TRANSFER MOLDING OF PMR-15 POLYIMIDE RESIN

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Transfer molding is an economically viable method of producing small shapes of PMR-15 polyimide. It is shown that with regard to flexural, compressive, and tribological properties transfer-molded PMR-15 polyimide is essentially equivalent to PMR-15 polyimide produced by the more common method of compression molding. Minor variations in anisotropy are predictable effects of molding design and secondary finishing operations.

INTRODUCTION

An intensifying interest in the aerospace community in PMR-15 polyimide resin is spawning programs to better characterize its physical properties, thereby leading to a variety of new applications. Because PMR-15 resin was designed for easy processing into structural composites, little has been done to utilize it for producing small components by common plastics molding techniques. Two years ago, however, we decided that the growing demands for a reasonably priced 600°F polymer warranted the effort to develop an economically feasible process for producing small parts from PMR-15 resin.

Among the standard molding techniques available for producing small parts, the first to suggest itself for mere simplicity is matched-die compression molding. Generally, however, cycle times greater than an hour are required to allow for heating and cooling the mold and for removing the molded piece from the mold cavity.

Hot isostatic pressing is suitable for making large billets, but the subsequent machining operations make this a rather expensive way of producing small parts. Similarly, extrusion yields rod stock which must then be machined into the finished shapes.

Injection molding has been developed to a high degree of sophistication and is probably capable of producing molded-to-size polyimide parts with minimum cycle times. But injection molding PMR-15 resin would be quite risky because of this resin's tendency to rapidly undergo extreme changes in viscosity during processing. An injection mold barrel frozen up with prematurely crosslinked PMR-15 polyimide would mean costly downtime.

A molding method with many of the good features of injection molding but less risk is transfer molding. Although it is less well-known than injection molding, transfer molding was the forerunner of injection molding, and it is still widely used for molding mundane thermosets such as phenolics. Because the mold itself is maintained at a single temperature and is capable of containing multiple cavities, transfer molding can produce a substantial number or parts with rather short cycle

times, and thus it can be a sound way of making small PMR-15 polyimide parts at a reasonable cost.

We have devoted enough effort to adapting transfer molding to the production of PMR-15 polyimide parts to have satisfied ourselves that the technique is economically sound as a manufacturing method. The subject of this paper is the results of our efforts thus far to demonstrate that the physical properties of transfer molded PMR-15 polyimide are equivalent to those of PMR-15 polyimide formed by the more usual compression molding.

PROCESS

The key to successful transfer or injection molding of a resin is the molding compound. Seldom are polymers molded neat. Fillers are selected to provide the particular blend of properties sought for in the final molded product. Once the formulation is decided upon, the processor proceeds as follows:

1. Blend the fillers into the resin solution.
2. Evaporate the solvent.
3. Imidize the resin.
4. Pulverize the imidized molding compound.
5. Press the powder into a preform pill.
6. Heat the pill immediately before inserting it into the transfer pot of the press.

The proper imidization of PMR-15 resin has been described in various technical papers (ref. 1-4). The imidized molding compound is reduced to a powder both as means of insuring homogeneity and of making it handleable. The powder, in turn, is compacted into a pill in a cold die in order to expel excess entrapped air. The size of the pill is determined by the size of the transfer pot and the volume of resin required to fill the mold cavities. The purpose of preheating the preform pills is to reduce the cycle time in the press.

The operation of the transfer press itself is easily described by referring to figure 1. The entire mold is maintained at the temperature required for curing the polymer. In the case of PMR-15 resin, the cure is effected by thermal crosslinking of the norbornenyl endcaps. At the start of the cycle, the mold is clamped shut. A hot preform pill of molding compound is dropped into the transfer pot of the mold and the hydraulic transfer ram is activated. The pressure of the ram and the heat of the mold rapidly liquify the molding compound. Molten material surges outward through narrow channels and into cavities in the mold base. A large enough preform pill is used to insure that a small amount of material remains in the hub (cull) directly under the ram, thereby keeping the curing resin under pressure. When enough time has passed to sufficiently cure the resin, the bottom platen drops down, lowering the lower half of the mold onto stationary ejector sleeves that force the molded pieces out of their cavities. The operator manually removes the pieces,

retracts the ram, and the cycle is ready to start over. The molded pieces themselves are later postcured in the free state to guarantee that the cure is complete and to enhance their oxidation resistance.

If the molding compound should setup prematurely, the worst that happens is that the cavities fill only partially and a thick cull remains. The hardened resinous mass can be ejected easily, the only loss being a small quantity of material and a few minutes of operating time.

