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THE EFFECTS OF EXTRUSION ON THE
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OF GENERAL-PURPOSE POLYSTYRENE.

The Ohio State University, Ph.D., 1973
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THE EFFECTS OF EXTRUSION
ON THE MOLECULAR AND RHEOLOGICAL PROPERTIES
OF GENERAL-PURPOSE POLYSTYRENE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Paul W. Springer, B.A., M.S.

* * * * *

The Ohio State University

1973

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SUMMARY

The effects of extrusion on the properties of general-purpose polystyrene were studied with particular attention on the molecular and rheological properties.

A new type of rheometer was designed because of the need to maintain constant operating conditions inside the extruder from recycle to recycle. A twin-slit concept was employed which permitted a variation of flow in one channel for the determination of rheology data without changes in the total extruder output. This was accomplished by use of a second flow channel. The slit geometry was chosen to enable flush mounts of the electronic pressure transducers which were located along the channel. With these, the axial pressure distribution was obtained. From this in turn, the wall shear stress was calculated. The apparent shear rate was determined by measurement of the polymer flow rate.

Two samples of general-purpose polystyrene were recycled 5 times through a 2 1/2-inch extruder, one at a high (100 RPM) and one at a low (50 RPM) screw speed. Rheological measurements were made on the material for each pass. For the 5 passes at the low screw speed, a 37% decrease in a low shear apparent viscosity (at 10 sec^{-1}) was observed. A single pass at 100 RPM reduced this apparent viscosity 18% below the Pass 1, 50 RPM material. The next 4 passes reduced the viscosity another 35%.

Changes in molecular weight were followed by gel permeation chromatography. Five passes created a 16% reduction in weight-average molecular weight. Number-average molecular weight changes were small and polydispersities decreased. This was true at both screw speeds.

An effect of extruder screw speed (prior shear) on the rheological measurements was discovered. The effect was evidenced by a 10% reduction of the intercept of the log weight-average molecular weight versus log low shear apparent viscosity curves. Further evidence of the screw speed effect was observed on the primary and secondary normal stresses.

The independent variables for this study were the extruder operating conditions. These variables were represented by a characteristic parameter, ΣE_D --the available energy for degradation. The characteristic parameter ΣE_D incorporated the mechanical and thermal energy effects which cause polymer degradation. Low shear apparent viscosity and the weight-average molecular weight followed an Arrhenius-type behavior with ΣE_D replacing temperature. The slope of a plot of $1/\Sigma E_D$ versus log weight-average molecular weight and log low shear apparent viscosity gives a measure of the speed of the degradation process. The influence of screw speed on polymer degradation was observed by comparison of the slopes. Up to a critical value of ΣE_D , the higher screw speed degraded the polymer more rapidly than the low screw speed. After the critical point, the influence of screw speed disappeared and the rate of degradation increased. With an assumed molecular polymer structure, the results can be interpreted. However, any such interpretation must be realized within the proper limits. That is, any model for the polymer melt structure is hypothetical.

Extensive measurements of the elastic properties were made by using the exit pressure technique. Recycle had no effect on these measurements; however, the effects of screw speed were present once again. The high screw speed level experiments decreased the values of the elastic parameters 2 to 3 fold.

CHAPTER I

INTRODUCTION

The processing of thermoplastics is a multi-million dollar industry that annually processes billions of pounds of material. In addition to the final product fabrication, most thermoplastics undergo some form of processing during production. During the processing steps, the thermoplastic is exposed to heat and shear. Extrusion, blow molding and injection molding are the three major processing techniques that employ both shear and heat. While material being vacuum-formed or thermo-formed is exposed to heat and very low shear, the material has been previously extruded. Thermal and mechanical energy are therefore necessary for both the production and processing of thermoplastic polymeric materials.

One or both of the above mentioned energy forms can provide the energy to break chemical bonds--the bonds that hold the polymer together--and cause degradation. The effects of the bond ruptures are witnessed in changes in polymer properties. The fundamental properties are the molecular weight and molecular weight distribution. Alterations of molecular structure will in turn cause changes in other properties. Melt rheology, most important from a processing point of view, is one of the properties that reflects changes in molecular weight and molecular weight distribution.

Of all the techniques employed to process a polymer, extrusion is the most important. Over one-half of all thermoplastic materials are processed by extrusion. With the large amounts of scrap generated by extrusion coupled with the current emphasis on recycle, thermo-

plastics are likely to undergo the extrusion process more than once. Conditions inside an extruder involve high temperatures (up to 600°F), high shear (100 sec^{-1} to 3000 sec^{-1}), and high pressure (up to several thousand pounds per square inch). These conditions will create an environment that degrades the polymer, especially if the polymer is recycled.

Up until the present, this subject has been treated by incorporating ingredients to inhibit the action of heat and shear. This process is called compounding. Only a few studies viewed degradation from a fundamental standpoint. And only one previous study was concerned with a fundamental, yet practical, approach. This was a pre-1960 study and suffered from the state-of-the-art of experimental equipment.

With these facts in mind and with the advances in technology of measurement devices, one should strive to obtain basic information about the degradation process yet keep in perspective the overall object--to study degradation under actual extrusion conditions. Such a study will be detailed in the following sequel.

CHAPTER II

LITERATURE REVIEW

Degradation Studies

Extensive studies have been made on the degradation of polystyrene from a mechanistic point of view. The purpose of these efforts was to establish a mechanism for the degradation reaction. Very little work has been done in the extrusion degradation of polystyrene with no studies reported from a practical outlook.

Staudinger (63) was the first to report experimental work in the area of thermal degradation of polystyrene. He employed the thermal breakdown of polystyrene to establish the head-to-tail configuration of the molecule. Jellinek (42) was the first to study the degradation reaction in detail. His experiments were conducted in vacuo over a temperature range of 275°C to 340°C. During the molecular breakdown, he discovered the narrow distribution of the initial polymer broadening with a subsequent narrowing over the later course of the reaction. He also studied thermo-oxidative degradation of polystyrene by heating the polymer in the presence of air. Temperature range for these experiments covered 180°C to 285°C. Plots of limiting viscosity versus time indicated the same initial rapid drop in molecular weight followed by a period of gradual drop in viscosity.

Jellinek postulated the "weak link" theory of polystyrene degradation. The polymer molecule was pictured with peroxide groups attached to the polymer chain backbone at random locations. This created weak links which were very susceptible to degradation and

4

caused the rapid initial breakdown. After destruction of the weak links, the process slowed and followed the slow degradation reaction of splitting C-C bonds.

Grassie and Kerr (28), Madorsky (46), Wagner and Patat (74), and a few others have picked up the previous work and included modifications to describe the path of the degradation reaction. All of these workers included a minor change in the mechanism, but produced the same experimental results.

J. G. Hendrickson (39) was the first to report a study on the degradation of polystyrene using gel permeation chromatography (GPC) for molecular weight analyses. He weathered commercial-grade polymers over different time periods and followed changes in molecular weight (MW) and molecular weight distribution (MWD). He reported a difficulty in following the degradation of broad distribution polystyrene. This was due to the presence of medium molecular weight species in the virgin sample which combine during reaction and replace the high molecular weight molecules as they break apart.

Chemical changes in polyolefins during extrusion have been studied by Burch (14). He details reactions that alter the polymer molecule. Free-radical reactions that are promoted by oxidation and homolytic-bond scission appeared most prevalent.

A few studies on the degradation of thermoplastics during a model extrusion process have been reported. Poller and Kotliar (49) reported a study on the degradation of polypropylene during processing. They employed a specially designed extrusion rheometer. The rheometer was of the gas-piston type with nitrogen pressure forcing polymer through a capillary die. Their experimental results illustrated the effects of degradation on the flow properties of the polypropylene. They attempted to relate the observed viscosity changes with $\overline{M}_w$ (measured by intrinsic viscosity). Part of the experimental results could be correlated with $\overline{M}_w$ but not all. Variations in MWD (which they did not measure) were used to explain the anomalous results.

Capillary rheometry was employed to study the thermal stability of poly(vinyl chloride) (PVC) by Collins and Krier (16). They extruded

PVC isothermally at constant shear rate and recorded viscosity versus time relationships. They discovered three distinct regions: (1) equilibrium viscosity obtainment; (2) constant viscosity period; and (3) period of rapid changing viscosity. A mathematical model of Collins' PVC degradation process was presented by Morrette and Gogos (47).

Recent studies by Porter and co-workers (2, 26) on the extrusion degradation of polystyrene have centered on a model extrusion process. His work included two narrow MWD polystyrene samples ($M_w = 670,000$ and $\overline{M}_w = 1,800,000$ and $P_d \approx 1.1$). Thermal and thermal-oxidative degradation of the polymer samples were checked and found to follow the established mechanism. Samples of the polystyrenes were recycled through an Instron capillary rheometer at various constant temperatures and shear rates. MWD were obtained by GPC. Their results indicated that the degradation of polystyrene was primarily due to thermal energy. However, the action of shear was seen to reduce the temperature level at which degradation first took place. Graphs of number of ruptured bonds versus $1/T$ showed a positive temperature coefficient. From this they deduced the extrusion degradation to be primarily a thermal process. The values of polydispersity greater than 2 (the value predicted by a theoretical treatment of random chain scission) were not explained.

Polyethylene resin processing was studied by Ford, Scott, and Wilson and the subsequent effects on the polymer flow properties reported (23). During the static compression molding tests, the melt viscosity increased and the solution viscosity decreased. A single-pass extrusion in a one-inch Killion extruder caused decreases in both solution and melt viscosities. From this they postulated a cross-linking reaction at low shear and a chain-scission reaction at high shear.

Studies of thermal and shear degradation on commercial-grade polymers from a practical viewpoint were few in number. Schott and Kaghn (57, 58) worked with a two-inch Davis-Standard extruder ($L/D = 22:1$) using commercial-grade polyethylene and polypropylene.

Capillary dies were fastened to the front of the extruder and used to measure the polymer flow properties during extrusion. Apparent viscosities were calculated and compared for various operating conditions. Molecular weight analyses were determined by solution viscosity measurements. To date this was the only work where a polymer was recycled through an extrusion process with the melt rheology being continuously monitored.

For their initial work on polyethylene, they employed three types of low-density material and one of high density. After four extrusions, two of the low density showed no change in intrinsic viscosity and identical flow curves. The third low-density polymer was processed eight times at 646°F. A seven percent decrease in intrinsic viscosity was observed. Melt viscosity measurements indicated a much stronger dependency with a 46% decrease. Melt viscosity appeared much more sensitive to change in molecular weight than solution viscosity. Two widely different temperatures with approximately the same shear rates were selected for repeated extrusion of the high-density polyethylene. An increase in both molecular weight (7%) and apparent viscosity (29%) was exhibited by the material extruded at the higher temperature, whereas the low temperature extrusion produced no change in the resin. Thermal energy appeared to be the cause of the reaction during this experiment.

Shear degradation was postulated from Schott and Kagh'n's work on polypropylene. The commercial-grade polymer was extruded six times at a high- and a low-flow rate while temperature was held constant. The molecular weights of the samples were identical. They calculated a specific degradation rate constant from an exponential relationship between apparent viscosity and the number of extruder passes. The slope of the semi-log plot of apparent viscosity versus N (number of passes) showed a straight-line relationship. The slope provided k (specific degradation rate constant). The high-shear-rate data produced a k five times greater than the low-shear-rate data. Thus, they concluded a definite effect of shear on the degradation process.

From examination of the previous studies, one immediately noticed

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From examination of the previous studies, one immediately noticed

a lack of work in the area of the effect of processing on polymers. The early workers provided valuable information about the chemistry of polymer degradation. The model extrusion processes of Poller and Kotliar, Collins and Krier, Porter and co-workers, and Ford, Schott and Wilson proved that there was an effect on polymer properties caused by processing. Experimental observation of these effects were without question but no one attempted to correlate the observed changes with processing conditions. Schott and Kaghni touched on this with pass number; however, pass number would not account for the myriad of possible extrusion conditions. Work in the area of polymer degradation was necessary with a specific desire for a correlation to relate measured changes in polymer properties with extruder operating conditions.

Rheological Studies

From a review of the literature and a previous study on impact-modified polystyrene (62), it was apparent that polymer melt rheology was affected by degradation to a great extent. Melt rheology was shown to be very important during polymer processing and therefore a review of effects of molecular weight and MWD on melt rheology was necessary. In addition, the measurement techniques for the continuous monitoring of melt rheology during extrusion was required for this appeared the best way to follow the effects of processing on the polymer.*

Several studies have covered the prediction of polymer processing behavior from melt rheology measurements. McCabe and Mueller (44) were concerned with elastomers and brought out the strong dependency of processing on the elastomer's rheological properties. They claimed that if provided with the flow curve, die swell, and extrudate smoothness information, they could determine a practical system for the

*Note: The basics of rheology will not be detailed. The reader is referred to any one of a number of texts on rheology for these reviews (10, 11, 21).

prediction of processability. Best (6) more or less postulated the same type of analysis.

In their study on high-density polyethylene, Shida and Cancio (59) related the processing behavior to the resin flow behavior over a wide range of shear rates. They maintained the flow property of a resin could be determined from the zero shear viscosity (μ_0), the maximum relaxation time (T_0), and the shape of the flow curve. From a correlation of the μ_0 and T_0 , they determined a shear sensitive parameter which is independent of molecular weight. With this parameter and μ_0 , one could predict the processing behavior of any resin. Their experiments were limited and only covered high-density polyethylene. Once again, no mention was given to extrusion conditions.

From a review of the attempts to predict processing behavior from melt rheology, one could understand the necessity of rheological measurements and the basic rheological information. But it was also realized that degradation also affects processing which the above authors never mentioned. Logically if one could determine the effect degradation has on rheological parameters, he could incorporate this information into the prediction of processing behavior.

Polymer melt rheology studies were in abundance with a number of good works on the effect of molecular structure on polymer flow properties. Polyethylene and polypropylene had been studied more recently (9, 60, 65) than polystyrene.

The study of polystyrene melt rheology dated back to Spencer and Dillion (61). They were the first to report rheological properties of polystyrene and established the basic fact that polystyrene melt behaved as a non-Newtonian fluid at certain levels of shear. In addition, they reported values for μ_0 , k (characterizes the degree of non-Newtonian behavior), and activation energy for viscous flow. The influence of temperature, molecular weight, and solvent content on μ_0 was also investigated. Among the values reported, a log-log relationship between μ_0 and molecular weight was found to fit the polystyrene data. This relationship was previously reported by Fox and Flory (24) for other polymers. The value of the slope of the

logarithmic plot was determined to be 3.4. These data were further substantiated by McCormick, Brower, and Kim (45).

These early studies on polystyrene melt rheology were hampered by the low availability of well-characterized narrow distribution polymer. Around 1960 anionic polymerization techniques were perfected which created an abundant source for narrow distribution polymer. Rudd (52) was the first to report an extensive study of polystyrene melt rheology using polystyrene from the anionic polymerization process. His study included twenty-five narrow distribution polystyrenes that ranged in weight-average molecular weight ($\overline{M}_w$) from 50,000 to 270,000 (polydispersity (P_d) $\approx$ 1.15). He also investigated the flow properties of seven broad distribution polymers (P_d from 1.9 to 2.9).

He reported values for μ_o versus $\overline{M}_w$ at 227°C. The log-log relationship of Flory (24) was indicated and appeared to hold quite well. The effect of $\overline{M}_w$ on the Newtonian-non-Newtonian transition region of the flow curve was studied. Rudd later extended his data to lower shear regions with a cone-and-plate viscometer in an extension of this study (53).

The data of Rudd was substantiated by Ballman and Simon (4). They also reported the effect of MWD on polystyrene. The logarithmic relationship between μ_o and $\overline{M}_w$ was determined and values for the exponent were in agreement with other investigators (values from 3 to 3.4). Ballman and Simon studied the effect of temperature on the μ_o versus $\overline{M}_w$ log-log plot. They established shifts in the intercepts but no deviation from the 3.4 power dependency. MWD had no effect on the curves; however, MWD did affect the shear rate level at which the polymer entered the non-Newtonian flow region. They also established that the high shear viscosity (measured at a shear stress of 700,000 dynes/cm²) was related to the number-average molecular weight ($\overline{M}_n$). Later investigations have also pointed to a 3 to 3.4 power dependency of the μ_o on $\overline{M}_w$ (27, 37).

Any study in the area of polymer degradation during processing would have to include detailed information of the polymer melt rheology. Changes in molecular weight would affect the flow curves of the polymer

and thus alter the processibility. A review of the available methods to study melt rheology in a processing environment (on-line with processing equipment if possible) was necessary. Many types of viscometers have been reported in the literature. Brabender, Siegloff-McKelvey, Melt Indexer, and Instron capillary rheometers were just a few (1, 3, 54). However, for reasons to be outlined in this manuscript, these off-line instruments were unacceptable. There were a few on-line viscometers reported in the literature with certain desirable features.

Five Japanese workers reported an on-line type of viscometer which was fed by a 30-mm extruder (66). Their study was concerned with flow instabilities of polyethylene, polypropylene, general-purpose polystyrene, and high-impact polystyrene. The polymers were of commercial-grade but they reported very few molecular properties, thus comparisons with this study are difficult. Their viscometer design was reviewed; however, a by-pass valve from the main polymer stream fed the viscometer and this was deemed undesirable for this study. The sudden change of direction the polymer must take will adversely affect the elastic properties of the polymer and have an undetermined effect on the viscous properties. If it were not for these factors, this design would be acceptable for degradation studies. However, it was encouraging to read of their success in measuring flow properties of polymers using an on-line viscometer.

During the 1960's, a study was initiated at TNO Laboratories, Delft, Netherlands by Janeschitz-Kriegl, Eswaran and Schiff (17, 18, 19, 22, 41, 70, 71, 72). The work has been carefully reviewed with respect to the type of viscometry. These workers were the first to use the slit geometry for measurement of polymer melt flow properties. They also introduced the concept of flush mounts for electronic pressure transducers inside the slit to determine axial pressure profiles. The data were obtained with a one-inch Killion extruder feeding the slit. Poly(vinyl chloride), high- and low-density polyethylene and polystyrene data were reported. The crudeness of the early pressure measurement devices limited the data considerably. Because of this, some of their interpretations appeared to be in error. First, they

reported no exit pressure and secondly, they found nonlinearities in the axial pressure profiles. These observations were not unreasonable because of the pressure levels that were attained during their experiments. Pressures up to 15,000 psi were reported. Thus, any extrapolation to a small exit pressure (< 100 psi) would be difficult. Their work included data on slit dimensions that were important. An aspect ratio (slit width divided by height) of ten was found to be sufficient for a one dimensional flow assumption.

Numerous articles on slit rheometry over the past four years have been reported by Han and co-workers (28, 32). His publications were too numerous to review in detail but a few highlights were important. He further established the technique for flush mounts of electronic pressure transducers and detailed a study to prove that no pressure hole error was observed (31). He showed the technique of on-line measurement of viscosity with an extruder was indeed possible.

He reported a great deal of data on general-purpose polystyrene and this will be reviewed in detail in another section of this report. The concept of the exit pressure and the relation of elasticity measurements to the exit pressure will be examined in the Theory section.

A general observation on the rheology literature showed a lack of experimental data. This author found a wealth of theoretical considerations but with little experimental data to prove or disprove them.

CHAPTER III

THEORETICAL AND EMPIRICAL CONSIDERATIONS

Degradation Studies

One of the goals of this study is to relate extruder conditions to the observed changes in polymer molecular and rheological parameters. From this relation the characteristic parameter for degradation would evolve. The following derivation details the development of this parameter-- E_D , the energy available for degradation.

From Figure 1, a simple heat and material balance around an extruder is completed.

Figure 1

F = mass flow rate -- LBM/SEC

- T_I = Temperature of incoming polymer -- $^{\circ}\text{F}$
 T_O = Temperature of polymer out -- $^{\circ}\text{F}$
 H_I = Enthalpy of incoming polymer -- BTU/LBM
 H_O = Enthalpy of polymer out -- BTU/LBM
 Q_{MECH} = Heat input from mechanical energy (screw) -- BTU/SEC
 Q_{ELECT} = Heat input from electrical energy (heaters) -- BTU/SEC
 Q_{LOSS} = Sum of all heat losses
 1. loss through insulation (radiation losses)
 2. loss through screw
 3. loss through thrust bearing
 4. frictional loss in gear train

Assumption I. All degradation occurs inside the extruder.

$$(R_{T_{\text{EXT}}} \gg R_{T_{\text{ADAPTER}}} + R_{T_{\text{DIE}}} + R_{T_{\text{VALVE}}}) \quad (\text{Shown in Appendix K})$$

$R_{T_{\text{EXT}}}$ = extruder residence time

$R_{T_{\text{ADAPTER}}}$ = adapter residence time

$R_{T_{\text{DIE}}}$ = die residence time

$R_{T_{\text{VALVE}}}$ = valve residence time

Assumption II. Q_{LOSS} term is of the same magnitude for all experiments.

$$\text{IN} + \text{GEN} = \text{OUT} + \text{ACC.} \quad (1)$$

at steady state $\text{ACC.} = 0$

$$\text{IN} = FH_I + Q_{\text{MECH}} + Q_{\text{ELECT}}$$

$$\text{OUT} = FH_O + Q_{\text{LOSS}} + \Delta H_m F$$

$$\text{GEN} = V\phi$$

V = volume occupied by polymer in extruder -- FT^3

ϕ = generation term associated with the available energy for polymer degradation

ΔH_m = heat of melting ($\Delta H_m = 0$ for amorphous polymers -
e.g., polystyrene)

Substituting for the terms in the overall property balance

$$FH_I + Q_{MECH} + Q_{ELECT} - V\phi = FH_O + Q_{LOSS}. \quad (2)$$

The volume occupied by molten polymer can be represented by

$$V = f_{50 \text{ RPM}} V_E \quad (3)$$

V_E = total void volume of extruder

$f_{50 \text{ RPM}}$ = fraction that accounts for density change of polymer

Rearranging Equation (2) gives

$$V\phi = F(H_O - H_I) + Q_{MECH} + Q_{ELECT} - Q_{LOSS}. \quad (4)$$

Assumption III. Electrical heaters supply little energy to the polymer and only enough to maintain the proper frictional coefficient between the polymer and the barrel.

$$V\phi = F(H_O - H_I) + Q_{MECH} - Q_{LOSS} \quad (5)$$

Division of Equation (5) by V places terms on a volume basis.

$$\phi + \frac{Q_{LOSS}}{V} = \frac{F(H_O - H_I) + Q_{MECH}}{V} \quad (6)$$

The Q_{LOSS}/V term and ϕ term cannot be separated unless details of all the major loss terms can be accounted for. But the energy that is responsible for polymer degradation is a part of the

$(Q_{\text{LOSS}}/V + \phi)$ quantity. Therefore, Q_{LOSS}/V and ϕ will be grouped together to yield,

$$\phi' = \frac{F(H_O - H_I) + Q_{\text{MECH}}}{V} \quad (7)$$

ϕ' = amount of energy available for degradation per unit volume per unit time.

A change to a mass basis is accomplished by dividing by ρ_{AVE}

$$\phi'' = \frac{F(H_O - H_I) + Q_{\text{MECH}}}{\rho_{\text{AVE}} V} \quad (8)$$

ϕ'' = amount of energy available for degradation per unit mass per unit time

ρ_{AVE} = average density of polymer calculated from the bulk density of polymer at inlet and density of molten polymer.

From experience, one knows the amount of degradation is also a function of time of exposure to heat and shear. Therefore, residence time must be included.

$$W = (F) \left(\frac{1}{\rho_{\text{AVE}}} \right) \quad (9)$$

W = volumetric flow rate -- $\frac{\text{FT}^3}{\text{MIN}}$

$$R_{\text{T}_{\text{EXT}}} = \frac{V_E}{W} \quad (10)$$

$R_{\text{T}_{\text{EXT}}}$ = residence time of polymer in extruder -- $\frac{\text{MIN}}{\text{PASS}}$

Finally, the energy available for degradation is calculated by,

$$E_D = (\varphi'') (R_{T_{EXT}}) \quad (11)$$

E_D = characteristic parameter which is the available energy for degradation per unit mass per pass through extruder.

From a knowledge of extruder conditions, i.e., temperature in and out, amperage reading, voltage level to motor, flow rate and enthalpy data, one can calculate E_D . A detailed knowledge of the loss term would be desirable but it is not essential during recycle studies if heater settings are maintained constant. E_D is a descriptive parameter and is characteristic of the extrusion conditions. It does not have fundamental significance and therefore comparisons of E_D values with polymer bond energies are not possible.

Polymer degradation or molecular weight change is a kinetic process and one would think an Arrhenius-type relation would apply. The corresponding low shear viscosity also follows an Arrhenius relation. These involve temperature, which can also be expressed at a heat content per unit mass ($c_p T$) just as is the term E_D . Thus, one might try the analogy of using E_D to replace temperature in these conventional relationships. The possibility of the Arrhenius-type functional dependency of $\overline{M}_w$ and μ_{10} on E_D exists and is postulated with the following equations:

$$\overline{M}_w = A e^{(K_{M_w} / \Sigma E_D)} \quad (12)$$

$$\mu_{10} = B e^{(K_{\mu_{10}} / \Sigma E_D)} \quad (13)$$

During extrusion degradation, E_D is increased by the recycle of the polymer. Therefore, the summation of E_D , referred to as ΣE_D , corresponds to an increase in temperature for the analogy to the Arrhenius relationship. The reciprocal of the ΣE_D values are plotted

against the logarithm of $\overline{M}_w$ and μ_{10} . The slopes of these plots, $K_{\overline{M}_w}$ and $K_{\mu_{10}}$, are related to the rate of the degradation process. Steeper slopes create higher K values and therefore, faster degradation rates. Determination of K values enables one to explore the effect of extruder operating conditions on the rate of polymer degradation.

Rheological Studies

Because of the rheological information being generated during this study of polymer degradation, a review of the theories of polymer melt structure and their influence on polymer melt rheology is necessary. Experimental results will be compared with the theories in a later section.

The first of these theories is the molecular theory for the viscosity-molecular weight dependence of polymer chains in bulk. This concept was advanced by Bueche in the early 1950's (12, 13). According to Bueche, the resistance to flow arises from the friction of one chain segment sliding past another. This holds for polymer chains short enough to have an average of less than one entanglement per molecule with a neighboring chain. Viscosity in this molecular weight region is proportional to chain length.

As the chain length is increased, the average number of entanglements per chain increases till a value of one is reached. These are the conditions for the formation of an infinite polymer melt network. If chain length is increased further, the viscosity would become infinite except this is not the case. Chain entanglements are not permanent but permit certain amounts of slippage between entangled chains. Resistance to flow arises from the viscous drag of the entangled chains which must be pulled along by a single molecule. Bueche postulated that in the limit of the very long slipping entangled

chain, viscosity is proportional to chain length to the 2.5 power. Bueche later points out a neglected section of the theory--the circulation effect--and now claims a 3.5 power dependency of viscosity on chain length. It is of interest to note that Bueche's theory followed the empirically determined 3.4 power of Flory and Fox (24).

