

Physical Properties of High Molecular Weight Acetal Resins

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INTRODUCTION

The purpose of this paper is to present information on the properties of the polyoxymethylene class of acetal resins: those properties where measurement is greatly facilitated by thermal stability greater than previously known polyoxymethylenes and properties of a mechanical nature characteristic of high molecular weight polymeric materials.^{1,2,4} The polymers used in this study were esterified polyoxymethylenes, of number-average molecular weights 45,000, unless otherwise noted. Molded objects used in testing were prepared by injection molding at melt temperatures of 190–200°C. into a cooled mold maintained at 100–120°C., except where otherwise stated.

MELTING TEMPERATURES

Acetal resins of this type behave as semicrystalline solids.³ The molded bars used in this study characteristically exhibited about 75% crystallinity. Values of the melting point or range are given in Table I.

TABLE I

Ref.	Method	Onset of melting, °C.	Melting complete, °C.
(3)	X-ray	173-178	178-181
(5)	Heat capacity	125-150	178-179
(6)	Visual (microscope)	175	180

The melting information obtained from heat capacity data is amplified in Figure 1. The characteristic melting range generally found in crystalline high polymers is clearly indicated. Onset of melting above 125°C. is associated with crystalline regions which are either very small or more readily melted for other energetic considerations.⁷ The sharp point as melting becomes complete shows up at 178–179°.

The effect of molecular weight on melting temperatures and boiling points may be used to compare polyoxymethylenes with hydrocarbon and fluorocarbon polymers. In Figures 2 and 3 the

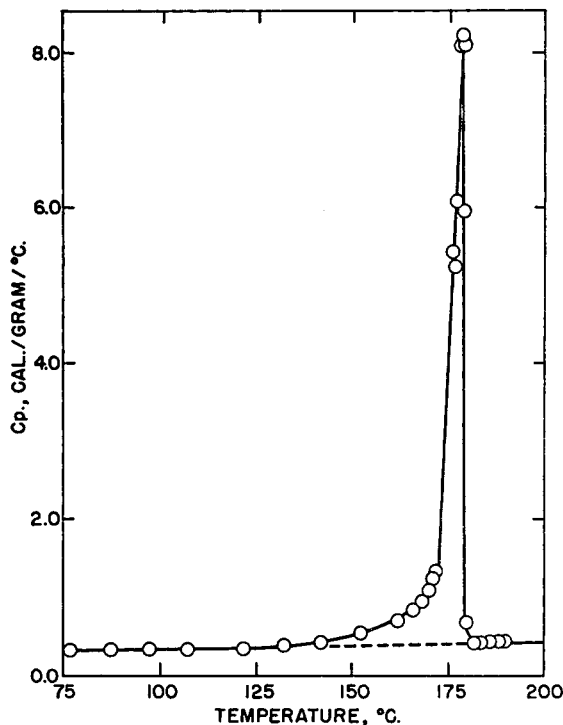


Fig. 1. Heat capacity of polyoxymethylene as a function of temperature.

melting points and boiling points are shown as a function of molecular weight. Data are from references 8–13. These three polymer structures are of special interest because they comprise probably the simplest straight chain polymers with no major side branching. The low molecular weight melting point data for polyoxymethylenes include the major part of the literature data. In all cases at low molecular weight it is plausible that the endgroups become significant.

The melting and boiling points of hydrocarbons and polyoxymethylenes in the low molecular weight range are similar, while those of the fluorocarbons are considerably lower. From the slopes of the boiling point curves it may be inferred that the heats of vaporization per structural unit of polyoxymethylene and polymethylene are similar, while that of the fluorocarbons is lower. This

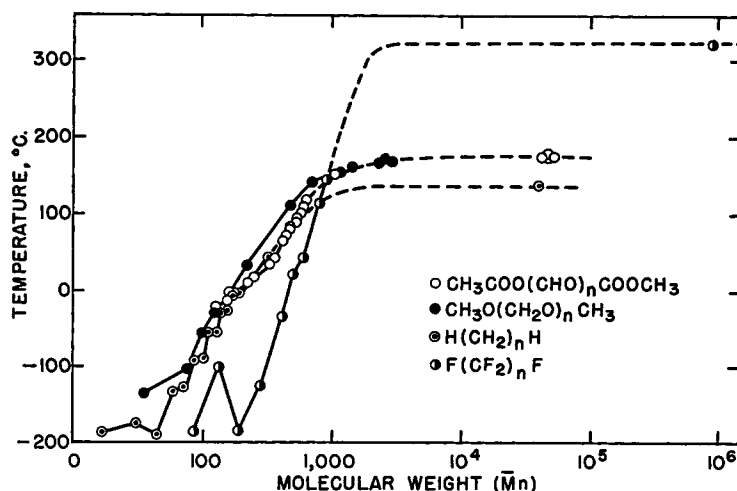


Fig. 2. Melting point vs. molecular weight for three different backbones.

may be an indication of the relative order of intermolecular forces.