RESULTS

Test Specimens

Figure 2 illustrates the three basic mold shapes from which specimens were taken for determination of physical properties. Rectangular plates as thick as 1.1 inch were formed by compression molding. Transfer-molded shapes included two cylinders, one being 1.50 in. OD x 0.37 in. ID x 1.16 in. and the other 1.03 in. OD x 0.53 in. ID x 2.41 in., and a standard test bar 4.0 x 0.50 x 0.25 inches. The point of resin injection ("gate") for the transfer-molded pieces is indicated in the sketch. Specimens were taken in two orientations 90° to each other as a check for anisotropy resulting from flow patterns into the mold cavity.

The flexural and compressive tests reported in this paper were run in accordance with ASTM D-790 and D-695, respectively. Wear tests were carried out in the conforming block configuration on a LFW-1 machine; a description of the test is given below.

Materials

Table I gives the composition of the material selected for this study. Material "N" is simply neat PMR-15 polyimide. The carbonaceous fillers found in materials "A," "B," and "C" represent typical formulations for self-lubricated, dry-running bearings and seals. The fillers consist of a high-quality natural graphite powder, a milled carbon fiber, and a calcined, finely divided amorphous carbon. The graphite provides lubricity, the carbon fiber reduces thermal expansion, and the amorphous carbon powder imparts hardness and wear resistance.

Flexural Properties

Table II presents a comparison of the four grades of PMR-15 polyimide in terms of the ultimate flexural strengths of specimens machined from compression-molded plates.

In table III, material "A" was chosen to illustrate the worst-case situation for the effect of the method of molding on the flexural strength. In the present context, "worst case" connotes the highest content of milled carbon fiber (33% by weight) and hence the most exaggerated anisotropy. The specimen orientations shown here favor preferred fiber orientation along the length of the specimens. The results are very much what one would normally anticipate. Because the transfer-molded test bar was end-gated, fiber orientation is dominant parallel to the length

of the bar, thereby providing maximum reinforcement. Resin flow downward into the cylindrical cavity is turbulent, giving the least reinforcement. In the compression-molded plate most fibers assume a horizontal posture but have no preferred orientation within the plane; this accounts for the intermediate flexural strength of compression-molded specimens.

Another factor that partially accounts for the variations in strength is the degree of machining required to prepare the test specimens. Thus, the transfer-molded tests bars were tested as-molded, the compression-molded specimens were machined only along their edges, but specimens from the cylinders had to be machined on all faces. Because machining operations run the risk of inducing localized stresses and microscopic flaws in the test specimens, it is not surprising that the flexural strength of these specimens decreases with the amount of machining to which they have been subjected.

To complete the profile of these materials, figure 3 shows the drop off in flexural properties (in this instance, for material "A") with elevated temperatures up to 600°F. The curves shown are for transfer-molded test bars. Data for compression-molded specimens generate nearly identical curves.

Compressive Properties

A comparison of the ultimate compressive strength of our four PMR-15 grades is made in table IV. There is an indication of slight anisotropy in the compression-molded specimens. For material "N" this anisotropy is attributable to poor thermal conductivity of the neat resin promoting curing from the outside inward, thereby causing stratification within the molded plate. (Poor thermal conductivity also makes the neat resin very difficult to transfer mold.) Although material "A" exhibits good thermal conductivity, the preferred horizontal orientation of fibers within the molded plate provides greater reinforcement to perpendicularly applied compressive loads (i.e., in vertical specimens) because the stresses so generated are principally shear stresses.

Table V is a more detailed look at the relationship between compressive strength and method of molding for material "A." Once again, material "A" represents the "worst case" situation because of its high fiber content. Average compressive strengths of the two orientations of transfer-molded specimens fall within the one standard deviation range of each other. Values for the two orientations of the compression-molded specimens, however, barely overlap at three standard deviations, which confirms their anisotropy.

Tribological Properties

Tribon makes extensive use of Falex model #1 ring and conforming block test machines in screening materials for friction and wear properties. These machines are still commonly referred to as LFW-1 machines, after their original designation. LFW-1 tests do not predict precisely the wear that will occur in a given application, but they do rank materials. An experienced tribologist can utilize LFW-1 data effectively in selecting candidate materials for new applications.

