

Generalization of the Temperature Dependence of Some Physical Properties of High-Strength Polyethylene using the Method of Given Parameters

Shixaliyev Kerem Sefi *

The Department of “Organic Substances and technology of high molecular compounds” Azerbaijan Oil and Industrial University. Baku, Azerbaijan

***Correspondence Author:** Shixaliyev Kerem Seyfi, The department of “Organic Substances and technology of high molecular compounds” Azerbaijan Oil and Industrial University. Baku, Azerbaijan.

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Abstract

In this paper, based on the study of high-strength polyethylene by dilatometric and rheological methods in a wide range of temperatures and cooling and deformation rates, we generalized the temperature dependence of the physical properties of polyethylene using the specified parameters method. Test specimens (cylinder size: height 12 mm, diameter 9.3 mm) were obtained both in the dilatometer's test cylinder itself and a specially designed injection mold using injection molding on a TP-125 injection molding machine. The temperatures in the experiments were added and maintained with an accuracy of 3.2. ° C. Defined by the dependence of ρ_{T_0} / ρ_{T_0} (relative reduced density of the polymer) on the reduced temperature $(T - T_0)$. Test specimens (cylinder size: height 12 mm, diameter 9.3 mm) were obtained both in the dilatometer's test cylinder itself and a specially designed injection mold using injection molding on a TP-125 injection molding machine. It was found that a reliable characteristic of the dilatometric properties of the crystallizing polymer, physically correctly and completely reflecting the features of the crystalline structure, can be obtained only in the mode of stepwise temperature changes when at each given temperature the equilibrium value of the specific sample of the primer is fixed. Thus, the practical value of the dilatometric method for studying crystallizing polymers is shown, especially when comparing the results of dilatometry with the results of rheological studies.

Keywords: dilatometry; viscosity; rheology; melt; high-strength polyethylene (HSPE); brittleness temperature; parameter

1. Introduction

HDPE, obtained by polymerization at moderate pressures, is characterized by high linearity of macromolecules, narrow MMD, and a high degree of crystallinity. These features of HSPE's chemical and physical structure must be considered when studying their behavior at high temperatures (in the molten state), as well as during the processing and operation of the products obtained from them. In connection with the foregoing, these generalizations of temperature dependence on HSPE's most important physical properties by the method of given parameters are of great scientific and practical interest [1-4].

The dilatometric properties of the polymer (temperature dependence of the specific volume) over a wide temperature range of 20-300 ° C, covering the crystallized and liquid state, were studied in the mode of rather slow stepwise cooling of the polymer into a dilatometer by the procedure described by the authors [5-9].

It was found that a reliable characteristic of the dilatometric properties of a crystallizing polymer, which physically correctly and fully reflects the features of the crystalline structure, can be obtained only in a step-change mode when the equilibrium specific volume is fixed at each given

temperature polymer sample. The calculation of the primary results of dilatometric measurements was carried out according to an improved method, which allows taking into account the change in the diameter of the sample studied in the dilatometer, which is associated with the actual shrinkage of polyethylene. [10-14].

2. Method

The temperature in the experiments was set and maintained with an accuracy of 0.2 ° C. Researched samples of HDPE production Socar Polymer with the following main indicators:

- 1) The average molecular weight is 83000, determined according to $[\eta]$ in decalin solution at 135 ° C;
- 2) Melt flow rate - 1.4 g for 10 minutes, determined at 190 ° C and a load of 5 kg.

Samples for testing (cylinder size: height 12 ± 1 mm, diameter 9.3 ± 0.5 mm) were obtained both in the test cylinder of the dilatometer and a specially designed casting mold using an injection molding method on a molding machine TP-125.

In the course of dilatometry at each fixed temperature, the measurement

of the temperature expansion or compression of the sample was performed with an accuracy of 0.001 mm. Further, the primary measurement results were processed and the specific volume v depended on the temperature T_c .

