AN INVESTIGATION INTO THE INJECTION MOLDING OF PMR-15 POLYMIDE

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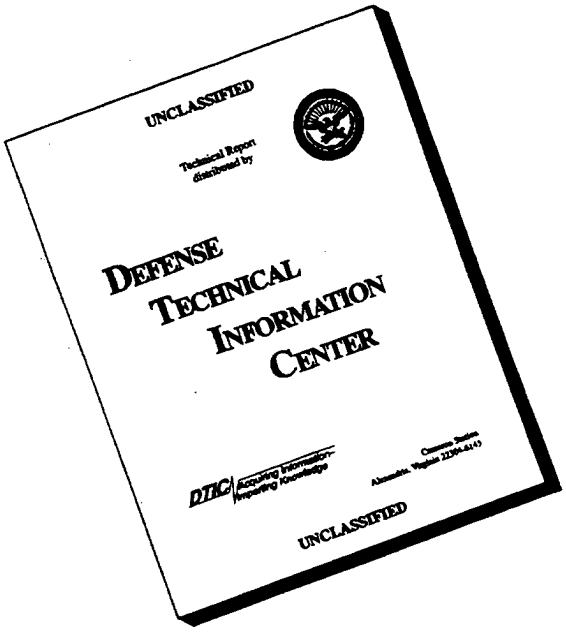

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I. INTRODUCTION

The excellent high temperature mechanical properties of polyimide resins have lead to their increasing use in high performance applications. Present employment of this material includes fiber-reinforced composite structures, bearings, seals, valve seats, bushings, piston rings, electrical connectors, switch components, abrasive wheel binders, aircraft interior panels, circuit boards, and jet engine parts including engine cowlings and high speed fan blades [1-6].

Both thermoplastic and thermosetting polyimides are commercially available. The thermosetting materials were developed first and are much more widely used than the newer thermoplastic resins. Early thermosetting polyimide systems were based on condensation reactions. They were difficult to process, requiring the use of high boiling point solvents. Solvent residues and reaction by-products lead to void formation and premature failure of fabricated parts.

A technique which allowed better control and easier processing of thermosetting polyimides was developed at the NASA Lewis Research Center [7]. Known as polymerization of momeric reactants of PMR, the method employs an easily evaporated solvent such as methyl alcohol to dissolve the monomers and form a low viscosity solution for fiber impregnation [5,7].

The cure of PMR polyimides is a two-step process. An initial imidization step accomplishes ring closure and the release of volatiles. Chain growth takes place through a

reverse Diels-Alder reaction of end caps [5,7,8]. PMR resins undergo four thermal transitions during cure: monomer melt, imidization, melt-flow and crosslinking [7,9].

The PMR approach is very flexible since the resin's flow and thermal characteristics as well as its mechanical properties can be adjusted over a wide range by changing the stoichiometry and nature of the monomer reactants [10,11]. A family of PMR resins have been developed [5,6,11,12]. PMR-15 has proved very successful in glass and carbon fiber prepreg tapes. A second-generation material, PMR-11, with significantly improved high temperature properties, has been developed [7,10,12].

Polyimide systems such as PMR-15 offer great opportunities for numerous applications if suitable resin compounds and processing techniques can be developed. The great flexibility of part size and shape, high production rates and consequent economics make injection molding an attractive processing technique for PMR-type polyimides.

II. SCOPE OF WORK

The present research program is directed toward developing a fundamental understanding of the relationships between material structure, processability and mechanical properties in an injection moldable PMR-15 compound. The specific objectives of this investigation are:

1. To characterize the chemorheological behavior of PMR-15 molding compounds.

Any study of the processing and mechanical behavior of thermosetting materials must begin with a fundamental understanding of the material's chemorheology [13]. Structural changes which occur during processing will influence the material's thermal, physical and flow properties. These properties will be strongly influenced by the chemical structure of the resin, fillers, additives, time and temperature.

2. To determine the range of suitable processing parameters for the injection molding of PMR-15 type materials in a reciprocating screw injection molding machine. The effects of such machine variables as mold temperature, barrel temperature, screw speed, back pressure and cycle time on the resin's flow behavior, reaction rate and state of cure will be examined.

3. To determine the effects of injection molding processing parameters on the mechanical behavior of molded PMR-15 parts. The processing conditions will affect the state of molecular orientation, residual stress and cure which will, in turn, determine the response of the molded part to mechanical loadings.

III. VISCOSITY MEASUREMENTS

A. APPARATUS AND PROCEDURES

1. Capillary Rheometer

Commercially available capillary rheometers have been designed for use with thermoplastic materials. Electric band

heaters are used to maintain the barrel temperature and a rather limited maximum load is available to force material from the barrel. Therefore, these devices are unsuitable for use with thermosets.

With these problems in mind, a capillary rheometer was designed specifically for use with thermosets. A schematic representation of the system built is shown in Figure 1 (see section VI. Figures). The rheometer barrel is heated by circulating Dowtherm G® fluid from a process heat transfer system through a surrounding jacket. Temperatures up to 288°C (550°F) can be attained with the heating elelent used. Higher temperatures up to the fluid's maximum of 343°C (650°F) can be reached with a more powerful heating unit. Temperature control is provided by a proportional temperature regulator monitoring the temperature of the fluid in the barrel jacket. The variation in temperature from the set point was approximately .5°C at 260°C (500°F). Fluid enters the jacket at the bottom and exits near the top, thus ensuring that the barrel is always covered to the same level. The capillary itself is placed relatively high up in the barrel in order to ensure that its temperature is close to that of the surrounding fluid. Several samples which cured in the barrel showed smooth surfaces indicating that the temperature was uniform along the barrel.

The barrel-jacket assembly is attached to a moveable frame which is inserted into a constant crosshead speed testing machine. Flexible stainless steel hoses allow the barrel-jacket

assembly to be separated from the heat transfer system. The testing machine provides up to 20,000 lbs of force. This allows any material which sets up in the barrel to be pushed out by the piston, since its length of travel extends past the capillary position in the barrel and extends past the capillary position in the barrel. Any material in the capillary is removed by the use of a thin steel rod.

A number of specific points are worthy of mention. In order to avoid leaks, especially vapor leaks, good sealing is necessary at all joints. Only metal-to-metal seals should be considered. Silicone and PTFE were initially used to seal the capillary barrel to the heating jacket. These seals proved unsuitable after limited use and the barrel was welded to the jacket and no further problems were encountered. For added safety, a well-ventilated work area should be used.