Gillespie advances a model of a polymer melt network that involves a system of extensible elements connected by entanglements or ordered regions (25). His model stemmed from an empirical equation developed by Williamson (77). He starts with a theoretical development and finally reaches the same form as the Williamson equation. This model is used primarily to predict the shear rate dependency of viscosity for polymer melts but it also serves as a possible pictorial representation for polymer melts.

A rather recent proposal of Busse suggests that the unit of supermolecular structure for molten polymers is a ball of coiled molecules (15). Molecular entanglements or interpenetration would dictate the internal structure of these balls. This ball of coiled molecules represents an additional complication over previous entanglement theories. The exact nature of how these balls rearrange and recombine to form clusters will have an effect on polymer melt behavior. This additional feature is necessary, however, to explain the influence of shear level on the polymer melt superstructure. The concept is advanced by Walczak in a recent investigation (67, 68, 69).

During this investigation, a number of rheological parameters were measured. Among these is the exit pressure (P_E) or residual pressure. The value of the exit pressure is determined from the experimentally measured wall normal stresses by plots of pressure versus flow channel axial distance. This plot will not yield a zero pressure at the channel exit. Through the theoretical considerations of Sakaidis (55, 56), the exit pressure is shown to be equal to the primary normal stress difference.

$$P_E = (P_{11} - P_{33}) = \sigma_1 \quad (14)$$

P_E = exit pressure -- psi

P_{11} = wall normal stress in x - x plane -- psi

P_{33} = wall normal stress in y - y plane -- psi

He has also shown that the secondary normal stress difference is the slope of the exit pressure versus $\ln \tau_w$ plot.

$$P_{22} - P_{33} = -\tau_w \frac{d P_E}{d \tau_w} = - \frac{d P_E}{d \ln \tau_w} = -\sigma_2 \quad (15)$$

τ_w = wall shear stress -- psi

P_{22} = wall normal stress in y - y plane

P_{33} = wall normal stress in z - z plane

His work is criticized by White (75) and therefore, his results are open to question. Recent studies in the area of normal stress measurement have been reported by Tanner (64), Williams and Olabisi (76).

Extensive experimental measurements of the exit pressure have been made by Han and co-workers (33, 34, 35) and by Blum, Yerushalmi, and Williams (7, 8). In the later study, eight electronic pressure transducers were mounted axially and profiles determined on viscous and viscoelastic fluids. Only the viscoelastic fluids yielded an exit pressure. Han has also performed similar studies plus investigations on polymer melts. He has further correlated exit pressure with shear

rate, shear stress and temperature. Comparison of our data with Han's for the same polystyrene will be reported in a later section.

CHAPTER IV

EXPERIMENTAL PROGRAM

Design of the BLS Twin-Slit Extrusion Rheometer

A major portion of this study centered on the design of a rheometer that would produce the desired rheological measurements without a hinderance to the degradation studies. Hopefully the polymer melt flow characteristics could be determined without a separate heat up procedure which would call for protection of the polymer from further degradation. This dictated on-line measurement of the viscous and elastic properties with the 2 1/2-inch extruder. Yet all the available technology of viscometer design was concerned with only rheological investigations with little regard to degradation studies.

The system employed by Schott and Kaghk measured the polymer flow properties; however, extruder conditions were altered as screw speed changed. Han's slit rheometer and the TNO equipment also called for changes in screw speed for the variation of flow rates. With a 2 1/2-inch machine, the temperature profile changed drastically with changes in screw speed and isothermal conditions would be difficult, if not impossible, to maintain. By-pass systems were rejected because of reasons stated earlier in Chapter 2. So the combined problems of not wanting to make off-line measurements yet desiring to maintain constant extruder conditions presented a formidable challenge.

This challenge was met with the twin slit-concept. If two flow channels were used, it would be possible to vary the flow in Channel A

and measure the pressure distribution. While Channel B could be employed for balance to the total flow, i.e., keeping total flow rate constant. If total extruder flow rate (processing flow rate) remained constant, head pressure would not change, thus extruder operating conditions would remain stable. This design would require a system of two slit flow channels and two valves. One channel would contain both temperature and pressure sensors while the second would have temperature sensors only.

The slit geometry was used so that flush mounts of the electronic pressure transducers could be possible. With accurate flush mounts of the transducer (i.e., $< \pm 0.001$ inch tolerance between transducer and flow channel), pressure hole effects can be avoided. The transducers were manufactured by Dynisco Division of Microdot Corporation (Westwood, Massachusetts) (20). They were produced in various pressure ranges from 0 to 100 psig up to 0 to 20,000 psig. The principle of operation was based on the strain gauge. A pressure was exerted on a thin stainless steel diaphragm and transmitted to a strain gauge via a tiny column of mercury. The strain gauge was connected into a Wheatstone bridge circuit and as the gauge expanded and contracted, a voltage was produced. The voltage was amplified and sent to an analog-to-digital converter. The digitized signal was processed by a computer with subsequent printout via teletype printer.

Calibration of the transducer was very critical. For this procedure, a piece of equipment (Figure 2) was constructed that included a steel block for mounting of the transducer, three pressure gauges, a reservoir tank, tubing, and valve connections. The block was tapped with a 1/4-inch diameter hole for admission of nitrogen pressure. Electrical heater bars were placed in the block to maintain calibration temperatures at the same level as extruder operating temperatures. Han reported very little temperature effect on the Dynisco transducers. This was not the case with the transducers used in this study. In conversations with the manufacturer, high temperature calibration was recommended. An extremely accurate Heise gauge (Heise Bourdon Tube Company, Newtown, Connecticut) was purchased and placed in series with

0 - 1500 PSIG HEISE GAUGE

0 - 3000 PSIG HEISE GAUGE

FIGURE 2 CALIBRATION APPARATUS

the steel block (38). Pressures were recorded from the gauge and the voltages were printed out by the computer. A least-squares analysis determined the equation for the best fit of the experimental data which in most cases proved to be linear.

Temperatures were measured by thermocouples produced by West Instrument Company (Chicago, Illinois). Calibration procedure was similar to that of the pressure transducers. A bath of heat transfer fluid provided the necessary thermal medium. A very accurate (calibrated to the nearest 0.1°C by NBS) mercury thermometer was positioned in the bath and temperature-voltage data recorded. Least-squares analysis again provided the calibration equations. Programs for the PDP-15 computer that handled these calibrations appear in Appendix A. The slit geometry also allowed flush mounts of the temperature probes.

The decision was made to study a commercial-grade general-purpose polystyrene with no additives. Two thousand pounds were donated by Dow Chemical Company. Physical data including viscosity-shear rate information, enthalpy data, PVT relation, thermal conductivity measurements and molecular weight properties were supplied. The trade name of this material was STYRON 686.* The weight-average molecular weight ($\overline{M}_w$), number-average molecular weight ($\overline{M}_n$) and polydispersity (P_d) were determined by gel permeation chromatography. Values for different determinations appear in Table 1. Results of this analysis yielded a $\overline{M}_w = 250,000 \pm 3,000$, $\overline{M}_n = 89,000 \pm 2,000$ and a $P_d = 2.83 \pm 0.05$.

TABLE 1
GPC RESULTS FOR STYRON 686

<u>RUN</u>	<u>SAMPLE</u>	<u>INTERVAL (COUNT)</u>	<u>$\overline{M}_w$</u>	<u>$\overline{M}_n$</u>	<u>P_d</u>
1	68600	0.2	250,200	89,250	2.80
1	68600	0.5	251,000	89,980	2.79
2	68601	0.2	252,800	91,910	2.75
2	68601	0.5	252,500	91,250	2.77
3	68602	0.2	249,500	86,650	2.88
3	68602	0.5	249,800	86,940	2.87

*STYRON is a registered trade name of The Dow Chemical Company.

Before the design of the rheometer, experience in extruder operating techniques had to be gained. This included pressure, temperature, and processing rate information. Some of this could be partially obtained from previous workers' data. However, there had been only one study completed on the extruder and the amount of data was limited.

The extruder used during the degradation studies was a 2 1/2-inch diameter, 24:1 L/D, NRM Spacemaker model (NRM Corporation, Akron, Ohio) (48). Reber and co-workers set up the extruder and the data acquisition system (43, 51). Temperature and pressure sensors were positioned in eight locations along the barrel. Figure 3 shows the positions of these probes and the extruder dimensions. Because of limitations in the number of data lines to the digital computer, only four melt temperatures and one pressure (head of extruder) could be obtained.

A valve was attached to the extruder for use by control studies. The adapter, which changes the flow geometry from circular to elliptical in preparation for the die, held the valve in place. A melt thermocouple probe was placed in the adapter to monitor the polymer temperature before entrance to the die.

Early investigations were completed with the die constructed by Hertenstein (40). Figure 4 contains the extrusion line for these studies. Polymer was pumped into the die and forced through 0.1-inch diameter holes. These "spaghetti" strands were cooled in a water trough and chopped into pellets by a grinder. This die was very convenient because the stranding operation was accomplished by a plate (3 in x 9 in x 1/2 in) attached to a larger piece of metal (6 in x 9 in x 4 in) which served as a reservoir. Hence, for experimentation with different flow areas (die resistances) and geometries, all that was necessary was to construct different plates. The plates were manufactured from cold rolled steel in the Ohio State University machine shop.

While waiting for the arrival of the shipment of general-purpose polystyrene, a series of experiments were conducted on an impact-modified polystyrene, STYRON 470. This material was in plentiful supply and had been used in previous extruder studies. However, the earlier

LEGEND

▼ MELT TEMPERATURE OR
PRESSURE TAP

SCALE 8:1

FIGURE 3 LOCATION OF MELT THERMOCOUPLES IN EXTRUDER BARREL

FIGURE 4 EXTRUSION LINE FOR RECYCLE STUDIES

studies did not include the necessary pressure, temperature, processing flow rate versus screw speed information for the rheometer design.

Table 2 and Figures 5 to 7 summarize the information obtained.

TABLE 2
DATA SUMMARY OF RUNS 1 TO 16
FOR STYRON 470

	Zone 1	Zone 2	Zone 3	Zone 4	Die	Die
Extruder controller setting	400	400	430	450	450	450
SCREEN PACK	YES	NO	NO	NO		
HOLES	13	13	8	8		
FLOW AREA (IN ²)	0.0981	0.0981	0.0603	0.0603		
FLOW RATE AT 100 RPM (LBM/HR)	183	183	183	183		
FLOW RATE AT 100 RPM/HOLE (IN ³ /SEC)	0.112	0.112	0.183	0.183		
HEAD PRESSURE psi	1295	890	950	1040		
DIE PRESSURE psi	440	435	520	580		
DIE TEMPERATURE °C	253	253	253	224		
HEAD TEMPERATURE °C	278	224	224	225		

This work involved two die plates, one with 8 holes and a second with 13 holes. Respective flow areas were 0.0603 in² and 0.0981 in². In addition to gaining valuable extruder operating experience, these runs revealed the linear relationship between screw speed and processing flow rate, the exponential relationship between screw speed and pressure, and temperature-screw speed data. One very valuable observation was the need for good metal-metal seals on all die, adapter, and valve surfaces. Leaks were a big problem because of the high extruder head pressures (i.e., > 1000 psi). Copper gaskets were found to be an excellent material to seal the metal-metal surfaces.

With the arrival of the general-purpose polystyrene, STYRON 686,

FIGURE 5 PRESSURE AS A FUNCTION OF SCREW SPEED FOR STYRON 470

FIGURE 6 TEMPERATURE AS A FUNCTION OF SCREW SPEED FOR STYRON 470

FIGURE 7 PROCESSING FLOW RATE AS A FUNCTION OF SCREW SPEED FOR STYRON 470

the extruder was cleaned out with solvent and purged with the new material. A two-slit plate was fabricated and attached to the die. Channel dimensions were: length (L) = 0.50 inch; width (W) = 1.0 inch; and height (H) = 0.050 inch. Extruder runs were made with one slit open and the other slit blocked. Pressure, temperature, and processing flow rates were recorded. The 8-hole plate was also used for a few runs to compare flow area effects. Figures 8 to 10 and Table 3 provide a summary of the experimental data.

TABLE 3
DATA SUMMARY OF RUNS 16 TO 51
FOR STYRON 686

Extruder temperature range 210°C to 230°C

SCREEN PACK	NO	YES	YES	YES	YES
FLOW AREA IN ²	0.102	0.0603	0.0603	0.051	0.051
FLOW RATE AT 100 RPM (LBM/HR)	180	180	175	173	168
FLOW RATE AT 100 RPM/HOLE(IN ³ /SEC)	0.705	0.180	0.172	1.38	1.34
HEAD PRESSURE psi	1100	1225	1385	1557	1689
DIE PRESSURE psi	300	605	436	642	663
DIE TEMPERATURE °C	209	240	210	220	220

Additional experience in operation of the extruder was obtained; this time with the STYRON 686. The slit geometry produced two "ribbons" of polymer. Pelletization of the ribbons was a messy operation because of the very brittle nature of the STYRON 686. During later experiments, the chopped ribbons (very flaky) were fed to the extruder. Drastic effects on extruder performance were observed. Bulk density measurement on the flakes revealed a 30 to 40% decrease when compared to the original pellets. A pelletizing operation was therefore

FIGURE 8 - PRESSURE AS A FUNCTION OF SCREW SPEED FOR STYRON 686

FIGURE 9 TEMPERATURE AS A FUNCTION OF SCREW SPEED FOR STYRON 686

FIGURE 10 PROCESSING FLOW RATE AS A FUNCTION OF SCREW SPEED

essential in recycle studies.

The basic information of extruder operation was established, and a channel was designed. This first prototype is pictured on the left side of Figure 11. The slit dimensions were $L = 4.00$ in, $W = 1.0$ in, and $H = 0.050$ in. For convenience the prototype was mounted on the 2-slit plate by $1/4$ -inch bolts, thus bringing the total slit length to 4.5 inches. A one-inch valve with 20 threads per inch was placed 2 inches from the slit exit. The channel was kept at temperature by an electrical heating tape.

Runs were made with the total extruder output passing through the slit channel. Die pressures (transducer located in reservoir section of die) approached 1200 psig while head pressures (transducer located at exit of extruder barrel) reached 2500 to 3500 psig. Data from Runs 60 through 68 (see Figure 9) indicated the large increase in pressure buildup with the addition of flow channel length from 0.5 inch to 4.5 inches. The shape of the P_{DIE} versus screw speed (RPM) is concave upward due to poor temperature control in the channel. But the magnitude of the die and head pressure was of sufficient magnitude to obtain the wall stress level of interest. After a check on the available polystyrene data (5), it was decided to obtain viscosity information up to a value of $\tau_w = 1.0 \times 10^6$ dynes/cm². All the previous experiments (large flow areas) developed pressures in too low a region for complete viscosity information. Data from these runs appear in Table 4 and Figures 8 through 10.

TABLE 4

DATA SUMMARY OF RUNS 52 to 68 FOR STYRON 686

HEATERS	450	450	450	450	DIMENSIONS OF FLOW
DIE	350	350			4.0 in x 1.0 in x 0.050 in
STYRON 686					$L = 4.0$ in + 0.5
SCREEN PACK					$H = 0.051$ in
TRANSDUCER NO. 2 IN DIE					
FLOW AREA = 0.051 IN ²					

1-inch valve -
20 threads/inch

1-inch valve -
40 threads/inch

4-inch Channel

5-inch Channel

FIGURE 11 PROTOTYPE MODELS FOR RHEOMETER DESIGN

TABLE 4 (Cont.)
DATA SUMMARY OF RUNS 52 to 68 FOR STYRON 686

RPM	3	4.4	10	25	50	75
P _{DIE} (PSI)	1184	1182	1100	963	911	845
T _{DIE} (°C)	220	223	223	228	238	244
FLOW RATE (LBM/HR)	6.2	9.3	17.0	38.8	76.8	109.2
FLOW RATE (IN ³ /SEC)	0.0496	0.0745	0.136	0.310	0.614	0.877
T _{SLIT} *	219.8	220.8	222.9	227.6	237.7	244.1

* Runs 60 to 68 check temperature in slit with TC in metal

This first prototype was constructed from 1/2-inch thick steel acquired from the University's lab storeroom. Thicker steel was required to mount a pressure transducer inside the channel and measure the wall normal stress, so a 1 1/2-inch thick piece of cold rolled steel was purchased from Brown Steel Company (Columbus, Ohio). Two 5-inch pieces of this material were cut and a slit one-inch wide by 0.050 inches high was milled from one piece. The pieces were tapped and bolted together. This prototype is shown on the right side of Figure 11. The standard pressure tap was made as outlined in Reference (18) exactly 3.25 inches from the slit exit. This left a distance of 0.5 inch between the outer edge of the one-inch valve and the pressure tap. A 0 to 1500 psig range Dynisco pressure transducer was flush mounted into the channel. The channel was mounted next to the four-inch channel on the slit plate (total channel lengths equaled 4.5 inches and 5.5 inches). The plate with the two channels was bolted to the die reservoir section as outlined previously.

The next phase of experimentation included extruder runs to test out the twin-slit and double-valve concept. Different temperatures and screw speeds were investigated. Heater bars were placed in the steel of both channels to obtain better temperature control. The one-inch valves were positioned up and down while the head pressure was examined.

With a ten-fold change in the flow rate of the 5-inch channel, the head pressure varied only 100 psi out of a total 3000 psi pressure. Summarizing this phase of the study, the twin-slit concept functioned quite well.

The only major modification was to mill out the channels to a 0.10 inch depth. This lowered the aspect ratio (W/H) to 10--still above the necessary value for one-dimensional flow according to the work of Han and the TNO workers. An aspect ratio of 20 created pressures inside the slit near the limits of the 0 to 1500 psi transducer. For protection against transducer over-pressure damage, a lower value of the aspect ratio was necessary. Pressure transducers were ordered from Dynisco with ranges of 0 to 1000 psi and 0 to 500 psi. By using the lower range transducers, a more accurate pressure reading could be obtained.

The single pressure measurement at constant flow rate from the 5-inch channel was placed on a plot of pressure versus axial distance and a straight line drawn to the slit exit. An example of this plot is shown in Figure 12. Pressure readings were taken from this line at different axial positions. In this manner, one could select the proper position of a given range transducer. Of course this plot holds only for the prototype channel (i.e., $L = 5.5$ inches, $W = 1.0$ inch, and $H = 0.10$ inch). Experimental data for STYRON 686 and 470 were obtained with the 5-inch channel and compared favorably with viscosity data reported by Bernhardt for similar types of polystyrene (5). Figures 13 and 14 show the viscosity data.

By a comparison of the axial distribution plots, the value of $H = 0.050$ inch created pressures too large and the $H = 0.10$ inch value created pressures too low. Therefore, the final slit height was set at 0.075 inch and the length at 6.0 inches. A one-inch value for width would yield a 13.33 ratio which would be acceptable. The four pressure transducers were placed 1 inch apart beginning 1 inch from the outer edge of the valve or a total distance from the slit entrance of 2.5 inches. Ranges of the transducers were 0 to 3000, 0 to 1500, 0 to 1000, and 0 to 500 psi. This would provide a large safety margin to protect against any over-pressures. Pressure transducers were custom

FIGURE 12 EXAMPLE OF AXIAL PRESSURE DISTRIBUTION
FOR STYRON 686 AT 230°C

FIGURE 13 EXAMPLE OF EXPERIMENTAL SHEAR DIAGRAM FOR STYRON 686

FIGURE 14 EXAMPLE OF EXPERIMENTAL VISCOSITY DATA
FOR STYRON 686

mounted to each hole. Even though these transducers were identical in thread size, the smallest difference in mount dimensions resulted in a slight protrusion or indentation from the slit. This was totally unacceptable and therefore, the custom mount was necessary. Two thread sizes, 20 and 40 threads per inch, were tried on the one-inch valves. Forty threads per inch was too fine and galled, therefore, 20 threads per inch was used.

The rheometer was constructed from 2 1/2-inch cold-rolled steel. Two pieces, each 2 1/2-inches x 7 inches x 6 inches, were cut and polished. Slits were milled from the top half and sensor holes drilled. This included six thermocouple holes, four opposite each pressure tap and two in the second slit. One-half-inch diameter Allen head bolts held the two halves together except on the extruder end of the rheometer. Because of space requirements, these two bolts were 3/8 inch in diameter (see Figures 20 and 21).

Detailed drawings of the BLS (Brodkey-Lynn-Springer) Twin-Slit Extrusion Rheometer are shown in Figures 15 through 19. The entire rheometer was mounted to the extruder adapter and fastened with 5/8-inch diameter Allen head bolts. Two holes for hooks were provided so that the chain over-head crane would be used to lift the rheometer into place (see Figure 22). Once bolted to the extruder, the chain was removed (see Figure 23). The 5/8-inch bolts were strong enough to support the rheometer.

Heater bars, four of which were 3/8 inch x 6 inches, two of which were 1/4 inch x 6 inches and two of which were 3/16 inch x 6 inches, were placed into their mount holes. The four heaters on each side of the rheometer were wired in series and plugged into separate variable voltage transformers. This permitted independent temperature control of each half, essential for constant temperature as the flow rate was varied.

Valves were marked with 5 large divisions and each large division was subdivided with 5 smaller marks. Hence a total of 25 divisions which corresponded to 0.002 inch of valve movement per mark. To travel the entire 0.075 inch height of the slit, a movement of 37.5 marks was

FIGURE 15

THE OHIO STATE
UNIVERSITY
BLS RHEOMETER
"FRONT VIEW"
PAUL W. SPRINGER
NOVEMBER 28, 1972
SCALE: 3/4" = 1"

FIGURE 18

THE OHIO STATE
UNIVERSITY
PLS RHEOMETER
"BOLTING DIAGRAM"
PAUL W. SPRINGER
NOVEMBER 28, 1972
SCALE: 3/8" = 1"

87

6.0 inches x 1.0 inch x 0.075 inch

FIGURE 20 BLS TWIN-SLIT EXTRUSION RHEOMETER -- FRONT AND TOP VIEWS

FIGURE 21 BLS TWIN-SLIT EXTRUSION RHEOMETER -- BACK VIEW

CHAIN MOUNTS

FIGURE 22 BLS TWIN-SLIT EXTRUSION RHEOMETER WITH STRANDING PLATE AND MOUNTING CHAINS

THERMOCOUPLE

PRESSURE TRANSDUCER

FIGURE 23 BLS TWIN-SLIT EXTRUSION RHEOMETER IN POSITION ON 2 1/2-INCH EXTRUDER

necessary. This was 1.5 turns of the valve.

Trial runs were made with the BLS rheometer and rheological information obtained. The pressure distributions were well within the limits of the transducers. Temperature measurements indicated no axial profile was developed above 200°C. With the extruder set at a given screw speed, the rheometer remained isothermal over a number of valve settings. However, at low flow rates ($< 300 \text{ sec}^{-1}$ apparent shear rate-- γ_{APP}), the variable voltage transformer had to be increased to maintain constant temperature conditions. Head pressure remained very stable as the viscosity information was obtained.

With the rheometer developed and ready, the final problem of product form was studied. Hopefully, a device could be designed to shape the polymer from the slit form to a strand. This was done by the design of a steel plate (3/8 inch thick) that bolted to the front of the rheometer. A 1/8 inch x 2 1/2 inch slot was milled out of one-half the plate thickness. Four 0.2 inch diameter holes were drilled through the plate and aligned with the twin slits. Polymer would exit the slits and enter the slot. Strands of polymer were formed as the material passed through the 0.2-inch diameter holes. The plate was removed for the determination of rheological data. When the regrind operation started, the plate was bolted in position. Figure 24 shows a detailed drawing of the plate.

Degradation Studies

With completion of the BLS Rheometer, on-line viscometric studies could be undertaken. Attention was focused on the degradation studies of general-purpose polystyrene. There were two goals of this study; first, to determine the effect of recycle on the polymer properties and second, to investigate the effect of shear on the polymer.

The decision was made to recycle polystyrene five times. One processing of the polymer included feeding to the extruder, extrusion

FIGURE 24

THE OHIO STATE
UNIVERSITY
BLS RHEOMETER
"STRANDING PLATE
DIAGRAM"
PAUL W. SPRINGER
NOVEMBER 28, 1972
SCALE: 3/4" = 1"

through valve-adapter-rheometer-stranding plate assembly, cooling in a water trough and pelletizing with the grinder. Twenty-five pounds of polymer were discarded before each pass to prohibit mixing of the polymer lots. A set of five recycle passes was made at a medium level of shear (extruder screw speed = 50 RPM) and another set at a high shear level (extruder screw speed = 100 RPM).

Controller settings on the extruder heaters were kept the same for all experiments. Motor amperage was recorded for each pass and DC motor voltages recorded for the two screw speeds. Twelve temperatures and six pressures were monitored with the following nomenclature:

T_1	=	melt temperature ($^{\circ}\text{C}$) at the end of zone 1 heater	
T_2	=	" " " " " " " 2 "	
T_3	=	" " " " " " " 3 "	
T_4	=	" " " " " " " 4 "	(head of extruder)
T_5	=	" " " in the adapter	
T_6	=	" " " entrance to rheometer	
* T_7	=	" " " right slit -- 0.5 inch from valve	
T_8	=	" " " " " -- 0.5 inch from exit	
T_9	=	" " " opposite first pressure transducer	
T_{10}	=	" " " " second " "	
T_{11}	=	" " " " third " "	
T_{12}	=	" " " " fourth " "	
P_H	=	extruder head pressure (psig)	
P_A	=	pressure at slit entrance (psig)	

* Right side is defined by viewing the extruder from the feed point. The right slit is used for balancing the flow. The left slit contained the pressure transducers and therefore was the channel of most interest.

P_3 = first slit pressure transducer (0 to 3000 psi)
 P_4 = second " " " (0 to 1500 psi)
 P_5 = third " " " (0 to 1000 psi)
 P_6 = fourth " " " (0 to 500 psi)

Figure 25 details a sketch that shows the location of the sensors. The data acquisition was tremendously aided by the departmental digital computer--a PDP Model 15 (Digital Equipment Corporation, Maynard, Massachusetts). Computer program listings appear in Appendix B. Signals from the sensors were sent to a bank of amplifiers and multiplied by 1000. The next step was signal conversion from analog to digital mode and then finally the signals were input to the computer. By means of the calibration equations, pressure and temperature appeared on the teletype next to the extruder.

Before the recycle operation and after the purge of the extruder, the flow curves--shear rate versus shear stress--were determined. The BLS Rheometer without the stranding plate was employed for this work. As polymer passed through the left slit, the ribbon was cut and weighed over measured time intervals (shear rates). Axial pressure distributions were recorded by the computer. At least 10 data points were taken over an apparent shear rate range of 10 sec^{-1} to 1000 sec^{-1} . The BLS Rheometer, with this set of pressure transducers, could measure wall stresses down to $200,000 \text{ dynes/cm}^2$. Polymer lots will be referred to as 50 RPM, Passes 1 to 5 and 100 RPM, Passes 1 to 5. The unextruded polystyrene will be called virgin material.