The material to be tested is machined into a block with a radius that conforms to the test ring (figure 4). In all the tests reported in this paper the specimens

were run against the standard S-10 ring (SAE 4620 steel; Rc 60-62 hardness; 10-12 microinch rms finish), although the test ring may be made from any suitable material. The test ring is mounted on an electric motor-driven spindle and can be run at speeds variable from 4.5 to 1,000 ft./min. Load is applied to the test specimen by dead weights through a 30-to-1 lever system. Friction is measured by a force gage mounted tangentially to the contact area.

The terms and symbols used in wear testing are summarized as follow:

P = unit load = load/area = F/A (lb./in.^{2})

d = diameter of test ring (in.)

w = width of test specimen (in.)

n = number of revolutions per minute

V = rubbing velocity = $\pi \cdot d \cdot n/12$ (ft./min.)

D = test material wear depth (in.)

Q = test material wear volume (in.^{3})

T = test length (hr.)

W = wear rate = D/T (in./hr.)

K = wear factor = Q/FVT $\left(\frac{\text{in.}^3}{\text{lb} \cdot (\text{ft/min}) \cdot \text{hr}}\right)$

The usual unit of measurement for the operating conditions of self-lubricated bearings is pressure-velocity (PV), i.e., the product of unit load times the rubbing velocity. Unit load is calculated by dividing the applied load by the area. The expression of area most common in LFW-1 testing is the actual area of the arc in contact with the test ring (0.16 in.^{2} in the present case). This expression differs sharply from the conventional expression used in journal bearing tests, which is for the projected area, namely, the shaft diameter multiplied by the bearing length, even though in actuality only an arc about the size of the LFW-1 test block supports the load. Ordinarily PV values derived from LFW-1 tests are considerably greater than those derived from journal bearing tests on the same material. We have found that if the PV values for LFW-1 tests are calculated as test ring diameter (d) times the test block width (w), LFW-1 wear rates approximate those obtained with journal bearing tests. Therefore, PV values reported below have been calculated on the basis of the conventional projected area.

The wear depth (D) of the test material is the difference in the height of the test block before and after tests. Wear rate (W), then, is calculated by dividing D by the test length (T). An alternate method of comparing wear rates of different materials under different operating conditions is by the wear factor K. This value, which is used extensively throughout the self-lubricated bearing industry, is normally a constant over the mild wear regime of a particular material. It is defined as the volumetric wear of the test material divided by the applied load, the rubbing velocity, and the test length. The ranges of K (all as 10^{-10} in English units) are:

1 to 50	Good self-lubricated materials such as carbon-graphites and graphite-filled polyimides, PTFE, nylons and acetals.
51 to 500	Unfilled polyimides, nylons and acetals.
501 to 5000	Unfilled PTFE and phenolics.
> 5000	Bronze and babbit.

Table VI gives the test parameters and wear rates of compression-molded material "A" tested under ambient conditions. It can be seen that the wear factor K is relatively constant over the regime of mild wear, and that the mild wear regime has been exceeded at 1,000 fpm and 131,000 PV. When the same data are put into graphic form (figure 5), K appears as the slope of the W vs. PV curve. The solid curve in figure 5 represents the average value of K, with the two dashed lines indicating the $\pm$ 3 standard deviations that would be used by design engineers. All plotted data easily fall within these limits. Although K is usually considered a constant, our tests show an apparent slight increase in K with increasing rubbing velocity.

A similar presentation of wear data for transfer-molded material "A" is given in table VII and figure 6. The average K of 15.9 for the transfer-molded material is within one standard deviation of the average K of 19.8 for the compression-molded material. The two dashed lines in figure 6 are the same $\pm$ 3 standard deviation limits for compression-molded material as appeared in the previous figure. Once again, the wear rate for the transfer-molded material falls well within these limits. In light of the wide scatter of data ordinarily encountered in wear testing, these data for material "A" exhibit quite reasonable agreement.

The wear data obtained with material "B" (table VIII) corroborate the results just shown for material "A," namely, that the wear characteristics of PMR-15 based materials is not changed significantly by the method of molding. Similarily, neither specimen orientation nor test temperatures up to 600°F had any significant effect on the wear rates.

Table IX is a composite of some data already presented plus new data for material "C" and additional high-temperature data. It further illustrates the consistently low wear rate of PMR-15 based materials, whether they be compression-molded or transfer-molded.

CONCLUSIONS

Starting from the premise that transfer molding is an economically viable process for producing small parts from PMR-15 polyimide, we set out to determine whether transfer molding yields results comparable to the more common compression molding. According to the criteria examined in this paper, namely, the flexural, compressive, and tribological properties of the molded pieces, it can be concluded that the two molding techniques give essentially equivalent results, certainly within the ranges of variation that would normally be employed by design engineers. The minor discrepancies that were encountered are differences familiar to plastics molders and fall into two general categories, viz.,

1) Orientation effects attributable to resin flow patterns within a particular shape of mold cavity, and

2) The degree of secondary finishing required after molding.

Because these minor differences are predictable, they can be anticipated and accounted for in engineering designs.

There are, of course, other important physical and chemical properties of PMR-15 polyimide that need to be confirmed before the case is closed on transfer- versus compression-molded PMR-15 polyimide. Our work is continuing along this line, with emphasis on the thermal properties and thermo-oxidative stability of the molded PMR-15 polyimide. Even though the focus of this report has been on small shapes and bearing-grade composites, there is no intent to imply that the efficacy of transfer molding is limited to this combination. In fact, our current development work is on the transfer molding of larger, structural-grade compositions, the results of which will be reported as they become available.

REFERENCES

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2. Lauver, R. W.: Kinetics of Imidization and Crosslinking in PMR-Polyimide Resin, NASA TM-78844, 1977.

3. Serafini, T. T., Delvigs, P., and Alston, W. B.: PMR Polyimides - Review and Update, NASA TM-82821/AVRADCOM TR 82-C-3, 1982.

4. Serafini, T. T.: PMR Polyimide Composites for Aerospace Applications, NASA TM-83047, 1982.

TABLE I

COMPOSITION OF MATERIALS TESTED

Material	Composition, % by wt.			
	PMR-15	Graphite Powder	Milled Carbon Fiber	Calcined Carbon
N	100	0	0	0
A	56	11	33	0
B	60	10	15	15
C	63	37	0	0

TABLE II

COMPRESSION-MOLDED PMR-15 POLYIMIDE-BASED MATERIALS

(Specimens Machined from Flat Plates)

Material	No. of Sets Tested*	Flexural Strength psi at 73°F	% Standard Deviation	
			Within Sets	Among Sets
N	10	18,200	8.1	14.6
A	9	13,600	6.7	3.8
B	1	11,700	2.5	-
C	7	14,500	4.8	8.6

* 5 specimens per set

TABLE III

EFFECT OF MOLDING MODE ON FLEXURAL STRENGTH OF MATERIAL "A"

Molding	Stock	Specimen Orientation	Flexural Strength psi at 73°F	% Standard Deviation	
				Within Sets	Among Sets
Compression	Plate	⊥ (horizontal)	13,600	6.7	3.8
Transfer	Bar	⊥ (lengthwise)	17,800	4.8	4.2
Transfer	Cylinder	∥ (vertical)	12,700	8.6	2.6

TABLE IV

COMPRESSIVE STRENGTH OF PMR-15 POLYIMIDE-BASED MATERIALS

Material	Compressive Strength, psi at 73°F			
	Compression-molded Plate		Transfer-molded Cylinder	
	Horizontal	Vertical	Horizontal	Vertical
N	24,300	27,100	-	-
A	26,200	29,900	27,700	26,800
B	30,600	-	30,600	30,300
C	27,300	-	-	-

TABLE V

COMPRESSIVE STRENGTH OF MATERIAL "A" ACCORDING TO METHOD OF MOLDING

Molding	Stock	Orientation	Compression, psi, at 73°F		No. of Tests
			Strength	% Std. Dev.	
Compression	Plate	⊥ (horiz.)	26,200	2.5	20
		∥ (vertical)	29,900	1.9	5
Transfer	Bar	⊥ (width)	28,500	2.2	15
		∥ (length)	27,800	2.3	21
Transfer	Cylinder	⊥ (horiz.)	27,700	2.8	8
		∥ (vertical)	26,800	3.6	13

TABLE VI

WEAR RATE OF COMPRESSION MOLDED MATERIAL "A" AT VARIOUS PV LEVELS

Rubbing Velocity ft/min	PV $\frac{lb}{in^2} \times \frac{ft}{min}$	Wear Rate in/hr	Wear Factor $\frac{in^3}{lb \cdot ft/min \cdot hr}$	Number Of Tests
26	9,100	3.7×10^{-5}	18.9×10^{-10}	1
	18,200	6.9	17.8	1
	36,300	11.9	15.3	1
	45,400	14.5	14.9	1
71	24,800	13.7	25.8	7
	49,600	21.3	20.0	7
	74,400	27.8	17.5	8
	99,100	32.2	15.2	7
	123,900	46.2	17.4	4
1000	43,600	25.5	26.2	2
	87,200	54.9	29.4	2
	131,000	197.3	70.5*	1
	174,000	427.4	114.6	2

* These values not included in average

AVERAGE WEAR FACTOR = 19.8×10^{-10}

STANDARD DEVIATION = 5.0×10^{-10}

NOTE: Calculations have been made to give values corresponding to typical journal bearing tests results (see text, p. 5 above). Multiply PV by 2.15 to obtain values in usual LFW-1 format.