Finding an adequate high temperature pump for the heat transfer system proved difficult. Only a few manufacturers carry the low capacity, low pressure pump required. Although these were stock pumps specifically modified for high temperature operation, the one selected gave considerable problems until additional internal clearances were cut. Manufacturer claims should be viewed as being optimistic at best.

The reservoir, rheometer heating jacket, as well as all the fluid lines must be well-insulated with high temperature insulation material.

The heat exchanger unit allows direct contact of the heating fluid and the electrical resistance heaters. Thus,

the maximum allowable watt density of the heat transfer fluid selected will control the maximum power of the heat exchanger. This requirement is necessary in order to avoid decomposition of the heat transfer fluid. If additional heating capacity is desired in order to decrease start-up time, a physically larger unit may be used.

By placing the heat exchanger, pump, controller and reservoir on a moveable cart, the system can be used with any available testing machine. This will also facilitate storage and transportation.

A filter to remove foreign matter from the fluid is recommended. It can be best placed on the return port to the reservoir since this location will make it easier to remove and clean. A simple wire element will do.

2. Experimental Procedure

Standard techniques for capillary rheometry were used [14,15]. The barrel was first heated with the capillary and capillary support in place. The temperature was monitored by placing a thermocouple down the barrel. When the temperature had stabilized, the piston was inserted and allowed to heat for 15 minutes. The sample material was then poured into the barrel and compressed by the machine until the load increased sharply.

The sample was heated according to the experimental program. Tests were then conducted with the piston descending at constant speed. The resulting force on the load cell of the testing machine was automatically plotted as a function of time.

The apparent viscosity η is given as

$$\eta = \frac{\tau_R}{\dot{\gamma}_R}$$

where τ_R is the shear stress and $\dot{\gamma}_R$ is the shear rate at the capillary wall. Ignoring entrance and exit affects

$$\tau_R = \frac{\Delta P R}{2L}$$

where ΔP is the pressure drop across the capillary, R is the capillary's radius and L is its length. The shear rate at the wall is given as

$$\dot{\gamma} = \frac{1}{\tau_R^2} \frac{d}{d\tau_R} (\tau_R^3 \, Q/\pi R^3)$$

where Q is the volumetric flow rate.

B. EXPERIMENTAL RESULTS

1. Thermoplastic Materials

Initial testing was conducted using thermoplastic materials in order to check the equipment and experimental techniques. Data taken was reproducible. Results obtained using the 2.54 cm (1 inch) capillary agreed closely with results obtained using the 3.81 cm (1.5 inch) capillary. Little data are available in the literature to compare the results obtained by this work. Frizelle and Norfleet [16] used a commercially available capillary rheometer with a

small L/D ratio of 3.8 to study two phenolic compounds. The phenolic compound studied in this investigation showed a viscosity in the same order as that of Frizelle and Norfleet, averaging between one-half and two-thirds their reported values.

2. Typical Thermosets

Six thermoset molding compounds were investigated: an alkyd polyester, a diallyl phthalate (DAP), a phenolic, a woodflour-filled phenolic, a mineral filled alkyd polyester and a woodflour-filled melamine. The instrument functioned satisfactorily with all these materials.

In the interest of brevity, only the results obtained with the woodflour-filled phenolic will be discussed since this material's behavior is typical of thermoset molding compounds. Details of the other materials' performances are available [17]. A capillary diameter of .16 cm and length of 3.94 cm, L/D = 24, was used in all the tests discussed below.

The apparent viscosity of the woodflour-filled phenolic as a function of shear rate at 121°C (250°F) and different heating times is shown in Figure 2. A power law type behavior is generally displayed. The effect of heating time at a barrel temperature of 121°C (250°F) and different shear rates is shown in Figure 3. The characteristic U-shaped curve has a minimum in the region of 1.5 to 2 minutes. At times greater than 4 minutes, crosslinking was great enough to prevent flow.

A similar behavior of viscosity with temperature at a fixed heating time of 3 minutes for different shear rates is shown in Figure 4. The shear rate in both Figures 3 and 4 seems to affect the magnitude of the viscosity but not the nature of its behavior with time or temperature.

By plotting the viscosity against the inverse of absolute temperature for a fixed heating time and shear rate, an apparent activation energy for viscous flow at constant shear rate can be determined. The data of Figure 5 was obtained for a heating time of 1 minute. The activation energy for flow of this material shows little shear rate dependence and has an average value of 8.23 Kcal/mole.

Heat transfer to the granular mass is governed by the contact thermal resistance at the barrel surface. Although thermal gradients between the outer and inner surfaces of the granular mass were not larger, the order of 5 to 10°F, the temperature of the mass tended to lag behind that of the barrel by a considerable amount. Thus, the temperature cited should be considered as nominal temperature for the material.

3. PMR-15

Difficulty was encountered determining the shear stress from capillary rheometry data taken with the PMR-15. Figure 6 illustrates typical PMR-15 data taken at 233°C. It is apparent that steady state load conditions were not realized and that reactions causing physical changes occured throughout the run period. Inspection of the PMR-15 sample after the

run revealed that gases had evolved resulting in bubbling and foaming in the sample. At this point it was decided to design tests to observe the physical changes occuring during sample heatup and to identify the source of the evolving gases. These are described in Section IV.

C. CONCLUSIONS

Capillary rheometry can be effectively used with thermosets if the equipment is designed to overcome some of the inherent problems of these materials. Most important is providing a uniform temperature in the barrel. This was accomplished by using a circulating hot oil system. Standard capillary rheometry methods can provide the dependence of thermoset apparent viscosity on shear rate, temperature and time.

IV. PHYSICAL RESPONSE OF PMR-15 DURING HEATING

A. APPARATUS AND PROCEDURE

A Piston and Cylinder Apparatus (PCA), shown in Figure 7, was constructed to observe the physical changes occuring during heating at constant pressure. A stainless steel rod was machined to fit loosely into a .95 cm nominal I.D. stainless steel tube. The tube was heated by heating tape wrapped around the bottom third of the tube. This whole assembly was wrapped to a thickness of 5 cm with high temperature insulation. A stainless steel plug fit tightly into the bottom

of the tube to prevent the loss of sample. A Type-K thermocouple was forced into a hole drilled in the plug. The movement of the upper end of the piston was measured with a linear variable differential transducer. The output was recorded on a strip chart along with the thermocouple output. A series of tests were conducted at various heating rates on the batch of PMR-15 that had been tested in the rheometer (Sample A) and a new batch of PMR-15 carefully prepared for these tests (Sample B). Samples (75 to 100 gms) were placed in the tube and heated at 5 to 50°C/min.

