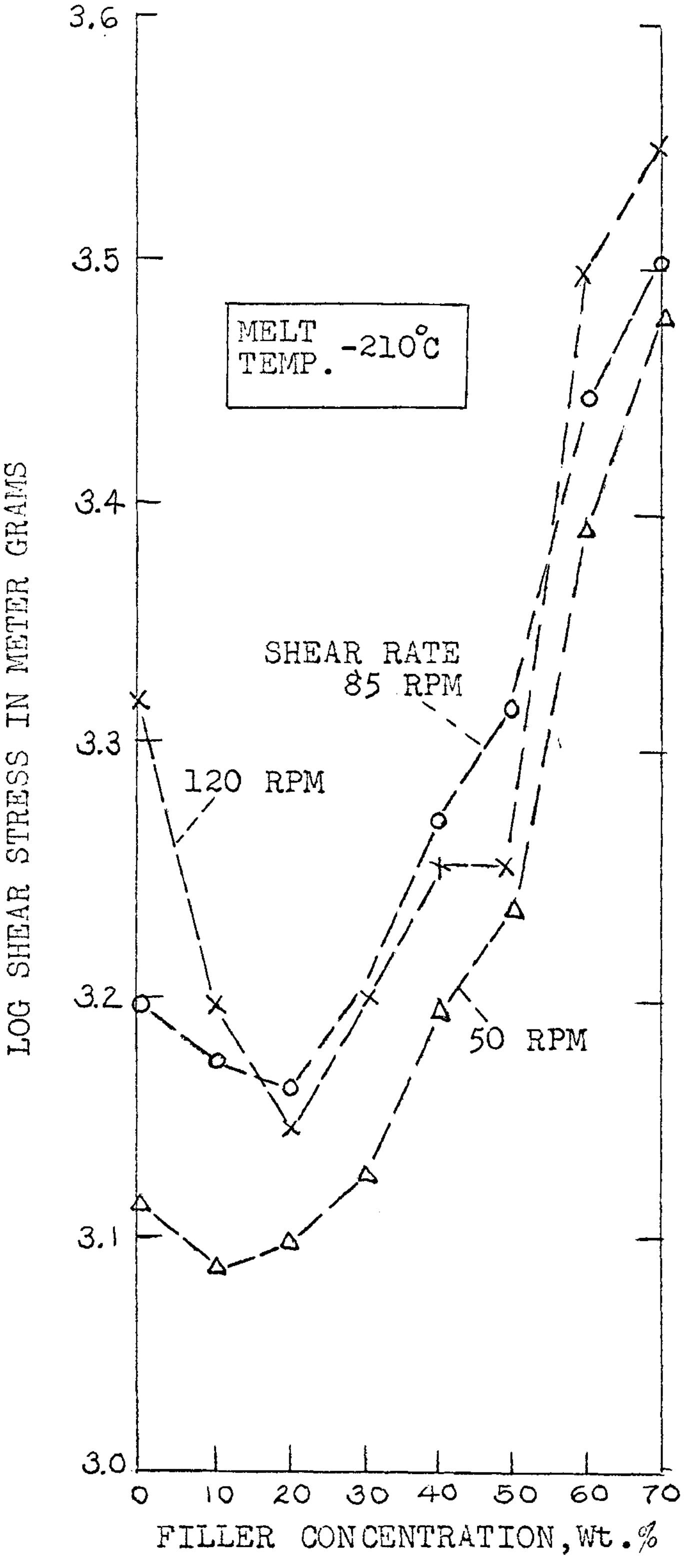
SHEAR STRESS AS A FUNCTION OF FILLER CONCENTRATION AT VARIOUS MIXING TIMES AND AT AN AVERAGE SHEAR RATE

FIGURE XIX



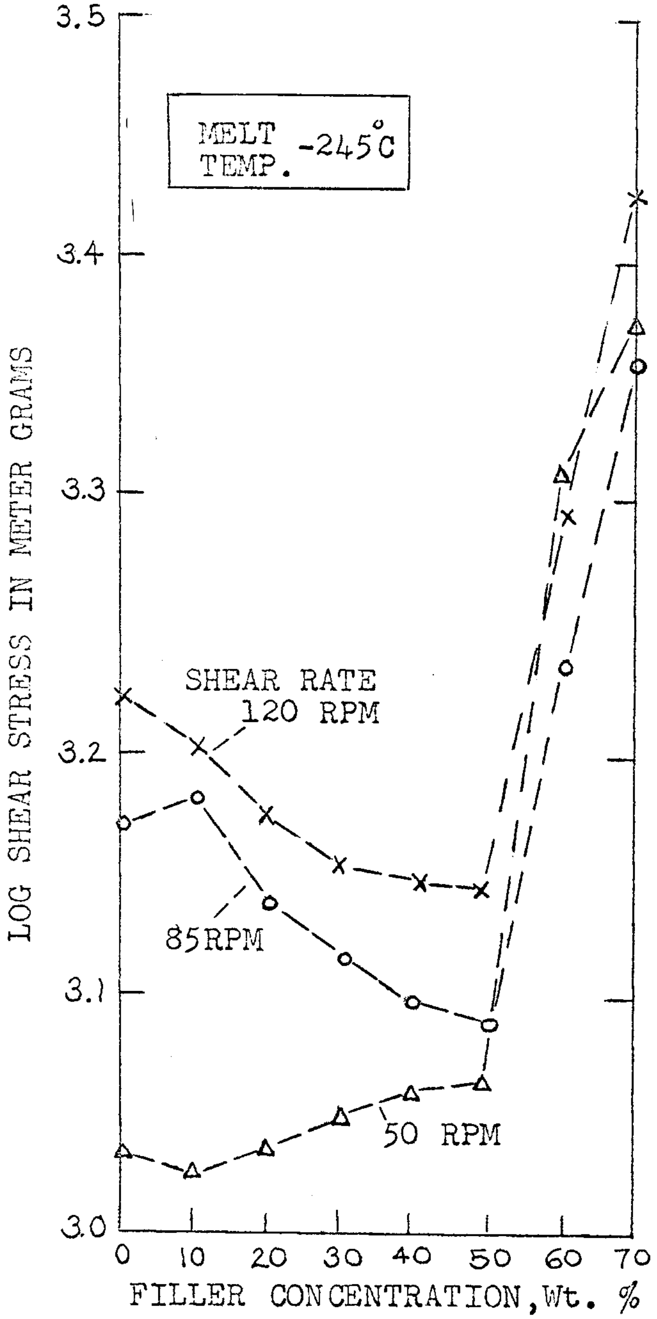
SHEAR STRESS AS A FUNCTION OF FILLER CONCENTRATION AT VARIOUS MIXING TIMES ,AT AN AVERAGE SHEAR RATE

FIGURE XX



SHEAR STRESS AS A FUNCTION OF FILLER CONCENTRATION AT VARIOUS SHEAR RATES, AVERAGED OVER TIME

FIGURE XXI



SHEAR STRESS AS A FUNCTION OF FILLER CONCENTRATION AT VARIOUS SHEAR RATES, AVERAGED OVER TIME levels, 210 and 245°C., and Figures XX and XXI indicate the relationship between log τ and concentration at three shear rates averaged over all time intervals.

As the shearing time increases, the shear stress decreases to a minimum shear stress which occurs at a higher concentration at the higher temperature of 245°C. After the minimum, the shear stress curves rise quickly and converge at a 70% filler concentration.

Since an increase in filler concentration increases the shear stress of the system and temperature decreases the shear stress of the polymer, it is evident from Figure XIX, that temperature plays a greater role in reducing shear stress at the lower concentrations, but gives way to the filler, which increases the shear stress at high filler loadings. This also explains the movement of the minimum shear stress value towards the higher concentration at the higher temperature.

If for example, the physical properties of a polyethylene clay system remained constant over the range of filler concentrations and it were desired to make use of the maximum output efficiency and cost economics of a particular mix in an extrusion operation, Figures XVIII and XIX would indicate that the curve at five minutes mix time and 245°C. offers the best economics. The residence time in the extruder would be short, the maximum loading high, and the output constant.

Extending this type of analysis to Figures XXX and XXXI, which are shear stress values at various concentrations of filler averaged over time at certain shear rates, shear stress will not change significantly up to 50% filler at 245°C. as a function of shear rate. Extruder output could then be increased by using the high shear rate.

The danger in going above 50% filler loading at 245°C. to attempt to lower raw material costs would be: (1) the inability to control material viscosity, (2) a greater chance of an error in formulation and (3) higher power requirements for the same shear rate.

VI CONCLUSIONS

Temperature Effects

A method has been devised by which the shear stress at a particular melt temperature can be converted to a corrected shear stress at a constant temperature in an isothermal system.

A plot of logτ vs $1/T_{abs.}$ at zero time(time at which the melt is homogeneous but not degraded by time) will predict a shear stress at any given temperature and be used to convert actual torque at various melt temperatures into a torque in a constant isothermal system temperature.

FigureVI, showing the change in log shear stress vs $1/T_{abs.}$ as a function of concentration describes the temperature dependency of shear stress. In a sense, the slopes in Figure VI indicate the energy of activation for flow.

Because of the frictional energy supplied to the material in the milling head by the action of the rotors, shear rate has a very significant effect on the rise of melt temperature. As the jacket temperature increased, the viscosity of the polymer-filler mixture decreased, thereby reducing the frictional heat build up and the amount of temperature rise in the polymer.

Flow Index

Analysis of the flow index, indicates increasingly non-Newtonian behavior at higher temperatures and a decrease in slope n (denoting more non-Newtonian behavior) with an increasing filler concentration.

The values for the flow index of virgin high density polyethylene obtained in this experiment are similar to those described in the literature.

The diluting effect of filler on polymer in the mixture does not follow the same effect experienced by the polymer in a Newtonian solution. As the polymer concentration decreases in the polymer-filler mixture, the behavior is more non-Newtonian. Conversely, as the polymer concentration increases in a Newtonian solvent, the fluid becomes increasingly non-Newtonian.

