THE STUDY OF ELECTRON BEAM IRRADIATION EFFECT ON MULTILAYER POLYMER MATERIALS

V. Tarasyuk[†], Russian Research Institute of Canning Technology, 142703, Vidnoye, Russia A. V. Prokopenko, National Research Nuclear University - Moscow Engineering Physics Institute, 115409, Moscow, Russia

N. R. Kil'deeva, N. A. Sazhnev, A.N.Kosygin Russian State University, 117997, Moscow, Russia A. V. Gordeev, State research center Burnasyan federal medical biophysical center, 123098, Moscow, Russia

N. E. Strokova, M.V. Lomonosov Moscow State University (MSU), 119991, Moscow, Russia

Abstract

The work is devoted to the investigation of a multilayer polyamide/polyethylene film material $80~\mu m$ thick after its processing with an electron beam with an energy of 10~MeV and doses of 3 to 18~kGy in the Burnasyan Federal Medical Biophysical Center of the federal medical biological agency. Infrared spectroscopy was used to study the structure of a polymer material before and after irradiation of each layer. Atomic emission microscope was used to study the surface of a film. Evolution of the film surface characteristics can lead to a change in the barrier properties of film material used for packaging in the food industry. Investigation of polymer film treated with fast electrons showed stable results on dispersion at doses up to 18~kGy.

INTRODUCTION

Radiation technologies of food processing and food packing is accurate radiation dosing of radiation, the possibility of exposure of packaged products, a high degree of efficiency and performance, and low operating costs [1]. High-energy electrons beam treatment reduces level of pathogenic bacteria and viruses. The applied dose is relatively different from 0.05 - 0.15 kGy to inhibit sprouting of potatoes and onions to 2.0 - 10 kGy to improve technological properties of food products and to 30 - 50 kGy for sterilizing meat products.

In the industry to maintain sterilization effects and increase the shelf life of foods often radiation sterilization is carried out in the package. Basically multilayer film materials of different composition are used. By combining multiple layers of different polymers, the manufacturer is able to create film materials with desired properties for each type of agricultural products, taking into account the respiratory processes.

During radiation sterilization by electron beam in polymeric materials can simultaneously undergo the process of crosslinking and degradation, followed by oxidation process and the appearance of such functional groups as:

-C=O, -OH, -O-O-H, -C-O-O-C- [2-5].

The structure of the polymer material surface under the action of irradiation changes and forms a variety of reliefs in the form of ripples, irregularities of granular type and through holes. This phenomenon is used for the manufacture of polymeric microporous membranes [6-9].

The aim of this work is to identify the dependence of surface structure of the polymer material with the change of functional groups in the IR spectra before and after fast electrons irradiation.

RESEARCH METHODS

When storing fresh agricultural produce best results showed the multilayer film materials composition of polyamide/polyethylene in a percentage ratio of 20:80 (PA/PE) [10-11].

PA/PE samples were irradiated by 10 MeV electrons at accelerator UELR-10-10-40 at doses from 3 to 18 kGy. Approximate (desirable) doses of irradiation of samples and real doses of irradiation of packs with samples according to indications of detectors in control points are presented in Table 1. The results are shown in Table 1.

Table 1: Absorbed Doses of Fast Electrons

Estab- lished	Irradiation on installations		
dose, kGy	UELR-10-10-40		
	Beam output dose, kGy	D, absorbed dose, kGy	
3	3.0 ± 0.3	3.2 ± 0.3	
6	5.8 ± 0.5	6.2 ± 0.6	
9	8.3 ± 1.1	8.3 ± 0.7	
12	11.5 ± 1.2	11.5 ± 1.1	
15	14.1 ± 2.6	14.1 ± 1.3	
18	16.7 ± 1.4	17.3 ± 1.4	

The infrared spectrum from 400 to 4500 cm⁻¹ are characteristic basic intense absorption bands to the PE-layer related to the stretching (2820-2980 cm⁻¹) and the deformation (1480 cm⁻¹, 725-740 cm⁻¹) fluctuations -CH₂-groups. Absorption bands related to deformation vibrations of -CH₃ groups are observed in the region 1380-1370 cm⁻¹. Characteristic absorption band for the PA-layer: the deformation vibration of the N-H in the region of 3040 cm⁻¹, 1550 - 1570 cm⁻¹ and the carbonyl group bending vibrations in the 1620-1680 cm⁻¹. The most characteristic absorption of functional groups in the test sample is presented at Table 2.