B. RESULTS AND DISCUSSION

1. Sample A Tests

A typical trace of piston movement is reproduced in Figure 8 for a heating rate of 15°C/min. Melt flow, expansion initiation, and maximum expansion are defined on the figure. These events were determined for several heating rates and the temperature at melt flow and expansion initiation along with the maximum expansion value are tabulated in Table I.

The results indicate that the maximum expansion can be reduced by reducing the heating rate and allowing time for the evolving gases to escape.

The melt flow temperatures and the temperature at expansion initiation are not greatly affected by heating rate, indicating that the sample size is small enough to assume uniform conditions in the sample.

The most important observation is that the expansion

always begins at temperatures slightly above the temperature specified for complete imidization. Hence, while the samples were imidized at 204°C (for 2 hours) during preparation, the expansion occurred in these tests in the range of 208 to 212°C. This is strong evidence that the samples were not completely imidized during preparation and that gases evolved during heating in the capillary rheometer were the result of the completion of the imidization reaction.

These observations seem to contradict the results of reference 9 which concluded that complete imidization would be accomplished at 204°C for times greater than 30 minutes. However, a caution expressed by the author of reference 9 gives a clue as to what is occuring. Lauver states "Neither the precision of the intensity data nor the control of temperature in the laboratory ovens used were adequate for a detailed kinetic analysis". It is very likely that by controlling oven temperatures at 204°C will result in actual sample temperatures different than 204°C. Also, the sample temperature in the NASA oven will likely be different than that in the Texas A&M University (TAMU) oven. It seemed possible that the resin prepared in the TAMU ovens was not completely imidized.

A new series of tests was conducted on a sample of PMR-15 (Sample B) prepared as was Sample A except that the temperature was controlled by a Type-K thermocouple placed about 10 cm above the sample. Samples were imidized at 205, 215 and 230°C for 75 minutes. These were heated in the PCA at a nominal

15°C/min and the temperature at melt flow and initial expansion and the maximum expansion were determined. These results are shown in Figures 9 through 11. From Figure 9 it can be seen that there is no evidence of melt flow or of gas evolution at temperatures comparable to imidization conditions, i.e., 204°C. Figure 10 shows that expansion did occur, but at temperatures (400 to 500°C) corresponding to the onset of crosslinking [9]. This is to be expected since gas is evolved during crosslinking. Melt flow temperature and expansion temperatures were relatively insensitive to imidization temperature. From Figure 11 it can be seen that the maximum amount of expansion did decrease as imidization temperature was increased, probably as a result of the onset of crosslinking during the 75 minutes at imidization temperature. The kinetics for the crosslinking reactions would result in an increasing amount of reaction as temperature increases [9].

It should be noted that at temperatures between 325 and 400°C, the PMR-15 flows without experiencing any gas evolution. Injection molding should be possible at these temperatures followed by curing above 400°C under pressure.

C. CONCLUSIONS

1. Process conditions resulting in complete imidization should be carefully defined. Specification of a controlled oven temperature is inadequate and can result in incomplete imidization.

2. For completely imidized PMR-15 heat at 15°C/min, melt flow without gas evolution occurs in the temperature range of 325 to 400°C.

V. REFERENCES

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Table I. Piston Cylinder Apparatus Data for Batch A

Heating Rate (°C/sec)	Melt Flow Temperature (°C)	Expansion Temperature (°C)	Maximum Expansion (%)
5	179	---	∿ 0
8	179	200	58
10	164	198	118
15	160	206	200
33	---	---	330
50	182	200	500

VI. FIGURES

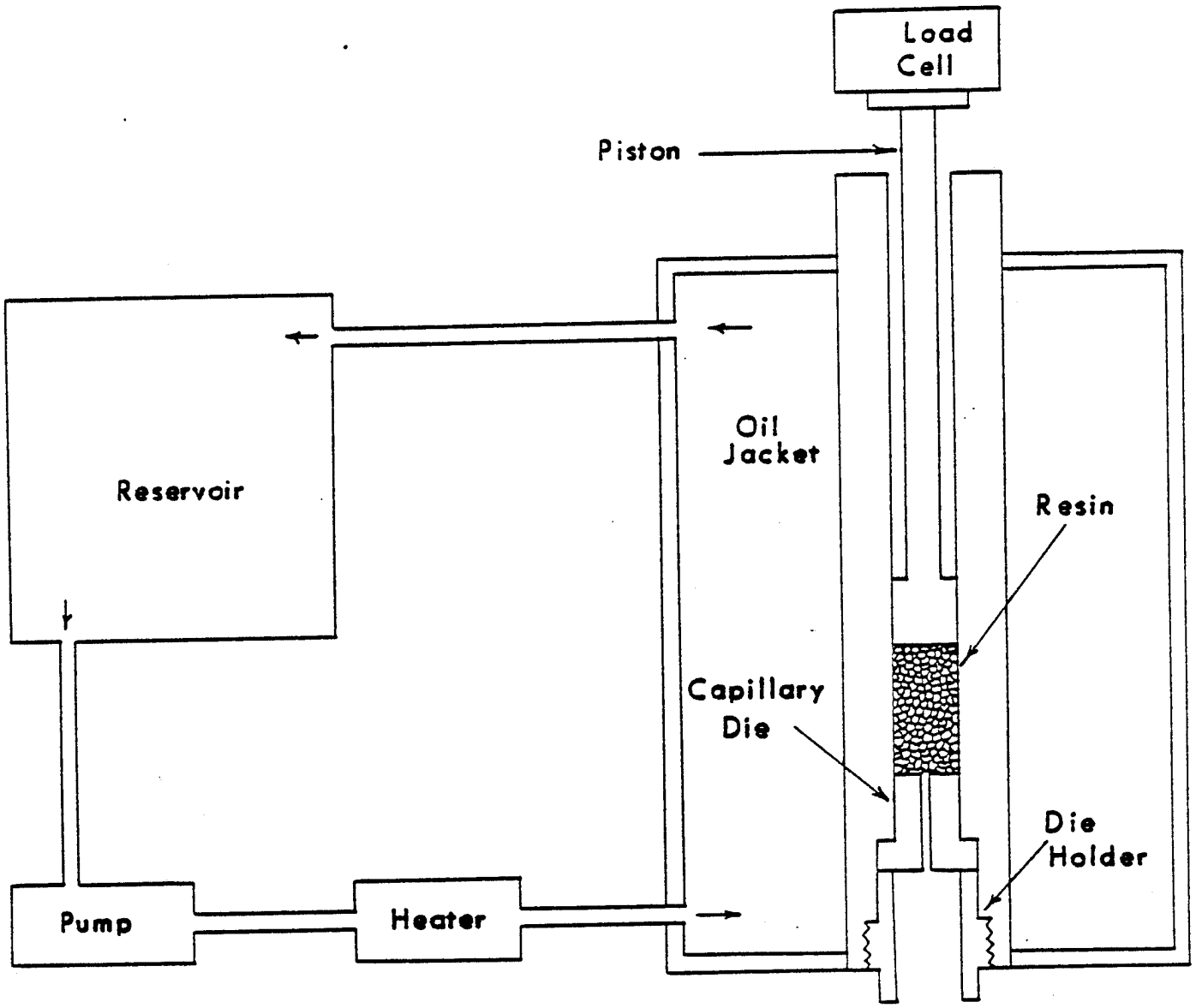

Figure 1. Schematic of thermoset capillary rheometer.

