Effect of electronic irradiation on the properties of polyethyleneterephthalate films of various producers

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Abstract. Studies on the effect of electron irradiation on the properties of polyethylene terephthalate films of various brands have been carried out. An analysis of the results shows that the relative elongation of the Mylar-type film is ~ 70%, for PET ε it is 48%. According to the strength properties, Russian-made PET is more resistant to electronic effects and is destroyed at doses of 10⁹ Gy, while the Mylar ones at 10⁵ Gy. The calculation made according to the proposed models (exponential and generalized) is in satisfactory agreement with experimental data.

1. Introduction
Most of the polyethylene terephthalate (PET) in the world goes to the production of films and fibers. Its widest application is observed in mechanical engineering, the chemical industry, food equipment, transport and conveyor technologies, medical industry, instrument making and household appliances [1 – 3].

Polyethylene terephthalate is a common thermoplastic, a representative of the class of polyesters, known under different brand names. For physical properties, it is a white solid, odorless. PET is durable, tough and lightweight material. In Russia, polyethylene terephthalate is called lavsan, in Great Britain – melinex, in the USA – dacron, mylar, in France – terfan, estar, etc., in Belgium – gevar, in Japan – tetorone, in Germany – hostafan, in Italy – motivele. It is a polyether of terephthalic acid and ethylene glycol, which can be obtained from various derivatives of terephthalic acid and ethylene glycol [4].

The main structural unit of the macromolecule of high-temperature resistant PET is:

\[-\text{O} – \text{CH}_2 – \text{CH}_2 – \text{O} – \text{CO} – \text{C}_6\text{H}_4 – \text{CO} – \text{]}_n\]

Polyethylene terephthalate is produced from petroleum products using similar technology by passing through several stages of heating and cooling. – O – CO – polar group, regularly located in the chain, enhances the intermolecular interactions and forms the rigidity of the material. Compared to polyimide, polyester films have a higher crystallinity of the structure [5].

To obtain the specified strength characteristics, the amorphous film is subjected to biaxial orientation, keeping it in a stretched state at elevated temperature for a certain time, which allows
achieving crystallization of the polymer and stabilization of its mechanical properties. PET products are highly durable. Ongoing research is aimed at the increase of the elastic-strength properties of polyethylene terephthalate by implementing technological processes for manufacturing products and by creating a more advanced, minimally diverse chemical structure [6]. The properties of PET are modified by introducing the derivatives of aliphatic and aromatic dicarboxylic acids, hydroxy acids, polyalkylene glycols, branched diols, substituted amines, etc. as comonomers in the process of synthesis. To ensure the best mechanical, physical, electrical properties of PET, the material is filled with various additives (glass fiber, molybdenum disulfide, fluoroplast) [7].

Radiation exposure also leads to modification of the substance. The restructuring of the supramolecular structure leads to a variety of properties of the polymer material, leading to an improvement or deterioration of its specific technical characteristics [4].

It is known that the mechanical properties of a polymer depend on its nature. Therefore, for polymers containing a benzene ring in the side chain, the degree of various changes is more significant (modulus of elasticity, creep rate, reduction of long-term strength, etc.) [4].

This work is devoted to the study of the properties of polyethylene terephthalate films of various brands under the influence of electron irradiation.

2. Experimental technique

In the work, polyethylene terephthalate films of various manufacturers were investigated: Mylar (USA) and PET (Russia).

Mechanical tests were carried out on a tensile testing machine of the RMU-0.05-1 type with a sliding speed of clamps of 36.09 ± 0.05 mm/min. Film samples were tested for uniaxial tension under normal conditions up to rupture (at T = 20 ± 2 °C, relative air humidity (45 ± 5)%). The studied samples were strips 5 x 50 and 10 x 100 mm in size, respectively, with a thickness of 100 μm.

The samples were irradiated in air in special holders on an electron accelerator of the ELU-6 type at 20 °C with an energy of 4 MeV, a current density of 0.5 μA/cm², a pulse duration of 5 μs at a repetition rate of 200 Hz. Absorbed doses (D) were 0 – 10^10 Gy.

3. Results and discussion

Figure 1 shows the graphs of the relative elongation and stress versus electron dose for polyethylene terephthalate films of various brands. As can be seen from the figure, the nature of the curves is similar and consists of 2 stages: 1) at D = 0 – 10^4 Gy, both for deformation and stress, the changes are minor and slowly decrease. The relative elongation of Mylar-type films to doses of ~ 10^4 Gy grows, which is associated with crosslinking processes. The second stage for a Mylar film lies in the range of 10^7 – 10^9 Gy, where there is a sharp drop of ε and σ to 0. For Mylar films, Stage 2 is in the range of 10^7 – 10^9 Gy.
We have considered 2 models: exponential and generalized. The simple physical model is used for constant static load changes for the interval $\sigma$ from $\sigma_0$ to $\sigma$, $\varepsilon$ from $\varepsilon_0$ to $\varepsilon$ and $D$ from 0 to $D$. Then we have:

$$
\varepsilon = \varepsilon_0 \exp \left( -\frac{D}{D_0} \right),
$$

(1)

$$
\sigma = \sigma_0 \exp \left( -\frac{D}{D_0} \right).
$$

(2)