Data of other investigators also show that within the non-Newtonian flow region, the flow behavior index increases slightly with increases in temperature. This phenomenon was verified with virgin polyethylene in this experiment.

The results of this experiment indicate the same is not true when polyethylene is filled with clay. The flow behavior index decreases with an increase in temperature.

As the melt temperature of the clay filled system increases, the "grindstone" effect of filler particle on polymer molecules becomes more significant, most likely producing a greater amount of crosslinking and thereby increasing the system viscosity. On the other hand, filler particles will also prevent polymer molecules from decreasing in size and redispersing into a random configuration necessary for Newtonian behavior. It is assumed that the net effect produces a decrease in the rate of change of shear stress with shear rate.

Statistical Analysis

It was possible statistically to submit mixing time and its effect on shear stress to analysis by separating the experiment into two distinct areas; Case I, in which the shear stress was a function of temperature, shear rate and filler concentration; and Case II, in which the shear stress was a function of the same three variables and mixing time.

By doing this, two important things were accomplished: (1) Case I described the behavior of the polymer-filler mix without the factor of time.

For high density polyethylene, equation (9) in the text was used sucessfully to predict the shear stress of a higher molecular weight polyethylene analyzed by another experimentor. Unfortunately, no melt data is available for filled polymer melts and further comparisons were impossible.

(2) By comparing the results of Case I and Case II, the net effect of time on shear stress was isolated. Generally, it can be said that melt temperature, the largest contributor to a change in shear stress, is relatively unaffected by time, but some of the interactions of variables with time are significant. Mixing time decreases the apparent viscosity of the polymer in the polymer-filler mix and is the second most important contributor to a change in shear stress.

Regression Equations - Regression relationships, obtained from a least square analysis, were fitted to the data.

In Case I, the equation explained 97% of the variability, denoting and excellent correlation of variables. The equation may be used to predict any shear stress under a given set of conditions for a clay filled high density polyethylene.

It was also concluded that the equation holds very well for virgin polyethylene not only of the type used in this experiment, but for another high density polyethylene with a higher molecular weight. The procedure for determining the shear stress of another molecular weight polyethylene is simple and only entails a recalculation of the regression coefficient for each molecular weight. The higher the molecular weight, the greater the numerical value of the coefficient.

In the analysis of Case II, it was quite evident that the variable time introduced some unexplained variability. The second order equation used in explaining 97% of the variability of Case I could only explain 84% of the variability of Case II. However, considering the type of experiment and the number of variables involved, the second order equation is adequate.

Commercial Operations

As the filler concentration increases in the system, the material loses its elastic properties both in the melt and solid phases. Because of this, it can be generally said that flexural strength will decrease, flexural modulus will increase and all other properties will change as a function of the added rigidity imparted by the filler.

Filler concentration would be chosen mainly on the basis of the physical properties desired in the formed product; however, rheological melt data of the type presented in this report may screen out certain types of formulations from a processing point of view.

In order to take advantage of the melt properties of a clay filled polyethylene of the type analyzed in this experiment , for extrusion, it must be assumed for the present that the physical properties of the polymer-filler mixture will not change as the concentration of filler changes.

The investigation of shear stress data involving the variables of concentration, shear rate, melt temperature and shearing time would indicate that 1) a higher temperature, 2) a low residence time in the extruder and 3) a high shear rate within the 0 to 50% filler range (preferably 40 to 50% filler), would offer the best economics in terms of output, raw material costs and process control.

The danger in loading above 50% filler at these conditions in an attempt to reduce raw material costs would be 1) the inability to control material viscosity, 2) a greater chance of an error in formulation and 3) higher power requirements for the same shear rate.

Brabender Plasticorder

The instrument is an extremely useful tool for evaluating the melt characteristics of thermoplastics. However, in the past, the non-isothermal effect gave misleading information. If a method of the type developed in this experiment to eliminate the effect of varying melt temperature is used, more information can be obtained from this device than from most other melt rheological instruments.

VII RECOMMENDATIONS

One of the main concerns in any experiment that leads to empirical relationships is the testing of that relationship under conditions other than that of the experiment itself.

Because of the time allotted for this experiment, further testing of derived equations was impossible.

It is recommended that:

(1) Other fillers such as calcium carbonate, carbon black and asbestos be incorporated into high density polyethylene, other polyolefins and thermoplastics of all types and results compared to the results obtained in this experiment.

(2) Brabender data on various molecular weight high density polyethylenes be collected and the equations derived in this experiment tested against these materials.

(3) Results obtained in this experiment be carefully compared to results obtained in capillary type rheometers under a controlled experiment.

(4) A device similar to the Brabender be constructed with accommodations for making the system isothermal.

VIII APPENDIX

NOMENCLATURE

A	Constant in Arrhenius Equation
b_o	Constant in regression equations
b_i, b_{ii}, b_{ij}	Regression coefficients for equations 1, 2, and 3
c	Filler concentration, weight %
E	Energy of activation for viscous flow
e	Natural log base
f	Degrees of freedom for statistical analysis
F	Statistical F test ratio
m	Constant equal to d log τ/d log 1/T in meter grams °K
n	Flow behavior index equal to d log τ/d log γ in meter grams rpm
R	Universal gas constant
r	Distance in ft. etc.:
T	Absolute temperature
t	Time under shear, minutes
u	Velocity, ft. per sec.
x_i	Main variable effect in units of rep, °C. or % conc.
x_i^2	Quadratic variable effect, rpm, °C or % conc.
$x_i\ x_j$	Interaction of variables, rpm, °C. or conc.
$\hat{y}$	Log of shear stress, meter grams
Greek	
T	Temperature rise of polymer above Brabender Jacket temperature, °C.
η	Newtonian viscosity, lb. sec/in.
τ	Shear stress, meter grams torque at melt temperature T
τ_o	Shear stress, meter grams torque at melt temperature T_o
$\dot{\gamma}$	Shear rate, rpm

TABLE VI

F TEST RESULTS

(CASE I)

VARIABLES	CALCULATED F RATIO $\left(\frac{\text{Mean Square}}{\text{Standard Error}}\right)$	TABULATED F VALUE $F_{.05}(f_1\ f_2)^*$
Temperature	240	F(1,14)= 4.60
Shear Rate	254	F(2,14)= 3.74
Temp.-Shear Rate	1.11	F(2,14)= 3.74
Concentration	319	F(7,14)= 2.76
Temperature-Concentration	3.54	F(7,14)= 2.76
Shear Rate-Concentration	2.65	F(14,14)=2.50

* .05=.05 probobility of a larger value of F

f_1= Degrees of Freedom for variable being tested

f_2= Degrees of Freedom for Standard Error

TABLE VII

F TEST RESULTS

(CASE II)

VARIABLES	CALCULATED F RATIO $\left(\frac{\text{Mean Square}}{\text{Standard Error}}\right)$	TABULATED F VALUE $F_{.05}(f_1 f_2)$
Time	194	F (3,42) = 3.45
Temperature	505	F (1,42) = 5.41
Time-Temp.	4.38	F (1,42) = 3.45
Shear Rate	166	F (2,42) = 4.02
Time-Shear Rate	4.30	F (6,42) = 2.72
Temp.-Shear Rate	3.68	F (2,42) = 4.02
Time-Temp-Shear Rate	1.61	F (6,42) = 272
Concentration	380	F (7,42) = 2.60
Time-Conc.	14.9	F (21,42)= 2.03
Temp.-Conc.	25.3	F (7,42) = 260
Time-Temp-Conc.	5.63	F (21,42)= 2.03
Shear Rate-Conc.	8.73	F (14,42)= 2.20
Time-Shear Rate-Conc.	1.26	F (42,42)= 1,86
Temp-Shear Rate-Conc.	4.83	F (14,42)= 2.20

TABLE VIII
REGRESSION COEFFICIENTS
CASE I

REGRESSION COEFFICIENT	NUMERICAL VALUE
b_1	$-1.93\text{x}10^{-3}$
b_2	$4.90\text{x}10^{-3}$
b_3	$-6.00\text{x}10^{-4}$
b_{12}	$-6.00\text{x}10^{-6}$
b_{13}	$1.20\text{x}10^{-5}$
b_{23}	$-1.60\text{x}10^{-5}$
b_{22}	$-6.50\text{x}10^{-6}$
b_{33}	$5.00\text{x}10^{-5}$

b_1 = Coefficient of Temperature
b_2 = Coefficient of Shear Rate
b_3 = Coefficient of Concentration

TABLE IX
REGRESSION COEFFICIENTS
CASE II

REGRESSION COEFFICIENT	NUMERICAL VALUE
b_1	$5.25\text{x}10^{-3}$
b_2	$-1.07\text{x}10^{-3}$
b_3	$3.05\text{x}10^{-3}$
b_4	$9.94\text{x}10^{-3}$
b_{11}	$2.30\text{x}10^{-4}$
b_{33}	$-1.27\text{x}10^{-5}$
b_{44}	$1.40\text{x}10^{-4}$
b_{14}	$-1.24\text{x}10^{-4}$
b_{13}	$-4.55\text{x}10^{-5}$
b_{12}	$-4.24\text{x}10^{-5}$
b_{23}	$7.00\text{x}10^{-6}$
b_{24}	$-5.66\text{x}10^{-5}$
b_{34}	$-2.66\text{x}10^{-5}$

b_1 = Coefficient of Time
b_2 = Coefficient of Temp.
b_3 = Coefficient of Shear Rate
b_4 = Coefficient of Conc.

TABLE XVII
RECORDED BRABENDER SHEAR STRESSES AND MELT TEMPS.

RUN NO.	JACKET TEMP.°C	SHEAR RATE rpm	FILLER CONC.%	MIX TIME 5 min		MIX TIME 10 min		MIX TIME 15 min		MIX TIME 20 min	
				TORQUE m-gms	TEMP. °C	TORQUE m-gms	TEMP. °C	TORQUE m-gms	TEMP. °C	TORQUE m-gms	TEMP. °C
1	177	50	0	1475	189	1475	189	1460	190	1450	189
			10	1575	191	1550	191	1500	191	1400	190
			20	1650	192	1625	192	1575	191	1460	191
			30	1800	193	1775	193	1625	193	1500	191
			40	2000	196	2000	196	1950	196	1825	195
			50	2200	197	2175	197	2175	198	2150	199
			60	2500	201	2475	201	2475	201	2475	200
			70	3150	210	3350	210	3350	210	3300	209
2	177	85	0	1750	201	1650	210	1550	207	1535	207
			10	1750	206	1550	210	1450	206	1350	204
			20	1780	210	1490	210	1370	205	1290	203
			30	1950	210	1650	210	1550	206	1400	204
			40	2250	215	1900	215	1675	211	1600	209
			50	2500	220	2350	222	1850	215	1500	206
			60	2850	217	2800	222	2700	228	2700	228
			70	3300	227	3200	237	3000	235	2850	233
3	177	120	0	1900	220	1750	227	1800	229	1850	230
			10	1800	226	1550	224	1500	221	1425	220
			20	1850	225	1500	222	1350	218	1300	216
			30	1900	227	1600	225	1400	220	1350	216
			40	2200	232	1650	225	1450	219	1300	214
			50	2300	238	1600	225	1400	215	1300	212
			60	2800	246	2500	248	2350	244	2200	240
			70	3150	250	2700	250	2600	246	2500	243

TABLE XVII CONTINUED

RUN NO	JACKET TEMP. °C	SHEAR RATE rpm	FILLER CONC. %	MIX TIME 5 min.		MIX TIME 10 min.		MIX TIME 15 min,		MIX TIME 20 min.	
				TORQUE m-gms	TEMP. °C	TORQUE m-gms	TEMP. °C	TORQUE m-gms	TEMP. °C	TORQUE m-gms	TEMP. °C
4	199	50	0	1375	206	1325	211	1300	212	1275	211
			10	1425	206	1350	212	1200	210	1050	209
			20	1475	210	1300	212	1200	211	1100	210
			30	1550	210	1400	213	1300	212	1225	211
			40	1850	212	1650	216	1450	214	1400	213
			50	2100	216	1900	219	1600	216	1350	213
			60	2500	215	2475	223	2400	224	2350	223
			70	3000	220	2975	228	2900	228	2800	227
5	199	85	0	1600	228	1575	228	1600	226	1625	220
			10	1650	224	1500	226	1450	226	1400	225
			20	1600	222	1450	223	1350	222	1300	220
			30	1800	226	1500	226	1300	222	1200	219
			40	2000	230	1600	228	1450	225	1300	220
			50	2300	233	1600	230	1300	221	1200	219
			60	2700	238	2450	243	2250	240	2050	237
			70	3000	244	2700	246	2500	244	2400	242
6	199	120	0	1700	236	1625	241	1675	245	1700	246
			10	1700	243	1700	246	1700	246	1700	246
			20	1700	242	1550	242	1550	242	1500	242
			30	1700	244	1450	240	1400	238	1400	238
			40	1800	246	1500	240	1300	234	1250	230
			50	2050	250	1350	238	1100	228	1000	224
			60	2500	260	2000	254	1500	243	1100	230
			70	2900	265	2400	260	2300	257	2250	256

TABLE XVII CONTINUED

RUN NO.	JACKET TEMP. °C	SHEAR RATE rpm	% FILLER CONC.	MIX TIME 5 min		MIX TIME 10 min		MIX TIME 15 min		MIX TIME 20 min	
				TORQUE m-gms	TEMP. °C	TORQUE m-gms	TEMP. °C	TORQUE m-gms	TEMP. °C	TORQUE m-gms	TEMP. °C
7	219	50	0	1250	224	1200	229	1200	229	1200	230
			10	1300	227	1225	230	1200	231	1200	230
			20	1350	228	1250	231	1200	230	1150	230
			30	1400	230	1350	232	1250	231	1200	230
			40	1650	233	1350	233	1300	231	1150	230
			50	1900	233	1450	234	1200	230	1125	230
			60	2325	237	2150	240	2000	239	1850	238
			70	2850	240	2550	244	2450	243	2325	240
8	219	85	0	1500	237	1500	243	1500	244	1500	245
			10	1525	240	1550	246	1550	246	1550	247
			20	1500	240	1400	246	1350	246	1350	247
			30	1500	242	1350	243	1250	241	1250	240
			40	1700	245	1350	242	1150	239	1050	237
			50	1900	250	1300	244	1000	237	850	233
			60	2300	253	1950	253	1600	247	1200	241
			70	2500	257	2200	259	2050	256	2000	255
9	219	120	0	1500	251	1450	257	1400	257	1300	256
			10	1600	255	1550	260	1450	258	1400	255
			20	1650	258	1500	258	1500	260	1500	259
			30	1600	257	1300	254	1300	252	1350	252
			40	1600	258	1250	252	1100	246	1100	245
			50	1700	262	1150	262	950	259	850	248
			60	2200	272	1700	265	1250	255	800	241
			70	2300	277	1950	268	1850	264	1800	260

TABLE XVIII

(Recorded and calculated Shear Stress Data-Case I)

Observation	Y Value	Y Estimate	Residual
1	3.12222	3.12774	-0.00552
2	3.15381	3.14446	0.00936
3	3.16879	3.17219	-0.00340
4	3.19033	3.21095	-0.02062
5	3.27875	3.26072	0.01803
6	3.33244	3.32152	0.01092
7	3.39794	3.39333	0.00461
8	3.45484	3.47616	-0.02131
9	3.21748	3.22326	-0.00578
10	3.24304	3.23438	0.00865
11	3.25042	3.25653	-0.00611
12	3.29003	3.28969	0.00035
13	3.36173	3.33387	0.02786
14	3.41497	3.38907	0.02591
15	3.45484	3.45529	-0.00044
16	3.49831	3.53252	-0.03421
17	3.30103	3.30292	-0.00189
18	3.30103	3.30845	-0.00742
19	3.30103	3.32500	-0.02397
20	3.34044	3.35257	-0.01212
21	3.42160	3.39115	0.03045
22	3.45025	3.44076	0.00949
23	3.50106	3.50138	-0.00032
24	3.57302	3.57302	-0.00248

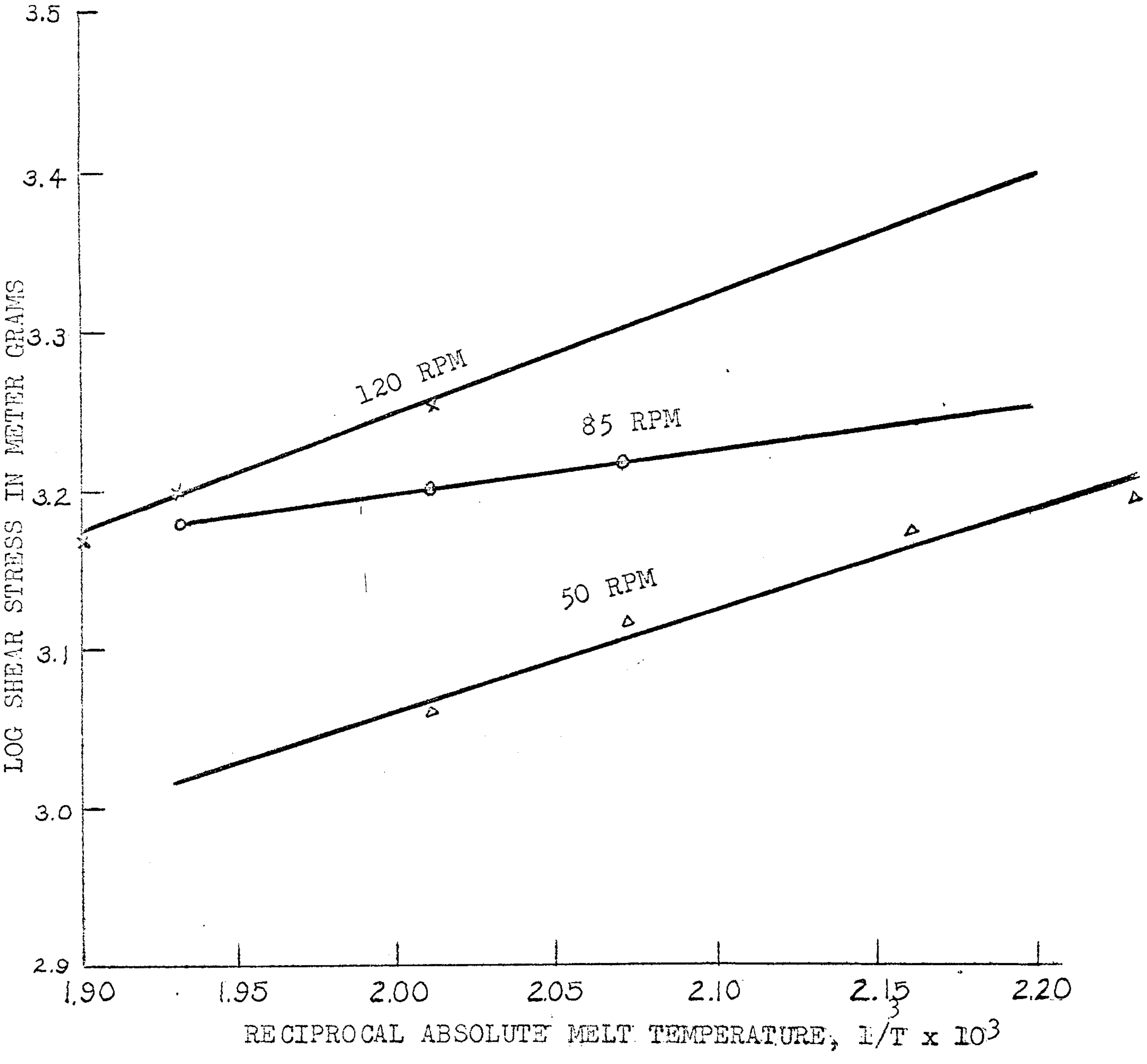
TABLE XVIII(continued)