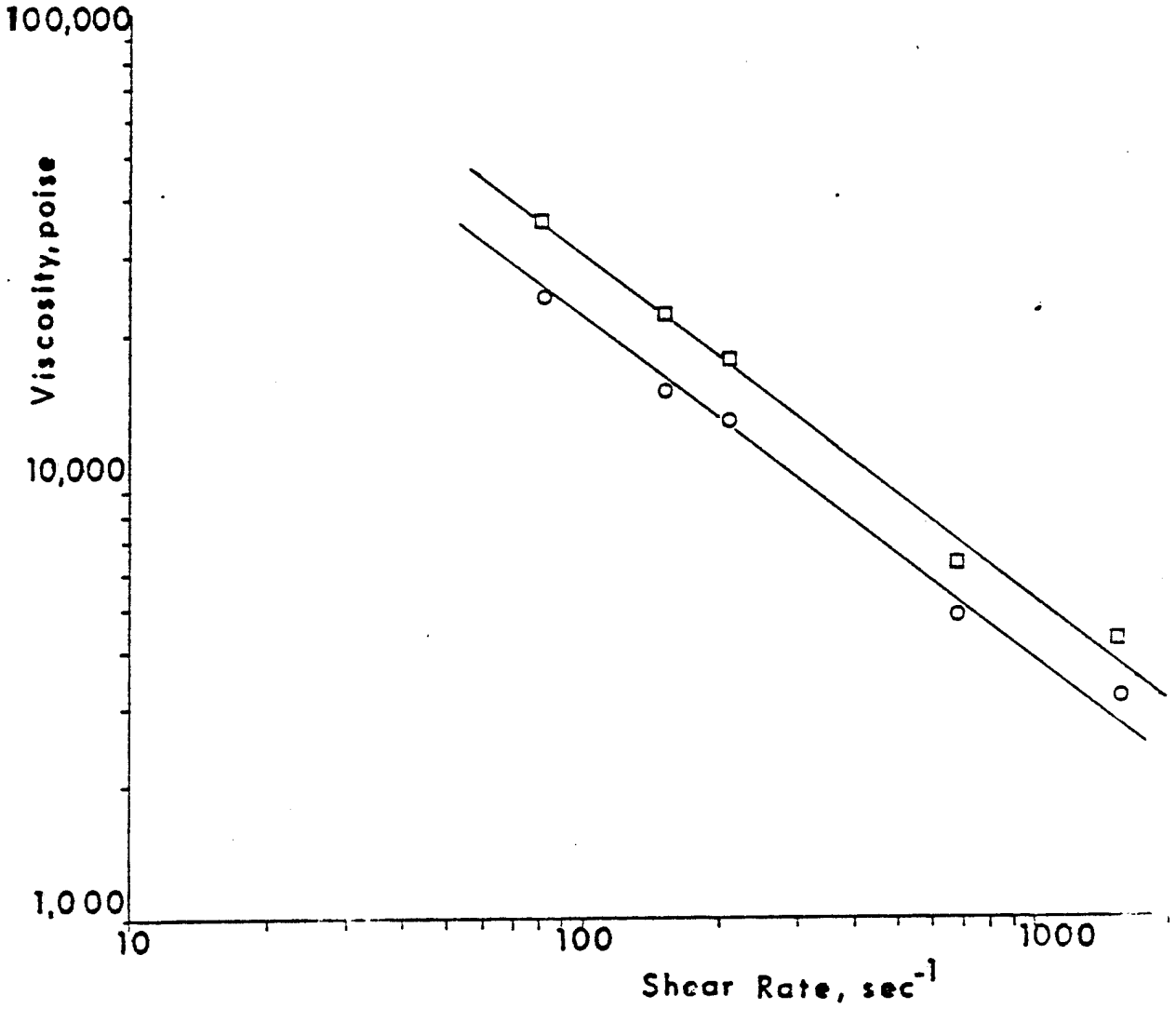

Figure 2. Effect of shear rate on the apparent viscosity of a woodflour-filled phenolic at 121°C (250°F). Legend for heating times: ○ - 1 min, □- 3 min.

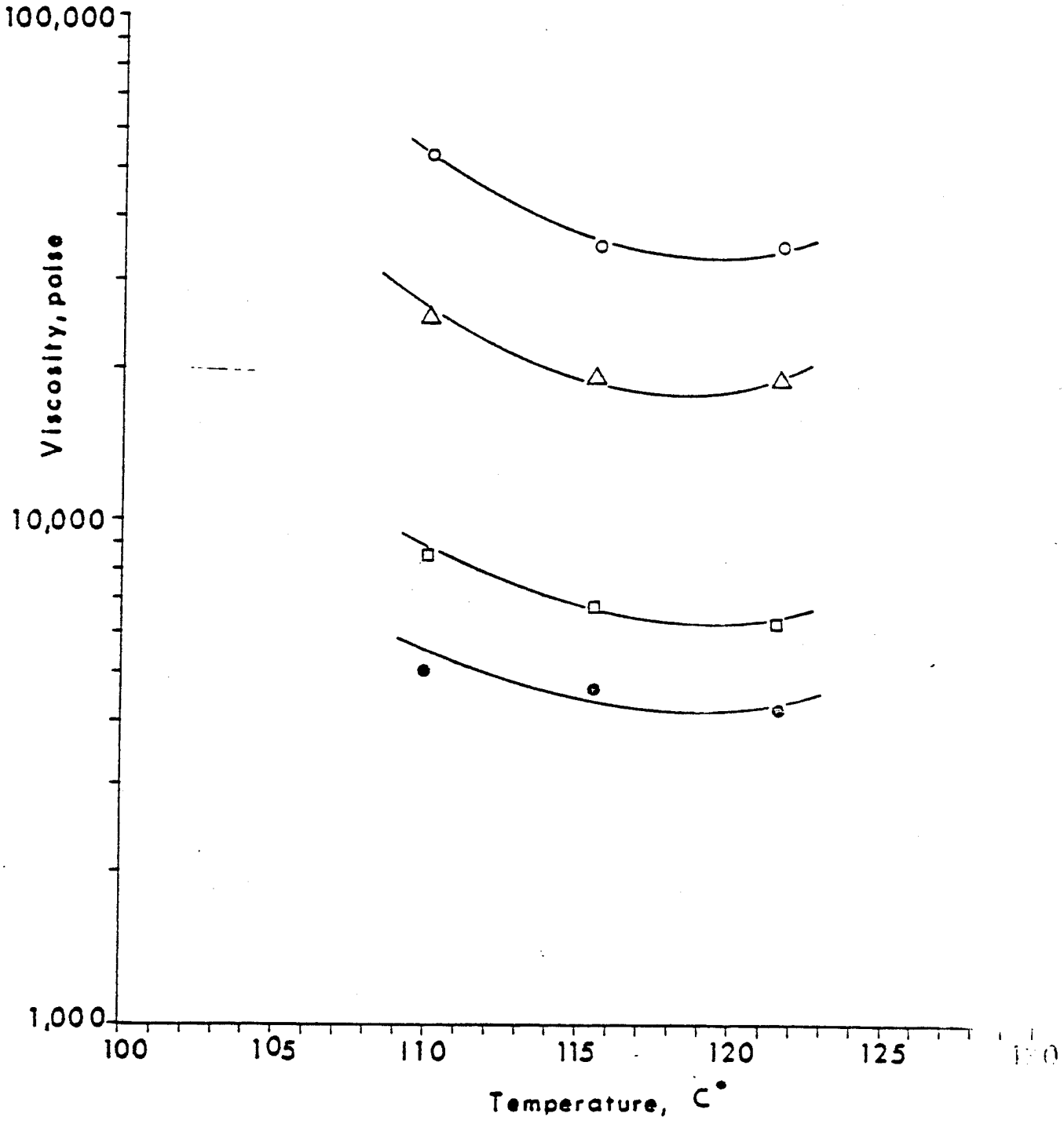

Figure 3. Apparent viscosity as a function of heating time for a woodflour-filled phenolic at 121°C (250°F). Legend for shear rates: ○ - 81.4 sec^{-1}, △-203.2 sec^{-1}, □ -684.2 sec^{-1}, ● -1535.4 sec^{-1}.

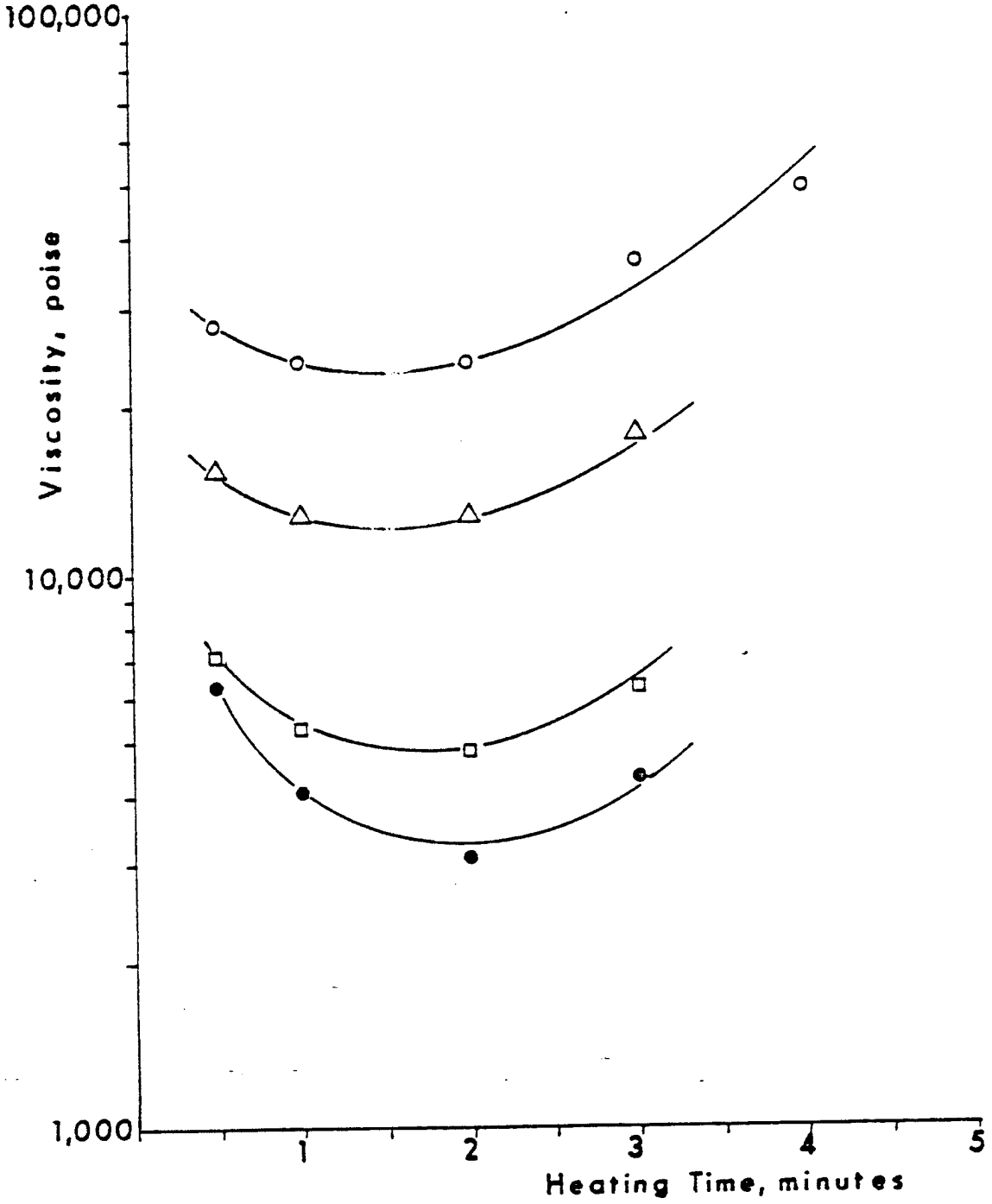

Figure 4. Apparent viscosity as a function of temperature for a woodflour-filled phenolic with a heating time of three minutes. Legend for shear rates the same as in Figure 3.

