EFFECT OF ELECTRON IRRADIATION ON CRYSTALLINITY OF POLYTETRAFLUOROETHYLENE

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Dose dependences of thermal conductivity and density of polytetrafluoroethylene (PTFE) were studied. It is found that irradiation of PTFE up to 1 MGy comes to increasing of crystallinity degree and at higher doses comes to decreasing.

Keywords: thermal conductivity, density, crystallinity, effect of irradiation, heat transition.

Interest in the problem effect of irradiation on thermal properties of the polymers is steadily growing. This interest is due to actual importance of knowledge thermal properties of the materials operating in the fields of ionizing radiations and information which their study can give for investigation of the molecular structure and heat transfer processes in the polymers.

Considerable attention is given to such important thermal properties of the polymers as thermal conductivity (\(x\)), specific heat (\(C\)), thermal diffusivity (\(a\)), density (\(\rho\)), thermal expansion coefficient (\(\beta\)) and also structural characteristics as crystalline degree (\(X\)) and temperature and heat transition.

The present paper conducts the analysis of crystallinity degree of PTFE dependence on irradiation dose on the base of the experimental data for thermal conductivity and density dependences on irradiation dose at temperatures 80 K, 160 K, 240 K, 293 K. So it was found \cite{1} that PTFE crystallinity increased from 65\% to 88\% for initial PTFE up to dose \(D=2\) MGy and then reduced to 81\% where PTFE exposed to dose \(D=9,4\) MGy. The crystallinity of Polychlortrifluoroethene behaves in a like manner (it is unchanged about 86\% up to \(D=2\) MGy and then reduces to 75\% at the dose \(D=6\) MGy).

This drop relates to disorder of crystallites. NMR data showed the rise of free motion of the polymer chains in crystal phase. It is clearly at same time that formation of macrostructure defects as result of radiolysis and decrease in \(X\) may be responsible for the lower thermal conductivity and density of PTFE values at high radiation doses. Dose dependence of density of PTFE is given in Fig. 1.

\begin{equation}
\rho \cdot 10^{-3}, \text{kg/m}^3
\end{equation}

Fig.1. Dose dependence of density of PTFE at different measurement temperatures: 1-80; 2-160; 3-240; 4-293 K.
The thermal conductivity of PTFE dependence on dose is presented in Fig. 2.

![Fig. 2. Dose dependence of thermal conductivity of PTFE at different measurement temperatures: 1-80; 2-160; 3-240; 4-293 K.](image)

The measurements of the thermal conductivity were conducted using transient method. The samples of PTFE were irradiated by 6 MeV electrons.

As is seen from Fig. 1,2 density and thermal conductivity increases with increasing irradiation dose. This indicates that crystallinity is increased. However, density and thermal conductivity decreases for each temperature starting with the dose \( D = 1 \text{ MGy} \) and hence in its crystallinity degree which is related to acceleration of depolymerization resulting in formation of more branched polymer. Similar results have been obtained in [2,3] where crystallinity degree was related to density.

The increase in the crystallinity degree in those reports was explained by the formation of small crystallites resulting from radiation destruction of the amorphous phase.

Considering that the density of the crystalline phase is higher than the amorphous phase \( X \) and \( \rho \) must be increased.

Let us consider the mechanism of radiated changes in thermal conductivity and crystallinity degree on irradiation.

Do similarly work [4] and let us find out dose and temperature dependence of thermal conductivities and density of the crystalline and amorphous phases of PTFE taking into account that there is a linear dependence between density and crystallinity [2].

\[
\rho = 2000 + 300X
\]  

(1)

The density values of the crystalline and amorphous phases are related by the relationship

\[
\rho = X + \rho_a (1 - X)
\]  

(2)

And thermal conductivity values of the corresponding phases are related by similar relationship

\[
\lambda = \lambda_c X + \lambda_a (1 - X)
\]  

(3)