By extrapolation, the dependence $v(T)$ in the temperature range in which the polymer is in a fluid state was calculated. On Based the same

dependence $v(T)$ in the region of the crystallized state, according to the published method of Tager A. A. [15–16], the glass transition temperature T_c of the polymer was determined. Since the HDPE dilatometric curves were obtained at different cooling rates at the time of crystallization (J), we were able to change the T_c of HSPE over a wide temperature range.

NO p/p	γ deg/min	T_c °K	FC
1	0,0056	167	0,0256
2	0,0083	184	0,0254
3	0,0333	237	0,0252
4	0,1	257	0,0248
5	0,2	273	0,0254
6	1,0	289	0,0251
7	3,1	301	0,0257
8	295,0	335	0,0255

Table 1: The value of T_c and f_c of HSPE samples obtained at different cooling rates at the time of crystallization (J)

Measurement of the rheological characteristics in a fluid state was carried out using a capillary viscometer according to the adopted method [17] in a wide range of shear strain rates, $\dot{\gamma} = [10]^{-1} - [10]^3 \text{ sec}^{-1}$, shear stresses $\tau = [10]^{-4} - 2 [10]^6 \text{ dyne/cm}^2$ and temperatures of 135-300 ° k. The melt flow of polyethylene was studied in a capillary with l/d equal to 16 and 32. For this τ , the corresponding value was determined by the formula $\dot{\gamma} = \dot{\gamma}_0 \cdot (3 + n)^{-1}$, where $\dot{\gamma} = Q / \Pi r^3$, and $n = d(l\dot{\gamma}) / d(\lg\tau)$.

The highest Newtonian melt viscosity, η_{nb} , was obtained by extrapolating the experimental dependence of $\lg\eta_{nb}$ from τ to the zero value of τ . And then build a temperature dependence.

It was previously shown [18-20] that when molding samples from HSPE with different cooling rates at the time of their crystallization, a polymer structure is formed, which differs sharply in density, degree of crystallinity, and relaxation properties. This results in the processing of HSPE to produce articles with properties that strongly depend on the molding conditions. The author and his collaborators, using the method of reduced parameters [15, 7], obtained general regularities for the change in the most important physical and mechanical properties of HSPE.

2.1 Determination of the manifestation of the characteristic physical properties of polyethylene

It is known that the most important kinetic characteristic of the τ -indicators, reflecting their structural features and determining the manifestation of characteristic physical properties, is the glass transition temperature T_c (Table 1). As can be seen from the data we obtained (Table 1), the value of T_g for HSPE varies greatly depending on the

cooling rate of crystallized samples. This fact is a consequence of the formation of structures of HSPE samples, characterized by different degrees of loosening and ordering. At the same time, polymer samples differ in the magnitude of the “free” volume and the temperature dependence of the “free” volume. Therefore, the eight HSPE samples studied, characterized by the same average molecular weight M_w , molecular weight distribution, and melt flow rate, depending on the cooling rate, have dilatometric characteristics approaching the dependence $v(T)$ either for a completely amorphous state or for an ideal crystalline state.

Thus, at any given temperature T , we have samples of HSPE that differ sharply in their most important structural characteristics: different ratios of “occupied” and “free” volumes, different ratios of amorphous and crystalline regions, different relaxation times of kinetic units of the structure, various density, viscosity, etc.

3. Result

However, all these physical characteristics should be proportional to [7-8] the difference $T - T_c$. To prove this position, the values of $v(T)$ at different T for all eight HDPE samples were processed taking into account the concept of “free” volume and are presented as a dependence of the volume fraction of the “free” volume of polymer samples $f = (v_T - v_{(t=0)}) / (v_{(T - T_c)} - v_{(t=0)})$ from the reduced temperature $T_n (T - T_c)$. This dependence off on $(T - T_c)$ is shown in Figure 1. As can be seen from Figure 1, at $T - T_c$, the value of f for all samples of polyethylene cooled at different speeds is located practically at one point, the ordinate of which is equal to the universal value $f_c = 0,025 \pm 0,0006$.

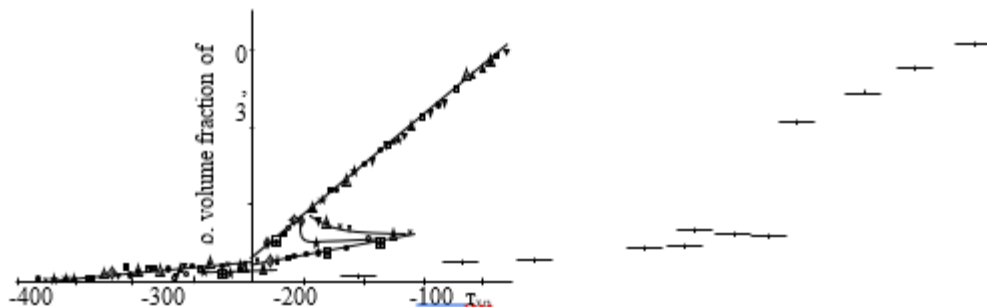


Figure 1: Dependence of the volume fraction of "free" volume (f) on the reduced temperature (T - Tc) for different samples of PES obtained at different crystallization rates (temperature-invariant characteristic of the volume fraction of "free" volume of linear polyethylene):

Further, depending on the values of $T - T_c$, all experimental data were located on two branches: the upper branch is a dependence off on $(T - T_c)$ for the polymer flowable state, and the lower one for the crystallized (solid) state. At the same time, the difference between the volume thermal expansion coefficients of the “free” volume of polyethylene for these

states is

$$d_2 = T > T_{\text{крист}} - (df)T < T_{\text{крист}} = 6,3 \cdot 10^{-4} - 1,5 \cdot 10^{-4} = 4,8 \cdot 10^{-4} (\text{deg}^{-1}) \tag{1}$$

This agrees well with many linear polymers' constant universal values [17–19].

At $T < T_c$, all experimental data are located on almost one dependence, the inflection point of which corresponds to the temperature of brittleness T_{xp} , equal to HSPE

$$T_{xp} = T_c - 77^\circ$$

(2)

The brittleness temperature corresponds to $f_{kp} = 0.014$.

Thus, the dependence on $T - T_c$ is the temperature-invariant characteristic of the "free" volume of the polymer. The existence of this dependence allows determining the value of the specific volume or density of the polymer (as well as the values of the specific "free" volume and f values) at any temperature and any cooling rate J if only the dependence of T_c on J is known and the value of the specific volume at one any temperature t .

On the other hand, this universal dependence confirms the fact that any physical property of polyethylene (and of polymers in general) is proportional to the reduced temperature $(T - T_c)$.

A dimensionless displacement parameter is usually used to construct the temperature-invariant characteristics of any physical properties of polymers by the method of the above parameters [16-19].

$$\alpha_T = \frac{\eta \cdot \rho_0 \cdot T_0}{\eta_0 \cdot \rho T} = \frac{Q}{Q_0} \quad (3)$$

where T is the temperature of reduction;

$\eta_0, \rho_0, Q_0, \eta, \rho, Q$ - viscosity, density, and generalized relaxation time, respectively, at a temperature of reduction T_0 and any other temperature T .

The works of M. Williams [8], P. Landel, D. Ferry [9], A. Tobolsky [10], Foy T. V., Flory R. J [14], Doolittle A. N [15] it was shown that α_T is a definite function $(T - T_c)$:

$$\lg \alpha_T = \frac{1}{2,303 f_c} (T - T_c) / \left(\frac{f_c}{\alpha_2} + T - T_c \right) \quad (4)$$

For the HSPE samples that we studied, the dependence of $\lg \alpha_T$ on $(T - T_c)$

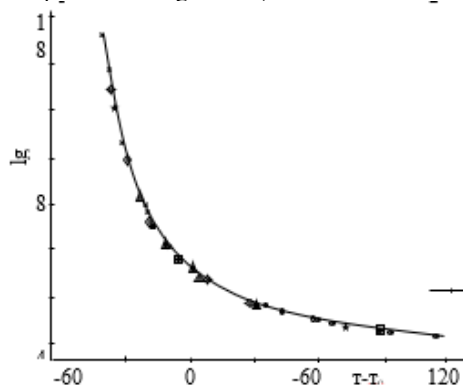


Figure 2: The dependence of the shift parameter α_T on the reduced temperature $(T - T_0)$ for linear PE

An important component of the value of α_T is also the ratio of viscosities at the temperature of reduction T_0 and any other temperature T , that is, η_0/η (if T_c is taken as the temperature of reduction, η_{Tc} is 1013 poise [21-24]. The dependence of the highest Newtonian viscosity of the melt η_{nb} for the investigated HDPE is shown in Figure 4. As can be seen from Fig. 4, in the region of temperature 423 ° K, i.e., long before reaching the equilibrium melting temperature (413 ° K) and the apparent melting point (405 ° K), viscosity increases especially sharply with decreasing

T_c) is shown in Fig.2. As can be seen from Fig. 2, this dependence is indeed temperature-invariant for all the samples studied. Knowing the value of α_T , it is possible at any temperature T to determine the physical size of the polymer of interest to us, if the value of this value is known at any temperature.

The component of the parameter is the relation $\rho_0 T_0 / \rho T$ equal to $(\eta_0/\eta) \alpha_T$ or equal to $\eta_0 Q / \eta Q$. The significance of this important component and its temperature dependence for many polymers is not known, in particular, for HSPE such data are absent in the literature. Many researchers usually take the value of $\rho_0 T_0 / \rho T$ equal to 1.

The dependence of $\rho_0 T_0 / \rho T$ on the reduced temperature $(T - T_0)$ for HSPE samples is shown in Fig.3. As can be seen from Fig. 3, depending on the temperature of the reduction T , the nature of the dependence of $\rho_0 T_0 / \rho T$ on $(T - T_0)$ changes dramatically, the smaller T_0 , i.e., the closer T_0 is to T_c , the more $\rho_0 T_0 / \rho T$ differs from 1 (curves 9-1 in Figure 1); the greater the temperature of the experiment T , at which $\rho_0 T_0 / \rho T$ is estimated, the more $\rho_0 T_0 / \rho T$ differs from 1. The dotted lines in fig. 2. The isotherms of $\rho_0 T_0 / \rho T$ versus $(T - T_0)$ are shown for various $T = \text{Const}$.

4. Discussion

Thus, even in a fluid state of the polymer, when $T > T_m$ (curve 9 in Figure. 3, on which data are plotted at temperatures from 423 ° K to 573 ° K, the equilibrium melting point of HSPE is $T_{pl} = 413$ ° K) differs from 1 by value to 0.18 (i.e. by 18%) depending on T . The maximum deviation $\rho_0 T_0 / \rho T$ from 1, equal to 0.6 (i.e. 60%), can be at $T = 573$ ° K if T_0 is taken to be equal to the equilibrium glass transition temperature $T_c = 167$ ° K. This feature of $\rho_0 T_0 / \rho T$ and its temperature dependence for HSPE is related to the high crystallinity of this linear polymer.

temperature. In this case, the magnitude of the apparent heat of activation of the flow increases sharply: from a value of 5–7 kcal/mol to a value of 12.6 kcal / mol. This circumstance is the result of the ordering of the polymer structure in the temperature region near T_m , which leads to an increase in the intermolecular interaction due to the formation in the melt of structures that are extremely prepared for crystallization. samples.

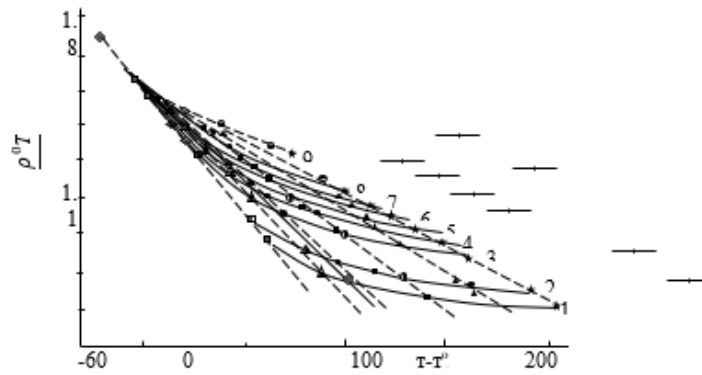


Figure 3: The dependence of $\rho_0 T_0 / \rho T$ (relative reduced density of the polymer) on the reduced temperature ($T - T_0$).