However, a theoretical calculation in this laboratory by W. Brandt¹⁶ of lattice energies and compressibilities at 0°K. of the high polymers of these three types indicates that the order of interaction energy is hydrocarbons > fluorocarbons > oxymethylenes. Due to the greater number of structural units per unit volume in polyoxymethylene the energy density and bulk

moduli are calculated to be about the same for polymethylene and polyoxymethylene and lower for polyfluorocarbons.

The much higher melting points of the high polymeric fluorocarbons and possibly the difference between high molecular weight polyoxymethylene and polymethylene indicate the importance of intramolecular degrees of freedom in determining transitions in high polymers. The stiffness imparted to the chain by the bulky fluorines greatly reduces the entropy increase upon melting.

It is also instructive to note the difference in melting points between polyethylene oxide and polyoxymethylene. Whereas high molecular weight materials of the latter structure melt at 178°C., polymers of the former structure melt at 66°C.¹⁷ Clearly, the additional methylene unit per oxymethylene unit disrupts the structural regularity important to crystallization.

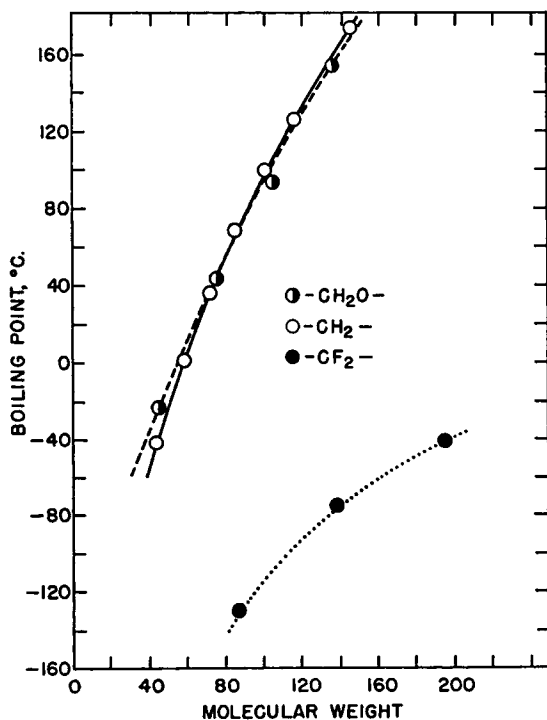


Fig. 3. Boiling point vs. molecular weight for three homologous series.

GLASS TRANSITION TEMPERATURE

The subject of transitions is complex; work now in progress in these laboratories is leading to results in some detail. Present information may give an indication of what these more precise measurements will show. ASTM brittleness tests on molded bars are made at various temperatures and the temperature corresponding to the breakage of 50% of the bars calculated. This is customarily considered an indication of transition from a state in which the chains in the noncrystalline regions are quite flexible and able to move to a state in which mobility is greatly restricted. From information in Figure 4 we may estimate a glass transition temperature in the range -40 to -60°C .

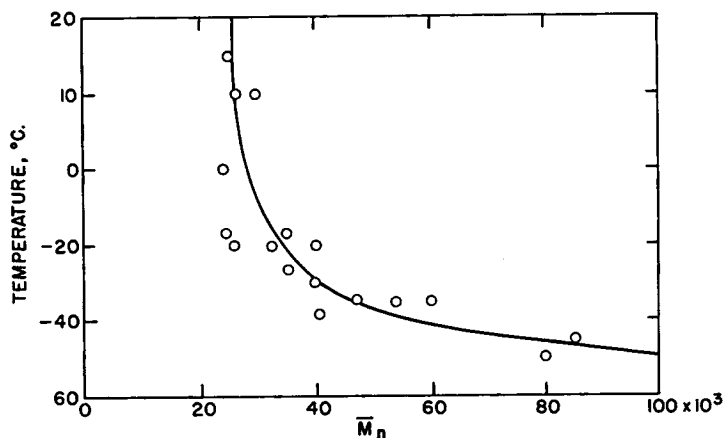


Fig. 4. ASTM brittleness temperature as a function of molecular weight.