Either it is famous Maxwell-Oyken equation for binary phase mixture
As follows from the analysis of the group of the model polymers such as polytetrafluoroethylene, polypropylene that thermal conductivity is related to density by the relationship

$$\frac{\lambda - \lambda_a}{\lambda_a} \approx 5.8 \frac{\rho - \rho_a}{\rho_a}$$

(5)

For calculation temperature dependences of $\rho_k$, $\rho_a$, $\lambda_k$, $\lambda_a$ the equation (4) was rearranged into the equation

$$\frac{\lambda - \lambda_a}{\lambda + 2\lambda_a} = X \left[ \frac{2 k_\perp - 1}{3 k_\perp + 2} - \frac{1}{3 k_\parallel + 2} \right]$$

(6)

with due to regard for the anisotropy of crystalline phase where $k_\perp = \frac{\lambda_k}{\lambda_a} \approx 1$, $k_\parallel = \frac{\lambda_k}{\lambda_a} \gg 1$. Here $\lambda_k\perp$ and $\lambda_k\parallel$ are thermal conductivities of the crystalline phase of PTFE lie along and transverse to the axes.

The theoretical estimations indicate $k_\parallel \approx 50$. It has been found experimentally [5] that $\lambda_k\perp$ values actual independent on temperature for these group of the polymers probably it was related by strong phonon scattering on defects in the crystallites of such polymers. The latter may be due to more complicated structure of the repeat units in the polymers of these groups.

Having determined $X$ from equation (1) for non-irradiated sample $\lambda_a$ was calculated on the basis of the density data for the same temperatures. Assuming the value of $k_\parallel \approx 50$ we can determine $k_\perp$ by equation (4). In this way for PTFE at temperature $T = 298$ K has been determined $\lambda_a = 0.179$ W/(m K), $k_\perp = 0.66$, $\lambda_k = \lambda_a = 0.118$ W/(m K).

Dose dependence of $\lambda_k$, $\lambda_a$ and $X$ can determine by solution equation systems (2), (3) and (5).

The calculations the crystallinity changes of PTFE dependence on irradiation dose at the temperature $T = 160$ K are tabulated in Table 1.

<table>
<thead>
<tr>
<th>$T_{\alpha}$, K</th>
<th>X, %</th>
<th>D (MGy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>0.04</td>
<td>0.2</td>
</tr>
<tr>
<td>60</td>
<td>0.65</td>
<td>0.67</td>
</tr>
</tbody>
</table>

The values of $X$ quantity can calculate by equation (2) without taking into account their dose changes of $\rho_k$ and $\rho_a$. The decrease in relative share of the amorphous phase $\varphi$ up to dose $D = 1$ MGy is described by the relationship

$$1g\left(\frac{\varphi}{\varphi_0}\right) = -\left(\frac{f_1}{f_2}\right) 1g \left[\left(\frac{D}{D_0}\right) + 1\right]$$

(7)

where $\varphi$ is a share of the amorphous phase in the initial sample, $f_1$ and $f_2$ are constants of the destruction kinetic equations, $D_0$ is an absorbed dose which an average of one scission is per molecule.

The increase in $X$ at the dose $D < 0.5$ MGy has been confirmed at the previous reports [6,7] when it was irradiated by electrons. The decrease in $X$ values at the dose $D > 0.5$ MGy can be
related to the formation of plenty defects in the crystalline phase which they are chain scissions, branchings and cross-linkings in the crystals.

An other hand the concept of the void volume resulting from destruction ("cage" effect) has been introduced to explain the decrease in $\rho_k$ and $X$ at the dose $D > 0.5$ MGy. The void volume $\nu$ referred to the unit volume of the polymer is related to the volume of one microspace $\nu_0$ by the relationship

$$\nu \equiv \nu_0 \left(\frac{\rho N_A}{M_n}\right) \left(\frac{D}{D_0}\right).$$

where $N_A$ is Avogadro’s number, $M_n$ is an average of molecular mass.

Thus proposed calculation of PTFE crystallinity degree depending on irradiation dose and temperature on evidence derived from thermal conductivity for different temperatures and dose are in good agreement with those obtained previously reports.

References: