Compressibility of Polyethylene Melts at Low Pressures

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Synopsis

Branched polyethylene has quite different rheological and physical properties from its linear homologue. Despite their many different properties, the densities of linear and branched polyethylene melts at atmospheric pressure have been reported to be identical at all temperatures. However, it was not known whether their melt densities at a given temperature would also be identical at all pressures. In this investigation, the compressibilities of one linear and two branched polyethylene melts at 160°C, 190°C, and 220°C were studied, and it was found that they had an identical compressibility over the present experimental pressure range of ca. 0–455 psi (0–31 atm). Both the specific volume and the density at each temperature could be very accurately expressed as linear functions of pressure for this pressure range. Time-dependent compressive property was not observed within the present low pressure range.

INTRODUCTION

Branched polyethylene has quite different rheological as well as physical properties from its linear homologue. Previous studies[1,2] have shown that the density of branched polyethylene melt is identical to that of linear polyethylene melt at the same temperature. However, these studies were performed only at atmospheric pressure, and it was not known whether the densities of branched and linear polyethylene melts at a given temperature would also be the same at different pressures. Such information is desirable not only for its practical application in engineering problems but also for the possible interpretation it can shed on the structure–property relationships of polyethylene melt.

Terry and Yang[3] studied the density dependence of a linear polyethylene on temperature and pressure using an Instron rheometer, but unfortunately their study did not include branched polyethylene. In the present investigation, the density dependences of both linear and branched polyethylene melts on pressure were studied using the same methods reported by Terry and Yang.[3]

EXPERIMENTAL

The experimental equipment was an Instron rheometer consisting of a heated $^3/_8$-in. (diam.) $\times$ $15^7/_{16}$-in. (L.) barrel, a plug to close off one end

of the barrel, a plunger to compress the polymer melt in the barrel, a compression load cell of 20–1000-lb-range, and a 10-in.-wide recorder.

The compressibilities of one linear polyethylene (LPE, melt index = 6) and two branched polyethylenes (BPE-A, melt index = 0.75; and BPE-B, melt index = 7.7) at 160°C, 190°C, and 220°C were measured with this equipment for the low-pressure range of ca. 0–455 psi (0–31 atm).

Packing the polymer inside the barrel without any inclusion of air bubbles was of essential importance for a successful experiment because any air bubbles trapped in the polymer melt gave an unreasonably large compressibility for the polymer melt. Some air bubbles trapped in the polymer melt column were inevitable when the solid polymer, usually in the form of pellets, was packed into the hot barrel at a temperature well above the melting point of the polymer. A preferred procedure described below was developed which resulted in an air-free polymer melt column. The barrel was first heated to a temperature somewhat below the melting point of the polymer, i.e., ca. 85°C for polyethylene samples. The weighed polymer pellets were packed into the barrel with a brass rod, charging a few grams at a time. The plunger was inserted, and the entire polymer charge was given a high pressure of 5,000–10,000 psi for ca. 30 min. Under this condition, an air-free, tightly packed polymer column could be formed since the polymer pellets were heated enough for easy deformation and yet not

TABLE I
Experimental Data

Force on plunger, lb	Polymer melt column height, in.		
	160°C	190°C	220°C
Linear polyethylene (sample weight = 14.0113 g)			
5	9.9797	10.1883	10.4052
15	9.9730	10.1806	10.3959
25	9.9663	10.1727	10.3868
35	9.9599	10.1650	10.3780
45	9.9534	10.1575	10.3691
Branched polyethylene A (sample weight = 14.0122 g)			
5	9.9435	10.1558	10.3726
15	9.9368	10.1478	10.3629
25	9.9302	10.1399	10.3538
35	9.9239	10.1323	10.3449
45	9.9176	10.1249	10.3361
Branched polyethylene B (sample weight = 14.0347 g)			
5	9.9466	10.1494	10.3677
15	9.9395	10.1412	10.3582
25	9.9329	10.1332	10.3488
35	9.9264	10.1256	10.3399
45	9.9199	10.1180	10.3314

[a] Based diameter = 0.3750 in.

TABLE II

Results of Linear Regression Analyses for Specific Volume (V, cm^3/g) and Density (ρ, g/cm^3) of Polyethylene Melt as Functions of Pressure (P, atm)[a]

Sample	160°C				190°C				220°C			
	V_0	$A \times 10^4$	ρ_0	$B \times 10^4$	V_0	$A \times 10^4$	ρ_0	$B \times 10^4$	V_0	$A \times 10^4$	ρ_0	$B \times 10^4$
BPE-A	1.2848	−1.356	0.7784	0.824	1.3123	−1.621	0.7621	0.945	1.3403	−1.908	0.7461	1.067
BPE-B	1.2831	−1.392	0.7794	0.848	1.3093	−1.641	0.7638	0.961	1.3376	−1.903	0.7476	1.068
Average of BPE, A and B	1.2840	−1.374	0.7789	0.836	1.3108	−1.631	0.7630	0.953	1.3390	−1.906	0.7469	1.068
LPE	1.2895	−1.378	0.7755	0.831	1.3166	−1.619	0.7596	0.937	1.3446	−1.889	0.7437	1.049
Average of BPE and LPE	1.2867	−1.376	0.7772	0.834	1.3137	−1.625	0.7613	0.945	1.3418	−1.897	0.7453	1.058

[a] $V = V_0 + A \cdot P$, where the unit of A is cm^3/g/atm; $\rho = \rho_0 + B \cdot P$, where the unit of B is g/cm^3/atm.

melted, allowing air to escape between the pellets. The barrel was then
heated to the final experimental temperature keeping ca. 2,000 psi pressure
on the plunger. The experiment was continued when the barrel tempera-
thus it could be concluded that the polymer melts did not have any mea-
surable time-dependent compressive properties within the present maximum
pressure of ca. 455 psi (31 atm) and the experimental time span of ca. 2 min.
ture became fully stabilized after ca. $1^1/_2$ hour. The maximum temperature
fluctuation from the set point and also the maximum temperature gradient
along the barrel were less than $1°C$.

The polymer melt column was compressed and decompressed by moving
the plunger up and down at a speed of 0.02 or 0.05 in./min while the corre-
sponding force on the plunger was continuously recorded. The force on
the plunger and the corresponding height of the polymer melt column were
later read out from the recording. An average of at least two recordings
were used for the calculation.

Leakage of the polymer melt past the plunger and the plug could be
avoided within the present experimental pressure range by installing Teflon
O-rings on the plunger and the plug. The pressure developed at a given
compression was observed to remain constant for a period of longer than 5
min, indicating no leakage of the polymer melt and no measurable effect
of the time-dependent compressive property within the maximum experi-
mental pressure of ca. 455 psi (31 atom). The time-dependent com-
pressive property of polymer melt under high pressures was previously re-
ported,[4,5] but it was not observed within the present low pressure range.

RESULTS AND DISCUSSION

The experimental data are summarized in Table I. The same experi-
mental data were obtained with the plunger speed of 0.02 or 0.05 in./min;

The pressure, the specific volume, and the density of the sample can be
calculated from Table I. Linear regression analyses were preformed to
obtain the linear relationships between the specific volume and the pressure,
and between the density and the pressure since the specific volume-versus-
pressure plot and also the density-versus-pressure plot were almost perfect
straight lines. The results of linear regression analyses are presented in
Table II.

The comparison of the average values of BPE-A and BPE-B with the
corresponding values of LPE in Table II shows that the specific volumes
(or the densities) of linear and branched polyethylene melts at atmospheric
pressure are identical within an experimental error of ca. $1/_2\%$ at all three
experimental temperatures. This finding agrees with the results of the
previous investigations.[1,2] Referring to Table III, the average specific
volumes of BPE and LPE shown in the last row of Table II are in excellent
agreement with the values reported by Richardson, Flory, and Jackson[1] and
also with the values reported by Terry and Yang[3] for linear polyethylene.

The compressibilities of linear and branched polyethylene melts are
also found to be identical within an experimental error of ca. 1% at all

TABLE III
Specific Volume of Polyethylene Melt at Atmospheric Pressure

	Specific volume, cm³/g		
	160°C	190°C	220°C
This investigation[a]	1.2867	1.3137	1.3418
Richardson, Flory, and Jackson[1a]	1.2928	1.3192	1.3456
Terry and Yang[3b]	1.2826	1.3109	1.3406

[a] Average value for linear and branched polyethylene.
[b] The value for linear polyethylene only.

three experimental temperatures. The linear regression coefficients for the density of linear polyethylene melt as a function of pressure obtained here, 0.831×10^{-4}, 0.937×10^{-4}, and 1.049×10^{-4} g/cm³/atm at 160°, 190°C, and 220°C, respectively, are in fair agreement with the values reported by Terry and Yang,[3] namely, 0.885×10^{-4}, 0.984×10^{-4}, and 1.083×10^{-4} g/cm³/atm at 160°C, 190°C, and 220°C, respectively.

CONCLUSIONS

The following conclusions can be drawn from the results of the present investigation:

1. The specific volumes of linear and branched polyethylene melts at atmospheric pressure are found to be the same at 160°C, 190°C, and 220°C, as is expected, and the values obtained here compare very well with the results of previous investigations.[1-3]

2. Linear and branched polyethylene melts have an identical compressibility up to 31 atm at 160°C, 190°C, and 220°C.

3. The specific volume and the density of polyethylene melt can be accurately expressed by linear functions of pressure up to ca. 31 atm. The validity of these linear functions above 31 atm is not known.

4. Time-dependent compressive property was not observed for polyethylene melt at 160°C, 190°C, and 220°C within the pressure of 31 atm and the time span of 5 min.

References

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