(Recorded and calculated Shear Stress Data-Case I)

Observation	Y Values	Y Estimate	Residual
25	3.01284	3.04886	-0.03602
26	3.08279	3.06978	0.01301
27	3.10037	3.10171	-0.00134
28	3.12057	3.14467	-0.02409
29	3.21219	3.19864	0.01355
30	3.28103	3.26363	0.01740
31	3.38021	3.33964	0.04057
32	3.41162	3.42667	-0.01505
33	3.17609	3.13651	0.03958
34	3.19033	3.15184	0.03850
35	3.16137	3.17818	-0.01681
36	3.17609	3.21554	-0.03945
37	3.23045	3.26392	-0.03347
38	3.34242	3.32332	0.01911
39	3.39794	3.39373	0.00421
40	3.44716	3.47517	-0.02801
41	3.22401	3.20830	0.01571
42	3.23045	3.21803	0.01242
43	3.23045	3.23878	-0.00833
44	3.23045	3.27055	-0.04010
45	3.27875	3.31333	-0.03458
46	3.38917	3.36714	0.02203
47	3.46240	3.43196	0.03044
48	3.51851	3.50780	0.01071

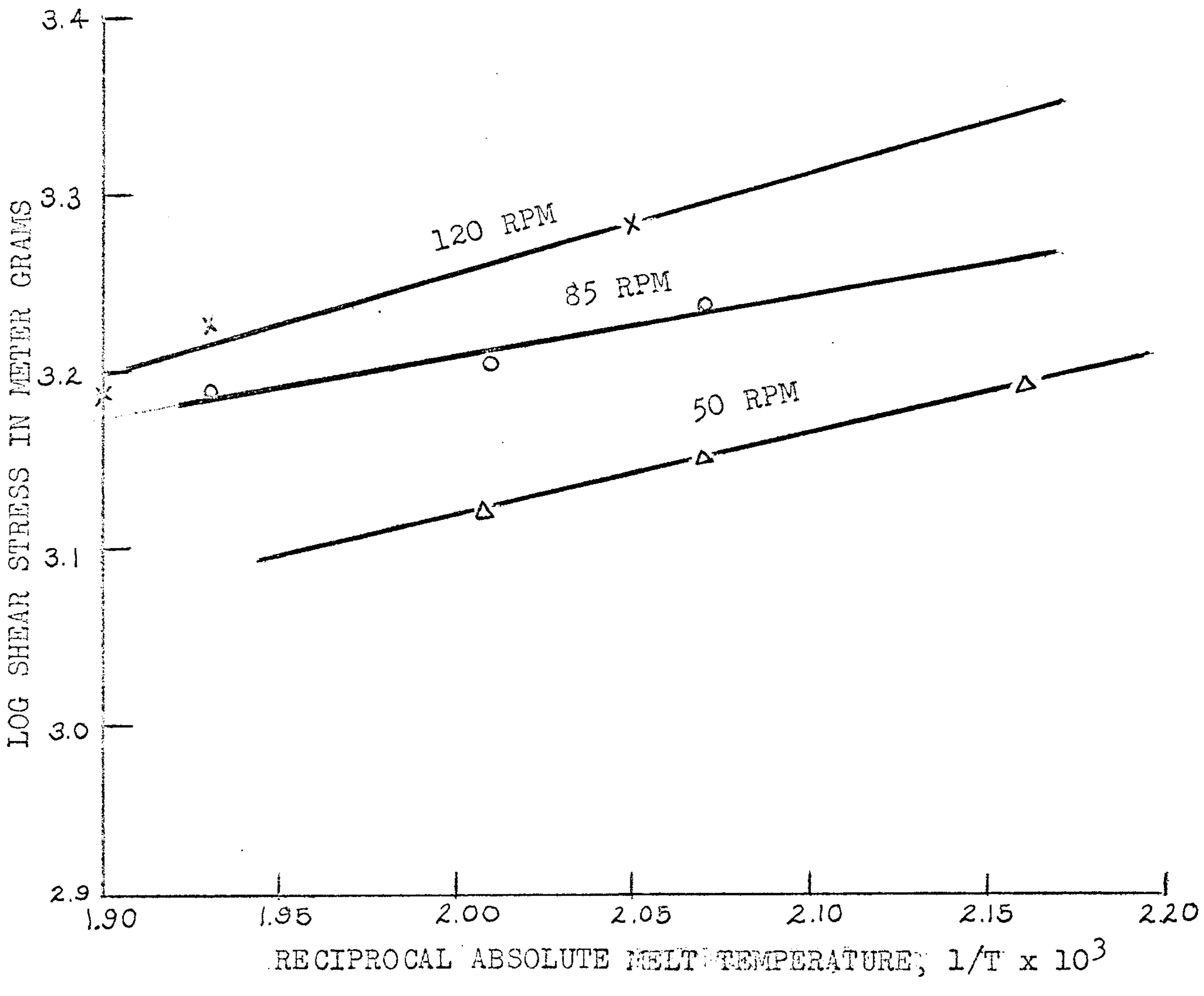
Test of Extreme Residuals Range of Residuals 0.081

FIGURE XXII



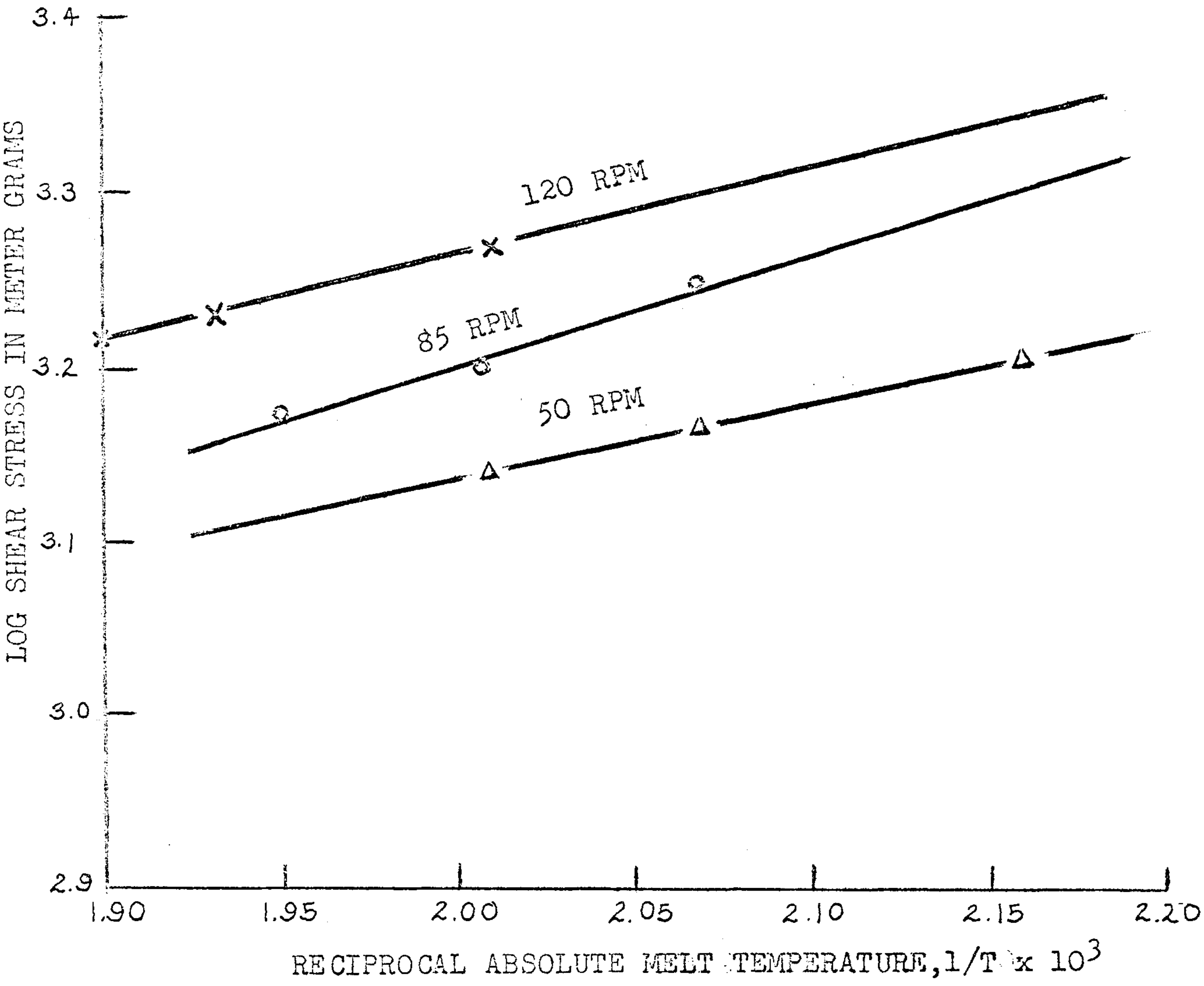
SHEAR STRESS AS A FUNCTION OF
ABSOLUTE MELT TEMPERATURE AT VARIOUS
SHEAR RATES
(0 % FILLER CONCENTRATION)

FIGURE XXIII



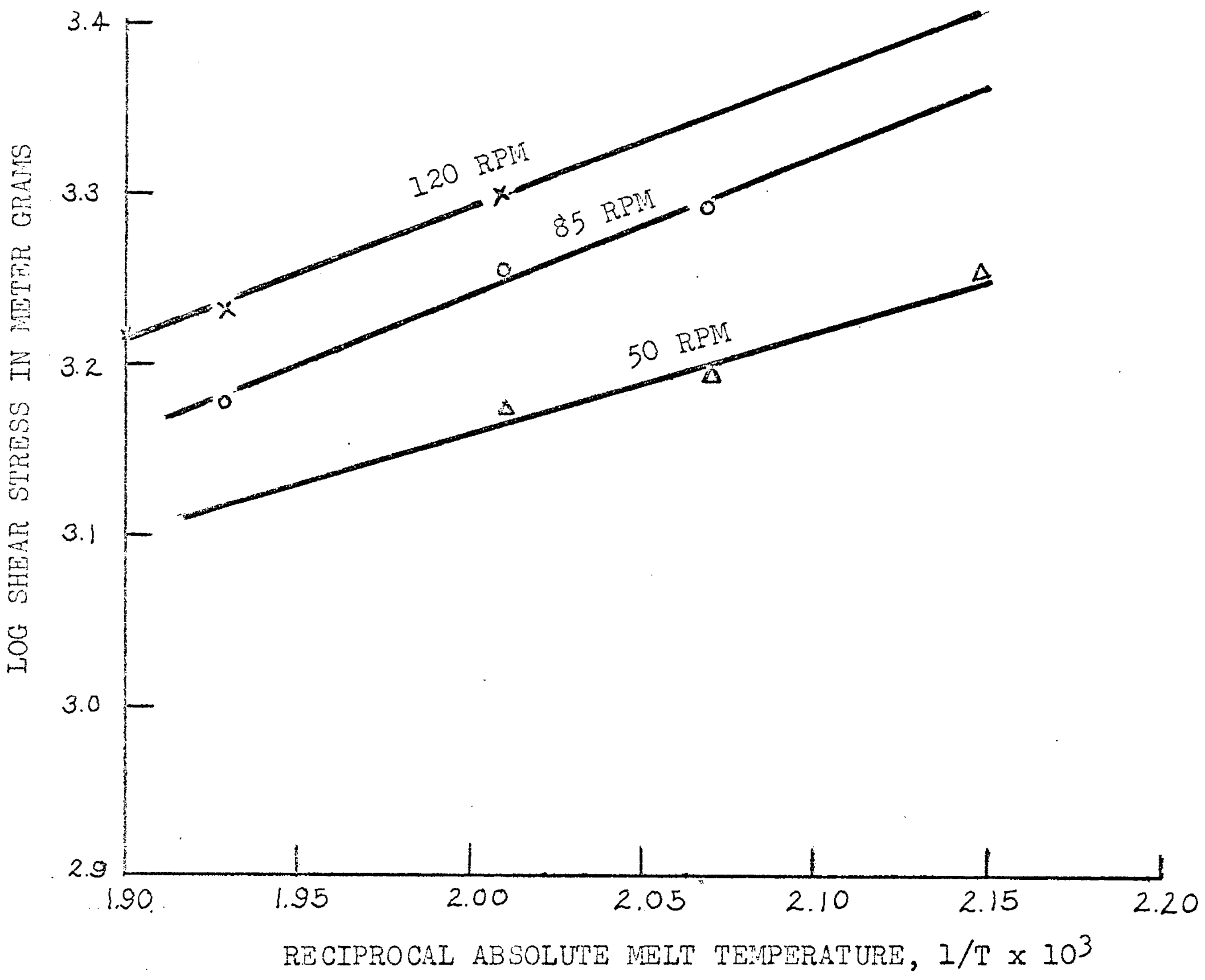
SHEAR STRESS AS A FUNCTION OF ABSOLUTE
MELT TEMPERATURE AT VARIOUS
SHEAR RATES
(10 % FILLER CONCENTRATION)

FIGURE XXIV



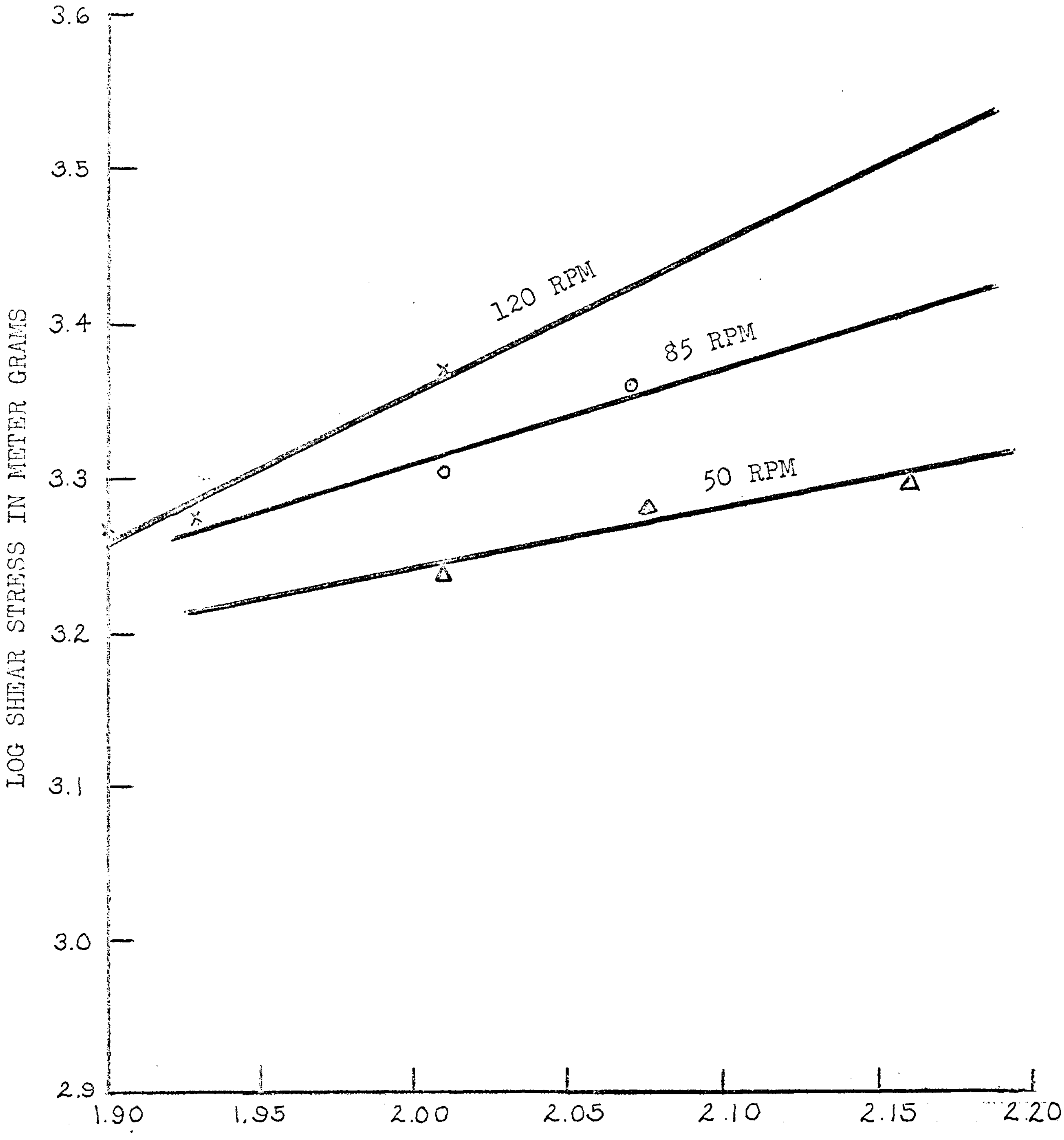
SHEAR STRESS AS A FUNCTION OF ABSOLUTE MELT TEMPERATURE AT VARIOUS SHEAR RATES
(20 % FILLER CONCENTRATION)

FIGURE XXV



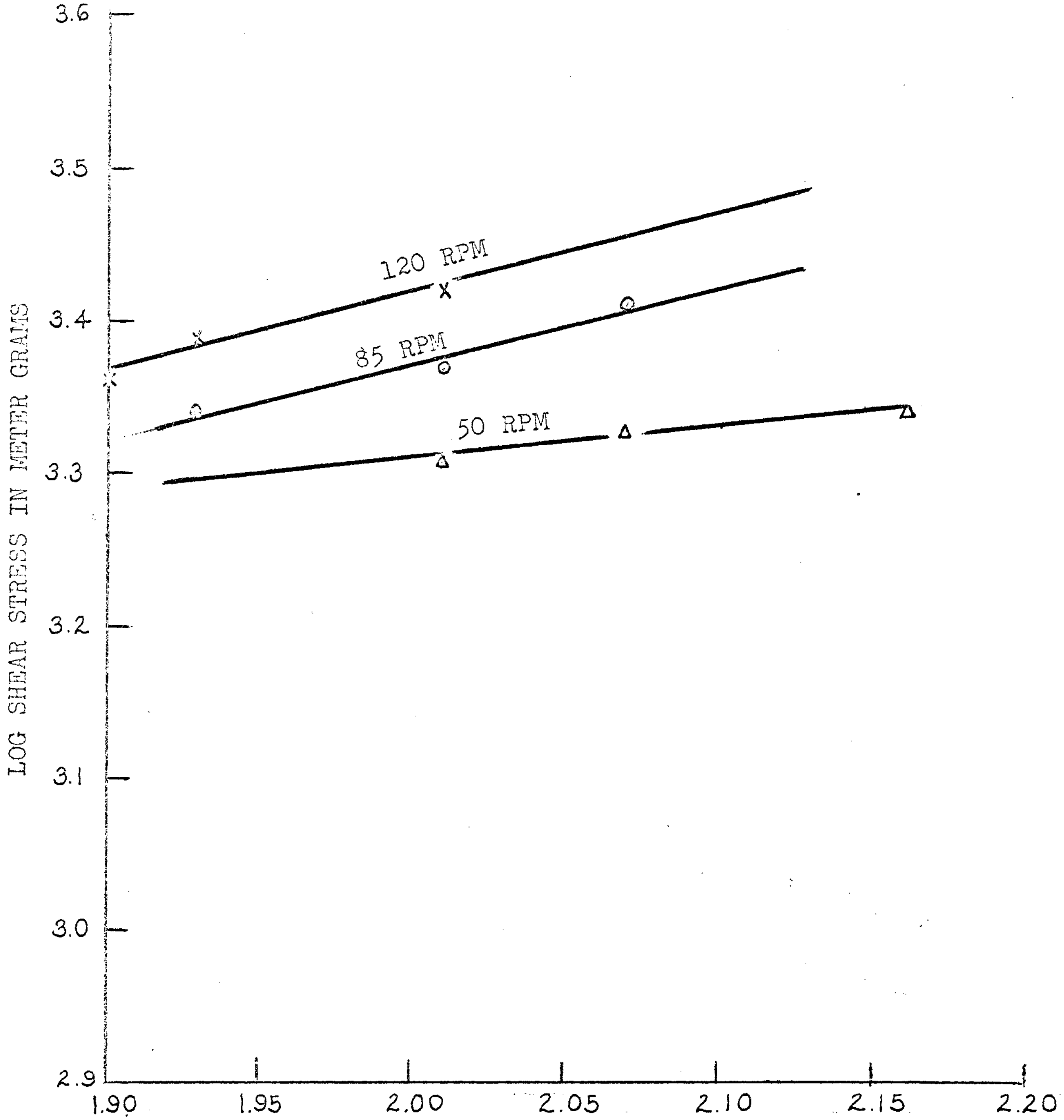
SHEAR STRESS AS A FUNCTION OF
ABSOLUTE MELT TEMPERATURE AT VARIOUS
SHEAR RATES
(30 % FILLER CONCENTRATION)

FIGURE XXVI



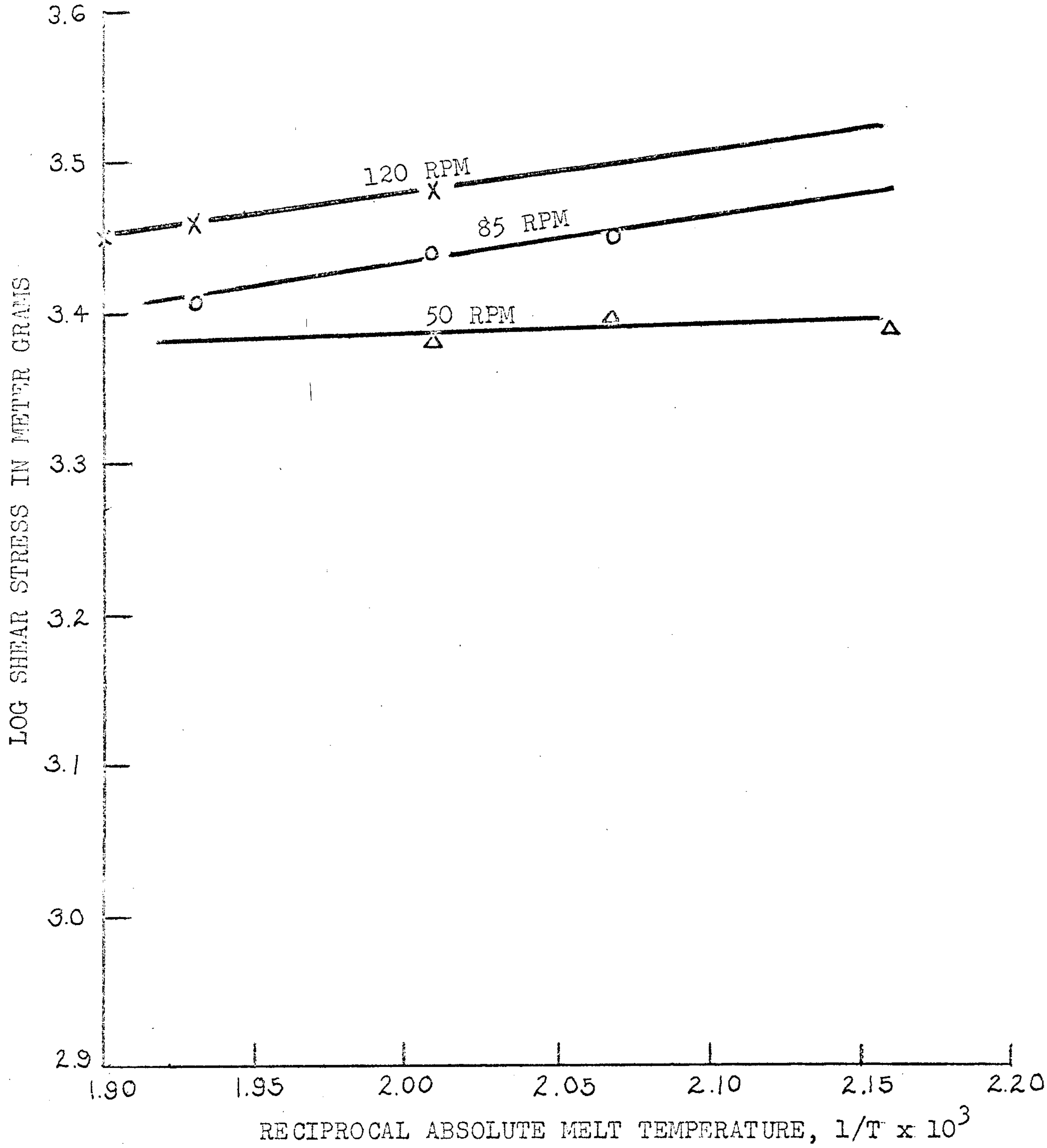
SHEAR STRESS AS A FUNCTION OF
ABSOLUTE MELT TEMPERATURE AT VARIOUS
SHEAR RATES
(40 % FILLER CONCENTRATION)

FIGURE XXVII



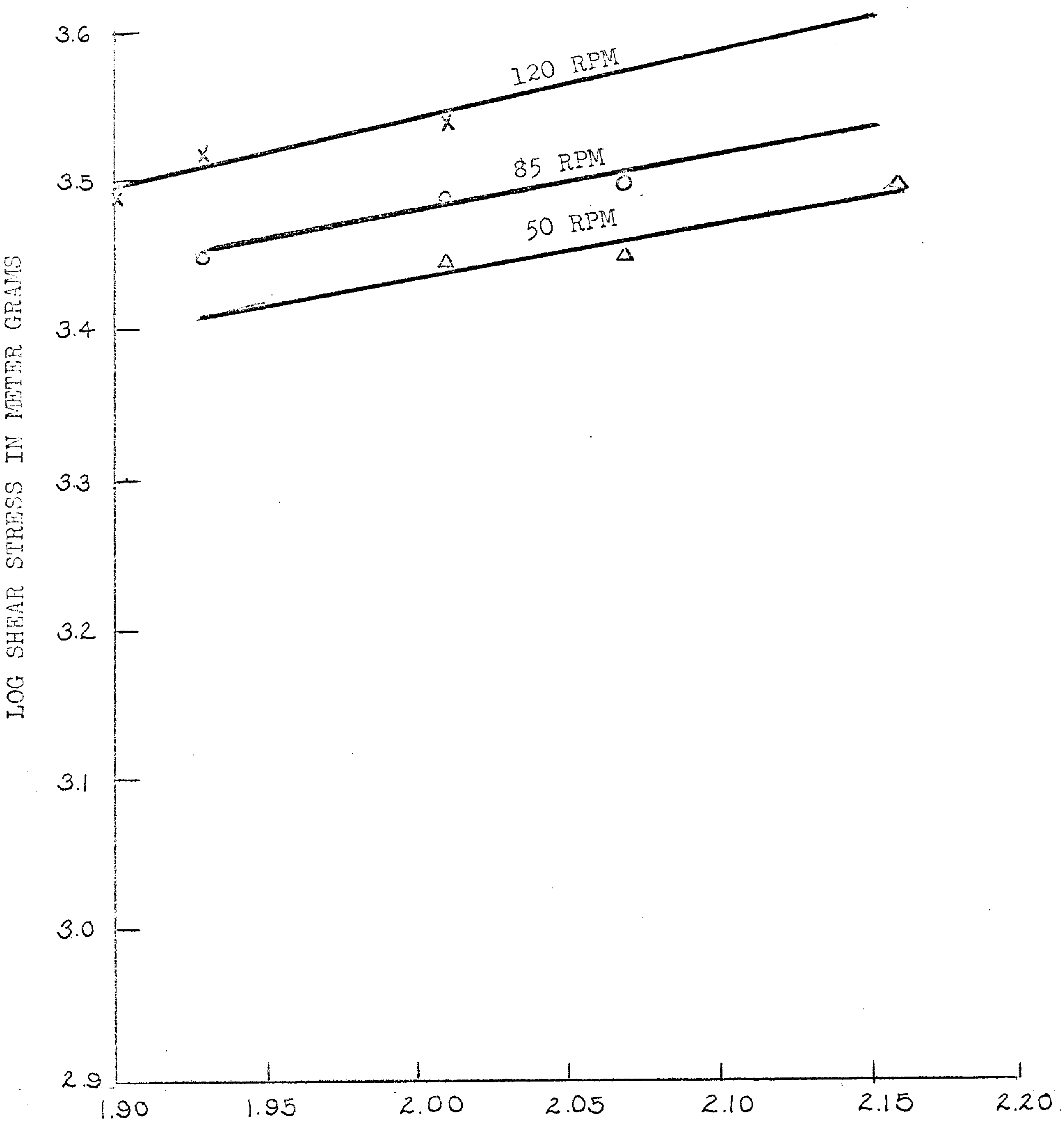
SHEAR STRESS AS A FUNCTION OF
ABSOLUTE MELT TEMPERATURE AT VARIOUS
SHEAR RATES
(50 % FILLER CONCENTRATION)

