Original Article

The Study of the Generalized Temperature Dependence of the Physical Properties of High-strength Polyethylene by the Method of given Parameters

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Abstract - In this paper, based on the study of high-strength polyethylene HDPE 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 in a specially designed injection mold using injection molding on a TP-125 injection molding machine temperatures in the experiments were added and maintained with an accuracy of 3.2. °C. Defined by the dependence of $\rho\_0 T\_0 / \rho T$ (relative reduced density of the Polymer) on the reduced temperature (T - T0). Est specimens (cylinder size: height 12 mm, diameter 9.3 mm) were obtained both in the dilatometer's test cylinder itself and in 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 theological studies.

Keywords - Dilatometry, Viscosity, Rheology, Melt, High-strength polyethylene (HDPE), Brittleness temperature, Parameter.

1. Introduction

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

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 dilatometerbyh the procedure described by the authors [1][2][3]

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.[4][5][6][7][8]

2. Method

The experiment temperature 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 [η] 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 in 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 υ depended on the temperature Tc.

The dependence υ (T) in the temperature range in which the Polymer is in a fluid state was calculated by extrapolation. Based on the same dependence υ (T) in the region of the crystallized state, according to the published method of Tager A. A. [9][10][11], the glass transition temperature Tc of the Polymer was determined. Since the HDPE dilatometric curves were obtained at different cooling rates at the time of crystallization (J), we could change the Tc of HDPE over a wide temperature range.

Table 1. The value of Tc and FC of HFCE samples were obtained at different cooling rates at the time of crystallization (J)

IN 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

Measurement of the rheological characteristics in a fluid state was carried out using a capillary viscometer according to the adopted method [6] in a wide range of shear strain rates, γ = 〚10〛 ^ (- 1) - 10〛 ^ 3 sec-1, shear stresses τ = 〚10〛 ^ 4 - 2 〚10〛 ^ 6 dyne / cm2 and temperatures of 135-300 ° C. 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 γ˙ = γ⁻. (3 + n). where γ = Q / Πr3, and n = d (lgγ) / d (lgτ).

The highest Newtonian melt viscosity, ηnb, was obtained by extrapolating the experimental dependence of lgηnb from τ to the zero value of τ. and then build a temperature dependence.

It was previously shown [9-10] that when molding samples from HDPE 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. It results in processing HDPE to produce articles with properties that strongly depend on the molding conditions. the author and his collaborators, using the method of reduced parameters [12][13][14][15], obtained general regularities for the change in the most important physical and mechanical properties of HDPE.

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

It is known that the most important kinetic characteristic of the ¬ indicators, reflecting their structural features and determining the manifestation of characteristic physical properties, is the glass transition temperature Tc (Table 1). As can be seen from the data we obtained (Table 1), the value of Tg for HDPE varies greatly depending on the cooling rate of crystallized samples. This fact is a consequence of the formation of structures of HDPE 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 HDPE samples studied, characterized by the same average molecular weight Mw, molecular weight distribution,n, and melt flow rate, depending on the cooling rate, have dilatometric characteristics approaching the dependence υ (T) either for a completely amorphous state or for an ideal crystalline state.

Thus, at any given temperature T, we have samples of HDPE 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 [8] the difference T-Tc. To prove this position, the values of υ (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 = (υ_т-υ_ (t = 0)) υ_ (t = 0) from the reduced temperature T_n (T-Tc). This dependence of f on (T - Tc) is shown in Figure 1. As seen from Figure 1, at T-Tc, the value of f for all polyethylene samples cooled at different speeds is located practically at one point, the ordinate of which is equal to the universal value fc = 0,025 ± 0,0006.
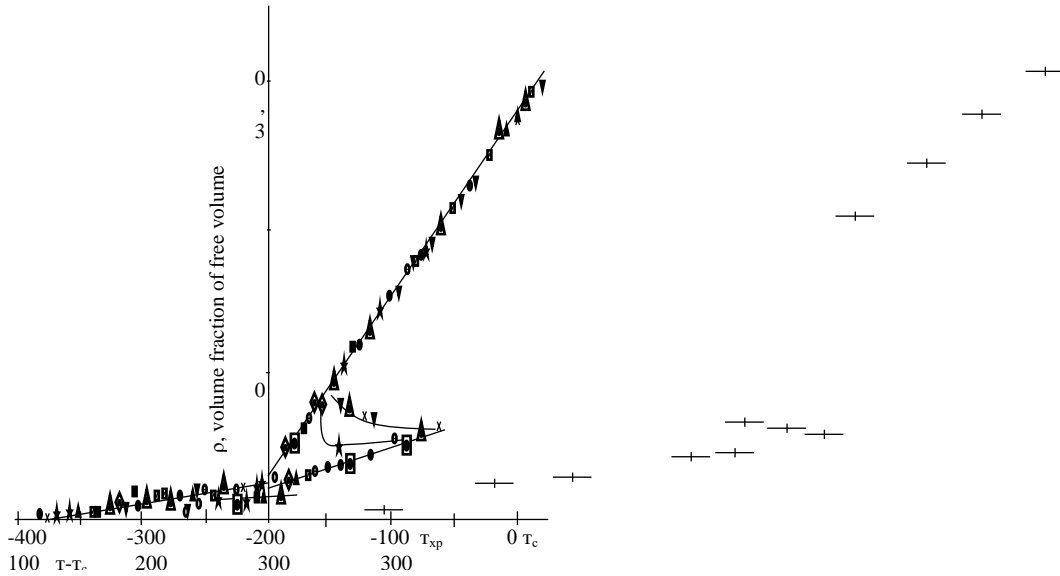
Fig. 1 Dependence of the volume fraction of "free" volume (f) on the reduced temperature (T - Tc) for different samples of PED obtained at different crystallization rates (temperature-invariant characteristic of the volume fraction of "free" volume of linear polyethylene)

Further, depending on the values of T-Tc, all experimental data were located on two branches: the upper branch is a dependence of f on (T-Tc) for the Polymer flowable state, 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

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

That agrees well with the constant universal value for many linear polymers [16-22]

At T < T.C., all experimental data are located on almost one dependence, the inflection point of which corresponds to the temperature of brittleness Txp, equal to HDPE

$$T_{XP} = T_C 77°C \qquad (2)$$

the brittleness temperature corresponds to keep = 0.014.

Thus, the dependence off on T-Tc 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 Tc on J is known and the value of the specific volume at one any temperature t.

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

To construct the temperature-invariant characteristics of any physical properties of polymers by the method of the above parameters [6][17][18][19], a dimensionless displacement parameter is usually used

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

where T is the temperature of reduction;

η_0, ρ_0, Q_0, η, ρ, Q - viscosity, density, and generalized relaxation time, respectively, at a temperature of reduction T0 and any other temperature T.

in the works of [20]][21][22][23], t was shown that αT is an Indefinite function (T - Tc):

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

for the HDPE samples that we studied, the dependence of lgα_T on (T - Tc) is shown in Figure2. As can be seen from the figure2, this dependence is indeed temperature-invariant for all the samples studied. Knowing the value of ss., It is possible at any temperature T to determine the physical size of the Polymer of interest to us if this value is known at any temperature.

The component of the parameter is the relation $\rho_0 T_0 / \rho T$ / ρT equal to (η_0/η) α_T or equal to $\eta_0 Q/\eta Q$. the significance of this important component and its temperature dependence for many polymers is unknown. in particular, for HDPE, 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 HDPE samples is shown in Fig.3. As can be seen from Figure. 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 $\rho_0 T_0/\rho T$ 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 Figur.2. the isotherms of $\rho_0 T_0/\rho T$ versus $(T – T_0)$ are shown for various T = Const.

4. Discussion

Thus, even in a fluid state of the Polymer, when T> Tm (curve 9 in Figure. 3, on which data are plotted at temperatures from 150 to 300 °C, the equilibrium melting point of HDPE is Tpl = 150 °C) 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 = 300 °C if T0 is taken to be equal to the equilibrium glass transition temperature Tc = 132°C. This feature of $\rho_0 T_0/\rho T$ and its temperature dependence for HDPE is related to the high crystallinity of this linear Polymer.
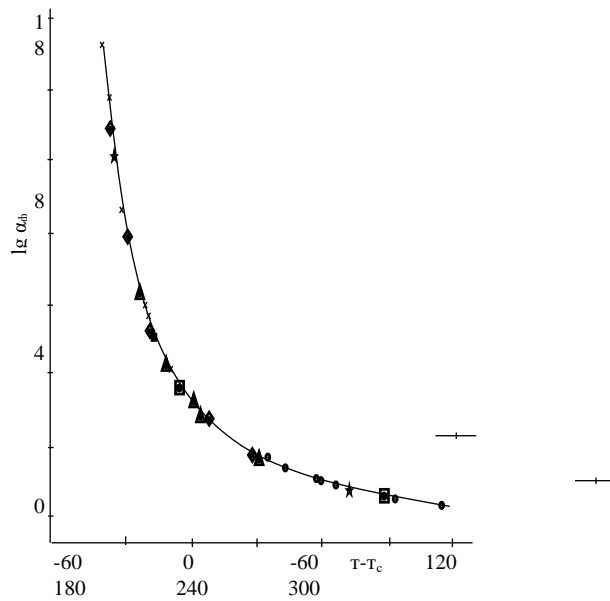

Fig. 2 The dependence of the shift parameter αT on the reduced temperature $(T – T_0)$ for linear P.E. samples.
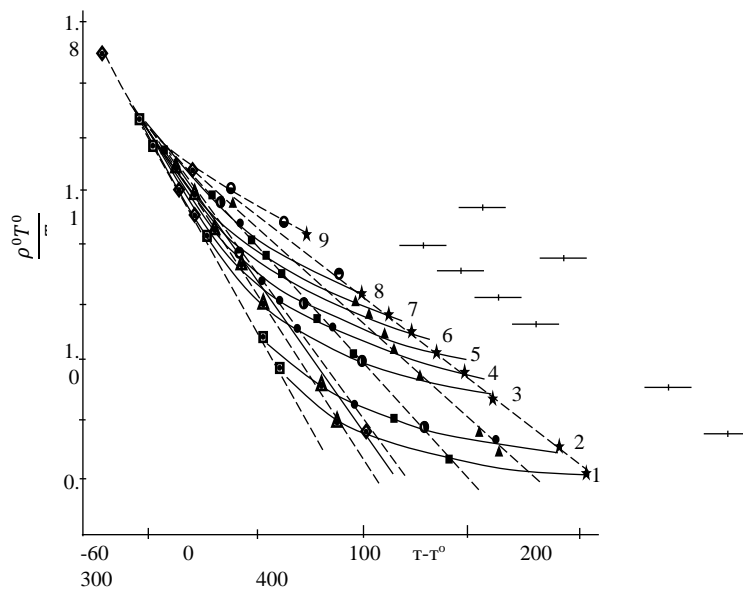

Fig. 3 The dependence of $\rho_0 T_0/\rho T$ (relative reduced density of the Polymer) on the reduced temperature $(T – T_0)$.

High-strength polyethylene, in the course of the research, has shown that it has two critical displacement temperatures - lower and true displacement criteria an important component of the value of at is also the ratio of viscosities at the temperature of reduction T_0 and any other temperature T, that is, η_0/η (if Tc is taken as the temperature of reduction, ηTc is 1013 poise [34][25] the dependence of the highest Newtonian viscosity of the melt ηnb for the investigated HDPE is shown in Figure4. As can be seen from fig. 4, in the region of temperature 150 °C, i.e., long before reaching the equilibrium melting temperature (132 °C) and the apparent melting point (132 °C), viscosity increases especially sharply with decreasing 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 results from ordering the polymer structure in the temperature region near Tm, which leads to an increase in the intermolecular interaction due to the formation in the melt of structures that are extremely prepared for crystallization. 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]

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 140 °C to 300°C), the dependence of the reduced parameter C = (L.G. η_T⁄η_c-lgM_w ^ (- 3.4) + lgα_T) was studied, and the reduced parameter (lgM_w ^ (- 3,4) + lgα_T) for the studied HDPE samples, characterized by a medium viscous molecular mass Mw = 8.3 x 104, (Figure 4and 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 HDPE and, apparently, of all linear polymers.

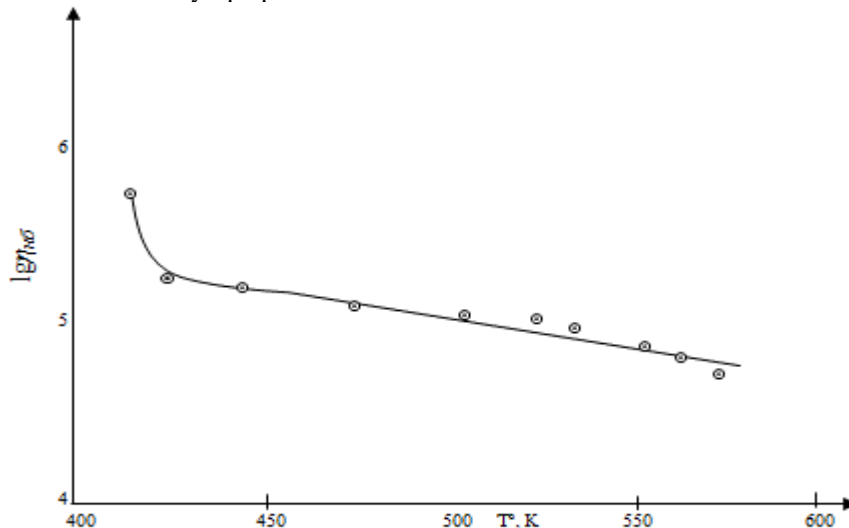$$\frac{\eta_T}{\eta_{Tc}} - lgMw^{-3,4} + lg\alpha_T = C$$

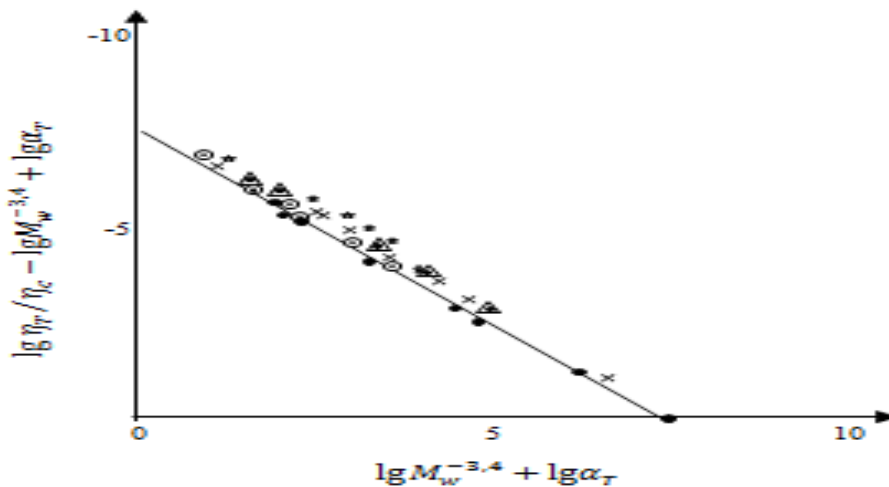**Fig. 4 Dependence of the greatest Newtonian viscosity of the melt, ηnb, on temperature T for PESD**

Fig. 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, ηnb 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 HDPE depends on the temperature and viscosity of average molecular weight. 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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