

REPLY TO REVIEW

Question: It will be interesting if authors could provide a more discussion regarding the competition between the influence of heating and gamma-irradiating on the structure changes of polytetrafluoroethylene. Is it possible to quantify separately these two influences?

Answer: The combined action of ionizing radiation and high temperatures in our case leads to the realization of two effects: i) ordering the crystal structure of polytetrafluoroethylene (PTFE) as a result of a decrease in the content of crystals with defects; ii) the disappearance of the system of micropores formed during the preparation of the polymer sample. Let's take a closer look at these effects:

i) The mechanisms of reactions proceeding under the influence of ionizing radiation and reactions excited thermally are different [1]. The formation of final and intermediate substances can occur as a result of processes such as radical reactions or ion-molecular reactions. The discussed structural changes in PTFE are a consequence of the course of radiation-induced processes of destruction and cross-linking of macromolecules [2]. In this case, the radiation destruction of the polymer differs from the thermal one, which occurs at higher temperatures. During the radiation destruction of PTFE in the melt, depolymerization and intense release of gaseous products of radiolysis are observed [3]. An increase in the PTFE irradiation temperature leads to an increase in the radiation-chemical yield of destruction in the amorphous phase of the polymer and, accordingly, to an increase in the degree of crystallinity [4]. In the case of irradiation of PTFE at a temperature of 303 K, a sharp decrease in the degree of crystallinity of PTFE occurs in the dose range from 3 to 10 MGy. An increase in the irradiation temperature to 453 K makes it possible to reduce the dose at which the degree of crystallinity of the polymer begins to decrease, to 1 - 3 MGy. The origin of this radiation effect can be associated with the intensification of the depolymerization processes, which leads to the amorphization of the polymer and the enhancement of chain branching in PTFE.

There are different points of view on the course of changes in the microstructure of PTFE during high-temperature radiation treatment: in [5], the decisive role of crosslinking processes is discussed, at the same time there are arguments in favor of amorphization of PTFE and the accumulation of defects during irradiation [4].

Such conclusions can be drawn from the currently available experimental material [1-5]. Further research is needed for a more substantive discussion of the competition between heating and gamma irradiation in structural changes in polytetrafluoroethylene. The above considerations have been added to the article in the "Discussion" section.

ii) b) Radiation-induced formation of a system of micropores is one of the main radiation effects leading to a change in the structure of condensed media [6 - 9]. Discussion of possible mechanisms of micropore formation during irradiation of condensed media showed that radiation-chemical processes of destruction and crosslinking, gas release have a decisive effect on the formation of a porous structure in irradiated solids [6, 9]. At the same time, the radiation heating of solids, which occurs as a result of the dissipation of the absorbed energy of ionizing radiation [1, 9], turns out to be insufficient for the development of pore formation processes.

This is evidenced by the results of a study by the method of X-ray computer microtomography of radiation-induced changes in the characteristics of the porous structure in foamed polyurethane samples, gamma-irradiated to various doses at room temperature [8]. It is shown that the observed changes in the porous structure of the polymer are caused by the processes of increasing the size of micropores and coalescence, which are caused by radiation crosslinking of macromolecules.

However, the conclusions [8] contradict the results obtained in our article. The reason for the contradiction may be related to the effect of temperature: probably, during irradiation in the melt, the processes of dissolution and coalescence of micropores proceed faster in comparison with the above-mentioned set of radiation-chemical processes, providing the appearance of pores in PTFE.

Therefore, the assessment of the contribution of temperature and radiation factors during the high-temperature radiolysis of PTFE should be carried out separately for both the processes of radiation-induced changes in the porous structure of the polymer and the processes developing in the crystalline phase of PTFE. These circumstances do not allow one to quantify the contributions to the change in the PTFE structure associated with the action of ionizing radiation and temperature.

References

1. Swallow A.J. // Radiation Chemistry of Organic Compounds. – Oxford London New-York Paris: Pergamon Press, 1960. - 380 p.
2. Wojna'rovits L. // 23 Radiation Chemistry // in: Handbook of Nuclear Chemistry / Attila Ve'rtés, Sa'ndor Nagy, Zolta'n Klencsa'r, Rezso" G. Lovas, Frank Ro'ssch (Eds.). - Springer Science+Business Media B.V., 2011. – pp. 1267 - 1331 doi:10.1007/978-1-4419-0720-2
3. E. Roland, R.E. Florin, M.S. Parker, L.A. Wall, The Mechanism of the Depolymerization of Polytetrafluoroethylene With Pyrolytic and Radiolytic Initiation, J. Res. Nat. Bur. Stand. A. Phys. Chem. 70 (1966) 115 – 131. doi: 10.6028/jres.070A.008
4. Briskman B.A., Tlebaev K.B. // Radiation Effects on Thermal Properties of Polymers. II. Polytetrafluoroethylene // High Performance Polymers. – 2008. - 20: 86. – pp. 86 – 114 doi: 10.1177/0954008307079540
5. Hill D.J.T., Whittaker A.K. // Radiation chemistry of polymers / in: Encyclopedia of polymer science and technology / ed. by Herman F. Mark. - John Wiley & Sons, 2016. – 58 p. doi: 10.1002/0471440264.pst488.pub2
6. Geguzin J.E. // Physics of Sintering. – Moscow: Nauka, 1984. – 312 p.
7. Sueo Machi, Silverman J. // Bubble Formation in Radiation-Induced Grafting of Styrene to Polyethylene // Journal of Polymer Science: Part A-1. – 1969. – V. 7. – pp. 2737 – 2740
8. Agrawal K., Singh B., Kashyap Y.S., Shukla M., Manjunath B.S., Gadkari S.C. // Gamma-irradiation-induced micro-structural variations in flame-retardant

polyurethane foam using synchrotron X-ray micro-tomography // Journal of Synchrotron Radiation. - 2019. - V. 26. - pp. 1797–1807 doi: 10.1107/S1600577519009792

9. Grogan J.M., Schneider N.M., Ross F.M., Bau H.H. // Bubble and Pattern Formation in Liquid Induced by an Electron Beam // Nano Letters. – 2014. – V. 14. – pp. 359 - 364 doi: 10.1021/nl404169a