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Physical Properties

Relations Between Expansivity, Compressibility and Density of Polyethylene

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SUMMARY

From a compilation of 17 different data sources on the expansivity and compressibility of polyethylene (PE) it is shown that these parameters are linearly related to the density (measured at 22°C) of the polymer. Since the correlations cover a wide range of density (0.9 to ~ 1 g/cm^3) and temperature (100 to 395 K), it is hoped that they may apply to all polyethylenes. The relationship between the thermal coefficient of pressure and density of PE as a function of temperature is also presented.

INTRODUCTION

The expansivity (also called thermal expansion coefficient) (α) and the isothermal compressibility (β) of polyethylene have been studied extensively over the years (1-14). Knowledge of α and β is of great interest not only because of the technical importance of PE but also because it allows evaluation of various polymer's properties such as the Grüneisen parameter or the internal pressure, among others. The electrostrictive coefficient of several materials is also known to be linearly related to the α and β values (10). The Grüneisen parameter γ, which measures the anharmonicity of intermolecular interactions is defined as(8,9,11)

$$\gamma = \frac{\alpha V}{\beta C_V} \qquad (1)$$

where V is the molar volume and C_V the heat capacity at constant volume. However, the γ values calculated at different temperatures by various authors(8,9,11) are significantly different, probably owing to the fact that most of the $\frac{\alpha}{\beta}$ values used were extrapolated rather than correct experimental values. The thermal coefficient of pressure $\frac{\alpha}{\beta}$, is also related to the polymer's internal pressure P_i, by

$$P_i = \frac{\alpha}{\beta} T \qquad (2)$$

It is well known that the values of α and β increase with decreasing crystallinities or densities and higher temperatures. However, the crystallinity dependence has rarely been evaluated for more than three different crystallinities at the same time. For example, White and Choy(8) give α values for just three PE samples and have extrapolated β values from ultrasonic measurements performed on different samples. More recently, Engeln et al.(9) have also extrapolated β values at various temperatures from results obtained at only 77 and 300 K. In fact, measurements of α and β have rarely been performed on the same sample(1,2). One purpose of this short note is to present a partial compilation of existing data for samples covering a wide crystallinity (~35 to 100%) and temperature (~100 to 395 K) ranges in the hope that it might prove a useful time-saving tool for future research calling for correct experimental α and β values. Density measurements at 22°C being much easier to perform than measurements of α and β (especially at low temperature), we feel that the correlations presented here could have some practical interest and value. We have also plotted the available $\frac{\alpha}{\beta}$ data as a function of crystallinity and temperature.

RESULTS AND DISCUSSION

Since experimental values for β are scarce below 150 K(8,9,10), we restricted ourselves to the 150-395 K temperature range. Note that β is nearly constant below 140 K(8) but that α varies by a factor of ≈ 2 between 0 and 150 K(8,9) although it remains nearly constant between 40 and 100 K(9). The expansivity values were determined either from bulk measurements(1,4,6) (i.e. from $\alpha = \frac{1}{V}\frac{dV}{dT}$) or from linear expansion(5,7-9) (the bulk value considered to be three times the linear value). Compressibility values were determined either from volume change under pressure ($\beta = -\frac{1}{V}\frac{dV}{dP}$)(1-4,6,11) or from ultrasonic wave propagation(13-14); both techniques give identical results within experimental error. The samples characteristics are given in Table 1. We retained only data for which a reliable density or crystallinity value was specified. As shown later, α and β are very sensitive to density variations and thus approximate classifications, such as low-density PE, are useless for our purpose.

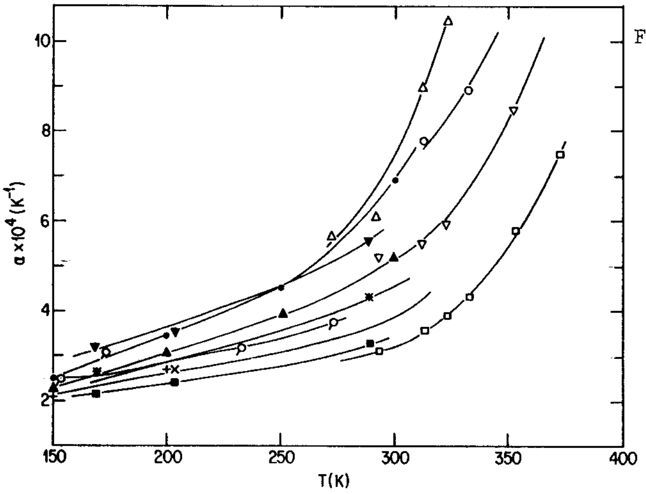

Fig.1- Variations of PE expansivity as a function of temperature and density (at 22^{0}C):0.91 (• ,Ref.8);o.922(Δ ,Ref. 2);o.928(▼ ,Ref.5);o.932 (▽ ,Ref.4);0.935(▲ ,Ref. 8);0.951(✱ ,Ref.5);0.963 (ρ ,Ref.6);0.966(+ ,Ref. 8);0.9748(■ ,Ref.5); 0.9794 (□ ,Ref.4). Density values are in g/cm^3.

Table 1. Samples Characteristics

Ref.	Density (22°C)	Remarks
1	0.9183	branched low-density (Lupolen 1811 H)
2	0.928	branched low-density (Du Pont)
3	0.98	linear high-density (unspecified origin)
4	0.9268	high molecular weight linear PE (Allied Chem. Co.)
	0.932	branched low-density (NBS specimen SRM 1476)
	0.9726	linear high-density (Marlex 9)
	0.9794	linear high-density (NBS specimen SRM 1475)
5	0.928	$\bar{M}_V$ = 4 400 000 } molecular weight fractions obtained from Marlex 50 or Hifax 28 linear PE
	0.951	$\bar{M}_V$ = 250 000
	0.9748	$\bar{M}_V$ = 7 000
6	0.963	slightly oxidized linear high-density (Marlex 6050)
8	0.910	branched low-density (WNF 15, ICI)
	0.935	linear high-density (Sclair 96A, Du Pont)
	0.966	linear high-density (Rigidex 50)
12	1.006	orthorombic crystal, high-density, $\bar{M}_w = 7.41 \times 10^4$, $\bar{M}_n = 8.41 \times 10^3$ (Sholex)
13	0.942	unspecified origin, annealed at 122°C
	0.962	unspecified origin, annealed at 129°C

Note: branching ratio and crystallite thickness were not reported for any of the above samples; only two references give molecular weight values.

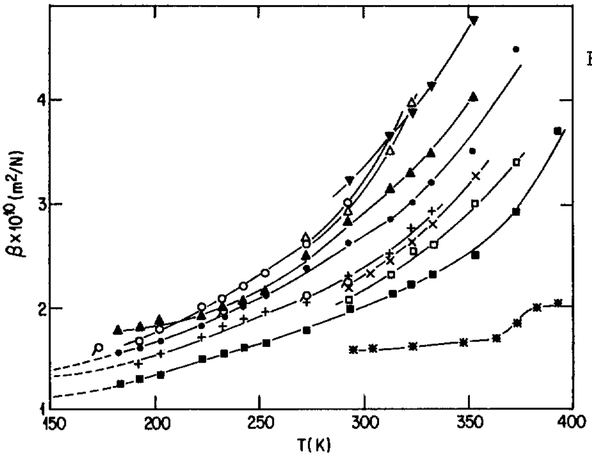

Fig.2- Variations of the isothermal compressibity of PE as a function of temperature and density. Density (in g/cm^3 and at 22°C): 0.918(○,Ref.1); 0.925(△,Ref.2);0.9268(▼, Ref.4);0.935(▲,Ref.8); 0.942(●,Ref.13);0.962(+, Ref.13);0.963(ρ,Ref.6); 0.9726(×,Ref.4);0.9794 (□,Ref.4);0.98(■,Ref.3); 1.006(✱,Ref.12).

Figures 1 and 2 show the temperature and density (i.e. crystallinity) dependence for various PE samples. Note that crystallinity is related to density ρ by the empirical Chiang and Flory relation(15)

$$\%\ \text{crystallinity} = 100\ (v_a - \bar{v})/(v_a - v_c) \qquad (3)$$

where v_a = 1.1722 cm^3/g is the amorphous specific volume at 22°C, $v_c \approx 1\ cm^3/g$ is the crystalline specific volume and $\bar{v} = 1/\rho$. Although some results over a restricted temperature range do not fit the general trend in Figs 1 and 2, it is clear that at a given temperature α and β decrease with increasing density as already observed(1,5,9). This is more obvious in Figs. 3 and 4, where the α and β values of Figs. 1-2 are plotted against density. It is interesting to note that the β values obtained by Ito(12) for orthorhombic PE (≈ 100% crystalline) fit very well the values obtained with samples of smaller density at the same temperature (Fig. 4).

From a limited number of experimental data Engeln et al.(9) proposed that above a 250 K this linear relation no longer holds for α. Figure 3 shows clearly that if all available data is considered the relation is still linear above 250 K although experimental values are more scattered here than at low temperature. The most likely sources of scatter are variations in molecular weight and crystallite thickness which can be very different for one given density. However, their influence should be of only secondary importance considering the good agreement observed between experimental results and the linear relations summarized in Table 2.

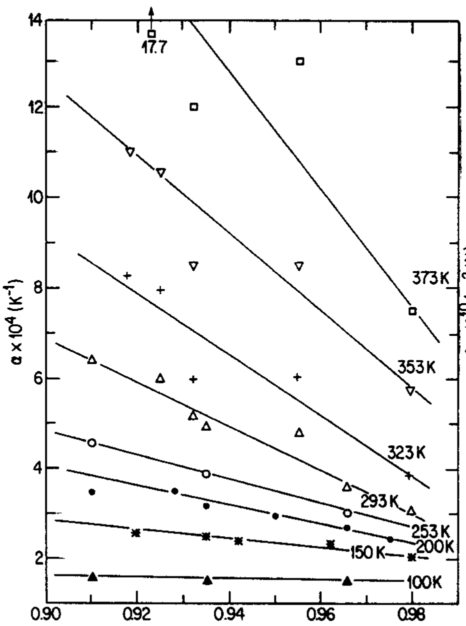

Fig.3-Variations of expansivity as a function of density and temperature (from Fig.1).

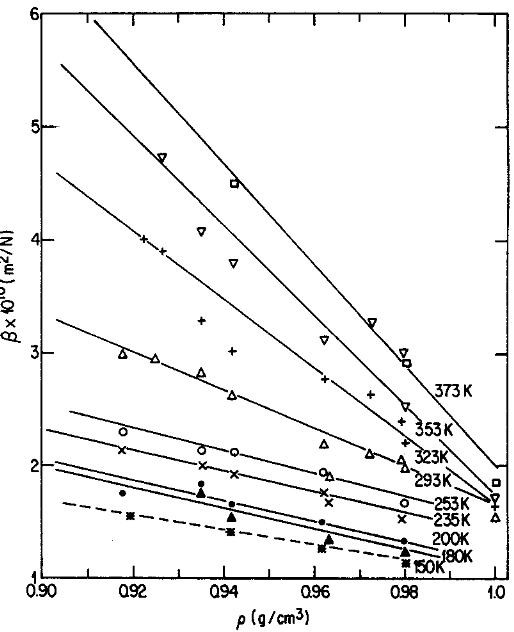

Fig.4- Variations of β as a function of density and temperature (from Fig.2). Results for $\rho = 1 g/cm^3$ are from Ref.12.

