

This is due to compression of gas bubbles in the melt. When the load is first applied, compression or compaction of the melt is occurring and the piston is moving rapidly but the amount of material forced out of the barrel is small. Since the reproducibility is poor, it seems unlikely that bubbles of volatile material in the polymer, i.e., monomer, are a major contributor to the effect; if this were so, consistent results would be expected. However, the trapping of air in the melt during loading would lead to the poorly reproducible behaviour observed. Since the effect occurs much more frequently in the piston instrument than in the gas operated instrument, the trapping of an air cushion between the piston and the melt seems to be the major factor. Although rapid movement of the piston observed when a load is first applied is mainly due to effect *C*, effect *B* also causes an increase in the rate of piston movement, which lasts over a longer period.

The swelling of the extrudate also varies with time. Over the long term change, (effect *A*) swelling and flow rate increase together, following the law:

$$\frac{\text{extrudate diameter}}{\text{capillary diameter}} = \text{constant } X \log (\text{flow rate})$$

In the initial period of extrusion, however, the swelling behaviour differs from that of the flow rate. It is initially low by some 3%, and increases slowly. The time period is of the same order as that of effect *B*. A few samples did not follow this pattern and the swelling decreased with time, paralleling the flow rate change.

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### *The Glass Temperature of Asphalt*

Very little is known about the glassy state properties of asphalt particularly about the glass temperature  $T_g$ , and the factors which affect it. Considering the important applications of asphalt which involve low temperature exposure it would seem very valuable to have an estimate of the  $T_g$  of this material. In addition, it has been reported that this property varies with asphalt composition,<sup>1</sup> and a measurement of  $T_g$  could conceivably provide an important and simple method for differentiating between various asphalt samples. Wada and Hirose have conducted specific volume-temperature measurements on a series of asphalt samples with varying asphaltene contents and have observed a direct relationship between asphaltene content and  $T_g$ .<sup>1</sup> It was observed that  $T_g$  decreased from 2° to -37.5°C. when the asphaltene content decreased from 61.9 to 0 weight percent. An asphaltene content of 28.6%, a value which falls somewhat above the range normally encountered (10-20%), had a  $T_g$  of -22.5°. In the present study broad-line nuclear magnetic resonance spectroscopy was applied to the

measurement of the glass temperatures of two samples of asphalt differing in softening point and penetration value. Asphalt I had an ASTM Softening Point (Ring and Ball Method, D-36-26) of 122.5°F. and a penetration value of 63 at 77°F. (ASTM D-5). Asphalt II had a softening point of 107.0°F. and a penetration value of 140.