DENSITY

Polymers of DP 1000–1500 were examined by the ASTM D-792 method. Results for density at 23°C. give 1.425 ± 0.001 g./cm.³ for 75% crystallinity.³ From a comparison with hydrocarbon and fluorocarbon polymers in Table II it may be seen that the greater density of the polyoxymethylenes cannot be attributed to monomer molecular weight alone.

TABLE II

Monomer molecular weight	Polymer	Density at 23°C., gm./cm. ³
30	—CH ₂ O—	1.425
28	—CH ₂ CH ₂ —	0.96
100	—CF ₂ CF ₂ —	2.2

Table III lists the unit cell dimensions, average distance between chains and the length of the recurrent structural unit. It may be seen that the high density of polyoxymethylene may be associated principally with the packing along the chain axis which can, in turn, be associated with the shortness of the C—O bond compared to the C—C bond.

Thus, the acetal linkages correspond to about 32% more recurrent units per unit of chain length in the lattice than the methylene linkages, about

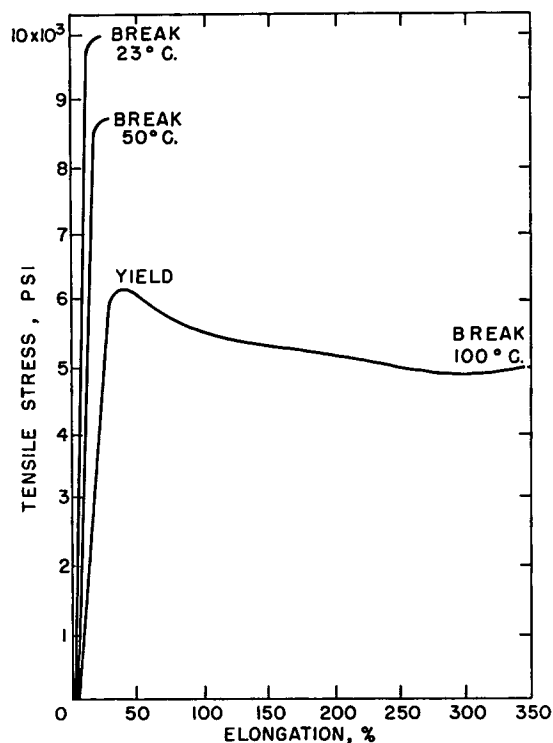


Fig. 5. Stress-strain curve at various temperatures.

TABLE III

Polymer	Cell dimensions, A.			Recurrent units/cell	Interchain distance, A.	Length of recurrent unit, A.
	<i>a</i>	<i>b</i>	<i>c</i>			
—CH ₂ O—	4.46		17.30	9	4.46	1.92
—C ₂ H ₂ —	7.40	4.93	2.534		4.30	2.534
—C ₂ F ₂ —	5.66		19.5	8	5.66	2.44

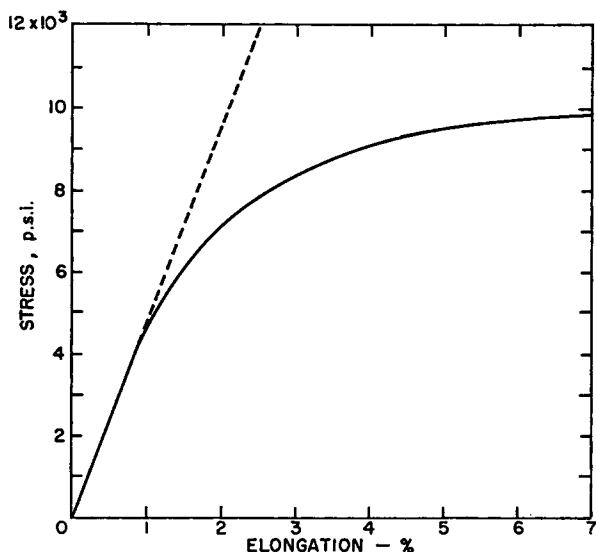


Fig. 6. Detail of stress-strain curve for 23°C.

7% more chains per unit cross-sectional area, and a monomer molecular weight about 7% greater.