TABLE VII

WEAR RATE OF TRANSFER MOLDED
MATERIAL "A" AT VARIOUS PV LEVELS

Rubbing Velocity ft/min	PV $\frac{lb}{in^2} \times \frac{ft}{min}$	Wear Rate in/hr	Wear Factor $\frac{in^3}{lb \cdot ft/min \cdot hr}$	Number Of Tests
71	24,800	14.4×10^{-5}	27.2×10^{-10}	4
	49,600	13.9	13.1	2
	74,400	18.4	11.6	2
	123,900	30.7	11.6	2

AVERAGE WEAR FACTOR = 15.9

NOTE: Calculations per method for journal bearing tests.
PV x 2.15 gives usual LFW-1 format.

TABLE VIII

WEAR FACTOR FOR MATERIAL "B"
FOR VARIOUS MOLDING METHODS

Molding Method	Orientation To Molding Direction	PV	K x 10^{-10}	
			Amb.	600°F
Compression	Perpendicular	24,800	17.2	19.0
		49,600	11.6	N/T
Transfer	Perpendicular	24,800	21.8	N/T
		49,600	12.5	N/T
Transfer	Parallel	24,800	17.8	17.0
		49,600	10.6	N/T

N/T - Not Tested

NOTE: Calculations per method for journal bearing tests.
PV x 2.15 gives usual LFW-1 format.

TABLE IX

EFFECT OF COMPOSITION ON WEAR FACTOR

Material	Molding Method	PV	K x 10^{-10}		
			Amb.	500°F	600°F
A	Transfer	24,800	27.2	33.0	34.3
		49,600	13.1	N/T	N/T
		74,400	11.6	9.0	N/T
		123,900	11.6	21.1	N/T
B	Compression	24,800	17.2	N/T	19.0
		49,600	11.6	N/T	N/T
	Transfer	24,800	17.8	N/T	17.0
		49,600	10.6	N/T	N/T
C	Compression	24,800	16.8	N/T	13.6
		49,600	9.6	N/T	N/T

N/T - Not Tested

NOTE: Calculations per method for journal bearing tests.

PV x 2.15 gives usual LFW-1 format.

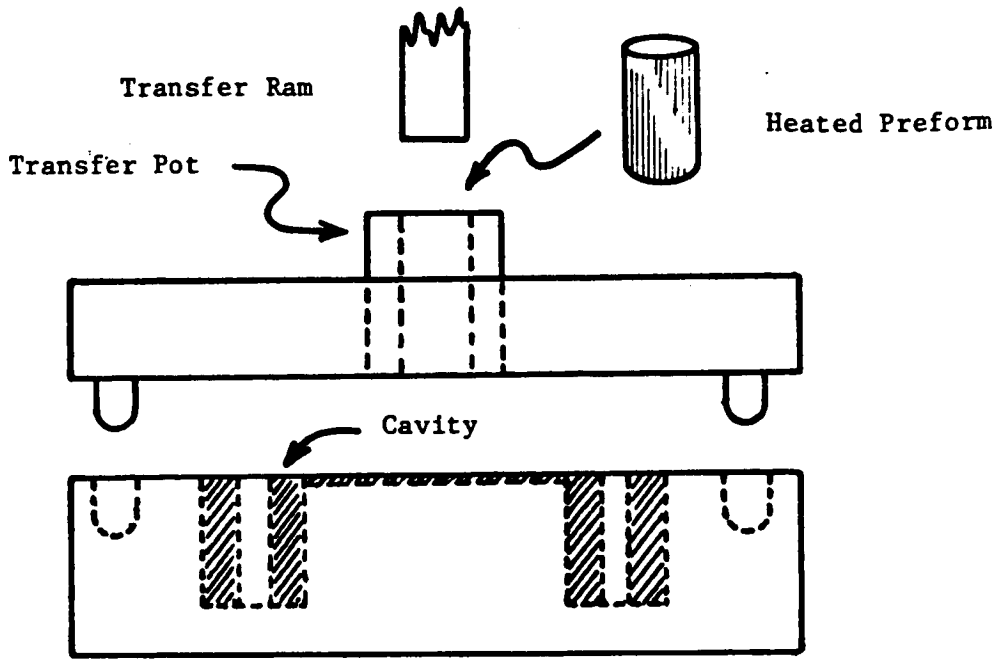

Figure 1. Simplified schematic of a typical transfer mold.

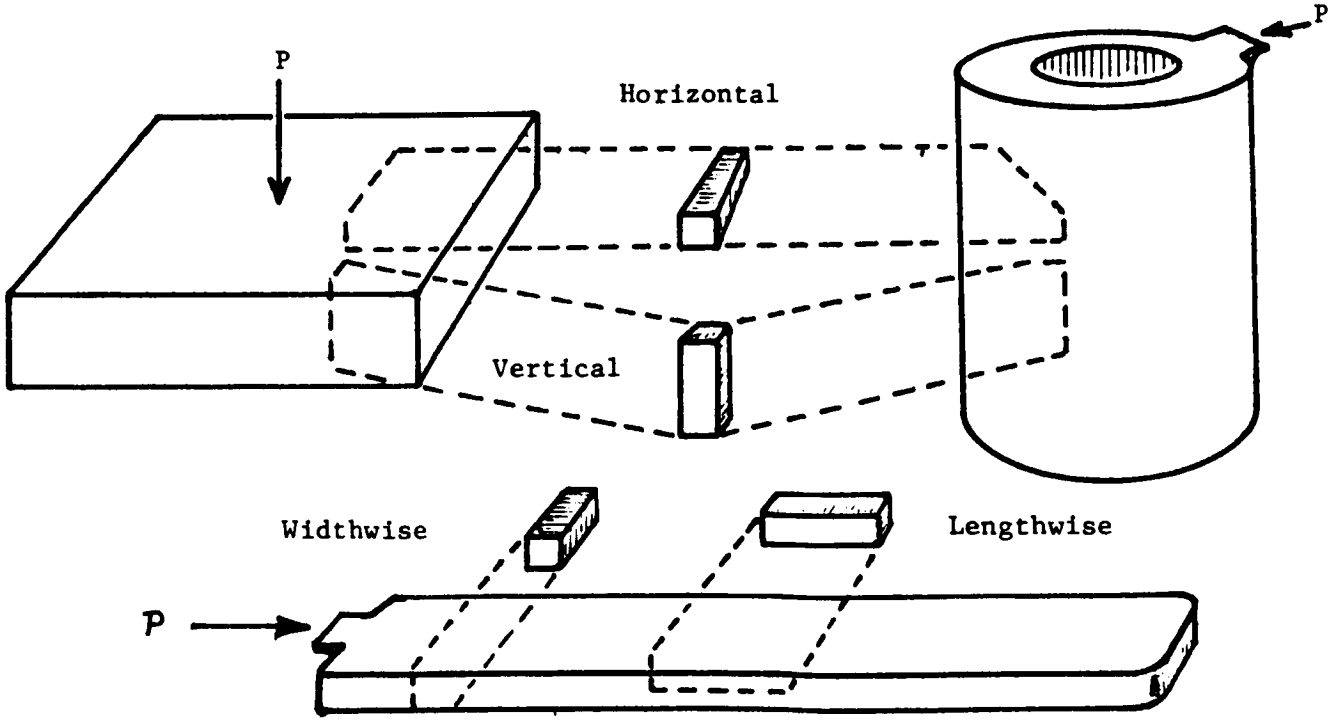

Figure 2. The three basic kinds of molded pieces from which test specimens were taken. "P" indicates the direction of applied pressure (compression molding) or the point of resin injection (transfer molding).