Calibration of the pressure transducers was critical and therefore, a calibration check was done after each flow curve determination. No significant changes in calibrations were discovered over the course of the 10 experimental runs.

FIGURE 25
LOCATION OF PRESSURE AND TEMPERATURE SENSORS

Molecular Weight Analyses

A Waters Model 200 GPC (gel permeation chromatograph, Waters Associates, Framingham, Massachusetts) was used for all molecular weight analyses. Operation conditions and calibration information are given in Appendix C. A study was completed to determine the effect of concentration on elution volume. The need for this information stemmed from a desire to run the polymer sample at the highest possible concentration. This would enable a lower recorder sensitivity setting and thus decrease base-line drift. Results from this study appear in Table 5. Only the higher molecular weight polymer ($\overline{M}_w > 400,000$) were susceptible to the shifting. These polymer fractions were present in low concentrations in the STYRON 686. The high molecular weight fraction's concentrations were approximated and compared with the concentration versus elution volume information. From this study, a concentration level of 3.0 milligrams per milliliter of solvent (tetrahydrofuran, reagent grade) was found acceptable. All the GPC polystyrene samples were made by solution of 300 milligrams of polymer in 100 ml of solvent. This solution was filtered through an asbestos pad and fritted stainless steel disc. Samples were then bottled and labeled to await analysis.

The strip chart recording from the GPC was analyzed by the measurement of peak heights every one-half count (one count = 5 ml of elution volume). A study was done to determine the effect of size interval on $\overline{M}_w$ and $\overline{M}_n$ calculation. The broad distribution STYRON 686 gave the same $\overline{M}_w$ and $\overline{M}_n$ for 0.5 count intervals and 0.1 count intervals.

A FORTRAN IV computer program computed the $\overline{M}_w$, $\overline{M}_n$, and P_d of the polystyrene sample. The program appears in Appendix C and is labeled GPCCALC. An IBM 370 computer was used for these calculations.

To check on the possibility of degradation from pelletization and shear in the rheometer, three samples were taken from each pass. Pelletized and unpelletized STYRON 686 comprised two samples. The third sample evolved during the flow curve determination. Shear rate for this sample was identical to the shear rate in the rheometer during the recycle operation (i.e., BLS rheometer with stranding plate in place).

TABLE 5

RESULTS OF GPC CONCENTRATION STUDIES

<u>SAMPLE</u>	<u>PEAK M</u>	<u>VOLUME ELUTED</u>	<u>CONC. (mg/ml)</u>
STAND 0	3.14×10^6	26.08	2.000
"	"	25.76	1.000
"	"	25.40	0.500
"	"	25.20	0.250
"	"	25.20	0.125
STAND 1	1.987×10^6	26.28	0.500
"	"	26.28	0.250
STAND 2	8.30×10^5	28.46	2.000
"	"	28.12	1.000
"	"	28.00	0.500
"	"	28.00	0.250
STAND 3	4.02×10^5	29.94	2.000
"	"	29.76	1.000
"	"	29.68	0.500
"	"	29.66	0.250
STAND 4	1.71×10^5	32.25	2.000
"	"	32.16	1.000
"	"	32.16	0.500
"	"	32.12	0.250
STAND 5	9.72×10^4	33.64	2.000
"	"	33.58	1.000
"	"	33.52	0.500
"	"	33.52	0.250
STAND 6	5.00×10^4	35.56	2.000
"	"	35.50	1.000
"	"	35.50	0.500
STAND 7	1.975×10^4	38.37	1.000
"	"	38.36	0.500
STAND 8	1.00×10^4	40.00	1.000
"	"	40.00	0.500
STAND 9	4.80×10^3	42.16	1.000
"	"	42.16	0.500

Two pounds of pelletized material were sealed in polyethylene bags and stored for further studies. The unpelletized strands and equal shear samples were also saved.

Oven Studies

A set of STYRON 686 samples were heated in an electric oven for time intervals of 1, 2, 3, 4, 5, 7.5, 10, 20, and 40 minutes. Oven temperature was set at 230°C. During the heating periods, the sample was exposed to an air atmosphere.

For nitrogen atmosphere oven studies, a specially-designed oven was employed. A block of steel was milled out until a disc of polystyrene (1 inch diameter by 0.030 inch thick) could fit inside. The steel block was heated by electrical heater bars (same design as those in the rheometer). A temperature of 230°C was maintained by a variable voltage transformer. Heating times were 30, 45, and 60 minutes with a continual flow of nitrogen gas inside the oven cavity.

Molecular weights were determined by the GPC with the same procedure as outlined above.

Die Swell Measurements

Experiments were conducted to determine the effect of recycle on the die swell behavior of general-purpose polystyrene. A 35-mm camera was employed to take die swell pictures at the exit of the BLS Rheometer. Measurements revealed no effect of recycle on the die swell; however, the investigation was not elaborate enough to draw any definite conclusions.

CHAPTER V

RESULTS

Degradation Studies

Rheological properties of Pass 1, 50 RPM (Run 128) polystyrene were determined from the raw experimental data that included pressure (P), temperature (T), and flow rate (F) data. Table 6 is a tabulation of these data. Appendix D (Tables 21 to 29) contains the P, T, F data for the other nine extruder runs (Runs 129 to 137). This included Passes 2 to 5, 50 RPM and Passes 1 to 5, 100 RPM.

Error in terms of voltages for temperature and pressure measurements was determined by a procedure that held a constant temperature or pressure on the sensor and recorded the output voltage. The voltage would scatter because of the noise on the sensor lines. Source of the noise was any external voltage in the sensor environment. Details of the noise level in voltages, pressures, and temperatures are given in Table 7. Errors in flow-rate measurements were much less than the error levels for pressure and temperature measurements.

Extruder conditions for the recycle experiments at 50 RPM were kept constant. At 100 RPM, problems occurred with the feed section of the extruder. This resulted in different process flow rates, motor amperage, and temperatures. Conditions for the 10 runs are given in Table 8.

For the determination of the rheological properties, apparent shear rate, γ_{APP} , is calculated from

$$\gamma_{APP} = \frac{6Q}{WH^2} (\text{sec}^{-1}) \quad (16)$$

TABLE 6

EXPERIMENTAL DATA FROM RUN 128

P = pressure -- psi T = temperature -- °C F = mass flow rate -- gr/min

Pass 1, 50 RPM

<u>T₁</u>	<u>T₂</u>	<u>T₃</u>	<u>T₄</u>	<u>T₅</u>	<u>T₆</u>	<u>T₇</u>	<u>T₈</u>	<u>T₉</u>	<u>T₁₀</u>	<u>T₁₂</u>	<u>P_H</u>	<u>P_A</u>	<u>P₁</u>	<u>P₂</u>	<u>P₃</u>	<u>P₄</u>	<u>F</u>
215	220	227	221	220	222	235	232	228	229	228	3194	2411	373	269	176	75	13.0
215	221	228	222	221	222	236	232	229	230	230	3167	2354	520	378	242	99	31.0
215	221	228	221	221	223	223	232	229	230	230	3150	2350	635	460	293	116	48.1
215	219	228	222	223	222	233	230	228	228	228	3034	2284	820	598	380	145	92.3
215	220	228	222	223	223	233	230	229	229	229	3041	2268	940	688	432	165	152.0
215	219	228	222	223	222	229	230	230	230	229	3078	2290	1044	766	478	183	232.0
214	219	227	222	222	222	232	229	231	231	231	3014	2206	1090	793	444	189	268.0
215	220	228	222	222	222	232	229	232	231	232	3075	2288	1123	817	506	195	307.0
215	221	227	222	221	220	226	225	230	229	229	3030	2253	1256	913	561	216	447.0
215	220	226	220	218	219	224	224	229	229	230	3050	2272	1300	938	577	223	499.0
215	220	227	221	221	220	221	222	231	230	230	3044	2266	1331	965	590	228	580.0
215	219	224	218	220	219	219	221	229	229	228	3040	2214	1375	992	608	235	618.0

TABLE 7

REPRODUCIBILITY FOR DYNISCO PRESSURE TRANSDUCERS

230°C

<u>Transducer Range</u>	<u>Pressure--psi</u>	<u>Voltage</u>	<u>Date</u>
0 - 3000	1400	3.88	3/27/73
"	"	3.89	4/20/73
"	"	3.87	4/24/73
"	"	3.87	5/16/73
0 - 1500	900	5.32	3/20/73
"	"	5.34	4/20/73
"	"	5.31	4/24/73
"	"	5.30	5/16/73
0 - 1000	400	4.12	3/20/73
"	"	4.18	4/20/73
"	"	4.16	4/24/73
"	"	4.15	5/16/73
0 - 500	150	3.75	3/20/73
"	"	3.78	4/20/73
"	"	3.77	4/24/73
"	"	3.74	5/16/73

TABLE 8

EXTRUDER OPERATING CONDITIONS FOR RECYCLE EXPERIMENTS - RUNS 128 to 137

50 RPM

Zone 1 Zone 2 Zone 3 Zone 4

Heater Setting 435 435 350 450

Adapter Variac 60
Die Variacs 65 65

Pass	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)	T_6 (°C)	T_8 (°C)	T_9 (°C)	T_{10} (°C)	T_{12} (°C)	P_H (psig)	P_A (psig)	P_1 (psig)	P_2 (psig)	P_3 (psig)	P_4 (psig)	F (lb/min)
1	213	220	226	222	220	226	228	228	228	2810	2020	1309	966	641	292	82.0
2	215	220	226	220	219	228	228	230	228	2590	1900	1180	867	573	263	81.5
3	215	218	224	220	217	230	231	232	230	2450	1720	1113	816	527	248	80.4
4	216	218	224	221	217	228	230	230	230	2400	1710	1118	814	524	247	83.0
5	215	219	222	218	217	229	228	229	230	2500	1820	1175	842	551	257	83.2

TABLE 8

(cont.)

EXTRUDER OPERATING CONDITIONS FOR RECYCLE EXPERIMENTS - RUNS 128 to 137

100 RPM

Zone 1 Zone 2 Zone 3 Zone 4

Heater Setting	435	435	350	450
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Adapter Variac 50

Die Variacs 45 45

Pass	T ₁	T ₂	T ₃	T ₄	T ₆	T ₈	T ₉	T ₁₀	T ₁₂	P _H	P _A	P ₁	P ₂	P ₃	P ₄	F
	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(psig)	(psig)	(psig)	(psig)	(psig)	(psig)	(lb/min)
1	223	225	228	230	212	230	231	232	233	2980	2090	1408	1108	680	322	152
2	219	220	225	228	217	229	231	229	228	2460	1870	1263	932	600	291	110
3	210	209	212	225	220	228	229	229	230	2530	1920	1266	921	618	291	121
4	210	211	215	225	214	227	226	227	226	2780	2140	1343	994	656	306	116
5	211	210	215	222	223	224	227	228	230	2510	1970	1268	944	622	289	125

Q = volumetric flow rate -- IN^3/sec
W = width of slit -- Inch (1.00 in)
H = height of slit -- Inch (0.075 in).

Volumetric flow rate is determined from the mass flow rate divided by the density (LBM/IN^3) at constant temperature (temperature for every run was $230^\circ\text{C} \pm 2^\circ\text{C}$). A P-V-T equation for STYRON 686 was supplied by Dow (68).

$$(P + 27,000) (V - 0.822) = 11.6 T \quad (17)$$

P = pressure -- psi
T = temperature -- $^\circ\text{K}$
V = volume -- cc/gram

Wall shear stress, $\tau_{W_{\text{EXP}}}$, is provided by a least-squares analysis of the four axial pressure data points. An example of the axial pressure profile is shown in Figure 26. The equation which relates the slope of the axial pressure profile to wall shear stress is

$$\tau_{W_{\text{EXP}}} = \frac{\Delta P}{\Delta L} \frac{H}{2} \quad (18)$$

$$\frac{\Delta P}{\Delta L} = \text{slope of axial pressure profile -- } \frac{\text{PSI}}{\text{IN}}$$

H = height of slit -- INCH (0.075 in).

The subscript EXP is used to signify experimental wall shear stress. Table 9 summarizes for Pass 1, 50 RPM the flow rate (F), volumetric flow rate (Q), γ_{APP} , slope of axial pressure distribution ($\Delta P/\Delta L$), and wall shear stress ($\tau_{W_{\text{EXP}}}$). The data from the remaining 9 runs appear in Appendix E, Tables 30 to 38.

The technique of least-squares polynomial analysis referred to

FIGURE 26 AXIAL PRESSURE DISTRIBUTION FOR RUN 123

TABLE 9

AXIAL PRESSURE DISTRIBUTION RESULTS FOR RUN 128

Pass 1, 50 RPM

<u>F</u> (gr/min)	<u>γ_{APP}</u> (sec^{-1})	<u>SLOPE</u> (psi/in)	<u>INTERCEPT</u> (psi)	<u>$\tau_{W,EXP}$</u> (psi)	<u>$\tau_{W,EXP} \times 10^{-5}$</u> (dynes/cm ²)
13.0	14.5	-98.7	618.0	3.70	2.55
31.0	34.0	-139.9	869.4	5.25	3.61
48.1	53.0	-172.4	1066.0	6.46	4.45
92.3	102.0	-225.3	1384.0	8.45	5.82
152.0	169.0	-259.1	1590.0	9.72	6.69
232.0	258.0	-287.6	1767.0	10.78	7.43
268.0	299.0	-300.7	1843.0	11.28	7.77
307.0	342.0	-310.0	1899.0	11.62	8.01
447.0	498.0	-347.2	2125.0	13.02	8.97
499.0	556.0	-359.2	2196.0	13.47	9.28
580.0	646.0	-368.4	2252.0	13.82	9.52
618.0	688.0	-380.4	2324.0	14.26	9.82

here and in subsequent sections of the report provided a good method to fit the experimental data. A copy of the FORTRAN IV computer program is included in Appendix F. A similar program is available from the Chemical Engineering Library (CHEPLS) written by H. C. Hershey. The significance of additional terms for the polynomial equation is tested at the 95% confidence level with the F-statistic. If the F_{CALC} value is greater than the F_{TABLE} , the next higher order term is significant. For the case of a F_{CALC} value below the F_{TABLE} value, the next higher order term is discarded. When the two F values are close (i.e., within 5.00), the test becomes questionable. Total number of viscosity data points for the 10 experimental runs was 123. A linear relationship between distance and P was found for every data point.

To smooth the $\gamma_{\text{APP}} - \tau_{\text{W}}$ experimental data, the least-squares analysis was employed. Figure 27 shows the apparent shear rate versus the calculated (line) and experimental (points) wall shear stresses. The calculated τ_{W} is referred to as $\tau_{\text{W,CALC}}$. Appendix G contains the remainder of these plots (Figures 58 to 66).

Rabinowitch (50) provided a relationship for calculation of true shear rate (γ_{T}) from apparent wall shear rate,

$$\gamma_{\text{T}} = \gamma_{\text{APP}} \frac{2}{3} + \frac{1}{3} \frac{d \ln \gamma_{\text{APP}}}{d \ln \tau_{\text{W,CALC}}} \quad (19)$$

By making the substitution of

$$\text{NPRIME} = \frac{d \ln \gamma_{\text{APP}}}{d \ln \tau_{\text{W,CALC}}} \quad (20)$$

into Equation (14), the following equation is provided:

$$\gamma_{\text{T}} = \gamma_{\text{APP}} \left(\frac{2}{3} + \frac{1}{3 \text{ NPRIME}} \right) \quad (21)$$

The least-squares analysis related γ_{APP} and $\tau_{\text{W,CALC}}$ in the following

SHEAR DIAGRAM FOR PASS 1 - 50 RPM - RUN 128

FIGURE 27

manner.

$$\log \gamma_{APP} = a_0 + a_1 \log \tau_{W_{CALC}} + a_2 (\log \tau_{W_{CALC}})^2 + \dots \quad (22)$$

The derivative with respect to $\log \tau_{W_{CALC}}$ gives

$$\frac{d \log \gamma_{APP}}{d \log \tau_{W_{CALC}}} = a_1 + 2a_2 \log \tau_{W_{CALC}} + \dots \quad (23)$$

which equal $1/NPRIME$. The FORTRAN IV computer program that computed $NPRIME$ and subsequent parameters is entitled RHEOCALC and is shown in Appendix H.

After the calculation of $NPRIME$, γ_T was calculated. Figures 28 to 30 show plots of γ_T versus $NPRIME$. With the values for γ_T and $\tau_{W_{CALC}}$, the flow curves for STYRON 686 can be constructed (Figures 31 to 33). Apparent viscosity, μ_{APP} , is calculated by the usual procedure,

$$\mu_{APP} = \frac{\tau_{W_{CALC}}}{\gamma_T} \quad (24)$$

Figures 34 to 36 show the shear rate-viscosity relationship for the entire degradation study. Table 10 contains the viscosity information for Pass 1, 50 RPM material. Data for the subsequent passes can be found in Appendix I, Tables 39 to 47.

Dow Chemical provided viscosity information on the virgin STYRON 686 (73). This information was determined by Caplastometer at 227°C . Appendix J summarizes these data. Figure 37 shows the Dow viscosity information and the Pass 1, 50 RPM data. The Dow data was determined under the comparatively mild conditions of the Caplastometer and should therefore not be directly compared with Pass 1, 50 RPM data. Figure 37 shows that the Pass 1, 50 RPM data is in the correct range of STYRON 686 viscosity information.

NPRIME AS A FUNCTION OF TRUE SHEAR RATE - 50 RPM γ_2

FIGURE 28

TRUE SHEAR RATE SEC-1

NPRIME AS A FUNCTION OF TRUE SHEAR RATE - 100 RPM ²⁷

FIGURE 29

NPRIME AS A FUNCTION OF TRUE SHEAR RATE

FIGURE 30

WALL SHEAR STRESS DYNES/CM**2

TRUE SHEAR RATE SEC-1

SHEAR DIAGRAMS FOR PASSES 1 TO 5 - 50 RPM

FIGURE 31

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SHEAR DIAGRAMS FOR PASSES 1 TO 5 - 100 RPM

FIGURE 32

WALL SHEAR STRESS DYNES/CM**2

TRUE SHEAR RATE SEC-1

COMPARISON OF SHEAR DIAGRAM FOR 50 RPM AND 100 RPM

FIGURE 33

APPARENT VISCOSITY AS A FUNCTION OF TRUE SHEAR RATE -50 RPM

APPARENT VISCOSITY AS A FUNCTION OF TRUE SHEAR RATE -100 RPM

FIGURE 35

FIGURE 36

TABLE 10

VISCOSITY DATA FOR RUN 128 PASS 1 50RPM

FOR THIS SET OF DATA THERE ARE 12 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.47581797D+01 B=0.64190607D+00 C=-.73724191D-01 D=0.0

THE VISCOUS PARAMETERS FOR THIS DATA SET ARE

APP. SHEAR RATE SEC-1	STRESS-EXP DYNES/CM**2	STRESS-CALC DYNES/CM**2	NPRIME	TRUE SHEAR RATE SEC-1	APP. VISCOSITY POISE
14.50	255000.	253647.	0.4707	19.94	12723.
34.00	361000.	370109.	0.4161	49.90	7416.
53.00	445000.	442395.	0.3877	80.91	5468.
102.00	582000.	562436.	0.3457	166.34	3381.
169.00	669000.	664269.	0.3134	292.41	2272.
258.00	743000.	754117.	0.2863	472.37	1596.
299.00	777000.	786095.	0.2769	559.31	1405.
342.00	801000.	815419.	0.2683	652.95	1249.
498.00	897000.	897841.	0.2442	1011.76	887.
556.00	928000.	921966.	0.2371	1152.17	800.
646.00	952000.	954671.	0.2275	1377.01	693.
688.00	982000.	968330.	0.2235	1484.73	652.

FIGURE 37 COMPARISON OF DOW VISCOSITY DATA WITH
PASS 1 - 50 RPM -- STYRON 686

To obtain a single shear rate viscosity, for comparison of different pass materials, a least-squares analysis was completed on the $\log \gamma_T - \log \mu_{APP}$ data. Quadratic relationships gave the best fit, and the coefficients appear in Table 11. The equations were evaluated at 10 sec^{-1} which yielded values for μ_{10} .

An extrapolation to a lower shear was also done (i.e., μ_1); but, the extrapolation range was too great and the scatter in the results increased. It should be noted, however, that even with the more drastic extrapolation, the results all showed the same tendencies.

Molecular weight analyses of the 10 polystyrene samples appear in Table 12. Averages of the three polymer samples taken per pass are also shown. Distributional changes are sketched in Figures 38 and 39.

Figure 40 is a log - log plot of $\overline{M}_w$ versus μ_{10} . Data determined at 50 RPM fall on one line while the data from the 100 RPM experiments fall on another. Once again, a least-squares analysis provided the best fit equation which was a linear relationship. A theoretical slope and slope of another worker's data at different levels of shear also appear. Table 13 summarizes the $\log \overline{M}_w - \log \mu_{10}$ data and provides the least-squares equations.

The remainder of the degradation results is concerned with E_D , the energy available for degradation. Appendix K gives the calculation for total extruder volume

$$V_E = 90.5 \text{ IN}^3$$

Volume of adapter plus valve is given ($V_{ADAPTER + VALVE} = 3.53 \text{ IN}^3$) and the volume of the slits is provided ($V_{DIE} = 0.9 \text{ IN}^3$). Values of the residence times at 50 RPM are also given.

Other parameters used to calculate E_D are the extruder volume and the fraction of total extruder volume filled. Details of these calculations are given in Appendix L. $V_{50 \text{ RPM}}$ and $V_{100 \text{ RPM}}$ equal 71.31 IN^3 and 66.89 IN^3 , respectively.

The calculation procedure for the determination of E_D was outlined in Chapter III. Table 14 furnishes the calculated values for E_D , ΣE_D ,

TABLE 11

SUMMARY OF LEAST-SQUARES POLYNOMIAL ANALYSIS

FOR APPARENT VISCOSITY (10 SEC^{-1})

AS A FUNCTION OF TRUE SHEAR RATE

<u>50 RPM</u>					
<u>Pass</u>	<u>a_0</u>	<u>a_1</u>	<u>a_2</u>	<u>F_{CALC}</u>	<u>F_{TABLE}</u>
1	4.74211	-0.40440	-0.06407	0.003	5.32
2	4.68387	-0.38145	-0.06508	0.285	5.59
3	4.64710	-0.36755	-0.06660	9.22	5.59
4	4.49886	-0.28679	-0.07699	2.81	5.99
5	4.42094	-0.26630	-0.07763	1.08	5.32

<u>100 RPM</u>					
1	4.56236	-0.28141	-0.08681	1.232	5.59
2	4.46988	-0.20170	-0.10494	1.125	4.611
3	4.8977	-0.26997	-0.08440	12.074	5.59
4	4.19086	-0.05814	-0.12088	1.118	4.96
5	4.28971	-0.20757	-0.08237	0.406	5.32

$$\log \mu_{\text{APP}} = a_0 + a_1 \log \gamma_T + a_2 (\log \gamma_T)^2$$

$$\text{Evaluate at } \gamma_T = 10 \text{ sec}^{-1} \quad \log \gamma_T = 1.0$$

$$\log \mu_{\text{APP}} = a_0 + a_1 + a_2$$

<u>50 RPM</u>		
<u>Pass</u>	<u>$\log \mu_{\text{APP}} (\gamma_T = 10)$</u>	<u>$\mu_{10} \text{ (poise)}$</u>
1	4.27364	18,800
2	4.23734	17,300
3	4.21295	16,300
4	4.13508	13,700
5	4.03701	11,900

<u>100 RPM</u>		
1	4.19714	15,600
2	4.16324	14,600
3	4.13540	13,600
4	4.01184	10,300
4	3.99977	9,900

SUMMARY OF GPC RESULTS
AVERAGED MOLECULAR WEIGHT ANALYSES

50 RPM

<u>Run</u>	<u>Pass</u>	<u>M_w</u>	<u>M_n</u>	<u>P_d</u>
128	1	246,000	93,100	2.64
129	2	234,000	87,800	2.67
130	3	228,000	90,100	2.53
131	4	218,000	84,500	2.58
132	5	209,000	84,400	2.48

100 RPM

<u>Run</u>	<u>Pass</u>	<u>M_w</u>	<u>M_n</u>	<u>P_d</u>
133	1	244,000	94,400	2.60
134	2	233,000	87,200	2.67
135	3	224,000	87,400	2.56
136	4	215,000	86,300	2.49
137	5	208,000	83,800	2.48

VIRGIN STYRON 686

$$M_w = 250,000$$

$$M_n = 89,000$$

$$P_d = 2.81$$

TABLE 12

SUMMARY OF GPC RESULTS

AVERAGED MOLECULAR WEIGHT ANALYSES

1. Pelletized		2. Unpelletized		3. $\gamma_{\text{App}} = 170 \text{ sec}^{-1}$			
50 RPM				100 RPM			
Sample No.	M_w	M_n	P_d	Sample No.	M_w	M_n	P_d
686-128-1	249,000	94,400	2.59	686-133-1	244,000	93,900	2.60
686-128-2	246,000	93,100	2.64	686-133-2	244,000	95,000	2.63
686-128-3	245,000	90,800	2.70	686-133-2	248,000	94,300	2.60
686-129-1	233,000	88,500	2.63	686-133-2	246,000	92,700	2.57
686-129-2	233,000	85,800	2.72	686-133-3	244,000	93,800	2.65
686-129-3	236,000	89,300	2.64	686-133-3	244,000	85,500	2.56
686-130-1	232,000	91,400	2.54	686-134-1	235,000	88,100	2.67
686-130-2	226,000	89,300	2.54	686-134-2	225,000	83,300	2.70
686-130-3	228,000	89,600	2.55	686-134-3	238,000	90,200	2.42
686-131-1	217,000	83,800	2.60	686-135-1	226,000	89,200	2.53
686-131-2	215,000	84,000	2.56	686-135-2	227,000	86,700	2.62
686-131-3	222,000	85,600	2.60	686-135-3	218,000	86,400	2.52
686-132-1	208,000	83,000	2.50	686-136-1	210,000	83,900	2.49
686-133-2	211,000	86,400	2.45	686-136-2	220,000	87,500	2.52
686-132-3	205,000	83,700	2.45	686-136-3	216,000	87,500	2.46
				686-137-1	206,000	83,500	2.47
				686-137-2	209,000	85,400	2.45
				686-137-3	206,000	82,600	2.49

FIGURE 38 MOLECULAR WEIGHT DISTRIBUTION CHANGES AT 50 RPM

FIGURE 39 MOLECULAR WEIGHT DISTRIBUTION CHANGES AT 100 RPM

FIGURE 40 APPARENT VISCOSITY AS A FUNCTION OF
WEIGHT-AVERAGE MOLECULAR WEIGHT

1. Theoretical Slope of 3.5 - Zero Shear Viscosity
2. Data of Rudd - Slope of 3.14 - Zero Shear Viscosity
3. 50 RPM Data - Slope of 2.90 - Viscosity at 10 sec^{-1}
4. 100 RPM Data - Slope of 3.05 - Viscosity at 10 sec^{-1}
5. Data of Rudd - Slope of 2.54 - Viscosity at $700,000 \text{ dynes/cm}^2$ (Approx. 400 sec^{-1})

SUMMARY OF LEAST-SQUARES POLYNOMIAL ANALYSIS FOR
 APPARENT VISCOSITY (10 SEC^{-1}) AS A FUNCTION OF MOLECULAR WEIGHT

<u>50 RPM</u>				
<u>Pass</u>	<u>μ_{10}</u>	<u>$\log \mu_{10}$</u>	<u>M_w</u>	<u>$\log M_w$</u>
1	18,800	4.27416	246,000	5.39094
2	17,300	4.23805	234,000	5.36922
3	16,300	4.21219	229,000	5.33984
4	13,700	4.13672	218,000	5.33845
5	11,900	4.07555	209,000	5.32015

$$\log \mu_{10} = 2.90 \log M_w - 11.3$$

F_{CALC}	F_{TABLE}
13.3	18.5

<u>100 RPM</u>				
<u>Pass</u>	<u>μ_{10}</u>	<u>$\log \mu_{10}$</u>	<u>M_w</u>	<u>$\log M_w$</u>
1	15,600	4.19312	245,000	5.38917
2	14,600	4.16435	232,000	5.36549
3	13,600	4.13354	224,000	5.35025
4	10,300	4.01284	214,000	5.33041
5	9,900	3.99564	208,000	5.31806

$$\log \mu_{10} = 3.05 \log M_w - 12.2$$

F_{CALC}	F_{TABLE}
6.32	18.5

DATA FOR ΣE_D CALCULATION AND THE CORRESPONDING ΣE_D VALUES

50 RPM

T_I	=	90°F	H_I	=	18 BTU/LBM
T_O	=	428°F	H_O	=	166 BTU/LBM
$I_{NO\ LOAD}$	=	12 AMPS	F	=	1.35 LBM/MIN
I_{LOAD}	=	52 AMPS	V_E	=	90.38 IN ³ /PASS
V_{OLT}	=	258 VOLTS	ρ_{AVE}	=	47.5 LBM/FT ³
$f_{50\ RPM} = 0.787$					

(Note: $I_{NO\ LOAD}$ = Reading from AMP gauge with screw removed from extruder)

<u>Pass</u>	<u>$\dot{Q}$ (BTU/LBM-SEC)</u>	<u>$R_{T_{EXT}}$ (SEC)</u>	<u>E_D (BTU/LBM-PASS)</u>	<u>ΣE_D</u>	<u>$1/\Sigma E_D$</u>
1	3.291	110	362	362	2.762×10^{-3}
2	3.291	220	362	784	1.381×10^{-3}
3	3.291	330	362	1396	0.9208×10^{-3}
4	3.291	440	362	1448	0.6906×10^{-3}
5	3.291	550	362	1810	0.5525×10^{-3}

DATA FOR E_D CALCULATION AND THE CORRESPONDING ΣE_D VALUES100 RPM

$$I_{\text{NO LOAD}} = 15$$

$$V_{\text{OLT}} = 503$$

<u>Pass</u>	<u>$T_I(^{\circ}\text{C})$</u>	<u>$T_O(^{\circ}\text{C})$</u>	<u>$I_{\text{LOAD}}(\text{AMPS})$</u>	<u>$H_O(\frac{\text{BTU}}{\text{LBM}})$</u>	<u>$F(\frac{\text{LB}}{\text{MIN}})$</u>
1	90	450	61	178	2.42
2	90	445	40	175	1.64
3	90	437	45	171	1.96
4	90	437	45	171	1.87
5	90	428	48	168	2.22

<u>Pass</u>	<u>$\phi = (\frac{\text{BTU}}{\text{LBM-SEC}})$</u>	<u>$R_{\text{T-EXT}}(\text{SEC})$</u>	<u>$E_D(\frac{\text{BTU}}{\text{LBM-PASS}})$</u>	<u>ΣE_D</u>	<u>$1/\Sigma E_D$</u>
1	8.946	58	519	519	1.927×10^{-3}
2	4.410	143	377	896	1.116×10^{-3}
3	5.377	214	385	1281	0.7806×10^{-3}
4	5.509	289	413	1694	0.5903×10^{-3}
5	5.884	352	372	2066	0.4840×10^{-3}

$$V_E = 90.38 \text{ IN}^3$$

$$\rho_{\text{AVE}} = 44.7 \text{ LBM/FT}^3$$

$$f_{100 \text{ RPM}} = 0.740$$

and $1/\Sigma E_D$ for the 10 experimental runs. Also included in Table 14 are the pertinent data for E_D calculation.

The correlation revealed in Chapter III that relates E_D and $\overline{M}_w$ and μ_{10} is plotted in Figure 41. Slopes taken from these plots are tabulated in Table 15. Per cent differences also appear.

Rheological Studies

By evaluation of the least-squares equations that relate axial distance and pressure at a distance of 6.0 inches (slit exit), the exit pressure (P_E) was determined. Table 16 lists for Pass 1, 50 RPM material the true shear rate, calculated wall shear stress, apparent viscosity, exit pressure ($f(x)$ at $x = 6$, where $f(x) = \text{Pressure} = a_0 + a_1(\text{axial distance})$), and recoverable strain ratio (stress ratio). Appendix M contains the exit pressure data from the 9 other experimental runs (Tables 48 to 56).

Han reported a logarithm dependency of shear rate on P_E following

$$P_E = A \gamma_T^b . \quad (25)$$

Figures 42 to 44 show the data of $\log \gamma_T$ and P_E . Least-squares analyses of the 10 data sets appear in Table 17. The $\ln \tau_{W_{CALC}}$ versus P_E data are shown in Figures 45 to 47. Table 18 summarizes the least-squares analysis of this data. Plots of true shear rate versus stress ratio (S_r), ratio of primary normal stress difference to wall shear stress, are shown in Figures 48 to 50.

Han published a summary of data on STYRON 686 in a recent article (30). The data included shear rate-viscosity information and shear rate-exit pressure data. These investigations were carried out at 200°C. A value of ΔE_T -- activation energy for viscous flow at constant shear stress--23 KCAL/MOLE for polystyrene was reported by Ballman and

FIGURE 4-1 MOLECULAR WEIGHT ($\bar{M}_w$) AND APPARENT VISCOSITY AS A FUNCTION OF $1/E_D$

TABLE 15

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VALUES OF $K_{\mu_{10}}$ AND K_{M_w}

$$M_w = A e^{K_{M_w}/E_D}$$

$$\mu_{10} = B e^{K_{\mu_{10}}/E_D}$$

$$\text{Units for } K_{\mu_{10}} \text{ and } K_{M_w} = \frac{\text{PASS-LEB}}{\text{BTU}}$$

<u>Region I</u>	<u>B</u>	<u>$K_{\mu_{10}}$</u>		<u>A</u>	<u>K_{M_w}</u>	
50 RPM	6,700	885	% = 7	185,000	264	% = 5
100 RPM	7,000	954		185,000	252	
AVE	6,850	919		185,000	258	
 <u>Region II</u>	 <u>B</u>	 <u>$K_{\mu_{10}}$</u>		 <u>A</u>	 <u>K_{M_w}</u>	
50 RPM	15,200	82.07	% = 65	223,000	38.52	% = 107
100 RPM	12,200	135.3		216,000	79.94	

Decrease of Rate of Degradation Region I to Region II

for $K_{\mu_{10}}$ 50 RPM = 11 Foldfor $K_{\mu_{10}}$ 100 RPM = 7 Foldfor K_{M_w} 50 RPM = 6 FOLDfor K_{M_w} 100 RPM = 3 FOLD

TABLE 16

EXIT PRESSURE DATA FOR RUN 128 PASS 1 50RPM

FOR THIS SET OF DATA THERE ARE 12 DATA POINTS

THE COEFFICEINTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.47531797D+01 B=0.64190607D+00 C=-.73724191D-01 D=0.0

THE ELASTIC PARAMETERS FOR THIS DATA SET ARE

TRUE SHEAR RATE SEC-1	STRESS-CALC DYNES/CM**2	APP. VISCOSITY POISE	EXIT PRESSURE DYNES/CM**2	EXIT PRESSURE PSI	RECOVERABLE STRAIN RATIO
19.94	253647.	12723.19	1779039.	25.80	7.0138
49.90	370109.	7416.38	2068650.	30.00	5.5893
80.91	442395.	5468.05	2178978.	31.60	4.9254
166.34	562436.	3381.25	2220351.	32.20	3.9477
292.41	664269.	2271.70	2441007.	35.40	3.6747
472.37	754117.	1596.46	2854737.	41.40	3.7855
559.31	786095.	1405.48	2675454.	38.80	3.4035
652.95	815419.	1248.83	2689245.	39.00	3.2980
1011.76	897841.	887.41	2882319.	41.80	3.2103
1152.17	921966.	800.20	2813364.	40.80	3.0515
1377.01	954671.	693.29	2868528.	41.60	3.0047
1484.73	968330.	652.19	2868528.	41.60	2.9623

EXIT PRESSURE AS A FUNCTION OF TRUE SHEAR RATE - 50 RPM

FIGURE 42

EXIT PRESSURE AS A FUNCTION OF TRUE SHEAR RATE - 100 RPM

FIGURE 43

EXIT PRESSURE AS A FUNCTION OF TRUE SHEAR RATE

SUMMARY OF LEAST-SQUARES POLYNOMIAL ANALYSIS FOR
EXIT PRESSURE AS A FUNCTION OF TRUE SHEAR RATE

$$\text{LOG } P_E = a_0 + a_1 \text{LOG } \gamma_T$$

50 RPM

<u>Pass</u>	<u>a₀</u>	<u>a₁</u>	<u>F_{TABLE}</u>	<u>F_{CALC}</u>
1	6.118	0.1111	5.12	1.43
2	5.991	0.1518	5.32	3.94
3	6.006	0.1144	5.32	0.175
4	5.972	0.1167	5.59	0.925
5	6.047	0.1186	5.12	2.041

100 RPM

<u>Pass</u>	<u>a₀</u>	<u>a₁</u>	<u>F_{TABLE}</u>	<u>F_{CALC}</u>
1	6.419	0.03388	5.32	1.22
2	6.305	0.04965	4.543	1.007
3	6.285	0.05586	5.32	14.36
4	6.439	0.00367	4.86	0.118
5	6.339	0.03321	5.12	9.62

$$P_E = \alpha \gamma_T^b$$

$$50 \text{ RPM Ave Slope} = 0.12252 = b$$

$$\text{Ave Intercept} = 6.0268 = \log a = \alpha$$

$$100 \text{ RPM Ave. Slope} = 0.03525 = b$$

$$\text{Ave Intercept} = 6.3574 = \log a = \alpha$$

EXIT PRESSURE AS A FUNCTION OF WALL SHEAR STRESS - 50 RPM

FIGURE 45

EXIT PRESSURE AS A FUNCTION OF WALL SHEAR STRESS - 100 RPM

FIGURE 46

EXIT PRESSURE AS A FUNCTION OF WALL SHEAR STRESS

FIGURE 47

TABLE 18

SUMMARY OF LEAST-SQUARES POLYNOMIAL ANALYSIS FOR
EXIT PRESSURE AS A FUNCTION OF WALL SHEAR STRESS

$$P_E = a_0 + a_1 \text{ LOG } \tau_w$$

<u>Pass</u>	<u>50 RPM</u>			
	<u>$a_0 \times 10^{-7}$</u>	<u>$a_1 \times 10^{-7}$</u>	<u>F_{TABLE}</u>	<u>F_{CALC}</u>
1	-0.8993	0.1982	5.117	1.665
2	-0.1034	0.2194	5.318	47.74
3	-0.6250	0.1424	5.318	4.959
4	-0.5215	0.1225	5.591	0.100
5	-0.6291	0.1485	5.117	4.291

<u>Pass</u>	<u>100 RPM</u>			
	<u>$a_0 \times 10^{-7}$</u>	<u>$a_1 \times 10^{-7}$</u>	<u>F_{TABLE}</u>	<u>F_{CALC}</u>
1	-0.1564	0.08248	5.318	0.365
2	-0.2925	0.09765	4.543	1.560
3	-0.2594	0.09164	5.318	0.860
4	+0.2513	0.005281	4.856	0.209
5	+0.01189	0.004405	5.117	2.894

$$P_{22} - P_{33} = \sigma_2 = -\tau_w \frac{dP_E}{d\tau_w} = -\frac{dP_E}{d \ln \tau_w}$$

Averaged values of a_0

$$50 \text{ RPM Ave. Slope} = -1.662 \times 10^6 = \sigma_2 \text{ dynes/cm}^2$$

$$100 \text{ RPM Ave. Slope} = -5.628 \times 10^5 = \sigma_2 \text{ dynes/cm}^2$$

STRESS RATIO AS A FUNCTION OF TRUE SHEAR RATE - 50 RPM

FIGURE 48

STRESS RATIO AS A FUNCTION OF TRUE SHEAR RATE - 100 RPM

FIGURE 49

STRESS RATIO AS A FUNCTION OF TRUE SHEAR RATE

FIGURE 50

Simon (4). This value was used to correct Han's data to 230°C by

$$\mu_{APP} = K e^{\frac{\Delta E}{RT} - \frac{\tau_w}{RT}}$$

Table 19 summarizes the information and Figure 51 compares Han's data and the Pass 1, 50 RPM data.

All of Han's published data for STYRON 686 was analyzed by the same procedures as the data from the degradation studies. This included least-squares analysis of the $\log \gamma_T$ versus $\log P_E$ and the $\log \tau_{W_{CALC}}$ versus P_E data. A summary of comparisons for the above information is included in Table 20.

Oven Studies

Results from the thermal stability tests on STYRON 686 in an air and nitrogen atmosphere are shown in Figures 52 to 54. These plots included time of exposure versus $\overline{M}_w$, $\overline{M}_n$, and P_d .

For comparison on an extruder residence time basis, Figures 55 to 57 were constructed. The independent variable was residence time in the oven (static) or residence time in the extruder (shear). Dependent variables were $\overline{M}_w$, $\overline{M}_n$, and P_d .

TEMPERATURE ADJUSTMENT FOR HAN DATA

$$\mu_{APP} = K e^{\Delta E/RT}$$

$$T_1 = 200^{\circ}\text{C} = 473^{\circ}\text{K}$$

$$T_2 = 230^{\circ}\text{C} = 503^{\circ}\text{K}$$

$$\Delta E_{T_w} = 23 \text{ KCAL/MOLE}$$

$$\log \mu_1/\mu_2 = \frac{\Delta E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$= 1.45848$$

$\gamma_T(\text{sec}^{-1})$	$\tau_w \left(\frac{\text{dynes}}{\text{cm}^2} \right)$	$\mu_{200}(\text{poise})$	$\mu_{230}(\text{poise})$
10	350,000	35,000	12,200
17	391,000	23,000	8,000
25	475,000	19,000	6,600
35	595,000	17,000	5,900
43	645,000	15,000	5,200
50	600,000	12,000	4,200
62	620,000	10,000	3,500
90	720,000	8,000	2,800

FIGURE 51 COMPARISON OF VISCOSITY DATA FOR STYRON 686 at 230°C

TABLE 20

COMPARISON OF EXIT PRESSURE MEASUREMENTS

<u>γ_T range (sec⁻¹)</u>	<u>Instrument</u>	<u>T (°C)</u>	<u>b</u>	<u>$\sigma_2 \times 10^{-6}$ (dynes/cm²)</u>	<u>Investigator</u>
17 - 90	Slit	200	0.3009	2.619	Han 1973
22 - 310	Slit	200	0.4471	4.743	Han 1971
20 - 1500 (50 RPM)	Slit	230	0.1225	1.662	Springer 1973
20 - 3500 (100 RPM)	Slit	230	0.0464	0.563	Springer 1973
110 - 560	Capillary	200	0.6236	5.327	Han 1971
135 - 490	Capillary	200	0.3009	2.619	Han 1973
140 - 640	Capillary	193	0.2754	6.612	Han 1971

FIGURE 52 WEIGHT-AVERAGE MOLECULAR WEIGHT AS A FUNCTION OF
OVEN TIME FOR STYRON 686 AT 230°C

FIGURE 53 NUMBER-AVERAGE MOLECULAR WEIGHT AS A FUNCTION OF
OVEN TIME FOR STYRON 686 AT 230°C

FIGURE 54 POLYDISPERSITY AS A FUNCTION OF
OVEN TIME FOR STYRON 686 AT 230°C

FIGURE 55 WEIGHT-AVERAGE MOLECULAR WEIGHT AS A FUNCTION OF RESIDENCE TIME FOR STYRON 686

FIGURE 56 NUMBER-AVERAGE MOLECULAR WEIGHT AS A FUNCTION OF RESIDENCE TIME FOR STYRON 686

FIGURE 57 POLYDISPERSITY AS A FUNCTION OF
RESIDENCE TIME FOR STYRON 686

CHAPTER VI

DISCUSSION OF RESULTS

Degradation Studies

The ability to reproduce experimental data over the course of any study is important. Reproducibility of the experimental flow curve data was good. Successive measurements of a given apparent shear rate (flow rate) at a given valve setting would fall within 1%. The pressure transducer reproducibility was somewhat worse. A rerun of the same experiment on a different day would yield pressure readings within a $\pm 1\%$ range. This was slightly greater than the 1% scatter from successive calibrations of the pressure sensors. At a given set of conditions, reproducibility for the recycle studies should fall within 2%.

The thermocouple for the position marked 11 (T_{11}) was not reported due to a malfunction. However, the other three temperatures from the left slit (T_9 , T_{10} , T_{12}) were sufficient to ensure good temperature readings.

Thermocouples 6 and 7 recorded the right slit temperature. These temperature were not maintained within the 228 to 232°C limit of the left slit. There was no reason to keep these temperatures inside the given temperature region. Experimentally, it would have been very difficult.

The 228 to 232°C range was selected after some amount of experimentation. It was impossible to keep all three thermocouples reading an identical temperature of 230°C. A reminder here is that these temperatures were of the polymer melt while under flow conditions and not

from a thermocouple immersed in the steel of the rheometer. Any such thermocouple in the rheometer would have given very isothermal measurements. This was experienced during earlier experiments with the prototypes.

Pressures at the head of the extruder were measured with a 0 to 10,000 psig transducer. The reproducibility of this transducer was in the 2% range. For all 10 runs, the head pressure was kept within a 200 psi range as the valve settings were changed for determination of the flow curve information.

The adapter pressure--pressure before entrance to the slits--was measured with a 0 to 5000 psig transducer. Readings for the 10 experiments were also kept within the reproducibility limits of this sensor.

At least 10 flow curve points were taken for each pass material. The average number of points was 12. For the 50 RPM experiments, the points were spaced over an apparent shear rate range from 13.0 to 700 sec^{-1} . The spacing of the points was completely arbitrary. Due to the large quantity of polymer flowing from the extruder during a run, a minimum amount of time to determine the flow curve was necessary. To make exact settings for equally spaced flow curve points would have been ludicrous. For the 100 RPM experiments, the γ_{APP} range covered 13.5 to 1000 sec^{-1} .

Constant extruder conditions were easy to maintain for the 50 RPM experiments. The 80 to 83 lbm/hour flow rate was handled by the chopping machine quite nicely. However, for the Pass 1 material at 100 RPM, a flow rate of 150 lbm/hour was produced. This was too much for the chopper to handle and produced large pellets of polymer. The larger pellets of polymer fed erratically to the extruder and created lower motor amperage for the four successive passes (Runs 134 to 137). The extruder temperatures were also lower. However, the lower extrusion temperatures at the higher shear level did not cause a problem for the recycle studies. Only a higher temperature would create the possibility of more thermal degradation. At any rate, for the 10 experimental runs, the extrusion temperatures never were above 230°C.

The axial pressure distribution was recorded for each flow rate.

One axial pressure distribution (4 pressure measurements) corresponded to one apparent shear rate or valve setting on the BLS Rheometer. Figure 26 shows give of the 11 apparent shear rates taken during Run 128, Pass 1, 50 RPM. The distributions are linear with little, if any, scatter. The least-squares polynomial analysis for the entire 123 apparent shear rates over all 10 runs yielded linear relationships only. Tables 9, 30 to 38 report values for the slopes and intercepts of these lines. Calculated values of the experimental wall shear stress are also given in psi and dynes/cm² units.

The experimental data were treated with the least-squares technique to reduce experimental scatter. Quadratic equations fit all but two of the 10 experimental flow curves--log γ_{APP} vs. log τ_w . The F-statistic at the 95% confidence level was employed to test for significance of any successive terms in the log γ_{APP} - log τ_w relationship. Figures 27, 58 to 66 show the log γ_{APP} vs log τ_w curves. Very little smoothing was necessary for most of the data. For all subsequent analyses, the calculated wall shear stress (calculated from the least-squares equation) and true shear rate values (corrected by Rabinowitsch relationship) are used.

The results of the rheology data for the low- and high screw speed experiments and a comparison of the two can be seen in Figures 28 to 36. The value of NPRIME for STYRON 686 decreases rapidly until a shear rate of 150 sec⁻¹ is attained. Therefore, a power law relationship should not be used for this material below 150 sec⁻¹ shear rates.

The most evident fact displayed in all nine figures, Figures 28 to 36, is the reduction of the dependent variables--NPRIME, wall shear stress, and apparent viscosity--at a given shear rate with pass number. The largest changes occurred in the low shear rate region of the curves (< 100 sec⁻¹). The Pass 5 material for both 50 and 100 RPM screw speeds show a slight effect above the 100 sec⁻¹ mark whereas the curves of the first four passes coincide above this shear rate. At a constant shear rate, the decrease in μ_{APP} with pass number in the lower shear rate region (< 100 sec⁻¹) corresponds to a higher NPRIME value and a lower wall shear stress value as shown in Figures 28 to 30 and 31 to 33,

respectively.

Each successive pass through the extruder lowered the viscosity curves further. The decrease of the curve was greater than the experimental scatter of the data points. Any temperature error would have also created scatter rather than the systematic decrease of the viscosity data. In short, the shift of the flow curves proved to be very real indeed. The recycle of STYRON 686 created definite changes in the rheological characteristics.

The second noticeable result is the large drop of the Pass 1, 100 RPM flow curve (Figure 33). This decrease in viscosity lowered the curve to coincide with the Pass 3, 50 RPM material. Subsequently, the data of the Pass 3, 100 RPM and the Pass 5, 50 RPM materials fell in the same region of the figure. The Pass 5, 100 RPM is lower than the other 9 materials.

For a better comparison of the 10 experimental runs, a low shear viscosity was calculated. This was completed by a least-squares analysis of the log true shear rate - log apparent viscosity data. Once again, quadratic relationships fit the data quite well. Table 11 provides a summary of the least-squares information. A value of 10 sec^{-1} was chosen for convenience in the calculation of a μ_{APP} . The log of 10 is 1 and therefore, a summation of the coefficients provided the log of the true shear rate at 10 sec^{-1} (μ_{10}). The anti-log of this value gave the viscosity of the 10 materials at 10 sec^{-1} .

The drop in viscosity at 10 sec^{-1} was substantial. Each pass at 50 RPM dropped the viscosity significantly with a total drop of 37%. One pass at 100 RPM dropped the value of μ_{10} to 15,500 poise. This is 18% below the value of the Pass 1, 50 RPM material. Total drop in viscosity for the five passes at 100 RPM was 53% below the Pass 1, 50 RPM material.

Gel permeation chromatography analysis was used to obtain the molecular parameter information. Because of the inaccuracies in the reduction of the GPC information, a scatter of molecular weight data of 4% is quite common. Therefore, one must never rely on a single determination of molecular weight by GPC, but rather a series of at least 3 to 5 samples.

For this study, 3 samples of STYRON 686 were taken at the extruder--the pelletized and unpelletized materials, and a sample taken from the rheometer at a shear rate of 170 sec^{-1} . This shear rate corresponded to the shear action supplied by the stranding plate. Table 12 summarizes all the molecular weight data obtained for the 10 experimental runs. The sample number is in 3 sections--first, the material number STYRON 686; second, the run number; and third, the type of sample. "1" corresponds to the pelletized polymer; "2" to the unpelletized polymer; and "3" to the $\gamma_{APP} = 170 \text{ sec}^{-1}$.

The difference in the $\overline{M}_w$, $\overline{M}_n$, and P_d for the pelletized, unpelletized and $\gamma_{APP} = 170 \text{ sec}^{-1}$ materials was never greater than the 4% reproducibility limit of the GPC analysis. Therefore, these samples were treated as the same material and averaged. The averaged molecular weight analyses are also given in Table 12 and represent 3 separate molecular weight determinations.

For Pass 1 at both screw speeds the $\overline{M}_w$ dropped slightly (~ 4000 to 5000) whereas the $\overline{M}_n$ increased slightly. This created a narrower molecular weight distribution (P_d decreased 7% from 2.81 to 2.64). The second pass decreased both $\overline{M}_w$ and $\overline{M}_n$. However, $\overline{M}_w$ dropped more than $\overline{M}_n$, and P_d remained the same. The last three passes show the same decrease in $\overline{M}_w$ as Pass 2 ($\sim 8,000$), but $\overline{M}_n$ decreases only slightly. P_d also had lower values of approximately 2.50. Comparison of the molecular weight data between 50 and 100 RPM experiments for a given pass proved to be interesting in that the values were the same.

Figures 38 and 39 show the changes in molecular weight distribution for Passes 1, 3, and 5 at the 50 and 100 RPM screw speeds. These are the actual GPC traces. The virgin STYRON with a 2.81 P_d is definitely broader than Pass 3 or 5 material. The Pass 3 shows a shift of the higher molecular weight tail (left side of figure) to lower values. The shift of the Pass 5 material is even greater. This shift is reflected in decreases of $\overline{M}_w$.

Extruder recycle affects the weight-average molecular weight more than the number-average molecular weight. Therefore, the long chain

molecules are broken first which caused decreases of $\overline{M}_w$. When a long-chain molecule is split into two molecules of roughly one-half their original length, the $\overline{M}_w$ is affected more than the $\overline{M}_n$. The two smaller molecules are the same length as many other molecules already present in the broad distribution virgin material, and the addition of 2 more has little effect on $\overline{M}_n$.

The changes in molecular weight distributions that were observed over the course of these studies were not characteristic of the distributional changes reported by Porter (2, 26). Porter's extrusion degradation studies employed very narrow distribution polystyrene ($P_d \sim 1.05$). The original distribution was so narrow that as the polymer chains broke apart there were noticeable effects on the GPC trace, specifically on the low molecular tail. Therefore, his polydispersities always increased. As indicated previously, the polydispersities of these experiments remained the same or decreased as the $\overline{M}_w$ decreased. Again, this is explained by the broad distribution of the virgin material and the ability of this polymer to mask the shorter chain molecules.