FIGURE XXVIII



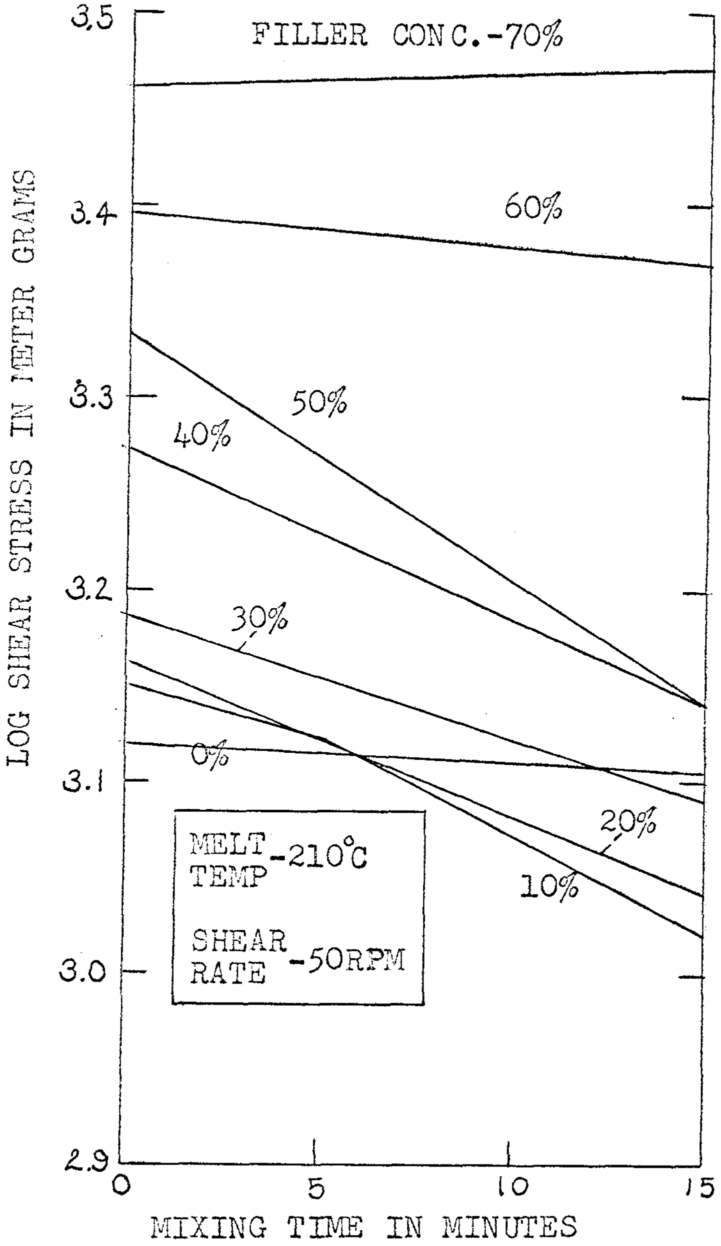
SHEAR STRESS AS A FUNCTION OF
ABSOLUTE MELT TEMPERATURE AT VARIOUS
SHEAR RATES
(60 % FILLER CONCENTRATION)

FIGURE XXIX



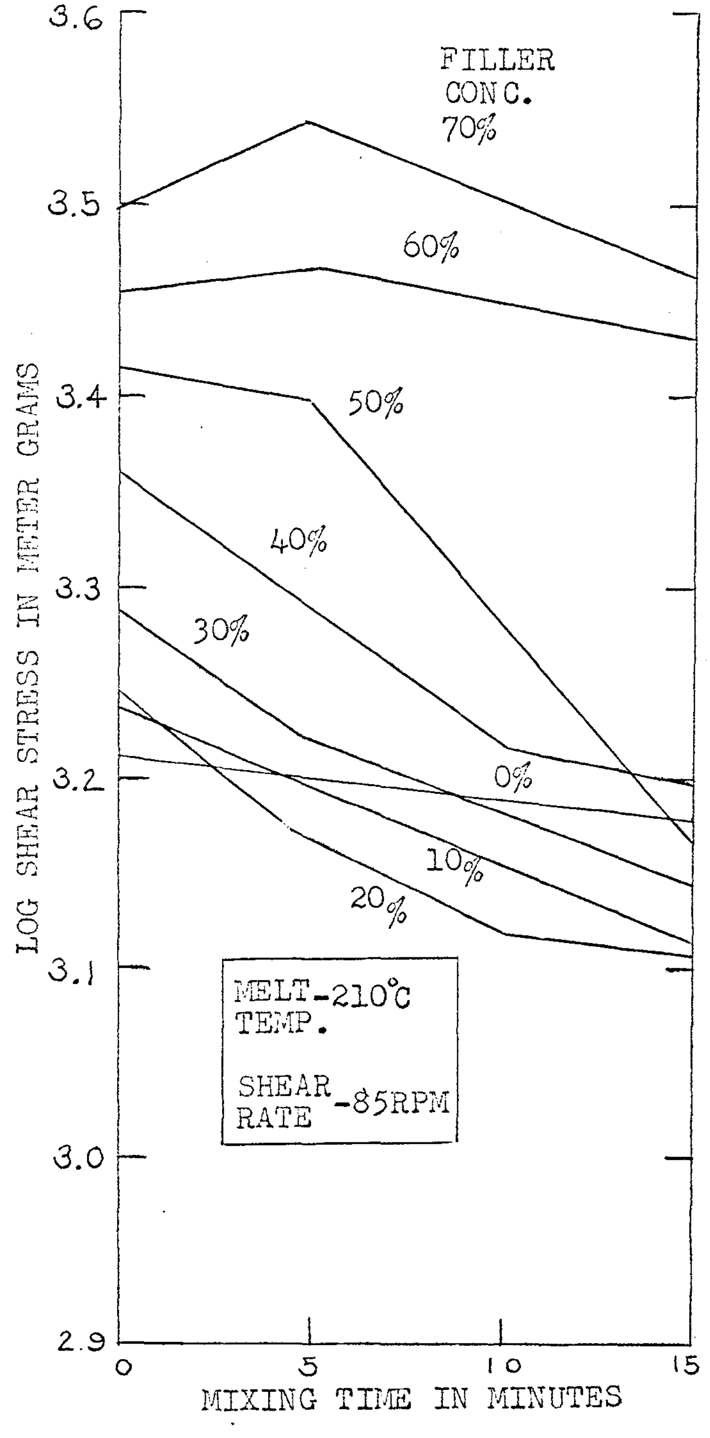
SHEAR STRESS AS A FUNCTION OF
ABSOLUTE MELT TEMPERATURE AT VARIOUS
SHEAR RATES
(70 % FILLER CONCENTRATION)

FIGURE XXX



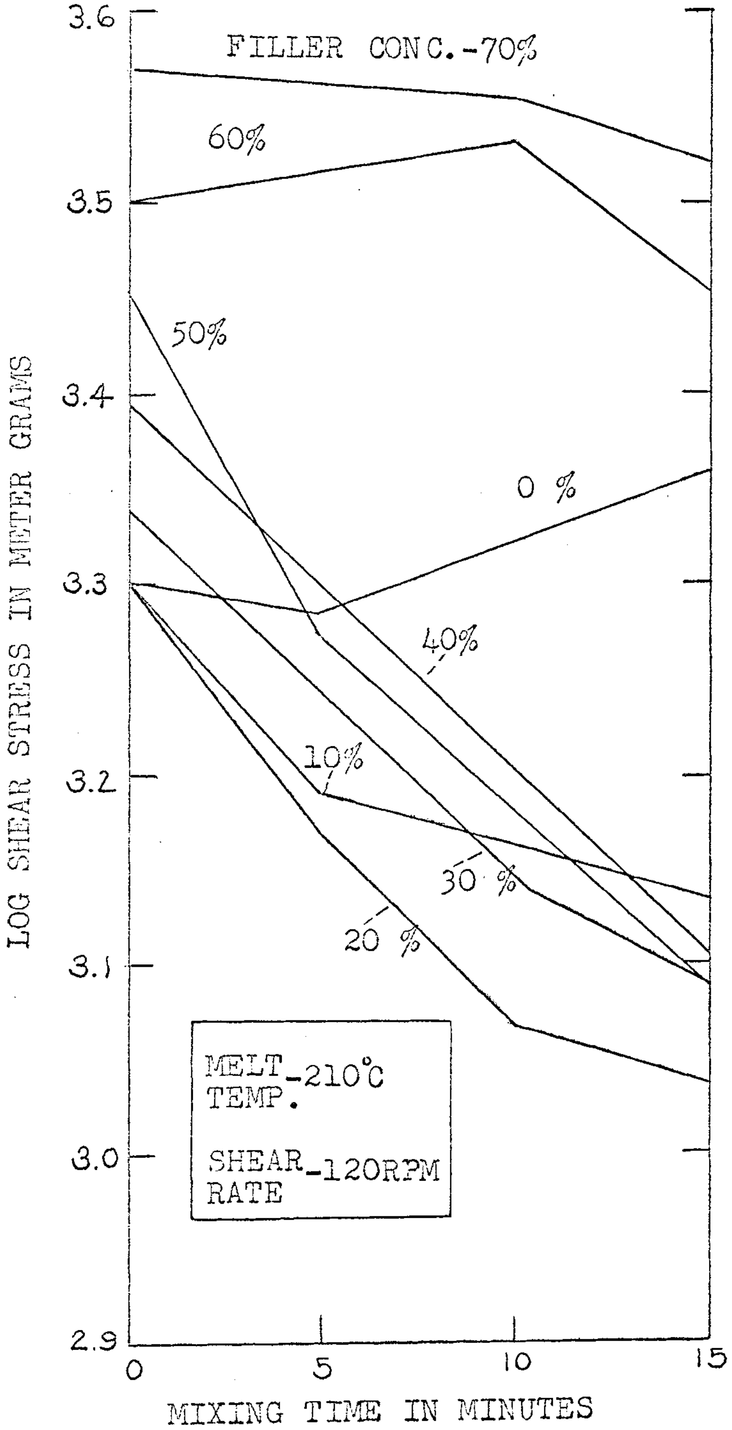
CONVERTED SHEAR STRESS AS A FUNCTION OF MIXING TIME AT VARIOUS CONCENTRATIONS OF FILLER

FIGURE XXXI



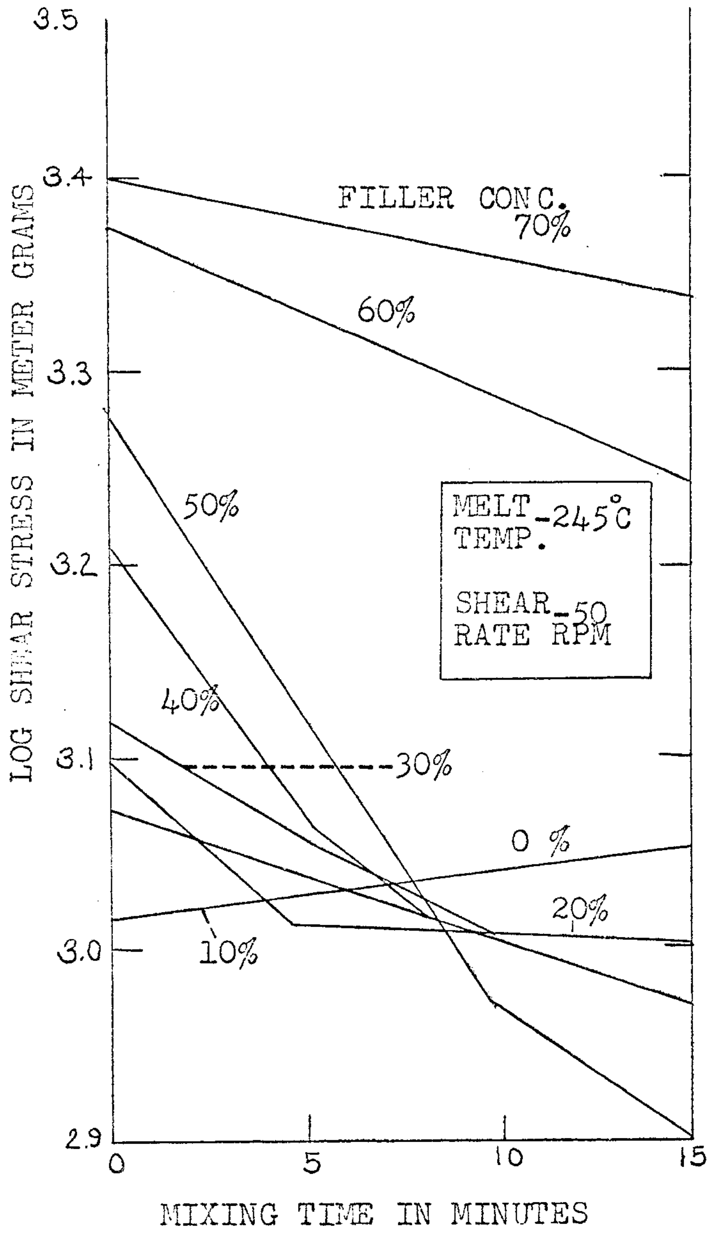
CONVERTED SHEAR STRESS AS A FUNCTION OF MIXING TIME AT VARIOUS CONCENTRATIONS OF FILLER

FIGURE XXXII



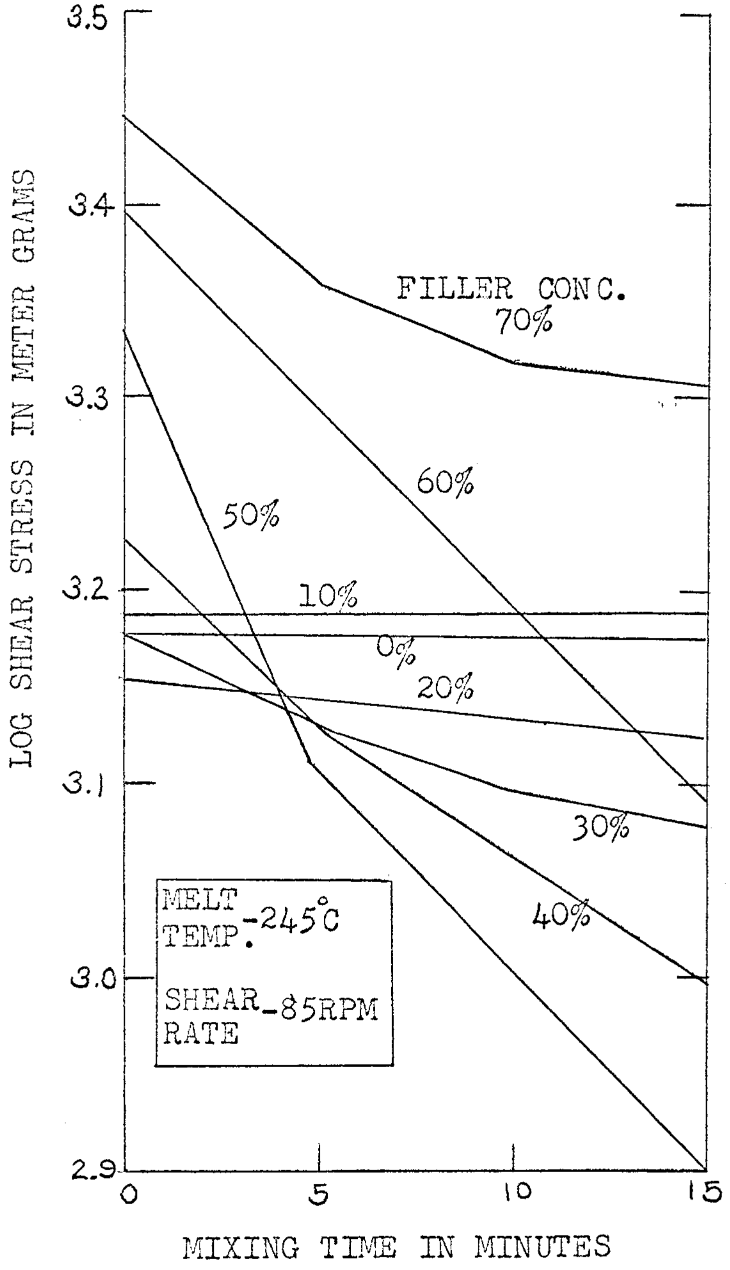
CONVERTED SHEAR STRESS AS A FUNCTION OF MIXING TIME AT VARIOUS CONCENTRATION OF FILLER

FIGURE XXXIII



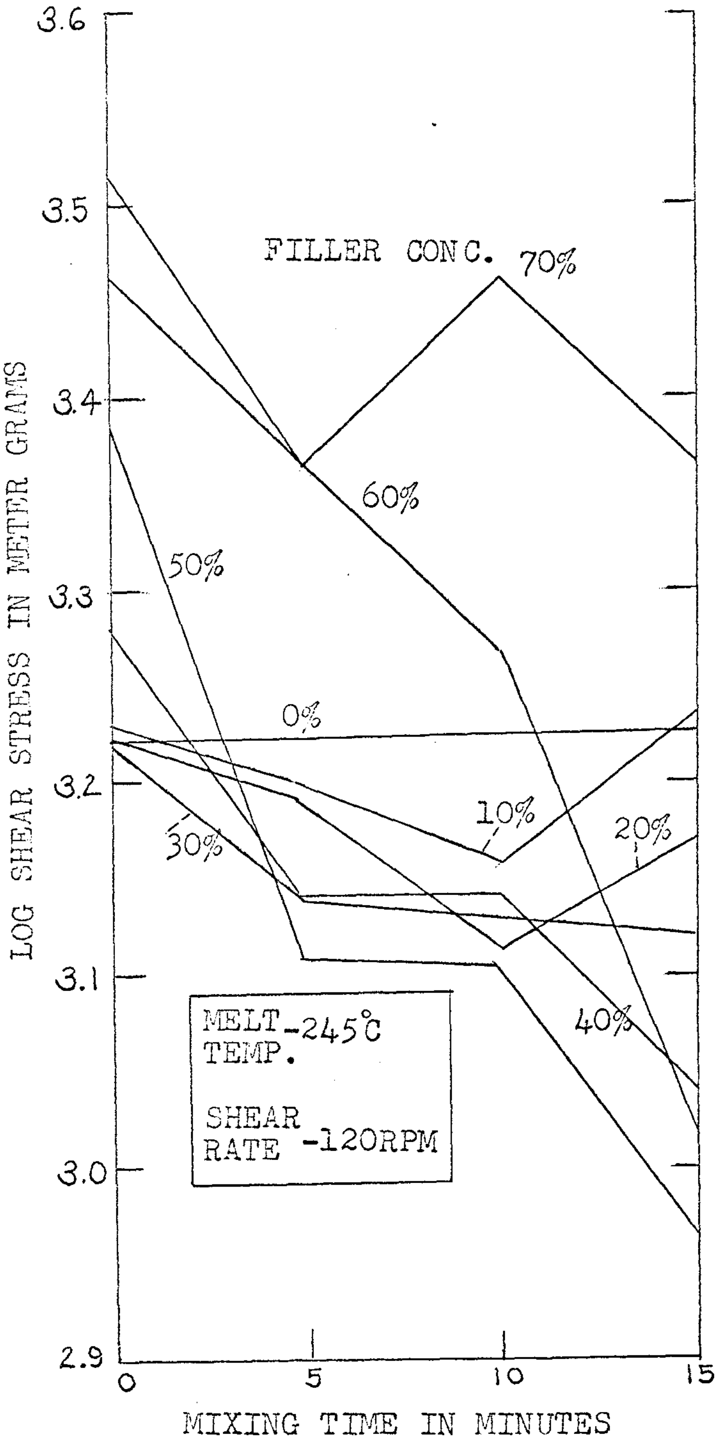
CONVERTED SHEAR STRESS AS A FUNCTION OF MIXING TIME AT VARIOUS CONCENTRATIONS OF FILLER

FIGURE XXXIV



CONVERTED SHEAR STRESS AS A
FUNCTION OF MIXING TIME AT VARIOUS
CONCENTRATIONS OF FILLER

FIGURE XXXV



CONVERTED SHEAR STRESS AS A FUNCTION OF MIXING TIME AT VARIOUS CONCENTRATIONS OF FILLER

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