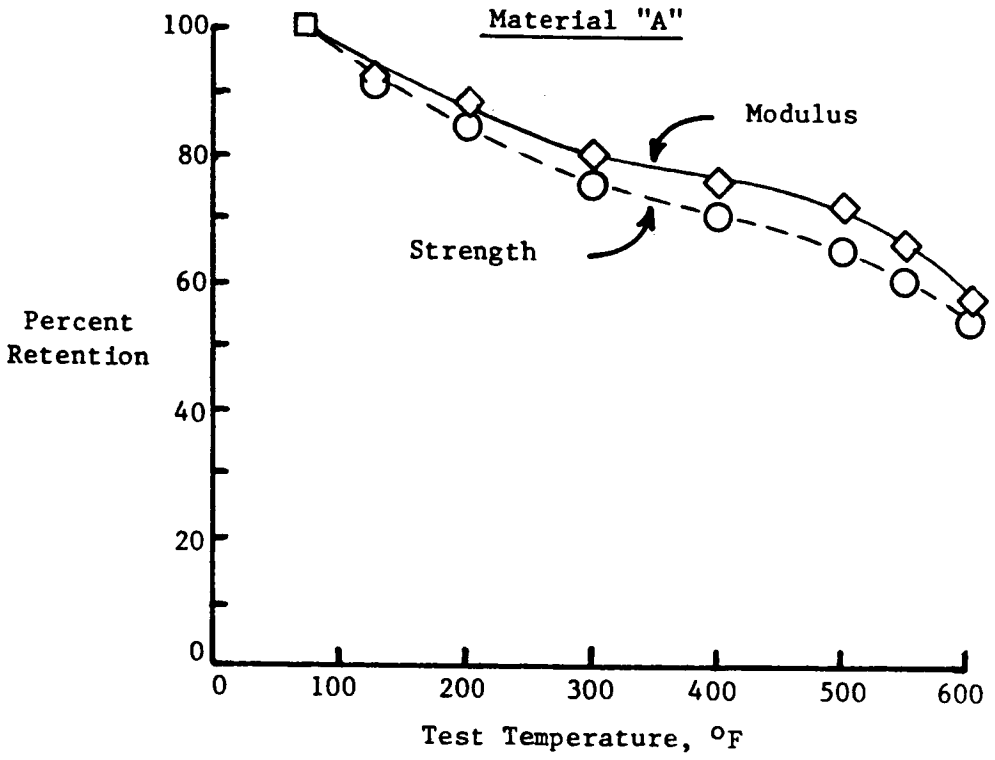

Figure 3. Effect of test temperature on the flexural properties of transfer-molded test bars of material "A".

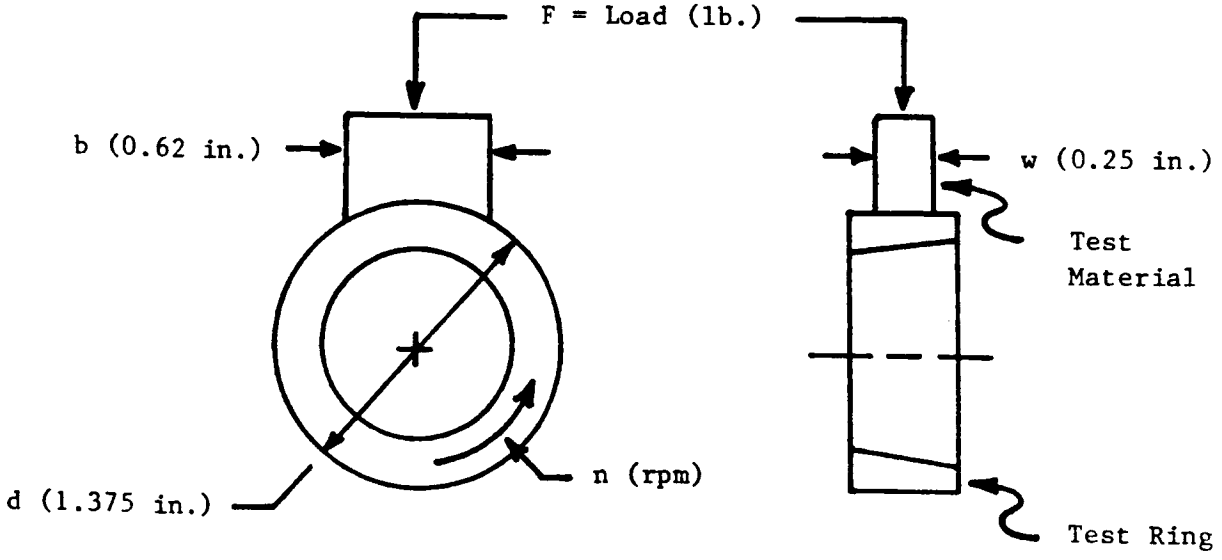

Figure 4. Ring and conforming block in the LFW-1 wear test.