This state can be characterized as a state of flow of melt structures, with kinetic units being oriented aggregates of segments of macromolecules moving in the melt as whole units [25-30].

The generalization of the obtained experimental results of rheological and dilatometric studies was performed using the well-known VLF equation [17]. To this end, at different temperatures (from 413 °K to 573 °K), the dependence of the reduced parameter $C = (\lg \eta_T / \eta_c - \lg M_w^{-3.4} + \lg \alpha_T)$ was studied, and the reduced parameter ($\lg M_w^{-3.4} + \lg \alpha_T$)

for the studied HSPE samples, characterized by a medium viscous molecular mass $M_w = 8.3 \times 10^4$, (Figure 5) The invariance of experimental data regarding temperature over the entire investigated range shows that the equation is generalized a characteristic of the temperature dependence of the most important physical properties of HSPE and, apparently, of all linear polymers.

$$\frac{\eta_T}{\eta_c} - \lg M_w^{-3.4} + \lg \alpha_T = C$$

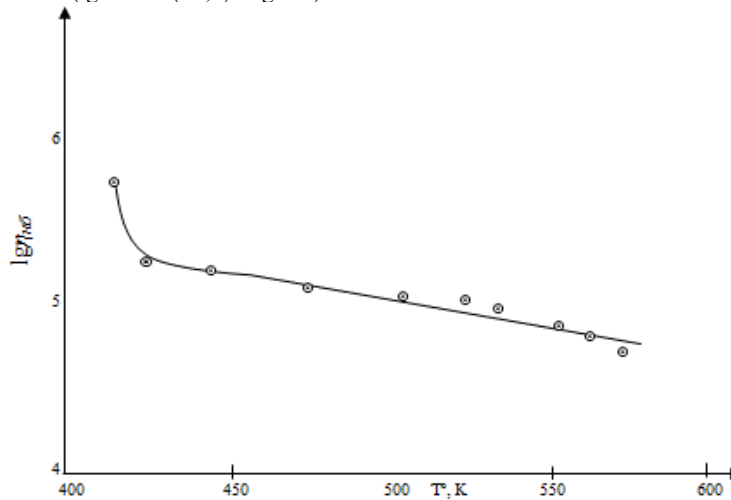


Figure 4: Dependence of the greatest Newtonian viscosity of the melt, η_{nb} , on temperature T for PESD

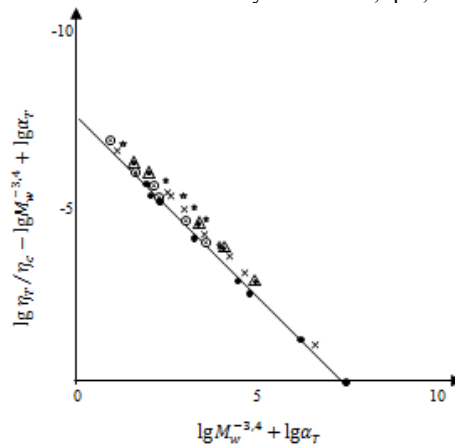


Figure 5: The dependence of the reduced parameter ($\lg \eta_T / \eta_c - \lg M_w^{-3.4} + \lg \alpha_T$) on the reduced parameter ($\lg M_w^{-3.4} + \lg \alpha_T$)

5. Conclusion

In this work, we studied the generalization of the temperature dependence of the physical properties of high-strength polyethylene using the method of given parameters

According to the above parameter's dependence and the melt's highest Newtonian viscosity, η_{nb} depends on the temperature.

Based on the research, it has been established that the invariance of experimental data on the temperature in the entire investigated range of the most important physical properties of HSPE depends on temperature and viscosity average molecular weight.

6. Recommendations

The shown difference between high-strength polyethylene from other polyethylenes should be taken into account during the processing and operation of materials obtained from them

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