Table 2. **Equations relating α, β and density of PE for various temperatures**

T (K)	$\alpha = \alpha_o - a\,\rho_T$		$\beta = \beta_o - b\rho_T$	
100	$3.225\text{x}10^{-4}-1.786\text{x}10^{-4}\ \rho$	(0.999)*	-	
150	$1.046\text{x}10^{-3}-8.433\text{x}10^{-3}\ \rho$	(0.9028)	$6.551\text{x}10^{-10}-5.531\text{x}10^{-10}\ \rho$	(0.9797)*
180	-		$1.253\text{x}10^{-9}-1.16\ \text{x}10^{-9}\ \rho$	(0.9197)
200	$2.00\ \text{x}10^{-3}-1.800\text{x}10^{-3}\ \rho$	(0.9474)	$1.073\text{x}10^{-9}-9.591\text{x}10^{-10}\ \rho$	(0.9178)
235	-		$1.162\text{x}10^{-9}-1.026\text{x}10^{-9}\ \rho$	(0.9806)
253	$3.077\text{x}10^{-3}-2.873\text{x}10^{-3}\ \rho$	(0.9967)	$1.292\text{x}10^{-9}-1.148\text{x}10^{-9}\ \rho$	(0.9667)
293	$4.98\ \text{x}10^{-3}-4.769\text{x}10^{-3}\ \rho$	(0.9794)	$1.919\text{x}10^{-9}-1.758\text{x}10^{-9}\ \rho$	(0.9922)
323	$6.57\ \text{x}10^{-3}-6.302\text{x}10^{-3}\ \rho$	(0.9279)	$2.973\text{x}10^{-9}-2.803\text{x}10^{-9}\ \rho$	(0.9891)
353	$8.17\ \text{x}10^{-3}-7.733\text{x}10^{-3}\ \rho$	(0.9418)	$3.534\text{x}10^{-9}-3.330\text{x}10^{-9}\ \rho$	(0.9719)
373	$1.38\ \text{x}10^{-2}-1.327\text{x}10^{-3}\ \rho$	(0.8386)	$4.26\ \text{x}10^{-9}-4.059\text{x}10^{-9}\ \rho$	(0.999)

*: Correlation coefficient.

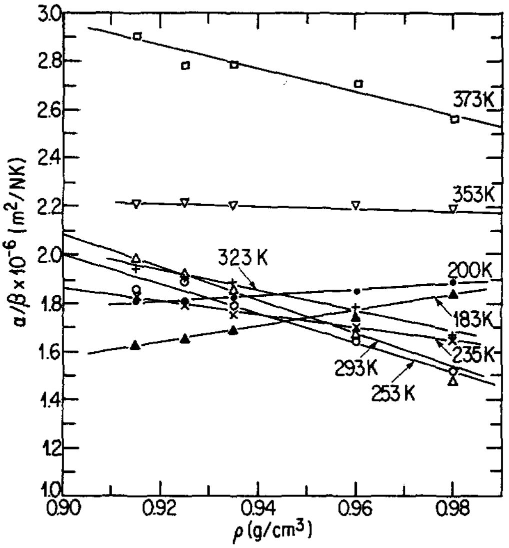

Fig.5- Variations of the thermal coefficient of pressure (deduced from Figs. 3 and 4 and Table 2) as a function of density for various temperatures.

From the average α and β values (see Table 2) we calculated the $\frac{\alpha}{\beta}$ ratio plotted in Fig. 5 as a function of density and temperature. The interesting feature in Fig. 5 is that below ≈ 200 K the $\frac{\alpha}{\beta}$ ratio increases with increasing density whereas above it it decreases with crystallinity. This means that below ≈ 200 K the internal pressure (Eq. 2) is larger in crystalline than in amorphous PE whereas above 200 K the contrary is true. This agrees with the fact that above 200-230 K the heat capacity (9,16) and the expansivity(8,9) of amorphous PE are much larger than for crystalline PE.

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