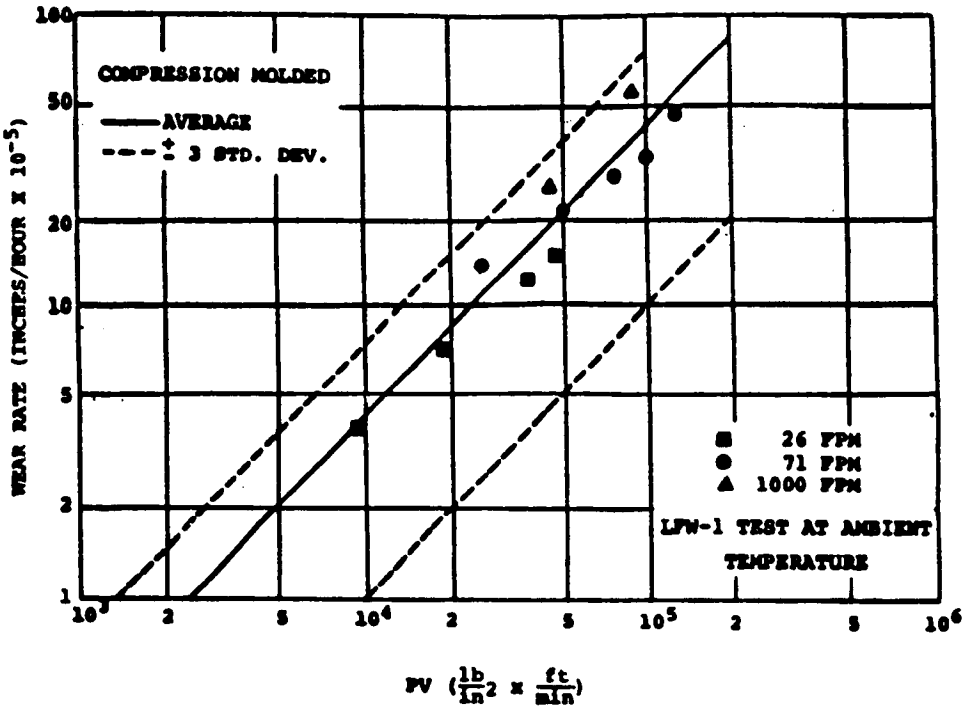

Figure 5. Wear of compression-molded material "A".

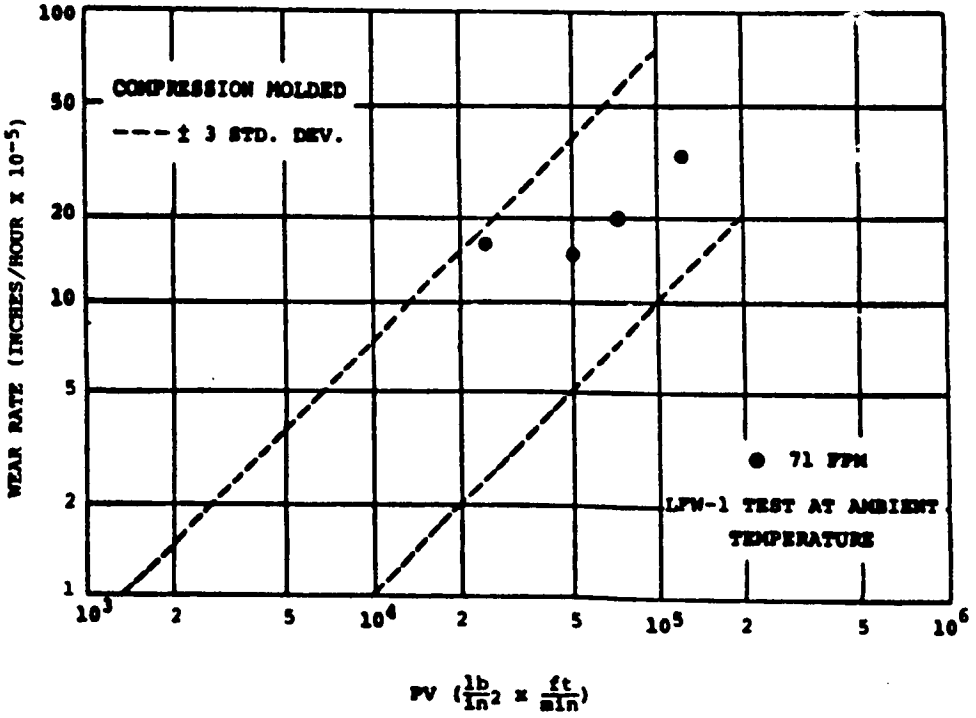

Figure 6. Wear of transfer-molded material "A".