Table 2: Characteristic Absorption in IR Spectra of the Sample PA/PE.

Func-	Characteristic absorption frequency, cm ⁻¹			
tional group	PE-layers	PA-layers	PA/PE	
Stretching vibrations				
-CH ₂ -	2820-2980			
	(s.)			
-C=O		1623-1680		
		(s.)		
		2020 (sl.)		
-C-O-		1120 (s.)		
C-		1257-1275		
		(s.)		
-COO-			2340 (sl.)	
-CH-			3268-3338	
			(s.)	
Deformation vibrations				
-CH ₂ -	1480 (s.)		718-733 (s.)	
	725-740 (s.)			
-NH-	3085 (s.)			
-CH ₃	1380-1371		1170 (s.)	
	(s.)			

After irradiation, the characteristic absorption bands of PE- and PA- layers do not undergo radical changes in the structure of the packaging material. Explore the intensity of absorption bands of functional groups present the change of their intensity.

The intensities of the absorption bands of functional groups at absorbed doses 0 kGy and 18 kGy are in Table 3. It is possible to speak about degradation or crosslinking in samples of films. We have found that almost no change occurs in the structure of multilayered sample PA/PE.

Table 3: Intensities of Absorption Bands in Films PA/PE

Absorption band, cm ⁻¹	Functional group	Intensities of the absorption band		
		PA/PE		
Dose 0 kGy				
1371-1366	-CH ₃	0.11±0.01		
2340	-COO-	0.76 ± 0.01		
3085	-NH-	0.19 ± 0.02		
Dose 18 kGy				
1371-1366	-CH ₃	0.10 ± 0.01		
2340	-COO-	0.76 ± 0.00		
3085	-NH-	0.18 ± 0.01		

Table 3 and Fig. 1 shows that the bands intensity of the functional groups of PA/PE samples under the influence of fast electrons from 3 to 18 kGy changes the intensity of the bands of the functional groups-CH₃ and -NH- decreases by 0.01 relative units, which can be attributed to the error limit.

The results of scanning probe microscopy showed that the surface structure of the PA/PE sample in the PE-layer before irradiation in the area of $50x50 \mu m$ has no evenness and holes (Table 4). With a detailed increase in the holes (in the area of $5x5 \mu m$), they can be attributed to the film production technology, since there are no through holes.

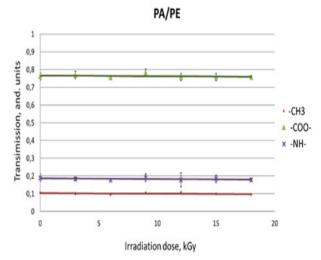


Figure 1: Dependence of fast electron irradiation doses on the intensity of absorption bands of functional groups.

After irradiation, the surface structure of the RE-layer becomes more loose and bumpy. The number of holes increases (in the area of 50×50 microns) after irradiation with a dose of 18 kGy more than 10 holes. In a more detailed study - the holes can be described as through. The structure of the surface in the PE-layer before irradiation has several non-through holes of 1 μ m, but after irradiation the number of holes increases and the size of the holes reaches 2 μ m.

Studies of the surface structure of the PA-layer in the PA/PE film before irradiation on the surface of the polymer film ($50 \times 50~\mu m$) has a lumpy rough surface (Table 4). On the plot with resolution $10 \times 10~\mu m$ we can be noted that deepening can be attributed to the technology of film production. After irradiation with doses of 18 kGy, the surface structure of the RA layer becomes smoother.

