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ON THE REPRODUCIBILITY OF THE MORPHOLOGY OF THE
POLYETHENE SAMPLE

1. Introduction

Increasing number of investigators pay attention on the relationship between the long term behaviour of polyethene and its morphology [1,2,3]. On the one hand, some theoretical models have been formulated which serve as a support to production of miniature cables, and on the other hand the morphology of the laboratory manufactured PE samples and its relations with ageing processes have been extensively investigated [4,5]. The best solution would be to investigate a reproducible sample (moulded piece or injection moulded piece) which reflects the morphology observed in the full-size cable insulation. Due to variety and difference of the technological parameters operating during production of sample (injection moulding or press moulding) and of insulation of cable (extrusion) it is a very complicated problem [6]. Confined the problem, it may be interesting to answer the following question: how to obtain the sample (i.e. the moulded piece) with reproducible morphology? The consequence of possibility of possessing of such sample seems to be evident as the limitation of scatter the results of life tests obtained in static voltage trials.

2. Concept of the morphology

Traditionally it has been accepted that the morphological structure

of cross-linked and low density polyethylene creates spherulites with the radii in the range from a few to tens of micrometers (max 150 μm) nucleating from the single lamella.

The size of these polycrystals increases as the function of thickness of the sample (insulation) and is controlled, first of all, by the degree of super-cooling, $\Delta T = T_M - T_C$ (T_M - melting temperature, T_C - crystallization temperature) and by the time of cooling.

A zone of homogenous structure of the material involves then spherulites with the similar radii exhibiting the longest time of crystallization and, therefore, located in the deepest layers of the sample (insulation) (about 500 μm from the surface). It seems impossible to obtain such a state in the full volume of the product. The reasons are as follows: the rapid freezing of the surface layer (forming about 50 μm thick zone of the amorphous material), orientation of the boundary region as a result of the melt flow in the injection or the extrusion (existing down to 200 μm from the surface) and, moreover, a very low conductivity of the PE in the temperature range of crystallization 90 - 110°C (about 0,25 - 0,3 W/mK) [7,8].

In light of the latest studies (improving of the chemical etching technique) existence of the spherulitic structure in cross-linked polyethylene (both in samples and cable insulation) has been excluded [9,10]. With the increase of concentration of the dicumyl peroxide (cross-linking agent) the rise of quantity of the transversal nodes C-C makes impossible twisting of lamellae and creating more ordered superstructures.

Opinions are not explicit in instance of the low density polyethene (LDPE) [10,11]. The possibility of existence of well formed spherulites in the cable insulation with regard to a large content of the impurities (microparticles of oxides, salts and blacks) increasing the amount of nuclei for crystallization is being excluded in LDPE, as well as the absence of these impurities in the laboratory samples. With regard to above consideration it seems that the concept of the morphology must be referred to the basic structure entities namely monocrystals (crystallites), eventually, to its compositions (lamellae).

The monocrystal is a rhomboidal or rectangular plate with the thickness of about 100 - 200 Å (0,01 - 0,02 μm) and the length varying from 1 to 10 μm . The thickness of the lamella oscillates from 300 to 1000 Å

(0,03 - 0,1 μm). As the quantity measure of the monocrystal content in the sample can serve the degree of crystallinity, η .

3. Cooling of the sample

A cooling time model is the key element in the analysis of morphology and crystallinity. A heat transfer during cooling is connected with the phase change of polymer melt into semicrystalline solid. During solidification, polyethene (on the contrary to i.e. amorphous sPE) creates the latent heat of crystallization, ΔH . Qualitatively, the cooling process may be described as follows: the melt which is initially at uniform $T > T_m$ is contained in a steel mold under pressure. At the zero time the outer surface of the mold is cooled by the cooling medium (i.e. water) which has a constant, average temperature. Solidification develops towards the center of the mole as temperature of the melt drops below the crystallization temperature region.

Quantitatively in order to obtain temperature profiles versus thickness (radius) of the sample and time of cooling, $T(x,t)$, the modified heat equation must be solved (i.e. for a sample of rectangular shape) [12]:

$$\frac{\partial T}{\partial t} = \alpha \left[\frac{\partial^2 T}{\partial x^2} + \frac{1}{k} \left\{ \frac{\partial k}{\partial T} \left(\frac{\partial T}{\partial x} \right)^2 + \frac{T}{c_p} \left(\frac{\partial v}{\partial T} \right) \varphi \frac{dP}{dt} \right\} \right] + \frac{\Delta H}{c_p} \frac{d\eta}{dt} \quad (1)$$