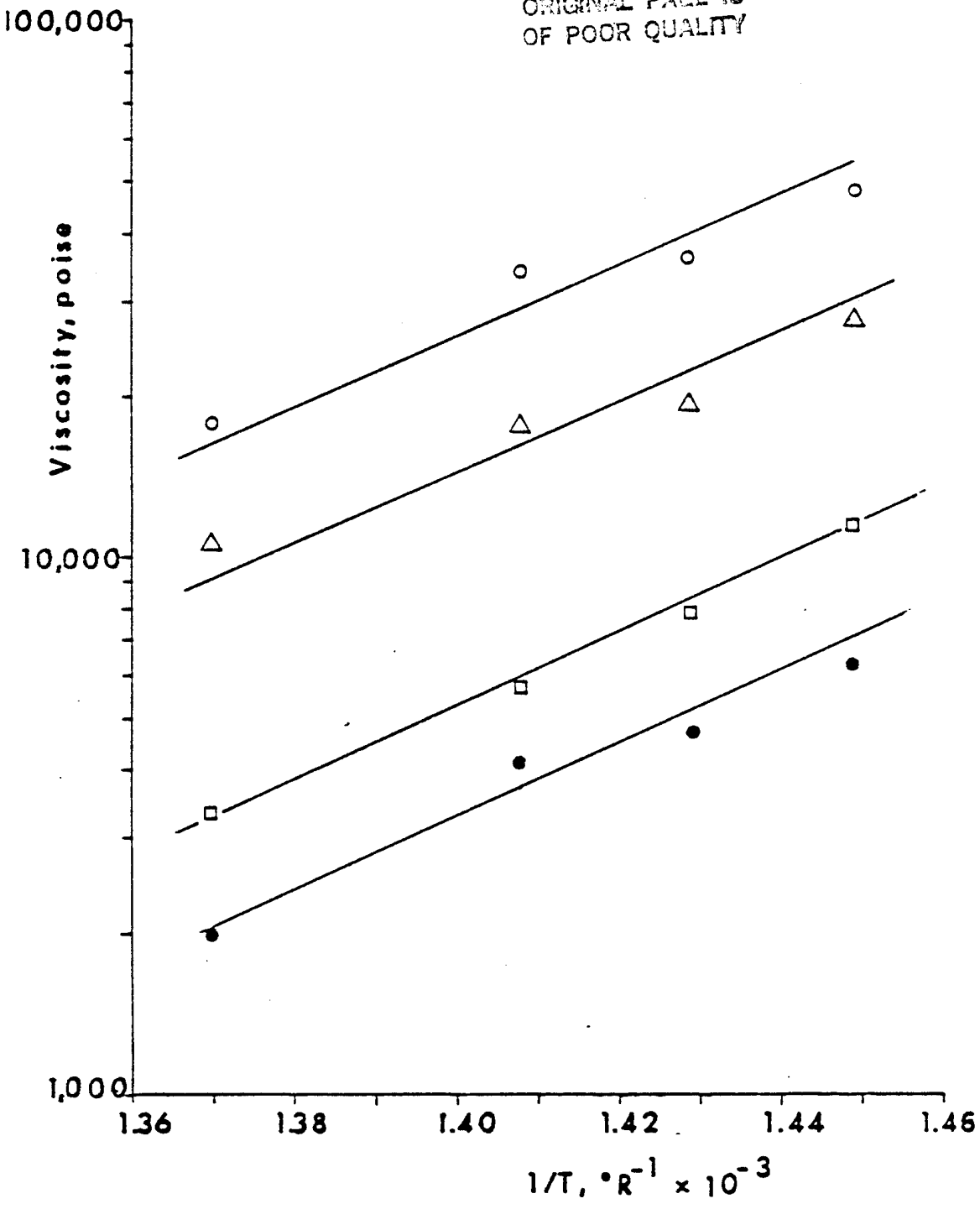

Figure 5. Apparent viscosity as a function of inverse temperature for a woodflour-filled phenolic with a heating time of one minute.
Legend for shear rates the same as in Figure 3.