TENSILE STRENGTH AND ELONGATION

Stress-strain behavior of molded bars is shown in Figures 5 and 6. The slope of the 23°C. curve shown gives a modulus of 450,000 psi. This again reflects the density and crystalline nature of the polymer, and can be compared with those for linear polyethylene and polytetrafluoroethylene (of *ca.* 50% crystallinity) (Fig. 7). Somewhat more detailed data are plotted in Figure 8 to show the effect of temperature. The increase in ductility

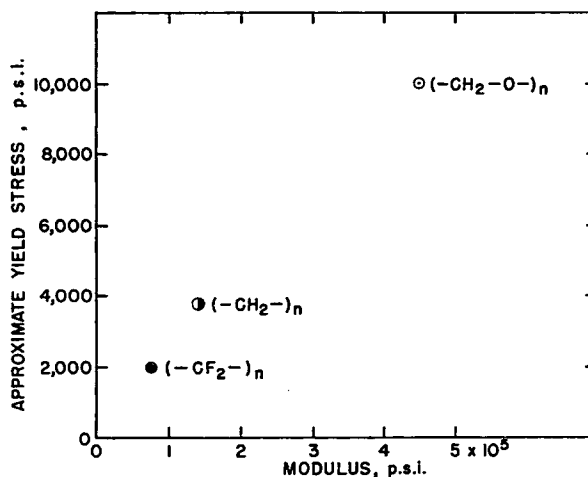


Fig. 7. Comparison of yield stress and modulus for high polymers of the oxymethylene, hydrocarbon, and fluorocarbon series.

in the 60–80°C. range is brought out. The effect of degree of crystallinity on polymer strength properties is best investigated on thin films; the thicker molded bars of this study showed only small variations in crystallinity (*ca.* $\pm 3\%$ absolute). However the importance of crystallinity is indicated by the influence of sample preparation on properties. An effect was observed on per cent elongation but not significantly on the tensile strength; for example, the elongation of $1/8$ -in. thick bars at 23°C. was increased from about 15% to about 30% by a change from 120°C. mold temperature to 60°C. mold temperature.

Figure 9 shows the effect of water on flexural

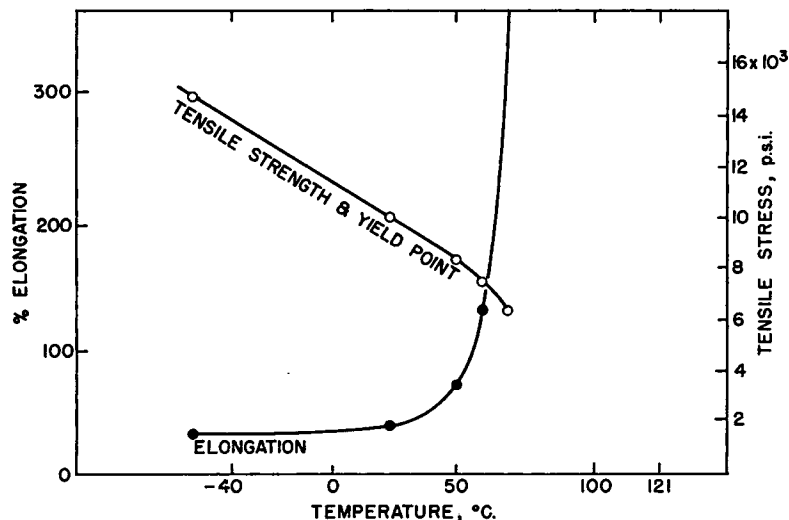


Fig. 8. Tensile strength and elongation as functions of temperature.

modulus at various temperatures. It is noteworthy that the effect is so small for this acetal structure in a resin. The effect of other solvents is given in another paper.⁴

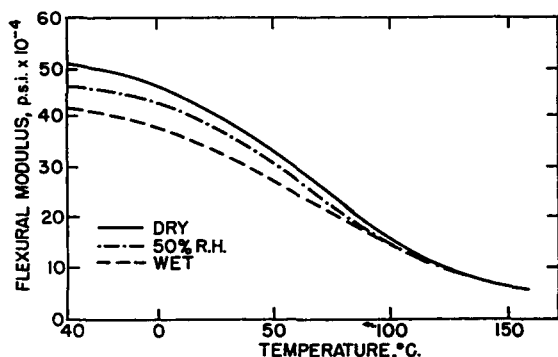


Fig. 9. Effect of moisture in environment on flexural modulus at various temperatures.