To obtain the generalized exponential model, we used the formula from [8]:

$$
\sigma^* = \sigma_0 \ln (\varepsilon + 1).
$$

(3)

Substituting (1) into (3) we get:

$$
\sigma^* = \sigma_0 \ln \left( \varepsilon_0 \exp \left( -\frac{D}{D_0} \right) + 1 \right).
$$

(4)

The calculated dependences of $\varepsilon$ and $\sigma$ on $D$, obtained using formulas (1 – 4) are shown in Figure 1. As follows from the results, the theoretical curves describe the experiment satisfactorily. In this case, the generalized and exponential models give almost identical results.
Analysis of the obtained results shows that, according to the deformation properties, Mylar films have an elongation of ~ 70 %, for PET (Russia) $\varepsilon$ is 48 %. By its strength properties, it is more resistant to electronic effects and is destroyed at doses of $10^9$ Gy of PET produced in Russia, whereas Mylar's are at $10^5$ Gy.

The effect of irradiation on the strength and inelastic characteristics of polymers is significant and affects the amorphous phase of the material [9 – 11]. The structure of the Mylar has a complex heterogeneous structure of amorphous regions, possessing a significant proportion of interfibrillar amorphous regions separating adjacent microfibrils, along with intrafibrillar amorphous layers [3, 4]. Basically, destruction occurs on the main chain, since high stresses occur in it.

The stress created by external loads propagates from the point of application of force along the sample at a certain rate. The weakened fragment of the film closest to the point of application of the load will be the point of rupture. The mechanical strength of the polymer is dramatically reduced by fragments of the introduced elements, which are loosely coupled with each other, which remain at very high doses.

For Russian-made PET films, this behavior of mechanical properties is associated with the features of film synthesis. Modification of properties in the process of producing polyester films is carried out by dimethyl adipate, dimethyl hexahydro-terephthalate, in consequence of which they are more durable, less creeping, and more resistant to repeated deformations [1, 2].

4. Conclusion

1. For 2 types of polyethylene terephthalate films studied (Mylar, PET), it was obtained that the character of the change of mechanical properties with the growth of the dose of electronic radiation is similar. Increasing the dose to $10^4$ Gy leads to a slow change in the deformation and stress for Mylar, and a further increase to $10^6$ Gy leads to a sharp decrease in them, which is associated with an increase in the destructive processes in the material. For lavsan films under irradiation to doses of ~ $10^7$ Gy, a gradual decrease in $\varepsilon$ and $\sigma$, is observed, and a further increase to $10^9$ Gy leads to a sharp decrease due to the features of the synthesis technology of this material.

2. Calculations were made according to the previously proposed models. The exponential physical model on the dependence of strain and stress on the electron dose of radiation is in satisfactory agreement with experimental data. Good agreement between the calculated and experimental data was also obtained for the generalized model.

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References

[1] White J L, Choi D, 2006 Polyethylene, polypropylene and other polyolefins (Sph.: Professiya)
[2] D Brooks, J Giles, 2006 Manufacture of packaging of PET, transl. from English (ed. by O.Y. Sabsay, SPb: Professiya)
[3] Ardekani S M, Dehghani A, Maadeed M A, Wahit M U, Hassan A, 2014 Mechanical and thermal properties of recycled poly(ethylene terephthalate) reinforced newspaper fiber composites Fibers Polym. 15 1531-1538
[4] Layus L A, Slutsker A I, Hoffman I V, Gilyarov V L, 2004 Interrelation of characteristics of reversible thermal and force deformations in solids of different structure Physics of a solid 46 6 1115-1122
[5] Kudashev S V, Urmantsev U R, Seleznev G V, Rakhimov N A, Zheltobryukhov V F 2012 Surface modification of PET granules by fluoride-containing urethanes Journal of Applied Chemistry 85 11 1860-1866
[6] Rouhi S, Alizadeh Y, Ansari R 2014 On the interfacial characteristics of polyethylene/single-walled carbon nanotubes using molecular dynamics simulations Applied Surface Science 292 958-970

[7] Gerasimenko N N, Voronova N A, Koytunets V A, Taipova B G, Kupchishin A I, Omarbekova Z A 2003 Study of the mechanical properties of polymer films effecting on their by static load and temperature Proceedings of the universities. Materials of electronic technology 6-12

[8] Kupchishin A I, Taipova B G, Kupchishin A A, Voronova N A, Kirdyashkin V I, Fursa T V 2016 Catastrophic models of materials destruction IOP Conf. Series: Material Science and Engineering 110 012037

[9] Kupchishin A I, Niyazov M N, Voronova N A, Kirdyashkin V I, Abdukhairova A T 2017 The effect of temperature, static load and electron beam irradiation on the deformation of linear polymers IOP Conf. Series: Materials Science and Engineering 168 012016

[10] Voronova N A, Kupchishin A I, Taipova B G, 2018 Nanoclusters and Electron Irradiation Effect on Mechanical Properties of Polyimide-Based Composite Key Engineering Materials 769 72-77

[11] Voronova N A, Kupchishin A I, Niyazov M N, Lisitsyn V M. 2018 Uniaxial Stress and Electron Irradiation Effects on Nanochains Straightening in Film Polymer Materials Key Engineering Materials 769 78-83