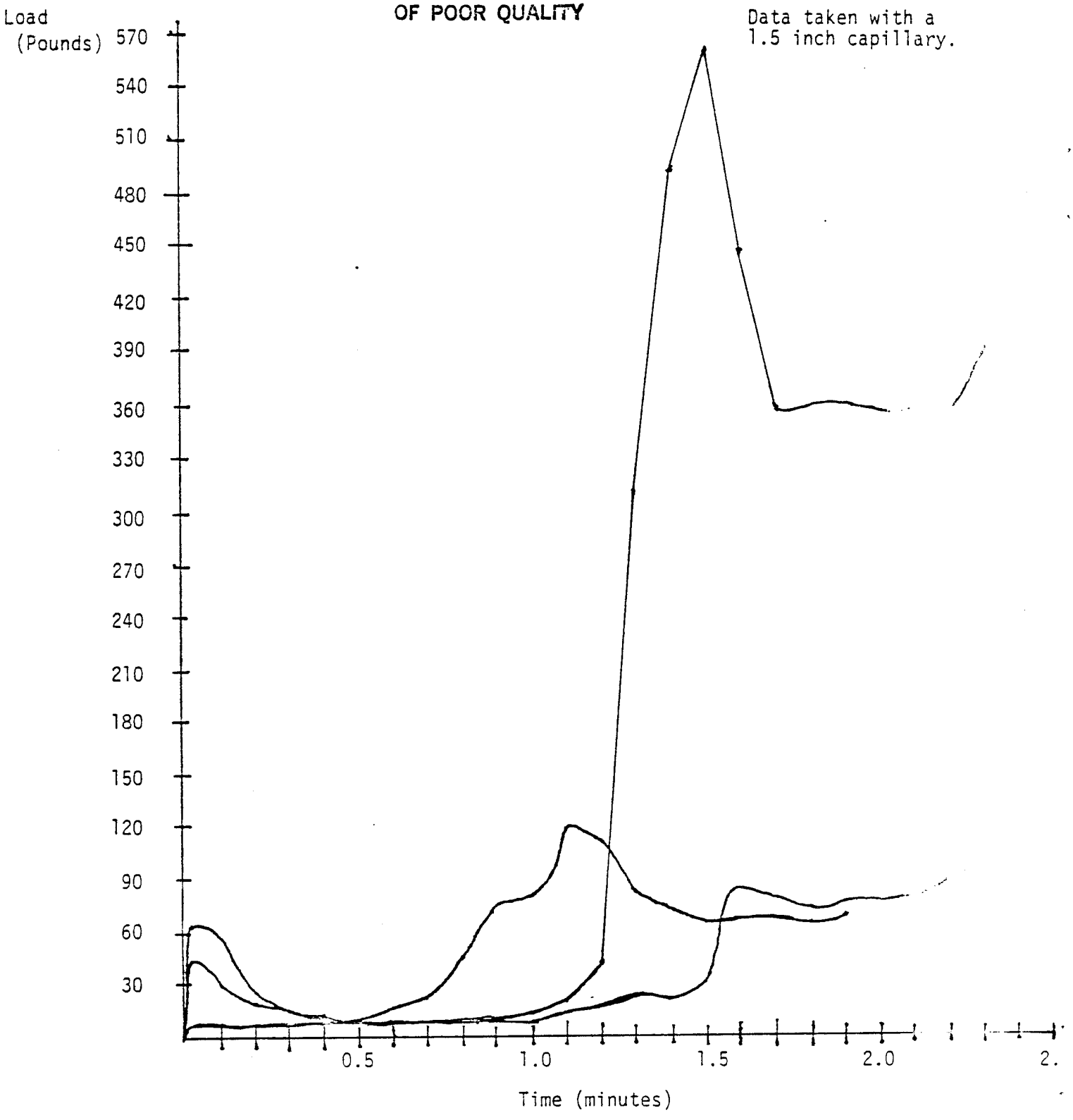

Figure 6. Load response for PMR-15 at 233°C and .03 cm^3/sec. (Three separate runs.)

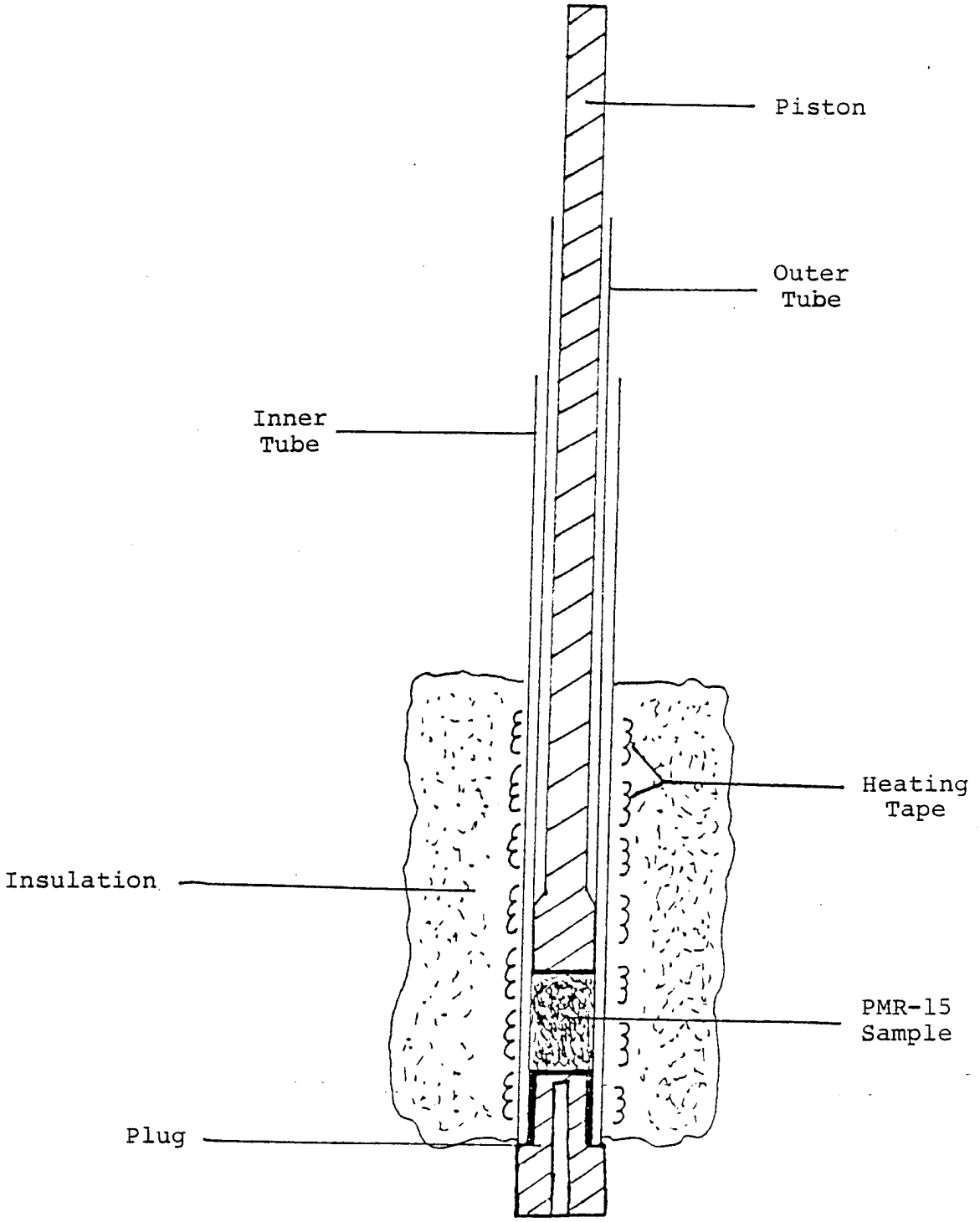

Figure 7. Piston-cylinder apparatus (PCA).

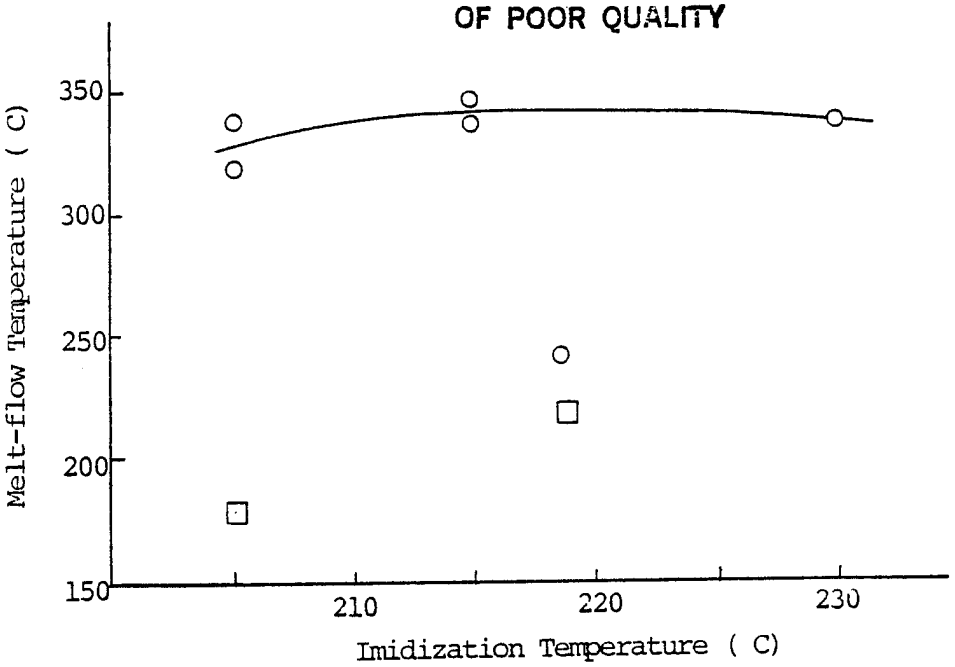

Figure 9. Effect of imidization temperature on the melt-flow temperature of PMR-15.