where: φ - density of PE, kg/m^3

k - thermal conductivity of PE, $[\text{W/mK}]$

α - thermal diffusivity of PE, $[\text{m}^2/\text{s}]$

c_p - specific heat at constant pressure of PE $[\text{J/kg K}]$

v - specific volume of PE, $[\text{m}^3/\text{kg}]$

ΔH - heat of crystallization of PE, $[\text{J/kg}]$

$d\eta/dt$ - rate of crystallization of PE, $[\text{1/s}]$

Exemplary, initial and boundary conditions for the equation (1) are as follows:

$$\text{for } t = 0 : T(x) = T_1, \quad P(x) = P_1, \quad \eta = 0 \quad (2)$$

$$\text{for } x = 0 : \partial T / \partial x = 0 \quad (3)$$

$$\text{for } x = x_0 : \partial T / \partial x = - \frac{B_1}{x_0} (T - T_0) \quad (4)$$

where: T_i, P_i - initial temperature and pressure, [K] and [Pa]
 x_0 - half thickness of plate, [m]
 $B_1 = h x_0 / k$ - Biot number,
 h - heat transfer coefficient, [$\text{W}/\text{m}^2 \text{K}$]
 T_0 - temperature of cooling medium, [K]

In the equation (1), the last three terms take into account the effect of changes of thermal conductivity k versus temperature, of enthalpy versus pressure and of the heat of crystallization versus time on variation of temperature being also a function of time. It must be emphasized that the equation (1) ought to be solved simultaneously with the relationship describing the development of crystallization versus supercooling ΔT , $d\eta / dt = f(\Delta T)$. This relationship will be discussed in the further part of this section. As can be seen, in order to solve the equation (1) one must know the derivatives of the thermal conductivity and specific volume with respect to temperature as functions of temperature and pressure. Traces of α , k and v in the wide range of temperature (-20 - 250 °C) at pressure changed from 0,1 to 150 MPa have been established for a given material using the method describing in the paper [13]. Knowledge of these characteristics permits a simple evaluation of both the value of material parameter and its derivative for a defined temperature and pressure [14]. With regard to geometrical simplicity of the sample (cylinder or rectangular prism) and to constant step of the operation application of the numerical method of finite difference would be suitable.

The solidified polyethene undergoes the nonisothermal crystallization i.e. the successive layers of the sample are cooled with different rates (different T_0). The process of overall crystallization contains nucleation and linear crystal growth. Below the equilibrium melting point material starts to create nuclei of amount increasing with higher degree of supercooling, ΔT . Quantitatively the process of isothermal crystallization is described by the Avrami equation [15]:

$$\eta(t) = \eta(\infty) \left[1 - \exp(-z \cdot t^n) \right] \quad (5)$$

where: $\eta(t)$ - degree of crystallinity at time t of cooling
 $\eta(\infty)$ - degree of crystallinity after infinite time of cooling
 ($\eta(\infty)$ can be obtained from DSC measurement),

$z(T)$ - rate constant depended on nucleation and growth rates,

n - constant characterizing a type of nucleation and geometry of crystal growth, n taking integer values from 1 to 4.

By taking the logarithm of the equation (5) twice one can obtain:

$$\log \left\{ -\ln \left[1 - \frac{\eta(t)}{\eta(\infty)} \right] \right\} = n \log t + \log z \quad (6)$$

Plot of $\log \left\{ -\ln \left[1 - \frac{\eta(t)}{\eta(\infty)} \right] \right\}$ versus $\log t$

is a straight line with a slope of n and shifting of $\log z$. The dependence of n and z on temperature is obtained from results of set of experiments carried out in the isothermal manner (cooling of samples to the different but constant crystallization points) [16]. Treating the nonisothermal crystallization as a sequence of isothermal crystallization steps, equation (5) leads to another one given in reference [17]:

$$\eta(t) = \eta(\infty) \left\{ 1 - \exp \left(- \int_0^t z(T) dt \right)^n \right\} \quad (7)$$

Where $T(t) = \left\{ z(T) \right\}^{1/n}$

and $z(T)$ and n are known from isothermal studies.

After differentiating, the equation (7) must be solved numerically (finite difference method) simultaneously with equation (1).

4. Conclusions

1. There is a necessity of quantitative description of manufacturing of sample in order to obtain both: the reproducible moulded piece utilized in ageing tests as well as the reference of this description to technological process of production of full-size cable insulation.

2. In lights of latest studies the former concept of the morphology of cross linked and low density polyethene must be verified [9,10,11]. The most adequate superstructure can be described by monocystals or its sequences (lamellae). The quantitative measure of the above structures is the degree of crystallinity and its progress versus sample cooling time, $\delta \eta / dt$.

3. Simultaneous solution of the equation (1) and (7) by the finite difference method permits to obtain temperature profiles $T(x,t)$ and to estimate rate of crystallinity as a function of the sample thickness, x and the time of cooling, t .

4. Control of values of technological parameters at the initial and boundary conditions allows to receive a controlled morphology of the sample at arbitrary chosen time of cooling.

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