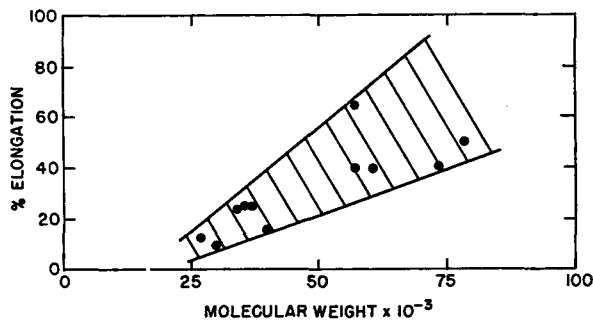


Fig. 10. Effect of molecular weight on elongation of tensile specimens at break.

Molecular weight affects properties as shown in Figure 10. A band of data points is found, probably because of the variations due to fabrication of these samples. While molecular weight is clearly a major factor in physical properties such as elongation, it is equally clear that other variables (e.g., mold temperature) are also important, as indicated previously.

FATIGUE

The fatigue endurance limit of a polymer is of interest where the material will be functioning under dynamic use conditions. In the test used here, a stress is alternately applied and released at the rate of 1800 cycles per minute until rupture occurs. The stress level is varied to find the highest stress at which the specimen will withstand 1,000,000 cycles without failure. The Sonntag fatigue tester used here has been adapted for plastics from a similar instrument used for metals. The speci-

men is a dumbbell shape prepared by injection molding with a test section $\frac{1}{8}$ -in. in diameter and 1 in long. Fatigue endurance limit stresses defined above were determined at 23°C. to be 5,000 psi for these polyoxymethylenes, compared with 2,000 psi for a number of linear polyethylenes. The fatigue test no doubt represents a special amplification of the importance of structural details. Presumably this stress is a measure of the resistance of the material to small but irreversible polymer chain slippages in the crystalline network.

CONCLUSIONS

1. The high molecular weight polyoxymethylenes studied possess the characteristic physical and mechanical properties of a semicrystalline material in the high molecular weight range.
2. The melting point, stiffness, and tensile strength of these polyoxymethylenes substantially exceed those for linear polyethylene. The close packing of repeat units along the acetal chain and the high crystallinity of this material increase the effective chain interaction beyond the amount due solely to intermolecular forces characteristic of small molecules of these series.

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Synopsis

Information is presented on those physical properties where measurement is greatly facilitated by thermal stability greater than previously known in polyoxymethylenes, and properties of a mechanical nature characteristic of high molecular weight polymeric materials. The high molecular weight polyoxymethylenes studied possess the characteristic properties of a semicrystalline material in the high molecular weight range. The melting point, stiffness, and tensile strength of these materials substantially exceed those for linear polyethylene, which suggests that the effective chain interactions are enhanced by ease of close packing of the chains. High density and high crystallinity are in accord with this picture.

Résumé

On fournit des renseignements au sujet des propriétés physiques des polyoxyméthylènes dont la mesure a été grandement facilitée par une stabilité thermique plus grande que prévue et au sujet des propriétés mécaniques des polymères de poids moléculaires élevés. Les polyoxyméthylènes

de hauts poids moléculaires possèdent les propriétés caractéristiques d'une substance semicristalline de hauts poids moléculaire. Le point de fusion, la rigidité et la résistance à la traction de ces substances dépassent substantiellement celles de polyéthylènes linéaires, ce qui suppose que les interactions effectives entre chaînes sont augmentées par la facilité avec laquelle les chaînes peuvent s'entasser. La densité élevée et la haute cristallinité sont en accord avec cette image.

Zusammenfassung

Angaben über solche physikalische Eigenschaften, deren Messung durch eine höhere thermische Stabilität, als sie früher bei Polyoxymethylenen bekannt war, stark erleichtert wird, und über mechanische Eigenschaften, die für hochmolekulare, polymere Stoffe charakteristisch sind werden gemacht. Die untersuchten hochmolekularen Polyoxymethylene besitzen die charakteristischen Eigenschaften eines semikristallinen Stoffes im hochmolekularen Bereich. Schmelzpunkt, Steifigkeit und Zugfestigkeit dieser Stoffe übertreffen die des linearen Polyäthylens wesentlich. Das spricht dafür, dass die massgebenden Wechselwirkungen zwischen den Ketten durch die Leichtigkeit einer dichten Packung der Ketten begünstigt werden. Hohe Dichte und hohe Kristallinität sind mit diesem Bild in Übereinstimmung.

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