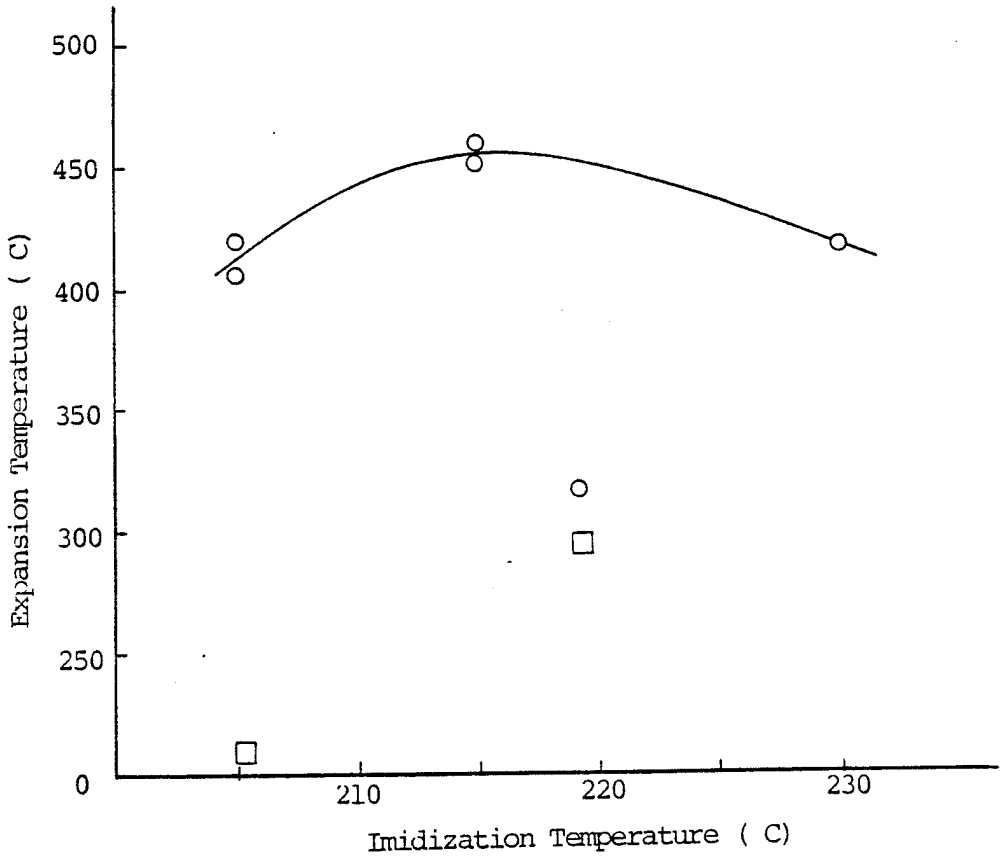

Figure 8. Effect of imidization temperature on the expansion temperature of PMR-15.

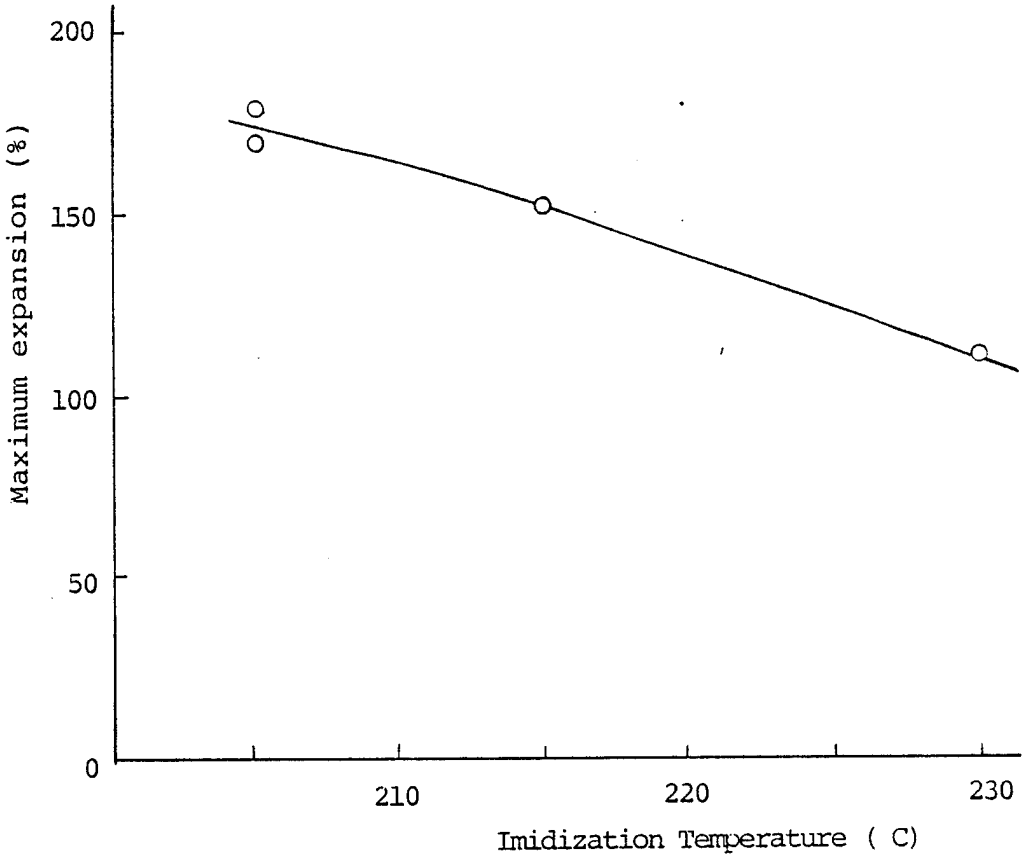

Figure 10. Effect of imidization temperature on the maximum percent expansion of PMR-15.

VII. APPENDIX

PUBLICATIONS

Malguarnera, S., Carroll, D., and Colaluca, M. A., "Design and Use of a Thermoset Capillary Rheometer", I&EC Product Research and Development, March 1984.

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