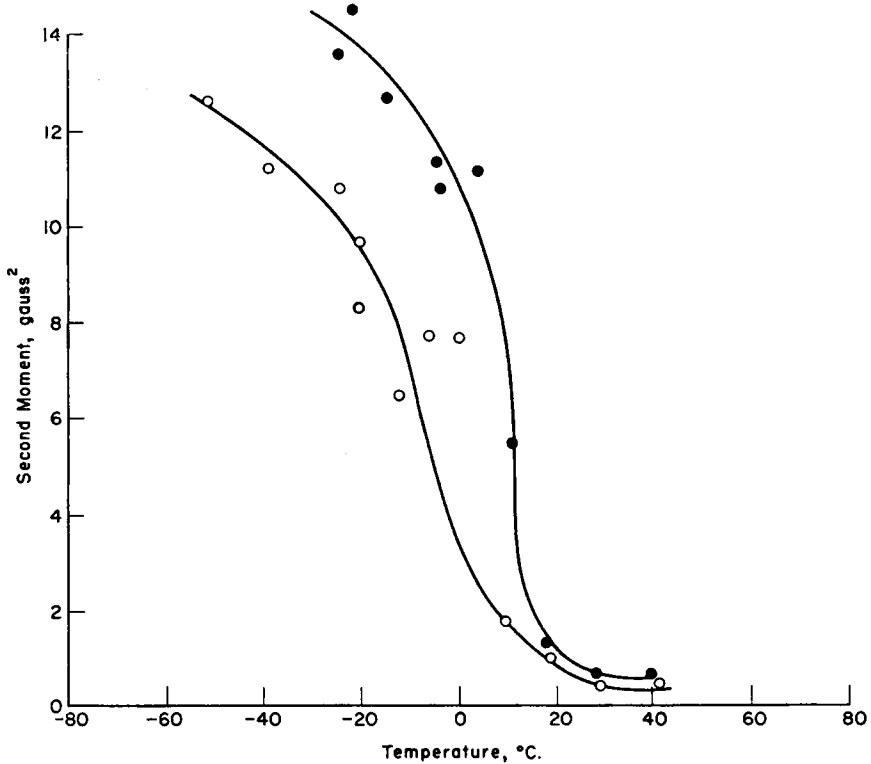


Fig. 1. Second moment as a function of temperature for two different asphalt samples: (●) Asphalt I; (○) Asphalt II.

Only one narrow peak was obtained for each of the two samples at room temperature, and the width of this line was found to be less than one gauss and averaged about 0.5 gauss. This value compares with a value of approximately 0.3 gauss for low density polyethylene at room temperature. No change in line width was observed over a period of two months, so that if any significant degree of age hardening of the asphalt occurred over that period it had no effect on the  $T_g$  being observed. Line width measurements were made from 40° to -25° for one sample and from 41° to -75° for the other. Second moments were calculated from the expression:

$$\langle \Delta H_2 \rangle^2 = \frac{1/2 \sum g'(H) (H - H_0)^3}{\sum g'(H) (H - H_0)}$$

where  $g'(H)$  is the ordinate of the derivative curve at an abscissa value of  $(H - H_0)$  and  $H_0$  is the maximum of the absorption curve. A modulation broadening correction,  $1/12 H_{\text{mod}}^2$ , was subtracted from this value of  $\langle \Delta H_2 \rangle^2$ .<sup>2</sup> For the instrument used,  $H_{\text{mod}} =$

0.043 *I*, where *I* is the modulation current in milliamps. The calculated second moment values for the two asphalt samples are tabulated below and plotted in Figure 1.

Asphalt I		Asphalt II	
Temp., °C.	Second moment, gauss <sup>2</sup>	Temp., °C.	Second moment, gauss <sup>2</sup>
+40	0.7	+41	0.5
+28	0.7	+29	0.4
+18	1.3	+19	1.0
+12	5.5	+10	1.8
+4	11.2	0	7.7
-3	10.8	-6	7.8, 8.0
-4	11.3	-12	6.5
-14	12.7	-20	8.3, 9.7
-21	14.5	-24	11.8
-24	13.6	-39	11.2
		-52	12.6
		-75	15.5

The second moment curves for the two asphalts indicate small but significant differences. The NMR transition for Asphalt I occurred in the interval +5–+15°, and for Asphalt II in the interval 0–+10°. The abrupt changes in second moment observed over these temperature intervals may be attributed, in both cases, to a rapid decrease in some type of molecular motion within the asphalt sample and can almost certainly be related to a glass transition. It may be concluded, therefore, that Asphalts I and II have glass temperatures of approximately 10° and 5°, respectively. This value of  $T_g$  should be in reasonable good agreement with values obtained by other methods, because in a number of cases involving synthetic polymers, it has been observed that the N.M.R. glass temperature corresponds fairly closely to glass transitions found by dielectric loss maxima, dilatometric studies, refractometric studies, specific heat measurements and dynamical mechanical measurements.<sup>3</sup> The N.M.R. transitions observed for the two asphalt samples and the line widths at room temperature are both close to the values of these properties observed for branched polyethylene. It appears likely, therefore, that the glass transition being observed is that of the paraffinic fraction and of the short polymethylene chains in the aromatic oil and asphaltene fractions. At sample temperatures above room temperature, when the predominant line became very narrow, the spectra of both asphalts showed the presence of a broader line. This broad line could be derived from the asphaltene protons, and if so, it would be of considerable interest to observe the effect of age hardening on the intensity of this absorption.

### Experimental

Broad-line N.M.R. measurements were made on a spectrometer which operates at 26 megacycles, and spectra are obtained with a marginal oscillator, lock-in amplifier and phase-sensitive detector. A gas-flow system surrounding the probe permits measurements at reasonably constant temperature from -160° to +100°. Asphalt samples were obtained from the Materials Research Laboratory of the Dept. of Civil Engineering of the Massachusetts Institute of Technology.

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