Thus, it is shown that the processing of PA/PE samples by fast electrons changes the number of functional groups on IR spectroscopy and is 0.01 relative units. This changes can be attributed to the error limit. However, the study of the surface structure of the samples by scanning microscopy confirms that after irradiation appear through holes mainly in the PE-layer, which proves the change in functional groups as a result of simultaneous processes of degradation and cross-linking (in the gap-hole) 0.01 relative units in the IR spectra, which refers not to the error, but to changes in the number of these groups.

Content from this

Table 4: Surface Structure of PA/PE Sample before and after Irradiation.

per l	after Irradiation.					
 - -	Resolu-	Dose, kGy				
bn	tion of		•			
Ĭ,	the					
×	micro-	0	18			
the	scope,					
ot ot	μm					
titļ	PE layer					
is work may be used under the terms of the CC BY 3.0 licence (© 2018). Any distribution of this work must maintain attribution to the author(s), title of the work, publisher,	50×50		8 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2			
maintain attributi	25×25					
of this work must	10×10					
Any distribution	5×5					
<u>8</u>		PA layer				
3.0 licence (© 201	50×50					
s of the CC BY	25×25		2 2 2 2 3 3 4 4 4 4 4 4 4 4 4 4 4 4 4 4			
ed under the terms	10×10		4 10 0 F			
s work may be use	5×5		_			

CONCLUSION

Polymer film materials with PA/PE composition as a percentage of the film 20:80 were processed by 10 MeV electrons at the accelerator UELR-10-10-40 with doses from 3 to 20 kGy. The study of the structure by IR spectroscopy showed that the irradiated PA/PE sample reduces the number of functional groups –CH₃ and –NH– by 0.01 relative unit entails a change in the surface of the polymer material. The results of reproducing the intensity of the absorption bands of the functional groups show minimal dispersion, which indicates uniform irradiation of all samples.

By confocal laser microscopy it was demonstrated that after irradiation in the PA/PE sample with doses of 18 kGy, the film surface becomes smooth in the PA-layer. There is lumpiness, roughness and through holes appear in the PA-layer. These characteristics can lead to changes in the barrier properties of the film material, as well as affect the shelf life of food.

ACKNOWLEDGEMENTS

The study was supported by the Ministry of Education and Science of the Russian Federation within the framework of the State Task (project no. 10.7554.2017/8.9).

REFERENCES

- [1] S.Yu. Gelfand *et al.*, Modern aspects of food radiation processing, *Storage and Processing of agricultural products*, vol. 2, pp. 25-31, 2013.
- [2] L. Bellamy, The Infrared spectra of complex molecules, London and New York: Chapman and hall, 1980.
- [3] A.V. Polyakov, *High-pressure polyethylene*. Moscow: Chemistry, 1988.
- [4] F. Bovey, Effect of ionizing radiation on natural and synthetic polymers. Moscow: Foreign literature, 1959.
- [5] M.B. Neiman, Aging and stabilization of polymers. Moscow: Nauka, 1964.
- [6] A.A. Kharchenko et al., Investigation of polimers surface modified by irradiation, Journal Potocki State University, Series C, N 12, 2013 pp. 83-90
- [7] A.V. Mitrofanov et al., Study of the surface of polyethylene terephthalate films modified by vacuum ultraviolet irradiation in air, Journal of Surface Investigation. X-Ray, Synchrotron and Neutron Techniques, N 7, pp. 30-35, 2009
- [8] A.A. Kharchenko et al., Radiation Modification of polymer, Journal of Surface Investigation. X-Ray, Synchrotron and Neutron Techniques, N 4, pp. 60-65, 2015.
- [9] V.F. Aristov *et al.*, New manufacturing technology of polymeric microporous membranes, *Technical Physics Letters*, vol. 28, issue 14, pp. 64-68, 2002.
- [10] V.T. Tarasyuk et al., Study of multilayer polymer materials after ionization treatment, IOP Conf. Series: Journal of Physics: Conf. Series, Vol. 941, 2017, 012084. doi: 10.1088/1742-6596/941/1/012084
- [11] A.Yu. Gracheova et al., Enhancement of efficiency of storage and processing of food raw materials using radiation technologies, Phys. Atom. Nucl., vol. 79, N 14, pp. 1682-1686, 2016. doi: 10.1134/S1063778816140118