The melt rheology and molecular weight data can be correlated and discussed most easily by Figure 40 and Table 13. This graph shows μ_{10} as a function of $\overline{M}_w$ for the 50 and 100 RPM experiments. Comparisons with the theoretical curve of Bueche (12, 13) and the data of Rudd are also given.

The slope of this plot has been treated theoretically in terms of the molecular entanglement theory of Bueche. A brief discussion of this theory was given in the Theoretical and Empirical Considerations chapter. However, the origin of the 3.4 or 3.5 power dependency of zero-shear viscosity on molecular weight ($\overline{M}_w$) was discovered by Flory (24) via empiricism.

Lines marked 2 and 5 show the slopes determined by Rudd (52, 53). His work was with polystyrene at two levels of shear. He reports a slope value of 3.14 at extrapolated zero shear and 2.54 at a higher shear of 400 sec⁻¹.

Least-squares analysis of the 50 and 100 RPM data for Passes 1 to 5 yielded slopes of 2.90 and 3.05, respectively. These values are at

10 sec^{-1} and lie between Rudd's values. The 10 sec^{-1} shear rate is much closer to the extrapolated zero-shear level of Rudd rather than the 400 sec^{-1} , and it is further noted that the 2.90 and 3.05 values are much closer to Rudd's 3.14 than the 2.54. Once again, the data reported from the degradation study appears to be good data. The comparison with other workers' data (Ballman and Simon's (4) data agrees with Rudd and therefore, agrees with the degradation study's data) is good, plus the agreement with the theoretical figure is fair (as good as others).

In addition to the fact that the 50-and 100 RPM data agree with previously reported information, the second important result is the difference of the intercepts of the 50 and 100 RPM lines. The 50 RPM degradation data lie above the 100 RPM data. This is a result of interest. An attempt to find the theoretical significance of the intercept of the $\log \overline{M}_w - \log \mu$ curve was made. However, the only statements concerning the intercept are given in terms of temperature differences and material differences.

To obtain the shift of intercept that appears in Figure 40 for Lines 3 and 4, a 10°C temperature difference would be required. This would have to be a systematic temperature drop for all experiments. As previously stated, the temperature range for all the rheological data was between 228°C and 232°C . By examining the experimental data (Tables 6, 21 to 29), one can see the temperatures scatter about in this range, and there is no systematic drop in temperature between the 50 and 100 RPM experiments.

By material differences, Flory and previous workers were concerned with different polymers, i.e., polystyrene and polyisobutylene. Granted that the 10 extruder runs produced 10 different materials; however, the materials were different by the molecular weight parameters only and they still remained general-purpose polystyrene.

The difference in intercepts could only point to an effect of the screw speed on the measurement of the rheological properties. The 50 RPM material has distinct rheological differences from the 100 RPM polymer. These differences lie in the structure of the polymer melt.

This fact is not surprising when compared with Walzac's (62, 63, 64) results. He also found an effect of screw speed on the melt structure.

If one subscribes to Busse's (13) model of a coiled ball of polymer molecules which form the polymer melt structure, the effect of screw speed would be quite evident. Rheological measurements are affected by the rearrangement of the coiled balls, by molecular interactions of the molecules that make up the balls, by the size of the coiled balls, and by interconnections between the coiled balls. Any number of these factors can be affected by screw speed which certainly appears to be the case in the 50 and 100 RPM studies.

The remainder of the degradation studies is concerned with the relation of the observed changes in molecular and rheological parameters to the extruder operating conditions. A calculation procedure for E_D --the available energy for degradation--was outlined in detail in Chapter III. Table 14 summarizes the information necessary to calculate E_D and records the E_D , ΣE_D and $1/\Sigma E_D$ values for the 50 and 100 RPM experiments. Because of constant extruder conditions during the 50 RPM recycle, E_D values for Passes 1 through 5 are the same (362 BTU/LBM-PASS). To obtain ΣE_D , one just multiplies by the pass number. However, due to the feeding problems, the 100 RPM E_D values vary. Changes in motor amperage were responsible for the different values of E_D . Slight differences in inlet and outlet polymer temperature had a small effect.

A correlation of E_D and the dependent variables of $\overline{M}_w$ and μ_{10} was derived from an Arrhenius-type behavior. Values of $1/\Sigma E_D$ were calculated and plotted against the log of $\overline{M}_w$ and the log of μ_{10} . This semi-log plot appears in Figure 42.

Examination of the plot provides the necessary insight into the effect of extruder recycle on general-purpose polystyrene. Two important observations are evident from this figure. First, the difference in slope of the 50 and 100 RPM lines and second, the definite break point in the lines at an $1/\Sigma E_D$ value of 0.8 to 0.9×10^{-3}

$$\frac{\text{lbm} \cdot \text{pass}}{\text{btu}} .$$

For simplification, Figure 42 will be broken into 2 regions. Formation of a single line characterizes Region I. The slope of the Region I line is much greater than the slopes of the Region II lines. Region I is before the break point (where the lines meet). In this region, the 50 and 100 RPM lines have similar slopes and intercepts.

In Table 15, the slopes and intercepts of these lines appear. The slopes have been labeled with $\underline{K}$ plus a subscript to denote the dependent variable. The large difference in the $\underline{K}$ values between the 50 and 100 RPM data (65% and 107%) indicate a much more rapid rate of degradation during the recycles at 100 RPM. This strongly indicates an effect of screw speed level on the degradation of general-purpose polystyrene, perhaps as much as a factor of 2.

In Region I, the difference in $\underline{K}$ values when calculated as separate lines was small (5 to 7%), therefore, a single line was fit to these data. Region I shows a more rapid rate of polymer degradation than Region II--a 7 to 11 fold increase in the rate of decrease of viscosity and a 3 to 6 fold rate of decrease in the molecular weight.

Before an attempt is made to explain this phenomenon at the molecular level, a reminder is given about the experimental data. The rheology data was determined via the BLS Twin-Slit Extrusion Rheometer. The molecular weight analyses were completed by GPC. These represent two very independent experimental observations. Yet both variables break at the same position on the graph, which is a most conclusive piece of evidence for the effects of screw speed on the extrusion degradation of polystyrene.

By consideration of the Busse model of a polymer melt, one can visualize the coiled balls of polymer molecules with the long chain molecules dangling from the main spherical element. These long chain molecules have a pronounced effect on zero-shear viscosity. As this element enters an energy field--which consists of mechanical and thermal energy--the protruding ends of the long chain molecules are most susceptible to bond cleavage. The shear level of the energy field would affect the rate at which the longer chain segments are broken--the higher the shear action, the greater the effect on these long chain

molecules.

After elimination of the dangling chain molecular segments, the average length of the molecules which make up the spherical element would be the same. Now the energy field would be permitted to operate on the coiled balls. As these molecules begin to degrade, the rate of bond breakage is increased. Here the effect of shear level disappears due to the lack of any dangling chain segments. The thermal and shear energy act on the polymer molecules together, and thus this accounts for the increase in rate of degradation. In this sense, the dangling chain segments act as an inhibitor against degradation in Region I. However, once the energy has been supplied to reduce the chain length down to the critical point (few dangling segments exist), the inhibitor effect is removed. While this may or may not represent a reasonable explanation of extrusion degradation on a molecular scale, it does represent an attempt that is made within the constraints of the current model of the polymer melt. One must realize that this model is purely hypothetical in nature.

Rheological Studies

This section of the study concerns measurements of the elastic properties of STYRON 686. The manifestation of the elastic character is witnessed by the non-zero pressure at the rheometer slit exit. The residual or exit pressure, as it is referred to, has been treated theoretically by Sakaidis (55, 56). He has shown a direct relationship between the exit pressure and the primary normal stress difference. It is well known that the primary normal stress difference is an elastic property of a polymeric material. Han has made experimental measurements of the exit pressure of several polymers, including STYRON 686. Comparisons of his data with the degradation study's data will be discussed.

At the onset of this study, a controversy over the exit pressure

existed. TNO Laboratories, through the publications of Eswaran, Schiff, den Otter and others, reported zero exit pressures. Han, Blum et al. and Arai concluded a definite measureable residual pressure at the exit of a flow channel. With this controversy in mind, the BLS Twin-Slit Extrusion Rheometer was designed to obtain the most accurate measurements of the axial pressure distributions to date. Chapter IV outlines the techniques used for calibration of the transducers and the design for placement of the pressure sensors. To this researcher's knowledge, the experimental data reported in this study represent the most extensive and accurate measurements of the exit pressure for polystyrene.

Exit pressures were calculated from the linear relationships between axial distance and pressure. These linear equations were determined by a least-squares analysis of the experimental pressure data. Therefore, the calculated exit pressures represent extrapolations of the axial pressure distributions to the slit exit. The exit pressure data appear in Tables 16, 48 to 56 in psi and dynes/cm² units.

As can be expected, the extrapolated values contain a great deal of scatter. Examination of the exit pressures as a function of shear rate show a general trend towards higher exit pressures as shear rate increases. For the 50 RPM experiments, the increase in exit pressure with shear rate is more pronounced than for the 100 RPM data.

Figures 42 to 44 show the exit pressure as a function of shear rate on a log - log basis. Han has reported this logarithmic relationship for several polymers, including STYRON 686. The data from each pass were fit via least-squares analysis, and the results appear in Table 17. The best-fit equations for all 5 passes at 50 RPM proved to be linear. The slope of the $\log \gamma_T$ versus $\log P_E$ line is represented by a_1 . For 4 passes, the values of a_1 are within 6%. The fifth slope (Pass 2 data) differs from the others by 20%. A 10% reproducibility error is associated with the measurements of the exit pressure. Most of this is due to the extrapolation. Examination of the intercept, a_0 , reveals no definite trend in the data with respect to recycle. At 50 RPM, recycle does not appear to affect the exit pressure data. At

100 RPM, the values of a_1 are small, approximately 1/3 of the values at 50 RPM. The lines appear almost horizontal on Figure 43. The intercepts vary less than the data from 50 RPM and again, there is no definite trend. Recycle at 100 RPM, as was the case for 50 RPM, does not affect exit pressure.

Slopes for the five passes at 50 RPM were averaged and compared with the average of the 100 RPM slopes. A difference by a factor of 3 resulted. Once again, the screw speed has affected a rheological measurement. Just as the viscosity data indicated a screw speed effect, so does the elastic data.

As pointed out earlier in Chapter III, the second normal stress difference (σ_2) is derived from exit pressure data. The negative of the derivative of the exit pressure with respect to the log of the wall shear stress equals the secondary normal stress difference.

$$P_{22} - P_{33} = \sigma_2 = - \frac{d P_E}{d \ln \tau_w} \quad (26)$$

This derivation was shown by Sakaidis (55, 56). Figures 45 to 47 contain the log wall shear stress-exit pressure data obtained from the degradation study. Table 18 summarizes a least-squares analysis of this information.

From 9 out of the 10 sets of the rheological measurements, a linear relationship between $\log \tau_w$ and P_E was found. This corresponds to a secondary normal stress difference that is independent of shear rate. A second-order dependency of σ_2 on shear rate has been suggested by theory (10). An explanation of the independence of σ_2 on shear rate found in this study can be attributed to two factors. First, the σ_2 values were determined from taking the slope of the extrapolated pressure distributions. Second, the wall shear stress range was only one decade. Within the narrow stress range and with all the experimental scatter, a first-order $P_E - \ln \tau_w$ relationship was the only one statistically permissible.

Once again, the slope and intercept data reflect an absence of any recycle affect on the secondary normal stress data. But the 50 and 100

RPM comparison indicates a 2 to 3 fold influence from the screw speed. The average slope value for the 50 RPM data is 1.662×10^6 dynes/cm² while the 100 RPM value is 5.628×10^5 dynes/cm². Standard deviation for σ_2 for the 5 data at each RPM level were $\pm 0.1288 \times 10^6$ and $\pm 0.1386 \times 10^6$, respectively.

Williams and Olabisi (76) and Tanner (64) reported negative values for the second normal stress in recent publications. Their work was in the area of polymer solutions. Magnitude for the σ_2 values were in the range $-0.10 \sigma_1$ to $-0.20 \sigma_1$. Values for σ_2 from this study depended on screw speed level and ranged from $-1.0 \sigma_1$ at 50 RPM to $-0.17 \sigma_1$ at 100 RPM. The 50 and 100 RPM data supported the contention that the second normal stress is opposite in sign from the primary normal stress and smaller in magnitude.

The strong elastic nature of the STYRON 686 is demonstrated by Figures 48 to 50. Values for the stress ratio (recoverable strain ratio) were calculated from the exit pressure (P_E) divided by the wall shear stress. At low shear rates ($< 150 \text{ sec}^{-1}$), the stress ratio values are high because of the lower wall shear stresses. With increases in shear rate, the stress ratio approaches a value of 1.0.

A recent article of Han (34) revealed a compilation of his previous data on STYRON 686. Han's data were taken on three instruments--a Weissenberg Rheogoniometer, a capillary, and a slit rheometer. A temperature of 200°C was maintained for all of his experimentation. Using a value for the activation energy for viscous flow (ΔE_T) of 23 KCAL/MOLE, Han's data was adjusted to 230°C. The results are summarized in Table 7. Figure 51 shows a comparison of the Han temperature-adjusted data, the BLS Pass 1, 50 RPM data, and the Dow Caplastometer data. Comparison of the Dow data with the Pass 1, 50 RPM data revealed lower viscosities at a given wall shear stress for the Pass 1, 50 RPM material. This was the expected result. The effect of screw speed (prior shear in the extruder) has been cited early in this chapter. From the fact that the Caplastometer applied almost no prior shear to the STYRON 686, it would be expected to produce higher viscosities. Han's data also behaved as expected. As he varied screw

speed to obtain the viscometric information, the screw speed level created scatter in the data.

Attention is turned to a comparison of the exit pressure data in Table 20. A 30°C temperature difference between Han's data and the BLS data is the first important factor. Han (36) reports an Arrhenius-type functional behavior of the exit pressure-temperature relationship

$$P_E = \alpha e^{\Delta E/RT} \quad (27)$$

However, he supports his contention with a limited amount of experimental information. The BLS data for $\underline{b}$ ($P_E = a \gamma_T^b$) at 230°C is lower than Han's figure by a factor of 3 at 50 RPM. Likewise, the 100 RPM data is even lower.

Han's wall shear stress-exit pressure data were taken from his publications and analyzed via the least-squares method. Linear relationships were observed for all these data. This produced a σ_2 value independent of shear rate--the same result produced from this study. In this respect, the BLS and Han data agree. Again, the magnitude of σ_2 is lower for the BLS data.

Attention should now be focused on Han's method for obtaining experimental exit pressure data. He employed a screw extruder just as this study did. However, he was forced to change screw speed to vary flow rate for determination of the rheological data. As proven by this study, the screw speed level experienced by a polymer melt prior to rheological investigation will affect the experimental measurements. Furthermore, the elastic properties appear to be affected more than the viscous properties. This is evidenced by the partial agreement with Han of the viscosity data but the factor of 3 difference in the elastic data.

At any rate, some doubt is cast on Han's experimental investigation until the influence of screw speed level on rheological measurements can be studied further. This is another plus for the BLS Twin-Slit design because the rheological measurements are determined without changes in the screw speed.

Oven Studies

Results of the static oven studies are shown in Figures 52 to 57. The STYRON 686 without inhibitors to protect against thermo-oxidative degradation is very susceptible to degradation. Not shown in the figures are the results from the nitrogen atmosphere experiments. During the course of one hour exposure to a 230°C temperature, the $\overline{M}_w$, $\overline{M}_n$, and P_d of several STYRON 686 samples did not change. Without air present, STYRON 686 is not susceptible to thermal attack.

Thought is now given to how much air the STYRON 686 comes in contact with inside the 2 1/2-inch extruder. During the extruder start-up, air present in the screw void spaces comes in contact with the polymer. This material was always discarded. However, after steady-state is attained, the pressure at the extruder head is several thousand pounds per square inch. From the extruder head to the throat, the pressure profile decreases. At some position between the second or third flight, the pressure inside the extruder will equal atmospheric conditions. This position marks the last contact point between air and the polymer. Air cannot push against the positive pressure profile of the polymer melt. This effectively seals off the extruder against air flow.

The initial 2 or 3 flights will have air entrapped in the channels, but temperature at this position is quite low (< 100°C) and the polymer will be primarily solid. Therefore little or no degradation occurs here.

Figures 55 to 57 compare the 50 and 100 RPM data with the static oven tests. The exposure time for the 50 and 100 RPM materials is equal to the extruder residence time. This includes time under the conditions of heat and shear. From a knowledge of the nitrogen atmosphere test results, one is able to view the effect of shear. Placing a polystyrene sample in a 230°C environment for 10 minutes that is void of oxygen will cause no degradation. But contained for the same period of time in a shear environment, the sample undergoes appreciable degradation. Increases in the screw speed (100 RPM data) causes the polymer

to degrade even faster.

In addition to showing the affect of shear, Figures 55 to 57 reveal the inability of static oven tests (air or nitrogen atmospheres) to provide insight into polymer degradation during processing. This fact has been pointed out by Porter (2, 26) and is further supported by this study.

CHAPTER VII

CONCLUSIONS

Degradation Studies

From results of the degradation study, the following conclusions were drawn:

1. The BLS Twin-Slit Extrusion Rheometer represents a novel design for extrusion rheometers. This design enables one to study the rheology of polymer melts over a large range of conditions. A temperature range of 200 to 250°C and a pressure range of 0 to 3000 psi can be achieved. In addition, the effect of levels of screw speed on polymer rheology can be investigated.
2. Axial pressure distributions for STYRON 686 were linear for all flow rates. Discussions with regard to non-linearities in the axial pressure distribution has been put forth by workers at TNO, Delft; however, for this study, non-linearities did not exist.
3. Slit rheometry is a simple method for the study of polymer melt rheology. Ease of construction and the simplification of calculations are two of the strong points. The ability to flush mount electronic pressure transducers is another outstanding feature.
4. General-purpose polystyrene undergoes degradation under the conditions of heat and shear. This breakdown is observed by decreases in melt viscosity and weight-average molecular weight.

Molecular weight distribution becomes narrower. The molecular weight viscosity relationship follows the previously established 3.4 power dependency ($\mu_{APP} \propto \overline{M}_w^{3.4}$).

5. Screw speed level affects viscosity measurements. The exposure of a polymer melt to a high screw speed prior to viscosity measurement will lower the viscosity reading.
6. A characteristic parameter, E_D , was developed and was descriptive of the extruder operating conditions. This parameter incorporates mechanical and thermal energy data that influences the polymer's degradation during the extrusion process.
7. The functional dependency of weight-average molecular weight and low shear apparent viscosity was related by an Arrhenius-type behavior. The term E_D is analogous to temperature in the Arrhenius relationship. An increase in temperature corresponds to the summation of E_D (ΣE_D).
8. Below a ΣE_D value of 1000 to 1250 btu/lbm - pass, general-purpose polystyrene's degradation is affected by screw speed. Above this value, the effects of screw speed are not separable. The rate of degradation increases above this level also.

Rheological Study

1. Elastic properties of polymer melts can be measured by the BLS Twin-Slit Extrusion Rheometer. Measurements of the exit pressure provide the necessary data.
2. A definite residual or exit pressure exists for polystyrene. For the 123 experimental points taken over the course of this study, the exit pressure was always observed as a positive pressure and attained a value between 18 and 44 psi.
3. The elastic properties of polystyrene are not affected by recycle. No changes with extruder recycle were observed in either the primary (P_E) or secondary (σ_2) normal stress

measurements.

4. Screw speed also affects elastic property measurements. The 50 and 100 RPM data reveal a factor of a 2 to 3 difference in the magnitude of the elastic parameters.

CHAPTER VIII

RECOMMENDATIONS

As a consequence of this study, the following areas of investigation could merit further work:

1. Improvement in the temperature control of the BLS Twin-Slit Rheometer is desirable. The heater bars should be changed from the present axial configuration to a lateral configuration. Thus, temperature control would be improved in the axial direction by individual control of the laterally placed heaters. This would be a good feature when investigating polymers that produce a great deal of viscous heat generation. An axial temperature profile would be created by this type of polymer.

In addition, the temperature range of the BLS instrument would be broadened. Temperatures below 200°C could not be maintained for general-purpose polystyrene due to an axial temperature profile.

2. More screw speeds should be studied to complete the study of general-purpose polystyrene. Screw rotation speeds of 25 and 75 RPM would be good selections. With this additional data, more light could be shed on the effect of screw speed rheological measurements and on polymer degradation.
3. The influence of screw speed on polymer melts merits further investigation. This includes both experimental and theoretical study.
4. Additional polymers should be studied. This would definitely

include work on poly(vinyl chloride) which is known to undergo rapid degradation during extrusion.

5. The data acquisition system for the GPC by a real-time computer should be completed.
6. With a modification of the present design, on-line viscosity measurements can be made during the processing of molten polymers. This can be done by providing different dimension channels and supplying each with two pressure measuring devices or a differential unit. Information concerning the elastic properties of the polymer melt would be possible with another pressure transducer located in the downstream cavity.

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APPENDIX A

CALIBRATION COMPUTER PROGRAM

C PROGRAM FILE NAME- CALIB

C PAUL SPRINGER-2/15/73

C THIS PROGRAM IS USED TO CALIBRATE THE 8 MELT THERMOCOUPLES
C ON CHANNELS 33 THRU 40 OR THE 6 MELT PRESSURE TRANSDUCERS
C ON CHANNELS 48 THRU 53 OR THE DIE THERMOCOUPLES ON CHANNELS 4,5,
C 41,46,47.

C 500 DATA POINTS ARE TAKEN PER CHANNEL AND THE MEAN
C VOLTAGE IS DISPLAYED.

C DIMENSION VOLTS(19),SUM(19),AVE(19),IDATE(6),ICHAN(18)
C DATA ICHAN/33,35,37,39,40,41,42,5,44,45,46,47,48,49,50,
C 151,52,53/

C INITIALIZE PROGRAM VARIABLES.

C N1=FIRST CHANNEL NUMBER.
C N2=LAST CHANNEL NUMBER.

C N1=13
C N2=18
C N=18
C DO 2 I=1,18
C SUM(I)=0.0
C AVE(I)=0.0
C 2 CONTINUE

CCC

1234

C

30
40

CCC

22

C

50

101

104

CALL EXIT

APPENDIX B

DATA ACQUISITION PROGRAM

```

C      PROGRAM FILE NAME-PWSEXT  5/24/73
C
C      THIS PROGRAM DISPLAYS THE MELT TEMPERATURES AND PRESSURES
C      DURING EXTRUSION.
C
C      500 DATA POINTS ARE TAKEN AND AVERAGED WITH THE MEAN
C      DISPLAYED.
C
C      DIMENSION VOLTS(18),SUM(18),AVE(18),IDATE(6),ICHAN(18)
C      DATA ICHAN/33,36,37,39,40,4,42,5,44,45,46,47,48,49,
C      150,51,52,53/
C
C      INITIALIZE PROGRAM VARIABLES.
C
C      N=18
C      DO 2 I=1,18
C      SUM(I)=0.0
C      AVE(I)=0.0
2      CONTINUE
C
C      START CLOCK.
C
C      CALL DATE(IDATE)
C
C      SAMPLE CHANNELS.
C
C      DO 40 I=1,500
C      CALL RTIN (N,ICHAN,VOLTS,IEV)
C      DO 30 J=1,18
30      SUM(J)=SUM(J)+VOLTS(J)
40      CONTINUE

```

C
C
C

DIVIDE BY 500 TO GET MEAN.

DO 50 I=1,18
AVF(I)=SUM(I)*0.002
CONTINUE

50

C
C
C

COMPUTE TEMPERATURES, AND PRESSURES.

TEMP1=119.36687-17.668676*AVE(1)
TEMP4=120.51-17.796*AVE(2)+0.0295*AVE(2)**2+0.0065*AVE(2)**3
TEMP5=119.18807-17.712716*AVE(3)
TEMP7=118.63771-17.714559*AVE(4)
TEMP10=120.92518-17.76860*AVE(5)
TPT=115.63627-18.363094*AVE(6)-0.080749218*AVE(6)**2
RB1=107.21275-20.279932*AVE(7)-0.21792847*AVE(7)**2
RB4F=109.75512-20.410698*AVE(8)-0.20184533*AVE(8)**2
RLT1=106.67603-20.654037*AVE(9)-0.23870850*AVE(9)**2
RLT2=109.04269-20.402865*AVE(10)-0.22784366*AVE(10)**2
RLT3=110.81438-20.495761*AVE(11)-0.22522248*AVE(11)**2
RLT4=106.77871-21.305310*AVE(12)-0.30763817*AVE(12)**2
PRESS1=65.232073-156.86365*AVE(13)
PRESS2=191.09656-312.48965*AVE(14)
PRESS3=-55.852924-58.817427*AVE(15)-0.89327598*AVE(15)**2
PRESS4=-63.935054-108.5.6679*AVE(16)
PRESS5=-108.82046-394.92348*AVE(17)
PRESS6=-107.14148-120.67114*AVE(18)+0.46296922*AVE(18)**2

C
C
C

WRITE OUT TIME, TEMPERATURES, AND PRESSURES.

WRITE(23,101)IDATE(4),IDATE(5),IDATE(6)
WRITE(23,102)TEMP1,TEMP4,TEMP5,TEMP7,TEMP10,TPT,RB1,RB4F,RLT1,RLT2
1,RLT3,RLT4,PRESS4,PRESS5,PRESS2,PRESS1,PRESS6,PRESS3
FORMAT(3I8)

101
102

FORMAT(1H,6F7.1/6F7.1/6F7.1)
CALL EXIT
END

	C	PAUL W. SPRINGER 4/8/73
	C	PROGRAM NAME - GPC CALC.
0001		REAL MOM0,MOM1,MOM2,INT,MW
0002		DIMENSION DAT(200),HT(200),WT(200),WX(200)
	C	READ IN NUMBER OF GPC CURVES (NUMBER)
0003	5	READ(5,10) NUMBER
0004	10	FORMAT(I5)
0005		DO 900 K=1,NUMBER
	C	READ IN RUN NUMBER AND SAMPLE NUMBER
0006		READ(5,15)NRUN,NSAM
0007	15	FORMAT(2I5)
	C	READ IN COUNT OF LAST DATA POINT -(DEND) AND INT.
0008		READ(5,12) DEND,INT
0009	12	FORMAT(2F5.2)
	C	READ IN GPC CURVE HEIGHT DATA AT COUNT DBEG BY INTERVALS INT
0010		DBEG=25.00
0011		NDATA=((DEND-DBEG)/INT)+1.0
	C	READ IN GPC CURVE HEIGHT DATA BEGINNING AT COUNT DBEG TO COUNT DEND AT
	C	INTERVAL INT
0012		READ(5,18) (DAT(I),I=1,NDATA)
0013	18	FORMAT(16F5.2)
	C	BEGIN CALCULATION OF MWD
	C	SUBTRACT BASELINE AND CORRECT FOR BASELINE DRIFT
	C	HT=CURVE HEIGHT CORRECTED FOR BASELINE;WT(I)=MW AT COUNT(I)
0014		BASE1=DAT(1)
0015		BASE2=DAT(NDATA)
0016		BDEF=BASE2-BASE1
0017		HTSUM=0.0
0018		DO 40 I=1,NDATA
0019		COUNT=FLOAT(I)*INT +DBEG-INT
0020		FRAC=(COUNT-DBEG)/(DEND-DBEG)
0021		HT(I)=DAT(I)- (BASE1+FRAC*BDEF)
0022		IF(HT(I).GT.0.0) GO TO 101
0023		HT(I)=0.0

```

0024      101  CAL=19.881248-0.97007969*COUNT+0.022702553*COUNT**2-0.0002090141*C
          10UNT**3
0025      WT(I)=10.**CAL
0026      HTSUM=HTSUM + HT(I)
0027      40  CONTINUE
0028      MOM0=0.0
0029      MOM1=0.0
0030      MOM2=0.0
0031      DO 60 I=1,NDATA
0032      HT(I)=HT(I)/HTSUM
0033      MOM0=MOM0+ HT(I)/WT(I)
0034      MOM1=MOM1+ HT(I)
0035      MOM2=MOM2+ HT(I)*WT(I)
0036      60  CONTINUE
0037      MOM2=MOM2/MOM1
0038      MOM1=MOM1/MOM0
0039      PDIS=MOM2/MOM1
          C  WRITE OUT HEADINGS,DATA,MW'S OF SAMPLE
0040      WRITE(6,150)NRUN
0041      150  FORMAT(1H ///,5X,'RUN NUMBER',8X,15/)
0042      WRITE(6,155) NSAM
0043      155  FORMAT(1H ,5X,'SAMPLE NUMBER',5X,15/)
0044      WRITE(6,170)
0045      170  FORMAT(1H ,5X,'COUNT NUMBER',10X,'GPC CURVE HEIGHT'///)

```



```

0046      DO 160 I=1,NDATA
0047      COUNT=(FLOAT(I)*INT)+DBEG-INT
0048      WRITE(6,165)COUNT,DAT(I)
0049      165 FORMAT(1H,9X,F5.2,19X,F5.2)
0050      160 CONTINUE
0051      WRITE(6,180)MOM1
0052      180 FORMAT(1H //,5X,'NUMBER AVER MOLECULAR WEIGHT',5X,E10.4/)
0053      WRITE(6,185)MOM2
0054      185 FORMAT(1H,5X,'WEIGHT AVERAGE MOLECULAR WEIGHT',5X,E10.4/)
0055      WRITE(6,190)PDIS
0056      190 FORMAT(1H,5X,'POLYDISPERSITY MW/MN',5X,F10.3///)
0057      WRITE(6,300)
0058      300 FORMAT(1H,5X,'MOLECULAR WEIGHT DISTRIBUTION'///)
0059      WRITE(6,305)
0060      305 FORMAT(1H,'CHAIN LENGTH',10X,'MOLECULAR WEIGHT'/)
0061      MWMON=104.14
0062      DO 250 I=1,NDATA
0063      J=NDATA-I+1
0064      COUNT=DBEG+FLOAT(J)*INT-INT
0065      CAL=19.881248-0.97007969*COUNT+0.022702553*COUNT**2-0.0002090141*C
0066      1COUNT**3
0066      MW=10.**CAL
0067      X=MW/MWMON
0068      WRITE(6,320)X,MW
0069      320 FORMAT(1H,4X,E12.4,12X,E12.4)
0070      250 CONTINUE
0071      900 CONTINUE
0072      CALL EXIT
0073      END

```

APPENDIX C

GPC OPERATING CONDITIONS, CALIBRATION EQUATION,
AND CALCULATION PROGRAM

The following conditions for the GPC operation were established and kept constant for all molecular weight determinations.

SOLVENT	=	Tetrahydrofuran (reagent grade)
TEMPERATURE	=	25°C
FLOW RATE	=	1.0 ml/min
CONCENTRATION	=	3.0 mg/ml
RECORDER SENSITIVITY	=	2 X
INJECTION TIME	=	2 min

Calibration standards were prepared and yielded these results:

<u>Sample</u>	<u>Chain length</u>	<u>Peak M_w</u>	<u>Elution Volume</u>
0	--	3,140,000	25.20
1	48,000	1,987,000	26.28
2	20,000	830,000	28.00
3	9,800	402,000	29.67
4	4,160	171,000	32.13
5	2,360	97,200	33.52
6	1,220	50,000	35.50
7	480	19,750	38.36
8	244	10,000	40.00
9	117	4,800	42.16

The elution volume - peak M_w data was analyzed via the least-squares technique which gave the following equation for the calculation of molecular weight:

$$\log M_w = 19.88 - 0.9700 * \text{COUNT} + 0.0227 * \text{COUNT}^2 - 0.0002091 * \text{COUNT}^3$$

where COUNT = Elution Volume

Column configuration included five columns and were arranged in order of increasing pore size:

2.0 - 5.0×10^3 , 5.0×10^3 - 1.5×10^4 , $1.5 - 5.0 \times 10^4$,
 6.5×10^4 , 5.0×10^6 .

APPENDIX D

TABLES 21 to 29EXPERIMENTAL DATA

TABLE 21

EXPERIMENTAL DATA FROM RUN 129

P = pressure -- psi T = temperature -- °C F = mass flow rate -- gr/min

Pass 2, 50 RPM

<u>T₁</u>	<u>T₂</u>	<u>T₃</u>	<u>T₄</u>	<u>T₅</u>	<u>T₆</u>	<u>T₇</u>	<u>T₈</u>	<u>T₉</u>	<u>T₁₀</u>	<u>T₁₂</u>	<u>P_H</u>	<u>P_A</u>	<u>P₁</u>	<u>P₂</u>	<u>P₃</u>	<u>P₄</u>	<u>F</u>
215	221	228	222	219	220	235	231	228	230	229	3037	2247	303	220	150	61	12.2
214	219	227	221	218	222	235	232	229	230	230	2844	2108	484	339	225	87	29.3
214	220	227	222	218	222	235	231	229	230	230	2826	2121	633	451	289	112	54.8
215	221	228	222	219	220	234	231	231	229	231	3052	2269	750	538	342	132	85.0
216	223	227	219	217	219	233	230	229	229	230	2924	2217	806	577	368	140	92.0
216	223	227	220	218	219	232	228	230	231	230	2959	2210	982	705	444	169	203.0
215	222	227	220	219	219	230	228	230	230	228	2971	2190	1081	775	489	185	269.0
216	221	227	221	217	220	231	228	232	232	229	2850	2101	1130	812	511	192	344.0
215	220	226	221	219	218	225	225	229	229	230	3016	2285	1214	874	549	207	417.0
215	221	225	221	219	217	221	222	229	229	230	3025	2296	1300	933	583	220	522.0
217	221	224	220	219	216	218	219	228	228	229	2950	2225	1354	972	608	229	610.0

TABLE 22

EXPERIMENTAL DATA FROM RUN 130

P = pressure -- psi T = temperature -- °C F = mass flow rate -- gr/min

Pass 3, 50 RPM

<u>T₁</u>	<u>T₂</u>	<u>T₃</u>	<u>T₄</u>	<u>T₅</u>	<u>T₆</u>	<u>T₇</u>	<u>T₈</u>	<u>T₉</u>	<u>T₁₀</u>	<u>T₁₂</u>	<u>P_H</u>	<u>P_A</u>	<u>P₁</u>	<u>P₂</u>	<u>P₃</u>	<u>P₄</u>	<u>F</u>
215	219	226	224	230	233	237	233	232	231	229	2882	2225	299	220	140	60	13.8
215	219	225	222	228	229	235	230	230	229	229	2850	2200	408	300	188	78	23.4
215	219	225	221	225	225	233	230	229	228	228	2873	2181	511	370	230	93	35.3
215	218	225	223	230	232	235	231	231	231	230	2800	2150	578	420	259	104	53.0
215	220	226	222	219	219	229	227	228	228	228	2970	2300	908	652	405	156	158.0
216	220	227	222	222	218	226	224	229	228	228	2997	2304	1100	784	485	185	286.0
215	220	227	222	218	218	225	225	228	228	229	2980	2270	1147	823	507	193	350.0
215	221	227	222	218	218	224	224	229	229	231	2978	2262	1203	864	530	203	422.0
215	221	227	222	217	217	224	223	229	228	229	3010	2300	1227	879	541	206	442.0
216	220	227	222	217	217	221	222	230	229	230	2980	2280	1297	927	570	216	524.0
215	221	227	222	217	217	220	221	230	229	228	2850	2150	1326	945	581	221	614.0

TABLE 23

EXPERIMENTAL DATA FROM RUN 131

P = pressure -- psi T = temperature -- °C F = mass flow rate -- gr/min

Pass 4, 50 RPM

<u>T₁</u>	<u>T₂</u>	<u>T₃</u>	<u>T₄</u>	<u>T₅</u>	<u>T₆</u>	<u>T₇</u>	<u>T₈</u>	<u>T₉</u>	<u>T₁₀</u>	<u>T₁₂</u>	<u>P_H</u>	<u>P_A</u>	<u>P₁</u>	<u>P₂</u>	<u>P₃</u>	<u>P₄</u>	<u>F</u>
218	215	221	218	213	220	234	232	228	231	229	2735	2077	275	188	124	58	13.7
217	217	222	218	213	220	234	233	228	231	231	2731	2067	344	241	156	70	21.4
217	217	223	219	213	220	234	233	229	231	230	2765	2120	438	309	195	84	33.2
217	218	224	220	214	220	235	233	229	232	230	2780	2101	530	373	235	97	48.9
217	219	224	220	214	220	235	233	229	232	229	2770	2137	658	467	290	118	81.6
219	220	224	217	214	220	234	231	230	231	231	2790	2120	775	549	338	136	120.0
218	220	226	218	215	219	231	228	228	228	228	2800	2200	980	701	433	171	222.0
217	220	226	220	215	219	230	227	230	231	230	2840	2200	1135	805	497	195	383.0
220	220	223	216	213	218	227	225	229	230	229	2940	2250	1182	837	517	201	437.0
217	219	224	219	210	214	218	219	228	228	229	2800	2060	1323	940	569	219	608.0

TABLE 24

EXPERIMENTAL DATA FROM RUN 132

P = pressure -- psi T = temperature -- °C F = mass flow rate -- gr/min

Pass 5, 50 RPM

<u>T₁</u>	<u>T₂</u>	<u>T₃</u>	<u>T₄</u>	<u>T₅</u>	<u>T₆</u>	<u>T₇</u>	<u>T₈</u>	<u>T₉</u>	<u>T₁₀</u>	<u>T₁₂</u>	<u>P_H</u>	<u>P_A</u>	<u>P₁</u>	<u>P₂</u>	<u>P₃</u>	<u>P₄</u>	<u>F</u>
213	218	222	216	220	225	234	231	230	231	228	2700	2024	268	196	124	63	15.7
213	218	222	216	221	228	235	231	231	232	229	2661	2025	353	256	160	75	26.7
214	218	223	218	223	229	237	232	231	232	230	2632	2006	429	309	191	85	38.1
213	218	223	219	225	230	237	232	231	232	230	2535	2000	483	354	219	95	50.2
213	214	222	219	226	230	237	232	232	232	230	2520	1954	606	442	272	115	83.9
214	212	222	219	227	230	237	232	232	232	230	2539	1943	727	522	318	133	126.0
214	210	221	221	219	228	233	236	230	231	231	2530	2012	906	652	396	162	238.0
213	215	221	219	229	231	236	230	232	231	232	2694	1968	959	695	419	172	266.0
214	216	221	217	230	231	235	230	231	232	229	2710	2000	1092	785	473	194	406.0
214	217	222	220	230	231	234	229	229	230	231	2725	2053	1177	838	509	206	521.0
214	217	222	220	227	226	230	225	230	231	232	2790	2052	1192	859	534	210	534.0
213	218	223	220	225	225	224	223	231	231	230	2682	2018	1278	919	557	222	630.0

TABLE 25

EXPERIMENTAL DATA FROM RUN 133

P = pressure -- psi T = temperature -- °C F = mass flow rate -- gr/min

Pass 1, 100 RPM

<u>T₁</u>	<u>T₂</u>	<u>T₃</u>	<u>T₄</u>	<u>T₅</u>	<u>T₆</u>	<u>T₇</u>	<u>T₈</u>	<u>T₉</u>	<u>T₁₀</u>	<u>T₁₂</u>	<u>P_H</u>	<u>P_A</u>	<u>P₁</u>	<u>P₂</u>	<u>P₃</u>	<u>P₄</u>	<u>F</u>
222	226	230	230	228	229	240	242	230	229	228	3010	2270	331	254	171	77	13.4
223	226	229	233	227	229	246	246	231	232	231	3095	2221	402	316	207	88	21.8
223	226	230	233	226	229	247	247	231	232	231	3073	2271	503	415	264	109	40.4
223	225	230	233	226	229	246	246	232	232	231	3085	2290	624	484	302	122	58.3
223	226	230	233	225	227	245	244	232	232	230	3088	2304	766	584	341	147	91.4
223	226	230	232	225	226	243	243	232	230	229	3130	2400	833	639	392	159	120.0
223	226	229	232	224	224	242	241	229	229	228	3124	2290	951	724	433	177	172.0
223	226	230	232	224	224	241	239	229	231	228	3132	2328	1036	783	463	191	236.0
223	226	229	232	224	222	237	234	230	232	231	3238	2500	1227	919	554	219	564.0
223	226	228	231	224	221	233	229	231	232	232	3266	2440	1343	1006	600	232	726.0
223	225	228	230	223	218	227	223	230	232	232	3264	2440	1411	1052	629	241	870.0

TABLE 26

EXPERIMENTAL DATA FROM RUN 134

P = pressure -- psi T = temperature -- °C F = mass flow rate -- gr/min

Pass 2, 100 RPM

<u>T₁</u>	<u>T₂</u>	<u>T₃</u>	<u>T₄</u>	<u>T₅</u>	<u>T₆</u>	<u>T₇</u>	<u>T₈</u>	<u>T₉</u>	<u>T₁₀</u>	<u>T₁₂</u>	<u>P_H</u>	<u>P_A</u>	<u>P₁</u>	<u>P₂</u>	<u>P₃</u>	<u>P₄</u>	<u>F</u>
218	211	211	228	217	215	237	237	230	232	231	2630	2070	271	221	140	63	12.4
219	220	225	228	231	230	241	239	232	232	230	2630	2035	333	261	174	74	21.2
218	212	212	228	217	214	237	236	230	231	230	2770	2120	415	309	202	85	24.8
217	212	212	227	217	215	236	235	227	228	228	2930	2221	563	420	266	107	44.8
218	212	214	228	218	213	236	235	229	230	229	2800	2150	609	442	287	115	56.4
218	220	225	227	231	228	239	237	232	231	230	2680	2125	624	465	291	116	63.9
218	212	213	229	219	213	234	233	228	228	227	2995	2270	778	575	359	144	95.2
218	212	212	226	217	214	235	234	229	229	229	3032	2250	841	624	386	151	134.0
219	212	212	230	219	212	231	229	228	227	227	2760	2190	862	635	396	155	135.0
218	211	213	226	217	214	233	232	229	229	230	2980	2280	956	698	434	170	200.0
219	212	212	231	220	212	230	228	229	227	227	2950	2280	1018	749	461	181	235.0
219	211	215	232	221	213	227	225	228	226	227	2770	2200	1142	821	509	200	341.0
218	219	223	223	229	226	231	228	232	230	230	2800	2225	1155	834	520	201	406.0
218	219	223	223	228	226	229	225	233	231	231	2740	2160	1202	855	539	208	506.0
219	212	215	233	221	233	221	225	231	229	230	2900	2260	1258	908	562	219	570.0
218	217	221	222	228	226	230	226	232	232	233	2930	2280	1271	915	564	220	620.0
219	212	216	234	222	214	220	219	232	230	233	2770	2100	1330	967	594	230	746.0
218	215	216	219	226	226	226	224	236	234	236	2890	2200	1386	993	611	235	850.0

TABLE 27

EXPERIMENTAL DATA FROM RUN 135

P = pressure -- psi T = temperature -- °C F = mass flow rate -- gr/min

Pass 3, 100 RPM

<u>T₁</u>	<u>T₂</u>	<u>T₃</u>	<u>T₄</u>	<u>T₅</u>	<u>T₆</u>	<u>T₇</u>	<u>T₈</u>	<u>T₉</u>	<u>T₁₀</u>	<u>T₁₂</u>	<u>P_H</u>	<u>P_A</u>	<u>P₁</u>	<u>P₂</u>	<u>P₃</u>	<u>P₄</u>	<u>F</u>
210	210	210	224	227	219	238	239	230	231	230	2940	2270	196	154	109	48	9.7
212	210	203	224	229	220	238	238	228	229	228	2840	2210	289	226	155	64	16.4
213	210	204	224	232	224	239	238	229	229	227	2850	2210	403	300	201	82	26.8
212	208	206	224	236	231	240	239	229	230	228	2770	2200	487	353	235	96	41.4
213	211	206	224	236	231	240	239	230	230	228	2770	2175	576	425	276	111	61.2
212	210	205	225	229	227	238	237	232	231	230	2770	2190	724	527	339	133	103.0
212	209	204	226	228	226	238	237	232	231	230	2800	2240	798	573	368	144	133.0
213	213	209	204	226	226	223	237	232	231	230	2820	2220	866	616	401	157	187.0
213	210	205	229	224	218	230	227	229	227	228	2790	2250	1140	804	515	199	392.0
212	209	207	228	223	216	225	222	229	227	228	2925	2300	1289	904	576	222	597.0
211	210	207	230	221	212	214	211	227	229	228	3120	2460	1380	953	614	234	892.0

TABLE 28

EXPERIMENTAL DATA FROM RUN 136

P = pressure -- psi T = temperature -- °C F = mass flow rate -- gr/min

Pass 4, 100 RPM

<u>T₁</u>	<u>T₂</u>	<u>T₃</u>	<u>T₄</u>	<u>T₅</u>	<u>T₆</u>	<u>T₇</u>	<u>T₈</u>	<u>T₉</u>	<u>T₁₀</u>	<u>T₁₂</u>	<u>P_H</u>	<u>P_A</u>	<u>P₁</u>	<u>P₂</u>	<u>P₃</u>	<u>P₄</u>	<u>F</u>
212	213	214	224	230	232	241	---	232	233	230	2520	2030	179	152	110	53	9.9
213	212	216	224	229	230	240	---	232	233	230	2580	2060	260	213	146	65	15.9
212	211	217	223	228	230	240	---	231	233	230	2700	2110	368	283	194	82	30.0
211	210	217	224	228	228	240	---	230	232	230	2770	2130	492	371	245	100	51.0
212	212	216	222	220	220	238	---	231	233	232	2750	2075	555	411	270	108	68.8
211	210	215	223	224	225	240	---	231	232	231	2870	2210	588	434	283	114	74.2
212	212	214	222	219	218	237	---	230	232	231	2650	2060	618	452	293	116	82.3
212	212	216	221	220	218	237	---	228	230	229	2840	2260	733	540	346	134	111.0
214	212	215	220	220	219	237	---	229	231	230	2850	2260	855	622	380	153	175.0
214	214	215	224	230	229	237	---	231	231	230	2520	2040	895	659	418	164	205.0
214	213	216	225	228	226	236	---	231	231	229	2750	2195	1048	780	479	184	328.0
213	212	218	225	224	222	232	---	228	228	228	2740	2180	1125	810	511	196	383.0
214	212	218	224	222	220	227	225	229	228	229	2870	2280	1265	900	567	215	630.0
214	213	219	223	221	218	221	219	229	229	230	2690	2140	1336	947	595	226	710.0

TABLE 29

EXPERIMENTAL DATA FROM RUN 137

P = pressure -- psi T = temperature -- °C F = mass flow rate -- gr/min

Pass 5, 100 RPM

<u>T₁</u>	<u>T₂</u>	<u>T₃</u>	<u>T₄</u>	<u>T₅</u>	<u>T₆</u>	<u>T₇</u>	<u>T₈</u>	<u>T₉</u>	<u>T₁₀</u>	<u>T₁₂</u>	<u>P_H</u>	<u>P_A</u>	<u>P₁</u>	<u>P₂</u>	<u>P₃</u>	<u>P₄</u>	<u>F</u>
208	215	220	225	219	215	238	238	229	231	230	2875	2144	169	139	95	52	10.6
209	210	217	225	220	216	237	237	229	230	229	2770	2131	265	207	137	66	19.5
218	217	222	226	222	217	239	239	230	231	230	2850	2180	376	285	186	83	35.2
208	217	222	226	222	218	239	239	230	231	230	2840	2150	473	354	223	99	55.8
209	211	218	225	227	222	238	237	230	231	230	2750	2130	620	459	287	120	95.7
208	211	221	226	230	226	240	238	232	232	231	2830	2160	696	515	320	133	132.0
205	211	221	226	232	228	239	237	233	232	231	2845	2160	786	574	360	146	182.0
208	211	219	225	232	229	238	236	233	232	231	2810	2150	879	640	398	160	240.0
208	211	216	225	232	228	237	234	233	232	231	2830	2240	971	707	733	174	321.0
210	210	218	226	232	225	233	228	230	228	228	2795	2170	1067	773	477	190	395.0
209	212	219	226	232	224	230	225	229	227	228	2800	2210	1146	824	509	200	482.0
208	212	219	226	233	224	225	219	230	228	229	2900	2250	1277	922	563	219	726.0

APPENDIX E

TABLES 30 to 38AXIAL PRESSURE DISTRIBUTION RESULTS

TABLE 30

AXIAL PRESSURE DISTRIBUTION RESULTS FOR RUN 129

Pass 2, 50 RPM

<u>F</u> (gr/min)	<u>γ_{APP}</u> (sec^{-1})	<u>SLOPE</u> (psi/in)	<u>INTERCEPT</u> (psi)	<u>$\tau_{W,EXP}$</u> (psi)	<u>$\tau_{W,EXP} \times 10^{-5}$</u> (dynes/cm ²)
12.2	13.6	-79.6	501	2.98	2.06
29.3	32.6	-130.5	806	4.89	3.37
54.8	61.0	-172.5	1061	6.50	4.46
85.0	94.6	-205.0	1261	7.69	5.30
92.0	102.0	-220.7	1355	8.28	5.70
203.0	226.0	-270.0	1655	10.12	6.97
269.0	299.0	-297.4	1822	11.15	2.68
344.0	383.0	-311.5	1907	11.68	8.05
417.0	465.0	-334.6	2049	12.55	8.65
522.0	582.0	-359.0	2195	13.46	9.27
610.0	680.0	-373.9	2286	14.02	9.66

TABLE 31

AXIAL PRESSURE DISTRIBUTION RESULTS FOR RUN 130

Pass 3, 50 RPM

<u>F</u> (gr/min)	<u>γ_{APP}</u> (sec^{-1})	<u>SLOPE</u> (psi/in)	<u>INTERCEPT</u> (psi)	<u>$\tau_{W,EXP}$</u> (psi)	<u>$\tau_{W,EXP} \times 10^{-5}$</u> (dynes/cm ²)
13.8	15.4	-79.7	498	2.98	2.06
23.4	26.0	-110.2	684	4.13	2.85
35.3	39.3	-139.4	859	5.23	3.60
53.0	59.0	-158.3	973	5.94	4.09
158.0	176.0	-250.3	1531	9.38	6.47
286.0	318.0	-304.4	1856	11.42	7.87
350.0	390.0	-317.8	1939	11.92	8.21
422.0	470.0	-333.4	2034	12.50	8.61
442.0	490.0	-340.1	2074	12.75	8.78
524.0	583.0	-360.0	2192	13.50	9.30
614.0	683.0	-367.9	2240	13.80	9.51

TABLE 32

AXIAL PRESSURE DISTRIBUTION RESULTS FOR RUN 131

Pass 4, 50 RPM

<u>F</u> (gr/min)	<u>γ_{APP}</u> (sec^{-1})	<u>SLOPE</u> (psi/in)	<u>INTERCEPT</u> (psi)	<u>$\tau_{W,EXP}$</u> (psi)	<u>$\tau_{W,EXP} \times 10^{-5}$</u> (dynes/cm ²)
13.7	15.2	-71.5	447	2.68	1.85
21.4	23.8	-90.7	566	3.40	2.34
33.2	37.0	-117.6	727	4.41	3.04
48.9	54.4	-143.7	884	5.39	3.71
81.6	90.8	-179.7	1102	6.74	4.64
120.0	134.0	-212.8	1301	7.98	5.50
222.0	247.0	-269.5	1649	10.11	6.97
383.0	426.0	-312.8	1909	11.73	8.08
437.0	486.0	-326.3	1989	12.24	8.43
608.0	677.0	-368.3	2236	13.81	9.52

TABLE 33

AXIAL PRESSURE DISTRIBUTION RESULTS FOR RUN 132

Pass 5, 50 RPM

<u>F</u> (gr/min)	<u>γ_{APP}</u> (sec ⁻¹)	<u>SLOPE</u> (psi/in)	<u>INTERCEPT</u> (psi)	<u>$\tau_{W,EXP}$</u> (psi)	<u>$\tau_{W,EXP} \times 10^{-5}$</u> (dynes/cm ²)
15.7	17.5	-68.7	437	2.57	1.77
26.7	29.8	-93.0	583	3.49	2.40
50.2	56.0	-129.9	807	4.87	3.36
83.9	93.5	-164.3	1016	6.16	4.24
126.0	140.0	-198.6	1219	7.45	5.13
238.0	265.0	-248.8	1524	9.33	6.43
266.0	296.0	-263.7	1616	9.89	6.81
406.0	452.0	-300.6	1838	11.27	7.77
521.0	580.0	-324.2	1979	12.16	8.38
534.0	595.0	-327.1	2007	12.27	8.45
630.0	702.0	-352.7	2155	13.23	9.12

TABLE 34

AXIAL PRESSURE DISTRIBUTION RESULTS FOR RUN 133

Pass 1, 100 RPM

<u>F</u> (gr/min)	<u>γ_{APP}</u> (sec^{-1})	<u>SLOPE</u> (psi/in)	<u>INTERCEPT</u> (psi)	<u>$\tau_{W,EXP}$</u> (psi)	<u>$\tau_{W,EXP} \times 10^{-5}$</u> (dynes/cm ²)
13.4	14.9	-84.5	546	3.16	2.18
21.8	24.3	-105.1	674	3.94	2.72
40.4	45.0	-141.4	895	5.30	3.65
58.3	64.9	-168.8	1058	6.33	4.36
91.4	102.0	-210.0	1299	7.88	5.43
120.0	134.0	-226.9	1413	8.51	5.86
172.0	191.0	-261.3	1616	9.80	6.75
236.0	263.0	-285.5	1760	10.71	7.38
564.0	628.0	-338.9	2085	12.71	8.76
726.0	809.0	-373.9	2291	14.02	9.66
870.0	970.0	-393.3	2406	14.75	10.28

TABLE 35

AXIAL PRESSURE DISTRIBUTION RESULTS FOR RUN 134

Pass 2, 100 RPM

<u>F</u> (gr/min)	<u>γ_{APP}</u> (sec^{-1})	<u>SLOPE</u> (psi/in)	<u>INTERCEPT</u> (psi)	<u>$\tau_{W,EXP}$</u> (psi)	<u>$\tau_{W,EXP} \times 10^{-5}$</u> (dynes/cm ²)
12.4	13.8	-70.5	455	2.64	1.82
21.2	21.2	-86.4	556	3.24	2.23
24.8	27.6	-109.7	691	4.11	2.83
44.8	49.9	-152.2	947	5.70	3.93
56.4	62.9	-163.7	1018	6.13	4.23
63.9	71.1	-169.8	1053	6.37	4.39
95.2	106.0	-211.8	1311	7.94	5.47
134.0	150.0	-230.8	1424	8.65	5.96
135.0	151.0	-235.4	1454	8.83	6.08
200.0	222.0	-262.2	1613	9.83	6.77
235.0	262.0	-279.9	1722	10.50	7.23
341.0	380.0	-313.8	1923	11.77	8.11
406.0	451.0	-317.6	1948	11.91	8.21
506.0	563.0	-329.8	2020	12.37	8.52
570.0	635.0	-346.3	2122	12.99	8.95
620.0	690.0	-350.7	2145	13.15	9.06
746.0	831.0	-367.3	2249	12.99	8.95
850.0	956.0	-383.5	2340	14.38	9.41

TABLE 36

AXIAL PRESSURE DISTRIBUTION RESULTS FOR RUN 135

Pass 3, 100 RPM

<u>F</u> (gr/min)	<u>γ_{APP}</u> (sec^{-1})	<u>SLOPE</u> (psi/in)	<u>INTERCEPT</u> (psi)	<u>$\tau_{W,EXP}$</u> (psi)	<u>$\tau_{W,EXP} \times 10^{-5}$</u> (dynes/cm ²)
9.7	10.8	-48.9	322	1.83	1.26
16.4	18.3	-74.6	482	2.80	1.93
26.8	29.8	-106.2	671	3.98	2.74
41.4	46.1	-129.1	809	4.84	3.34
61.2	68.1	-154.4	965	5.79	3.99
103.0	115.0	-196.1	1215	7.35	5.07
133.0	148.0	-216.7	1338	8.13	5.60
187.0	217.0	-258.2	1482	9.68	6.67
392.0	436.0	-311.2	1909	11.67	8.04
597.0	664.0	-352.9	2159	13.23	9.12
892.0	993.0	-377.7	2306	14.16	9.76

TABLE 37

AXIAL PRESSURE DISTRIBUTION RESULTS FOR RUN 136

Pass 4, 100 RPM

<u>F</u> (gr/min)	<u>γ_{APP}</u> (sec^{-1})	<u>SLOPE</u> (psi/in)	<u>INTERCEPT</u> (psi)	<u>$\tau_{W,EXP}$</u> (psi)	<u>$\tau_{W,EXP} \times 10^{-5}$</u> (dynes/cm ²)
9.9	11.1	-37.4	265	1.58	1.09
15.9	17.7	-65.2	432	2.44	1.68
30.0	33.4	-94.7	611	3.55	2.45
51.0	56.8	-130.2	833	4.88	3.36
68.8	76.6	-148.2	929	5.56	3.83
74.2	82.6	-157.3	984	5.90	4.06
82.3	91.6	-166.5	1036	6.24	4.30
111.0	124.0	-199.1	1235	7.47	5.14
175.0	195.0	-234.8	1442	8.80	6.07
205.0	229.0	-243.4	1508	9.13	6.29
328.0	365.0	-289.3	1760	10.85	7.48
383.0	426.0	-308.6	1895	11.57	7.97
630.0	701.0	-348.3	2130	13.06	9.00
710.0	790.0	-368.2	2249	13.81	9.52

TABLE 38

AXIAL PRESSURE DISTRIBUTION RESULTS FOR RUN 137

Pass 5, 100 RPM

<u>F</u> (gr/min)	<u>γ_{APP}</u> (sec^{-1})	<u>SLOPE</u> (psi/in)	<u>INTERCEPT</u> (psi)	<u>$\tau_{W,EXP}$</u> (psi)	<u>$\tau_{W,EXP} \times 10^{-5}$</u> (dynes/cm ²)
10.6	11.8	-41.8	283	1.46	1.01
19.5	21.7	-66.7	435	2.50	1.72
35.2	39.2	-97.8	624	3.67	2.53
55.8	62.1	-125.3	788	4.70	3.24
95.7	106.0	-167.2	1140	6.27	4.32
132.0	147.0	-188.4	1170	7.06	4.87
182.0	202.0	-213.4	1320	8.00	5.51
240.0	267.0	-239.9	1479	8.99	6.20
321.0	358.0	-266.5	1637	9.99	6.89
395.0	440.0	-292.7	1796	10.98	7.57
482.0	536.0	-315.3	1931	11.82	8.14
726.0	808.0	-353.3	2158	13.25	9.13

APPENDIX F

LEAST-SQUARES POLYNOMIAL ANALYSIS PROGRAM


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C LEAST SQUARES CURVILINEAR REGRESSION
C ASSIGNMENT 11 ,DUE-DEC.4,1970
C PAUL SPRINGER CH.E.779
0001 IMPLICIT REAL*8(A-H,G-Z)
0002 DIMENSION B(11,12),XPX(11,12),XPY(11),NZ(11),LABEL(20),X(800),Y(80
10),RESID(11),WRM(11,12)
C INITIALIZE GENERALIZED I/O VARIABLES
0003 IN=5
0004 IO=6
C INITIALIZE COLUMN AND ROW DIMENSIONS
0005 NRDIM=11
0006 NCDIM=12
C THIS SECTION READS IN DATA AND WRITES DATA OUT
C NPTS= NUMBER OF DATA POINTS(CANNOT BE GREATER THAN 800)
C IHIGH= HIGHEST ORDER OF POLYNOMIAL TO BE CALCULATED(CANNOT BE
C GREATER THAN 9)
0007 1 TT=1.000
0008 CALL SCLOK1
0009 READ(IN,100) NPTS,IHIGH
0010 IF(NPTS.EQ.0)GO TO 1004
0011 IF(NPTS.GT.800) GO TO 1003
0012 IHI=IHIGH
0013 WRITE(IO,201)
0014 WRITE(IO,202)
0015 WRITE(IO,203) NPTS,IHIGH
C LABEL= IDENTIFICATION STATEMENT
0016 READ(IN,101) (LABEL(I),I=1,20)
0017 WRITE(IO,204)(LABEL(I),I=1,20)
C X= INDEPENDENT VARIABLE
C Y= DEPENDENT VARIABLE
0018 READ(IN,102) (Y(I),X(I),I=1,NPTS)
0019 WRITE(IO,205)

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```

0020      ISTU=2
0021      I=1
0022      5  ISTU=ISTU+1
0023      IF(I+1.GT.NPTS) GO TO 6
0024      WRITE(IO,206) ISTU,X(I),Y(I),X(I+1),Y(I+1)
0025      I=I+2
0026      IF(I.LE.NPTS) GO TO 5
0027      GO TO 7
0028      6  WRITE(IO,206) ISTU,X(I),Y(I)
0029      IF(IHIGH.EQ.0) GO TO 4
0030      IF(IHIGH.GE.10) GO TO 4
          C  INITIALIZE SUMMATION VARIABLES
0031      7  TSS=0.000
0032      DO 15 I=1,10
0033      XPY(I)=0.000
0034      RESID(I)=0.000
0035      DO 15 J=1,11
0036      B(I,J)=0.000
0037      15  XPX(I,J)=0.000
          C  CALCULATION OF TOTAL SUM OF SQUARES
0038      DO 20 I=1,NPTS
0039      20  TSS=TSS+ Y(I)**2
0040      WRITE(IO,207) TSS
          C  CALCULATION OF AUGMENTED MATRIX XPX
0041      NROW1=IHIGH+2
0042      SUMY=0.000
0043      DO 30 I=1,NPTS
0044      30  SUMY=SUMY+ Y(I)
0045      XPX(1,1)=DFLCAT(NPTS)
0046      XPY(1)= SUMY
0047      I=1
0048      DO 35 J=2,NROW1
0049      II=J-1
0050      DO 35 K=1,NPTS
0051      XPX(I,J)=XPX(I,J)+ X(K)**II
0052      35  XPY(J)= XPY(J)+ Y(K)*X(K)**II
0053      DO 45 I=2,NROW1
0054      DO 40 J=2,NROW1

```

```

0055      40 XPX(I,J-1)=XPX(I-1,J)
0056      II=II+1
0057      SUM=0.000
0058      DO 42 K=1,NPTS
0059      42 SUM=SUM+ X(K)**II
0060      45 XPX(I,NROW1)=SUM
      C    CALCULATION OF COEFFICIENTS
0061      ICOUNT=1
0062      NROW=2
0063      NCOL=3
0064      50 DO 80 I=1,NROW
0065      DO 80 J=1,NROW
0066      80 B(I,J)=XPX(I,J)
0067      DO 70 I=1,NROW
0068      70 B(I,NCOL)=XPY(I)
0069      DO 72 I=1,NROW
0070      DO 72 J=1,NCOL
0071      72 WRM(I,J)=B(I,J)
      C    DIAGONALIZATION OF AUGMENTED MATRIX AND CALCULATION OF RESIDUALS
0072      CALL DIAGON(B,NZ,NROW,NCOL,NRDM,NCDIM,&1001)
0073      DO 90 I=1,NROW
0074      90 B(NCOL,I)=B(I,NCOL)
0075      DO 95 I=1,NROW
0076      95 RESID(ICOUNT)=RESID(ICOUNT)+B(NCOL,I)*XPY(I)
0077      NDGFDM=NPTS-(ICOUNT+1)
0078      IF(ICOUNT-1.EQ.0) GO TO 110
      C    CALCULATION OF ADV TABLE
0079      ICD=ICOUNT-1
0080      ADJ=RESID(ICOUNT)-RESID(ICD)
0081      ERROR=TSS-RESID(ICOUNT)
0082      IF(NDGFDM.LE.0) GO TO 110
0083      SSME=ERROR/DFLOAT(NDGFDM)
0084      FCALC=ADJ/SSME
0085      CALL FSTAT(NDGFDM,TABLE)
      C    WRITE OUT OF ADV TABLE
0086      WRITE(IO,215)
0087      WRITE(IO,227)
0088      WRITE(IO,216) NPTS,TSS

```

```

0089      ICI=ICOUNT+1
0090      WRITE(10,217) ICOUNT,ICI,RESID(ICOUNT)
0091      WRITE(10,218) ICO,ICOUNT,RESID(ICO)
0092      L=1
0093      WRITE(10,219) L,ADJ,ADJ,FCALC,TABLE
0094      WRITE(10,220) NDGFDM,ERROR,SSME
0095      IF(FCALC.GT.TABLE) GO TO 110
0096      IF(1H1.EQ.0) GO TO 98
0097      IF(1H1.GE.10) GO TO 98
0098      IF(NROW.LE.1HIGH+1) GO TO 110
0099      GO TO 130
0100      98 WRITE(10,222)
0101      130 TIME=RCLK1(TT)
0102      WRITE(10,228) TIME
0103      GO TO 1

      C
0104      110 WRITE(10,209) ICOUNT
0105      WRITE(10,210) (B(NCOL,I),I=1,NROW)
0106      WRITE(10,211)
0107      WRITE(10,212) ((WRN(I,J),I=1,NROW),J=1,NCOL)
0108      WRITE(10,213)
0109      WRITE(10,208)
0110      DO 120 K=1,NPTS
0111      YCAL1=0.0D0
0112      DO 119 I=2,NROW
0113      I1=I-1
0114      YCAL1=YCAL1+B(NCOL,I)*X(K)*I1
0115      YCAL2=YCAL1+B(NCOL,1)
0116      DIFF=YCAL2-Y(K)
0117      120 WRITE(10,214) X(K),Y(K),YCAL2,DIFF
0118      IF(NDGFDM.LE.0) GO TO 1005
0119      NROW=NROW+1
0120      NCOL=NCOL+1
0121      ICOUNT=ICOUNT+1
0122      GO TO 50
0123      1001 WRITE(10,224)
0124      GO TO 130

```

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0125      1003 WRITE(10,226)
0126      GO TO 130
0127      1005 WRITE(10,229)
0128      GO TO 130
0129      4 IHIGH=9
0130      WRITE(10,225)
0131      GO TO 7
0132      1004 WRITE(10,223)
0133      201 FORMAT('1', 'THE INPUT DATA CARDS ARE')
0134      202 FORMAT('0', 9X, 'NPTS', 4X, 'IHIGH')
0135      203 FORMAT('0', 'CARD 1', I5, I7)
0136      204 FORMAT('0', 'CARD 2', 5X, 20A4)
0137      205 FORMAT('0', 17X, 'X', 16X, 'Y', 17X, 'X', 18X, 'Y')
0138      206 FORMAT(' ', 'CARD', I3, 4E18.8)
0139      207 FORMAT('0', 'THE TOTAL SUM OF SQUARES IS', E16.8)
0140      209 FORMAT('0', I2, 1X, 'DEGREE LEAST SQUARES POLYNOMIAL. THE COEFFICIENTS
      1(A+BX+...) ARE')
0141      210 FORMAT('0', 4E18.8)
0142      211 FORMAT('0', 'FOR DEBUGGING PURPOSES THE LEAST SQUARES SOLUTION MATR
      1IX IS')
0143      212 FORMAT('0', 4E18.8)
0144      213 FORMAT('0', 'THE RESIDUALS ARE')
0145      208 FORMAT('0', 22X, 'X', 27X, 'Y', 21X, 'Y(CALCULATED)', 16X, 'DIFFERENCE')
0146      214 FORMAT(' ', 4F28.8)
0147      215 FORMAT('0', 'THE ANALYSIS OF VARIANCE TABLE IS')
0148      227 FORMAT('0', 'SOURCE', 12X 'DEG OF FDM', 4X, 'SUM OF SQUARES', 3X 'MEAN SU
      1M OF SQUARES', 3X, 'F-CALCULATED', 5X, 'F-TABLE VALUE')
0149      216 FORMAT(' ', 'TOTAL', I19, E22.8, 41X, '(95 PER CENT LEVEL)')
0150      217 FORMAT(' ', 'DUE TO DEGREE', I3, I8, E24.10)
0151      218 FORMAT(' ', 'DUE TO DEGREE', I3, I8, E24.10)
0152      219 FORMAT(' ', 'ADJUSTED', I16, E22.8, F19.8, F15.3, F18.3)
0153      220 FORMAT(' ', 'ERROR', I19, E22.8, E19.8)
0154      222 FORMAT('0', 'THUS THE NEXT HIGHER ORDER COEFFICIENT IS NOT SIGNIFIC
      1ANT')
0155      223 FORMAT('0', 'PROGRAM TERMINATES DUE TO NPTS=0')
0156      224 FORMAT('0', 'PROGRAM WILL NOT CALCULATE SINGULAR MATRIX')

```

0157	225	FORMAT('0','PROGRAM HAS SET IHIGH=0 DUE TO ITS HAVING A READ IN VA ILUE OF 0 OR GREATER THAN 9.')
0158	226	FORMAT('0','PROGRAM WILL HANDLE A MAXIMUM OF 800 DATA POINTS(NPTS 11S GREATER THAN 800)')
0159	228	FORMAT('0','EXECUTION TIME=',F6.4,1X,'SECONDS')
0160	229	FORMAT('0','THE NUMBER OF DEGREES OF FREEDOM =0')
0161	100	FORMAT(215)
0162	101	FORMAT(20A4)
0163	102	FORMAT(4E18.8)
0164		STOP
0165		END

APPENDIX G

SHEAR DIAGRAMS FORPASSES 2 to 5, 50 RPM and PASSES 1 to 5, 100 RPMFIGURES 58 to 66

SHEAR DIAGRAM FOR PASS 2 - 50 RPM - RUN 129

FIGURE 58

SHEAR DIAGRAM FOR PASS 3 - 50 RPM - RUN 130

FIGURE 59

WALL SHEAR STRESS DYNES/CM**2

SHEAR DIAGRAM FOR PASS 4 - 50 RPM - RUN 131

FIGURE 60

SHEAR DIAGRAM FOR PASS 5 - 50 RPM - RUN 132

FIGURE 61

WALL SHEAR STRESS DYNES/CM**2

SHEAR DIAGRAM FOR PASS 1 - 100 RPM - RUN 133

FIGURE 62

WALL SHEAR STRESS DYNES/CM²

APPARENT SHEAR RATE SEC-1

SHEAR DIAGRAM FOR PASS 2 - 100 RPM - RUN 134

FIGURE 63

APPARENT SHEAR RATE SEC-1

SHEAR DIAGRAM FOR PASS 3 - 100 RPM - RUN 135

FIGURE 64

SHEAR DIAGRAM FOR PASS 4 - 100 RPM - RUN 136

FIGURE 65

WALL SHEAR STRESS DYNES/CM**2

SHEAR DIAGRAM FOR PASS 5 - 100 RPM - RUN 137

FIGURE 66

APPENDIX H

RHEOCALC PROGRAM FOR
CALCULATION OF RHEOLOGICAL PARAMETERS

	C	PAUL W. SPRINGER
	C	PROGRAM NAME- RHEO CALC
	C	THIS PROGRAM CALCULATES VARIOUS RHEOLOGICAL PARAMETERS FOR THE
	C	DETERMINATION OF THE ZERO SHEAR VISCOSITY.
0001		IMPLICIT REAL*8(A-H,L,M,C-Z)
0002		DIMENSION AGAMMA(20),STRESS(20),PEXIT(20),SR(20),TGAMMA(20),LABEL(
		120),PNPRIME(20),MU(20),DUM(20),LAGAM(20),LTGAM(20),LSTRE(20),LSTRC(
		120),LMU(20),LPEX(20),STRESC(20),SIGMA1(20),SIGMA2(20),ELASK(20),DE
		IR(20),FNSR(20),SNSR(20),PEXITP(20)
	C	READ IN NUMBER OF DATA SETS-NSET
0003		READ(5,100)NSET
0004		N=36
0005		DO 50 I=1,NSET
	C	READ IN NUMBER OF DATA POINTS FOR THIS SET-NDATA
0006		READ(5,101)NDATA
	C	READ IN LABEL
0007		READ(5,102)(LABEL(J),J=1,20)
	C	READ IN COEFFICIENTS FOR SHEAR EQUATION-A,B,C,D,E,F
0008		READ(5,103)A1,B1,C1
0009		READ(5,103)D1,E1,F1
	C	READ IN APPARENT SHEAR RATE(INDEPENDENT VARIABLE),STRESS(DEPENDENT
	C	VARIABLE),AND EXIT STRESS-AGAMMA,STRESS,AND PEXIT
0010		READ(5,104)(STRESS(J),AGAMMA(J),J=1,NDATA)
0011		READ(5,105)(DUM(J),J=1,NDATA)
	C	READ IN SECONDARY NORMAL STRESS--SIGMA2
0012		READ(5,106)SIGMA2(I)
	C	REVERSE PEXIT DATA.
0013		ICT=NDATA
0014		DO 10 J=1,NDATA
0015		PEXIT(J)=DUM(ICT)
0016		PEXITP(J)=PEXIT(J)
0017		ICT=ICT-1
0018		10 CONTINUE

```

0019      N=N+1
          C PRINT OUT SECTION OF PROGRAM.
0020      WRITE(6,199)N
0021      WRITE(6,202)
0022      WRITE(6,203)A1,B1,C1,D1
0023      WRITE(6,204)
0024      WRITE(6,205)
0025      WRITE(6,206)
          C CALCULATION SECTION OF PROGRAM FOR TRUE SHEAR RATE,NPRIME,STRESS
          C RATIO,AND APPARENT VISCOSITY-TGAMMA,NPRIME,SR,MU
0026      DO 40 J=1,NDATA
0027      LAGAM(J)=DLOGIO(AGAMMA(J))
0028      STRESC(J)=A1+B1*LAGAM(J)+C1*LAGAM(J)**2+D1*LAGAM(J)**3+E1*LAGAM(J)
          1**4+F1*LAGAM(J)**5
0029      STRESC(J)=2.202585*STRESC(J)
0030      STRESC(J)=DEXP(STRESC(J))
0031      PNRIME(J)=B1+2.000*C1*LAGAM(J)+3.000*D1*LAGAM(J)**2
0032      TGAMMA(J)=(AGAMMA(J)/3.000)*(2.000+1.000/PNRIME(J))
0033      MU(J)=STRESC(J)/TGAMMA(J)
0034      PEXIT(J)=PEXIT(J)* 6.8955E04
0035      SR(J)=PEXIT(J)/STRESC(J)
0036      SIGMA1(J)=PEXIT(J)+SIGMA2(I)
0037      ELASK(J)=2.000*STRESC(J)*TGAMMA(J)/SIGMA1(J)
0038      DEB(J)=SIGMA1(J)/(2.000*STRESC(J))
0039      PNSR(J)=SIGMA1(J)/STRESC(J)
0040      SNSR(J)=SIGMA2(I)/STRESC(J)
0041      WRITE(6,207)AGAMMA(J),STRESS(J),STRESC(J),PNRIME(J),TGAMMA(J),MU(J)
          1)
0042      40 CONTINUE
          C PUNCH OUT SECTION OF PROGRAM.
0043      WRITE(6,208)N
0044      WRITE(6,213)(LABEL(J),J=1,20)
0045      WRITE(6,201)NDATA
0046      WRITE(6,202)
0047      WRITE(6,203)A1,B1,C1,D1
0048      WRITE(6,209)

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0049      WRITE(6,210)
0050      WRITE(6,211)
0051      DO 45 J=1,NDATA
0052          45 WRITE(6,212)TGAMMA(J),STRESC(J),MU(J),PEXIT(J),PEXITP(J),SR(J)
0053          50 CONTINUE
0054          100 FORMAT(I5)
0055          101 FORMAT(I5)
0056          102 FORMAT(20A4)
0057          103 FORMAT(3E14.8)
0058          104 FORMAT(4E18.8)
0059          105 FORMAT(4E18.8)
0060          106 FORMAT(E18.8)
0061          199 FORMAT('1'/////////49X,'TABLE',I4)
0062          201 FORMAT('0',30X,'FOR THIS SET OF DATA THERE ARE',I5,3X,'DATA POINTS
1')
0063          202 FORMAT('0',12X,'THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHE
1AR RATE VS. SHEAR STRESS DATA ARE')
0064          203 FORMAT('0',23X,'A=',E14.8,3X,'B=',E14.8,3X,'C=',E14.8,3X,'D=',E14.
18)
0065          204 FORMAT('0',32X,'THE VISCOUS PARAMETERS FOR THIS DATA SET ARE')
0066          205 FORMAT('0',7X,'APP. SHEAR RATE',4X,'STRESS-EXP',5X,'STRESS-CALC',5
1X,'NPRIME',4X,'TRUE SHEAR RATE',2X,'APP. VISCOSITY')
0067          206 FORMAT(' ',13X,'SEC-1',7X,'DYNES/CM**2',4X,'DYNES/CM**2',26X,'SEC-
11',10X,'POISE')
0068          207 FORMAT(' ',2X,F16.2,2F16.0,F16.4,F16.2,F16.0)
0069          208 FORMAT('1'/////////49X,'TABLE',I4)
0070          213 FORMAT('0',30X,'EXIT PRESSURE DATA FOR',20A4)
0071          209 FORMAT('0',32X,'THE ELASTIC PARAMETERS FOR THIS DATA SET ARE')
0072          210 FORMAT('0',7X,'TRUE SHEAR RATE',3X,'STRESS-CALC',3X,'APP. VISCOSIT
1Y',3X,'EXIT PRESSURE',4X,'EXIT PRESSURE',4X,'RECOVERABLE')
0073          211 FORMAT(' ',13X,'SEC-1',7X,'DYNES/CM**2',7X,'POISE',9X,'DYNES/CM**2
1',10X,'PSI',5X,'STRAIN RATIO')
0074          212 FORMAT(' ',2X,F16.2,F16.0,F16.2,F16.0,F16.2,F16.4)
0075      CALL EXIT
0076      END

```

APPENDIX I

VISCOSITY DATA FORPASSES 2 to 5, 50 RPM and PASSES 1 to 5, 100 RPMTABLES 39 to 47

TABLE 39

VISCOSITY DATA FOR RUN 129 PASS 2 50RPM

FOR THIS SET OF DATA THERE ARE 11 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.41409219D+01 B=0.14693133D+01 C=-.44866109D+00 D=0.56333155D-01

THE VISCOUS PARAMETERS FOR THIS DATA SET ARE

APP. SHEAR RATE SEC-1	STRESS-EXP DYNES/CM**2	STRESS-CALC DYNES/CM**2	NPRIME	TRUE SHEAR RATE SEC-1	APP. VISCOSITY POISE
13.60	206000.	205118.	0.6693	15.84	12950.
32.60	337000.	340526.	0.4984	43.53	7822.
61.00	446000.	451475.	0.4060	90.75	4975.
94.60	530000.	533395.	0.3561	151.62	3518.
102.00	570000.	547742.	0.3488	165.48	3310.
226.00	697000.	705290.	0.2935	407.35	1731.
299.00	768000.	764530.	0.2836	550.73	1388.
383.00	805000.	819620.	0.2791	712.80	1150.
465.00	865000.	865113.	0.2782	867.09	998.
582.00	927000.	921011.	0.2803	1080.23	853.
680.00	966000.	962295.	0.2835	1252.75	768.

TABLE 40

VISCOSITY DATA FOR RUN 130 PASS 3 50RPM

FOR THIS SET OF DATA THERE ARE 11 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

$$A=0.44703717D+01 \quad B=0.85091284D+00 \quad C=-.11268973D+00 \quad D=0.0$$

THE VISCOUS PARAMETERS FOR THIS DATA SET ARE

APP. SHEAR RATE SEC-1	STRESS-EXP DYNES/CM**2	STRESS-CALC DYNES/CM**2	NPRIME	TRUE SHEAR RATE SEC-1	APP. VISCOSITY POISE
15.40	206000.	209861.	0.5833	19.07	11006.
26.00	285000.	281040.	0.5320	33.62	8358.
39.30	360000.	347210.	0.4916	52.85	6570.
59.00	409000.	420558.	0.4518	82.86	5075.
176.00	647000.	649962.	0.3448	287.47	2261.
318.00	787000.	783500.	0.2869	581.44	1349.
390.00	821000.	829058.	0.2669	747.00	1110.
470.00	861000.	869914.	0.2487	943.33	922.
492.00	878000.	879776.	0.2442	999.58	880.
583.00	930000.	915711.	0.2276	1242.55	737.
683.00	951000.	948141.	0.2121	1528.76	620.

TABLE 41

VISCOSITY DATA FOR RUN 131 PASS 4 50RPM

FOR THIS SET OF DATA THERE ARE 10 DATA POINTS

THE COEFFICEINTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.44055878D+01 B=0.85059483D+00 C=-.10515819D+00 D=0.0

THE VISCOUS PARAMETERS FOR THIS DATA SET ARE

APP. SHEAR RATE SEC-1	STRESS-EXP DYNES/CM**2	STRESS-CALC DYNES/CM**2	NPRIME	TRUE SHEAR RATE SEC-1	APP. VISCOSITY POISE
15.20	185000.	183644.	0.6020	18.55	9900.
23.80	234000.	238355.	0.5611	30.01	7944.
37.00	304000.	302608.	0.5208	48.35	6259.
54.40	371000.	367375.	0.4856	73.61	4991.
90.80	464000.	465519.	0.4388	129.51	3594.
134.00	550000.	548397.	0.4032	200.11	2741.
247.00	697000.	689877.	0.3474	401.68	1717.
426.00	808000.	822445.	0.2976	761.17	1080.
486.00	843000.	854658.	0.2856	891.32	959.
677.00	952000.	934800.	0.2553	1335.34	700.

TABLE 42

VISCOSITY DATA FOR RUN 132 PASS 5 50RPM

FOR THIS SET OF DATA THERE ARE 12 DATA POINTS

THE COEFFICEINTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.43638282D+01 B=0.83472436D+00 C=-.97420772D-01 D=0.0

THE VISCOUS PARAMETERS FOR THIS DATA SET ARE

APP. SHEAR RATE SEC-1	STRESS-EXP DYNES/CM**2	STRESS-CALC DYNES/CM**2	NPRIME	TRUE SHEAR RATE SEC-1	APP. VISCOSITY POISE
17.50	177000.	178194.	0.5925	21.51	8284.
29.80	240000.	241360.	0.5475	38.01	6350.
42.40	297000.	291224.	0.5176	55.57	5241.
56.00	336000.	335234.	0.4941	75.11	4463.
93.50	424000.	427090.	0.4507	131.48	3248.
140.00	513000.	508798.	0.4166	205.36	2478.
265.00	643000.	652383.	0.3626	420.29	1552.
296.00	681000.	678732.	0.3532	476.67	1424.
452.00	777000.	782245.	0.3174	776.03	1008.
580.00	838000.	844444.	0.2963	1039.17	813.
595.00	845000.	850833.	0.2941	1070.96	794.
702.00	912000.	892209.	0.2801	1303.30	685.

TABLE 43

VISCOSITY DATA FOR RUN 133 PASS 1 100RPM

FOR THIS SET OF DATA THERE ARE 11 DATA POINTS

THE COEFFICEINTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.45275785D+01 B=0.80598440D+00 C=-.10484917D+00 D=0.0

THE VISCOUS PARAMETERS FOR THIS DATA SET ARE

APP. SHEAR RATE SEC-1	STRESS-EXP DYNES/CM**2	STRESS-CALC DYNES/CM**2	NPRIME	TRUE SHEAR RATE SEC-1	APP. VISCOSITY POISE
14.90	218000.	213224.	0.5600	18.80	11340.
24.30	272000.	277367.	0.5154	31.92	8691.
45.00	365000.	374521.	0.4593	62.66	5977.
64.90	436000.	440422.	0.4260	94.05	4683.
102.00	543000.	529013.	0.3848	156.36	3383.
134.00	586000.	585589.	0.3599	213.43	2744.
191.00	675000.	661474.	0.3277	321.64	2057.
263.00	738000.	731152.	0.2985	469.00	1559.
628.00	876000.	915945.	0.2193	1373.41	667.
809.00	966000.	965421.	0.1962	1913.83	504.
970.00	1020000.	998918.	0.1797	2446.33	408.

TABLE 44

VISCOSITY DATA FOR RUN 134 PASS 2 100RPM

FOR THIS SET OF DATA THERE ARE 18 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

$$A=0.43146290D+01 \quad B=0.99064714D+00 \quad C=-.14537887D+00 \quad D=0.0$$

THE VISCOUS PARAMETERS FOR THIS DATA SET ARE

APP. SHEAR RATE SEC-1	STRESS-EXP DYNES/CM*2	STRESS-CALC DYNES/CM*2	NPRIIME	TRUE SHEAR RATE SEC-1	APP. VISCOSITY POISE
13.80	187000.	179867.	0.6592	16.18	11119.
21.20	223000.	235946.	0.6050	25.81	9140.
27.60	283000.	275564.	0.5717	34.49	7989.
49.90	393000.	378129.	0.4969	66.74	5666.
62.90	423000.	422799.	0.4677	86.76	4873.
71.10	439000.	447313.	0.4522	99.81	4482.
106.00	547000.	530478.	0.4018	158.61	3345.
150.00	596000.	605262.	0.3579	239.69	2525.
171.00	608000.	606701.	0.3571	241.62	2511.
222.00	677000.	689717.	0.3084	387.93	1778.
262.00	723000.	724618.	0.2875	478.43	1515.
380.00	811000.	799366.	0.2406	779.89	1025.
451.00	821000.	831451.	0.2189	987.36	842.
563.00	852000.	870115.	0.1909	1358.32	641.
635.00	895000.	889525.	0.1757	1627.91	546.
690.00	906000.	902211.	0.1652	1852.00	487.
831.00	895000.	928330.	0.1418	2508.14	370.
956.00	991000.	945781.	0.1241	3206.07	295.

TABLE 45

VISCOSITY DATA FOR RUN 135 PASS 3 100 RPM

FOR THIS SET OF DATA THERE ARE 11 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.42056326D+01 B=0.10348128D+01 C=-.14709396D+00 D=0.0

THE VISCOUS PARAMETERS FOR THIS DATA SET ARE

APP. SHEAR RATE SEC-1	STRESS-EXP DYNES/CM**2	STRESS-CALC DYNES/CM**2	NPRIME	TRUE SHEAR RATE SEC-1	APP. VISCOSITY POISE
10.80	126000.	131202.	0.7308	12.13	10820.
18.30	193000.	189494.	0.6634	21.39	8857.
29.80	274000.	257922.	0.6011	36.39	7087.
46.10	334000.	331214.	0.5454	58.91	5622.
68.10	399000.	405786.	0.4955	91.21	4449.
115.00	507000.	516936.	0.4286	166.11	3112.
148.00	560000.	573625.	0.3963	223.14	2571.
217.00	667000.	661359.	0.3475	352.85	1874.
436.00	804000.	816993.	0.2583	853.30	957.
664.00	912000.	900529.	0.2046	1524.64	591.
993.00	976000.	967739.	0.1531	2823.33	343.

TABLE 46

VISCOSITY DATA FOR RUN 136 PASS 4 100 RPM

FOR THIS SET OF DATA THERE ARE 14 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.40871803D+01 B=0.10795641D+01 C=-.14834101D+00 D=0.0

THE VISCOUS PARAMETERS FOR THIS DATA SET ARE

APP. SHEAR RATE SEC-1	STRESS-EXP DYNES/CM**2	STRESS-CALC DYNES/CM**2	NPRIME	TRUE SHEAR RATE SEC-1	APP. VISCOSITY POISE
11.10	109000.	113131.	0.7694	12.21	9266.
17.70	168000.	159740.	0.7093	20.12	7940.
33.40	245000.	244198.	0.6275	40.01	6104.
56.80	336000.	334623.	0.5591	71.73	4665.
76.60	383000.	393249.	0.5205	100.12	3928.
82.60	406000.	408843.	0.5108	108.97	3752.
91.60	430000.	430726.	0.4975	122.44	3518.
124.00	514000.	497818.	0.4585	172.82	2881.
195.00	607000.	604616.	0.4002	292.44	2068.
229.00	629000.	643707.	0.3794	353.84	1819.
365.00	748000.	757580.	0.3194	624.28	1214.
426.00	797000.	794687.	0.2995	758.18	1048.
701.00	900000.	907888.	0.2353	1460.43	622.
790.00	952000.	932924.	0.2199	1724.23	541.

TABLE 47

VISCOSITY DATA FOR RUN 137 PASS 5 100RPM

FOR THIS SET OF DATA THERE ARE 12 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.35361298D+01 B=0.19109789D+01 C=-.57878241D+00 D=0.71932782D-01

THE VISCOUS PARAMETERS FOR THIS DATA SET ARE

APP. SHEAR RATE SEC-1	STRESS-EXP DYNES/CM**2	STRESS-CALC DYNES/CM**2	NPRIME	TRUE SHEAR RATE SEC-1	APP. VISCOSITY POISE
11.80	101000.	101877.	0.9181	12.15	8385.
21.70	172000.	169047.	0.7494	24.12	7009.
39.20	253000.	252658.	0.6145	47.40	5331.
62.10	324000.	328474.	0.5292	80.52	4080.
106.00	432000.	426523.	0.4517	148.88	2865.
147.00	487000.	491407.	0.4158	215.84	2277.
202.00	551000.	558358.	0.3893	307.64	1815.
267.00	620000.	620886.	0.3727	416.77	1490.
358.00	689000.	691423.	0.3622	568.14	1217.
440.00	757000.	744758.	0.3590	701.90	1061.
536.00	814000.	799407.	0.3591	854.83	935.
808.00	913000.	927925.	0.3696	1267.35	732.

APPENDIX J

DOW VISCOSITY DATA FOR STYRON 686 AT 230°C

τ_W (psi)	$\tau_W \times 10^{-5}$ (dynes/cm ²)	$\dot{\gamma}_T$ (sec ⁻¹)	μ_{APP} (poise)	$\log \dot{\gamma}$	$\log \mu_{APP}$
5.53	3.81	45.8	8300	1.66087	3.91908
7.37	5.08	97.4	5210	1.98856	3.71684
9.22	6.35	182	3480	2.26007	3.54158
11.06	7.62	312	2430	2.49415	3.38561
12.90	8.89	514	1720	2.71096	3.23553
14.66	10.10	802	1260	2.90417	3.10037
16.54	11.40	1120	1010	3.04922	3.00432

source: Caplastometer

LEAST-SQUARES POLYNOMIAL ANALYSIS

$$\log \mu_{APP} = a_0 + a_1 \log \dot{\gamma}_T + a_2 (\log \dot{\gamma}_T)^2$$

a_0	a_1	a_2	F_{CALC}	F_{TABLE}
4.83960	-0.49455	-0.035546	4.859	10.13
$\log \mu_{10}$	μ_{10} (poise)			
4.30950	20,400			

APPENDIX K

EXTRUDER VOLUME DATA AND RESIDENCE TIME CALCULATION

For use in extruder modeling work, Reber measured the physical dimensions of the screw and extruder barrel. He divided the extruder into 10 zones with the following void volumes:

<u>ZONE</u>	<u>VOLUME (IN³)</u>
1	12.35
2	12.35
3	12.22
4	10.92
5	10.80
6	8.04
7	5.73
8	6.15
9	5.93
<u>10</u>	<u>6.01</u>
Total = V _E	90.5 IN ³

For residence time calculations, the volume of the adapter, valve and die were also needed.

$$V_{\text{ADAPTER} + \text{VALVE}} = \pi r^2 h = \pi (0.375 \text{ in})^2 (8.0 \text{ in}) = 1.125 \pi$$

$$r = 0.75 \text{ in}/2 = 0.375 \text{ in}$$

$$h = 8.0 \text{ in}$$

$$V_{\text{ADAPTER} + \text{VALVE}} = 3.53 \text{ in}^3$$

$$V_{\text{DIE}} = 2 (1.0 \text{ in}) (0.075 \text{ in}) (6.0 \text{ in}) = 0.9 \text{ IN}^3$$

$$F \text{ at } 50 \text{ RPM} = 1.36 \text{ lb/min}$$

$$= 0.8185 \text{ in}^3/\text{sec}$$

$$R_{\text{T}_{\text{EXT}}} = 90.63 \text{ IN}^3 / 0.8185 \text{ IN}^3/\text{sec} = 110 \text{ sec}$$

$$R_{\text{T}_{\text{ADAPTER} + \text{VALVE}}} = 4.31 \text{ sec}$$

$$R_{\text{T}_{\text{DIE}}} = 1.10 \text{ sec}$$

$$\therefore R_{\text{T}_{\text{EXT}}} \gg R_{\text{T}_{\text{ADAPTER} + \text{VALVE}}} + R_{\text{T}_{\text{DIE}}}$$

APPENDIX L

CALCULATION OF FRACTION OF EXTRUDER FILLEDf_{50 RPM} and f_{100 RPM}

$$\rho_{RPM} = (V_P \rho_P + V_M \rho_M) / V_E$$

$$V_E = 90.5 \text{ in}^3$$

$$\rho_P = 37.4 \text{ lbm/ft}^3$$

$$P = \text{solid polymer}$$

$$\rho_M = 60.4 \text{ lbm/ft}^3$$

$$M = \text{molten polymer}$$

Assume at 50 RPM first 4 zones are pellets

$$V_P = 50.4 \text{ in}^3$$

$$V_M = 39.92 \text{ in}^3$$

$$\begin{aligned}\rho_{50 \text{ RPM}} &= \frac{(50.4 \text{ IN}^3) (37.4 \text{ LBM/FT}^3) + (39.92 \text{ IN}^3) (60.4 \text{ LBM/FT}^3)}{90.5 \text{ IN}^3} \\ &= 47.5 \text{ LBM/FT}^3\end{aligned}$$

Assume at 100 RPM first 5 zones are pellets

$$v_P = 61.58 \text{ IN}^3$$

$$v_M = 28.80 \text{ IN}^3$$

$$\begin{aligned}\rho_{100 \text{ RPM}} &= \frac{(61.58 \text{ IN}^3) (37.4 \text{ LBM/FT}^3)}{90.5 \text{ IN}^3} + \frac{(28.80 \text{ IN}^3) (60.4 \text{ LBM/FT}^3)}{90.5 \text{ IN}^3} \\ &= 44.7 \text{ LBM/FT}^3\end{aligned}$$

$$f_{50 \text{ RPM}} = \frac{47.5}{60.4} = 0.787$$

$$f_{100 \text{ RPM}} = \frac{44.7}{60.4} = 0.740$$

$$v_{50 \text{ RPM}} = 0.787 (90.38 \text{ IN}^3) = 71.3 \text{ IN}^3$$

$$v_{100 \text{ RPM}} = 0.740 (90.38 \text{ IN}^3) = 66.9 \text{ IN}^3$$

APPENDIX M

EXIT PRESSURE DATA FORPASSES 2 to 5, 50 RPM and PASSES 1 to 5, 100 RPMTABLES 48 to 56

TABLE 48

EXIT PRESSURE DATA FOR RUN 129 PASS 2 50RPM

FOR THIS SET OF DATA THERE ARE 11 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.41409219D+01 B=0.14693133D+01 C=-.44866109D+00 D=0.56333155D-01

THE ELASTIC PARAMETERS FOR THIS DATA SET ARE

TRUE SHEAR RATE SEC-1	STRESS-CALC DYNES/CM**2	APP. VISCOSITY POISE	EXIT PRESSURE DYNES/CM**2	EXIT PRESSURE PSI	RECOVERABLE STRAIN RATIO
15.84	205118.	12949.56	1675607.	24.30	8.1690
43.53	340526.	7822.01	1565278.	22.70	4.5957
90.75	451475.	4974.77	1792830.	26.00	3.9711
151.62	533395.	3518.01	2137605.	31.00	4.0075
165.48	547742.	3309.94	2123814.	30.80	3.8774
407.35	705290.	1731.40	2413425.	35.00	3.4219
550.73	764530.	1388.20	2592708.	37.60	3.3912
712.80	819620.	1149.85	2620290.	38.00	3.1970
867.09	865113.	997.72	2854737.	41.40	3.2993
1080.23	921011.	852.61	2827155.	41.00	3.0696
1252.75	962295.	768.15	2937483.	42.60	3.0526

TABLE 49

EXIT PRESSURE DATA FOR RUN 130 PASS 3 50RPM

FOR THIS SET OF DATA THERE ARE 11 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.44703717D+01 B=0.85091284D+00 C=-.11268973D+00 D=0.0

THE ELASTIC PARAMETERS FOR THIS DATA SET ARE

TRUE SHEAR RATE SEC-1	STRESS-CALC DYNES/CM**2	APP. VISCOSITY POISE	EXIT PRESSURE DYNES/CM**2	EXIT PRESSURE PSI	RECOVERABLE STRAIN RATIO
19.07	209861.	11006.14	1406682.	20.40	6.7029
33.62	281040.	8358.35	1592861.	23.10	5.6677
52.85	347210.	6569.81	1530801.	22.20	4.4089
82.86	420558.	5075.34	1627338.	23.60	3.8695
287.47	649962.	2260.97	2013486.	29.20	3.0979
581.44	783500.	1347.51	2041068.	29.60	2.6051
747.00	829058.	1109.85	2220351.	32.20	2.6782
943.33	869914.	922.17	2316888.	33.60	2.6634
999.58	879776.	880.14	2303097.	33.40	2.6173
1242.55	915711.	736.96	2206560.	32.00	2.4097
1528.76	948141.	620.20	2247933.	32.60	2.3709

TABLE 50

EXIT PRESSURE DATA FOR RUN 131 PASS 4 50RPM

FOR THIS SET OF DATA THERE ARE 10 DATA POINTS

THE COEFFICEINTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.44055878D+01 B=0.85059483D+00 C=-.10515819D+00 D=0.0

THE ELASTIC PARAMETERS FOR THIS DATA SET ARE

TRUE SHEAR RATE SFC-1	STRESS-CALC DYNES/CM**2	APP. VISCOSITY POISE	EXIT PRESSURE DYNES/CM**2	EXIT PRESSURE PSI	RECOVERABLE STRAIN RATIO
18.55	183644.	9900.34	1254981.	18.20	6.8338
30.01	238355.	7943.56	1475637.	21.40	6.1909
48.35	302608.	6258.79	1468742.	21.30	4.8536
73.61	367375.	4990.76	1475637.	21.40	4.0167
129.51	465519.	3594.38	1641129.	23.80	3.5254
200.11	548397.	2740.54	1668711.	24.20	3.0429
401.68	689877.	1717.46	2206560.	32.00	3.1995
761.17	822445.	1080.50	2220351.	32.20	2.6997
891.32	854658.	958.86	2151396.	31.20	2.5173
1335.34	934800.	700.04	1806621.	26.20	1.9326

TABLE 51

EXIT PRESSURE DATA FOR RUN 132 PASS 5 50RPM

FOR THIS SET OF DATA THERE ARE 12 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.43638282D+01 B=0.83472436D+00 C=-.97420772D-01 D=0.0

THE ELASTIC PARAMETERS FOR THIS DATA SET ARE

TRUE SHEAR RATE SEC-1	STRESS-CALC DYNES/CM**2	APP. VISCOSITY POISE	EXIT PRESSURE DYNES/CM**2	EXIT PRESSURE PSI	RECOVERABLE STRAIN RATIO
21.51	178194.	8283.66	1751457.	25.40	9.8290
38.01	241360.	6349.88	1723875.	25.00	7.1423
55.57	291224.	5240.70	1620443.	23.50	5.5642
75.11	335234.	4463.12	1923844.	27.90	5.7398
131.48	427090.	3248.31	2082441.	30.20	4.8759
205.36	508798.	2477.60	1889367.	27.40	3.7134
420.29	652383.	1552.21	2151396.	31.20	3.2977
476.67	678732.	1423.89	2330679.	33.80	3.4339
776.03	782245.	1008.00	2372052.	34.40	3.0324
1039.17	844444.	812.61	2330679.	33.80	2.7600
1070.96	850833.	794.45	3061602.	44.40	3.5984
1303.30	892209.	684.58	2675454.	38.80	2.9987

TABLE 52

EXIT PRESSURE DATA FOR RUN 133 PASS 1 100RPM

FOR THIS SET OF DATA THERE ARE 11 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.45275785D+01 B=0.80598440D+00 C=-.10484917D+00 D=0.0

THE ELASTIC PARAMETERS FOR THIS DATA SET ARE

TRUE SHEAR RATE SEC-1	STRESS-CALC DYNES/CM**2	APP. VISCOSITY POISE	EXIT PRESSURE DYNES/CM**2	EXIT PRESSURE PSI	RECOVERABLE STRAIN RATIO
18.80	213224.	11339.98	2703036.	39.20	12.6770
31.92	277367.	8690.74	2965065.	43.00	10.6901
62.66	374521.	5977.25	3220198.	46.70	8.5982
94.05	440422.	4682.66	3116766.	45.20	7.0768
156.36	529013.	3383.28	2689245.	39.00	5.0835
213.43	585589.	2743.70	3558078.	51.60	6.0761
321.64	661474.	2056.55	3323631.	48.20	5.0246
469.00	731152.	1558.96	3240885.	47.00	4.4326
1373.41	915945.	666.91	3558078.	51.60	3.8846
1913.83	965421.	504.44	3282258.	47.60	3.3998
2446.33	998918.	408.33	3185721.	46.20	3.1892

TABLE 53

EXIT PRESSURE DATA FOR RUN 134 PASS 2 100RPM

FOR THIS SET OF DATA THERE ARE 18 DATA POINTS

THE COEFFICEINTS FOR THE POLYNCMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.43146290D+01 B=0.99064714D+00 C=-.14537887D+00 D=0.0

THE ELASTIC PARAMETERS FOR THIS DATA SET ARE

TRUE SHEAR RATE SEC-1	STRESS-CALC DYNES/CM**2	APP. VISCOSITY POISE	EXIT PRESSURE DYNES/CM**2	EXIT PRESSURE PSI	RECOVERABLE STRAIN RATIO
16.18	179867.	11118.03	2261724.	32.80	12.5744
25.81	235946.	9140.36	2599603.	37.70	11.0178
34.40	275564.	7989.07	2303097.	33.40	8.3573
66.74	378129.	5665.69	2303097.	33.40	6.0903
86.76	422799.	4872.93	2385843.	34.60	5.6430
99.81	447313.	4481.64	2358261.	34.20	5.2721
158.61	530478.	3344.54	2771991.	40.20	5.2255
239.69	605262.	2525.17	2703036.	39.20	4.4652
241.62	606701.	2510.98	2868528.	41.60	4.7281
387.93	689717.	1777.95	2744409.	39.80	3.9790
478.43	724618.	1514.58	2937483.	42.60	4.0538
779.89	799366.	1024.97	2771991.	40.20	3.4677
997.36	831451.	842.10	2923692.	42.40	3.5164
1358.32	870115.	640.58	2840946.	41.20	3.2650
1627.91	889525.	546.42	3047811.	44.20	3.4263
1852.00	902211.	487.15	2813364.	40.80	3.1183
2508.14	928330.	370.13	3116766.	45.20	3.3574
3206.07	945781.	295.00	2689245.	39.00	2.8434

TABLE 54

EXIT PRESSURE DATA FOR RUN 135 PASS 3 100 RPM

FOR THIS SET OF DATA THERE ARE 11 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.42056326D+01 B=0.10348128D+01 C=-.14709396D+00 D=0.0

THE ELASTIC PARAMETERS FOR THIS DATA SET ARE

TRUE SHEAR RATE SEC-1	STRESS-CALC DYNES/CM**2	APP. VISCOSITY POISE	EXIT PRESSURE DYNES/CM**2	EXIT PRESSURE PSI	RECOVERABLE STRAIN RATIO
12.13	131202.	10819.75	1999695.	29.00	15.2413
21.39	189494.	8857.01	2365157.	34.30	12.4814
36.39	257922.	7087.42	2351366.	34.10	9.1166
58.91	331214.	5622.40	2385843.	34.60	7.2033
91.21	405786.	4448.91	2620290.	38.00	6.4573
166.11	516936.	3112.03	2647872.	38.40	5.1222
223.14	573625.	2570.74	2606499.	37.80	4.5439
352.85	661359.	1874.35	2882319.	41.80	4.3582
853.30	816993.	957.45	2882319.	41.80	3.5280
1524.64	900529.	590.65	2868528.	41.60	3.1854
2823.33	967739.	342.77	2744409.	39.80	2.8359

TABLE 55

EXIT PRESSURE DATA FOR RUN 136 PASS 4 100 RPM

FOR THIS SET OF DATA THERE ARE 14 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.40871803D+01 B=0.10795641D+01 C=-.14834101D+00 D=0.0

THE ELASTIC PARAMETERS FOR THIS DATA SET ARE

TRUE SHEAR RATE SEC-1	STRESS-CALC DYNES/CM**2	APP. VISCOSITY POISE	EXIT PRESSURE DYNES/CM**2	EXIT PRESSURE PSI	RECOVERABLE STRAIN RATIO
12.21	113131.	9266.38	2806468.	40.70	24.8073
20.12	159740.	7940.21	2799573.	40.60	17.5253
40.01	244198.	6103.56	2923692.	42.40	11.9726
71.73	334623.	4664.92	2868528.	41.60	8.5724
100.12	393249.	3927.87	2730618.	39.60	6.9437
108.97	408843.	3752.03	2765096.	40.10	6.7632
122.44	430726.	3517.87	2551335.	37.00	5.9233
172.82	497818.	2880.57	2785782.	40.40	5.5960
292.44	604616.	2067.50	2289306.	33.20	3.7864
353.84	643707.	1819.21	3282258.	47.60	5.0990
624.28	757580.	1213.52	3047811.	44.20	4.0231
758.18	794687.	1048.15	2992647.	43.40	3.7658
1460.43	907888.	621.66	2771991.	40.20	3.0532
1724.23	932924.	541.07	2744409.	39.80	2.9417

TABLE 56

EXIT PRESSURE DATA FOR RUN 137 PASS 5 100RPM

FOR THIS SET OF DATA THERE ARE 12 DATA POINTS

THE COEFFICIENTS FOR THE POLYNOMIAL FIT OF THE SHEAR RATE VS. SHEAR STRESS DATA ARE

A=0.35361298D+01 B=0.19109789D+01 C=-.57878241D+00 D=0.71932782D-01

THE ELASTIC PARAMETERS FOR THIS DATA SET ARE

TRUE SHEAR RATE SEC-1	STRESS-CALC DYNES/CM**2	APP. VISCOSITY POISE	EXIT PRESSURE DYNES/CM**2	EXIT PRESSURE PSI	RECOVERABLE STRAIN RATIO
12.15	101877.	8384.51	2268619.	32.90	22.2631
24.12	169047.	7008.85	2434112.	35.30	14.3990
47.40	252658.	5330.52	2544439.	36.90	10.0707
80.52	328474.	4079.59	2523753.	36.60	7.6833
148.88	426523.	2864.80	2537544.	36.80	5.9494
215.84	491407.	2276.76	2730618.	39.60	5.5557
307.64	558358.	1814.99	2730618.	39.60	4.8904
416.77	620886.	1489.76	2730618.	39.60	4.3979
568.14	691423.	1217.00	2620290.	38.00	3.7897
701.90	744758.	1061.06	2744409.	39.80	3.6850
854.83	799407.	935.17	2703036.	39.20	3.3813
1267.35	927925.	732.17	2634081.	38.20	2.6387