Study of multilayer polymer materials after ionization treatment

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Abstract. Electron-beam technologies of food products processing involves the use of modern packaging materials in form of polymer films of different composition. The objective of the research is to study the impact of accelerated electrons on the structure of the polymeric packaging materials used for storage of agricultural products. It was investigated radiation exposure on film material PE/PA (80/20) with a thickness of 80 mkm. This film used for storage of vegetables and fruits and has the necessary indicators for gas and vapor permeability. Electron beam treatment of the films was performed on a compact radiation sterilization installation with local bio-protection with electron energy of 5 MeV. A polymer films were irradiated with doses from 1 to 10 kGy. Changing the structure of the film composition was monitored by IR spectrometry. As a result of irradiation by accelerated electrons with doses up to 18 kGy is established that the polymer film is modification of the polymeric material in the form of a partial degradation with subsequent intra-molecular cross-linking. This improves the physico-mechanical properties in the transverse direction, and such film can be used for food packaging before electron-beam treatment.

1. 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.

In radiation sterilization process it is possible to observe in polymers the processes of crosslinking and degradation. The impacts of electron beams in the presence of oxygen could be form of oxygen-containing groups: \(-\text{C}=\text{O}\), \(-\text{OH}\), \(-\text{O-O-H}\), \(-\text{C-O-C}\). Groups \text{C}=\text{O} are formed of different types: acid, ketone, aldehyde, ester, percolate, perepisnye. These groups have characteristic absorption bands in the IR spectrum [2]. When exposed to radiation on the macromolecules of the polymers, they can break down into free radicals with rupture of the C-H, C-C etc [3].

There are works on studying of influence of irradiation on the structure of single-component film materials and their physical and mechanical properties [4-6]. At this work the radiation impact on the suitability of multi-component film materials for packaging agricultural products before irradiation in order to increase its shelf life are studied.

2. Research methods

Researched polymer packing film polyamide/polyethylene (PA/PE) at a ratio of 20:80, thickness 80 \(\mu\)m manufacture by Dmitrov factory of flexible packaging was studied.

Installation of X-ray sterilization plant with local bio-protection is located in the radiation technologies center of Moscow Radiotechnical Institute Russian Academy of Sciences. X-ray sterilization plant has the following characteristics: energy of accelerated electrons - 5 MeV, power of the electron beam - 1.5 kW radiation performance - 3600 Mrad· kg/hour, maximum dimensions of sterilized products - 57 cm \(\times\) 38 cm \(\times\) 27 cm.

IR spectra of polymer packing film are recorded on device FMS-1201 (Russia) at M.V. Lomonosov Moscow State University. The device has the following characteristics: spectral range of 400-4000 cm\(^{-1}\); spectral resolution – 1 cm\(^{-1}\); source of infrared flux – nichrome; IR-receiver flow – pyroelectric. The film samples are placed in the experimental cell perpendicular to the light flux. IR absorption spectrum of polymer packing film is recorded before and after irradiation.

Water vapor permeability of packing film before and after irradiation is determined according to GOST 21472-81 "Sheet materials. Gravimetric method for determining water vapor permeability" at room conditions of temperature (25.0 \(\pm\) 0.5) °C and humidity (75 \(\pm\) 2) %.

3. Research results

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) [7-8].

Samples of the polymer film PA/PE has been exposed to radiation at a dose of from 3 to 18 kGy in 10 replicates. Actual doses were determined in comparison with film detectors which were irradiated together with the samples. Film detectors were manufactured by "Scientific Production Enterprise "Doza" and are accredited in Rostest Moscow. The absorbed dose is determined by comparing the optical density of the film detector relative to the control sample on spectrophotometer Varian Cary 100 Scan. Spectrophotometer is in the Russian Research Institute of Canning Technology. The results are shown in table 1.

| Established dose (kGy) | Optical density of film | Absorbed dose, (kGy) |
|------------------------|-------------------------|----------------------|
| 3                      | 0.061                   | 3.3                  |
| 6                      | 0.117                   | 5.3                  |
| 9                      | 0.177                   | 8.3                  |
| 12                     | 0.261                   | 12.8                 |
| 15                     | 0.302                   | 14.9                 |
The study of the structure of samples before and after irradiation was conducted. It was removed IR spectra in the range of 400-5000 cm\(^{-1}\). The infrared absorption spectrum of the polymer film PA/PE after electrons irradiation with 18 kGy is shown in figure 1.

![Infrared absorption spectrum of PA/PE](image)

Figure 1. The infrared absorption spectrum of the polymer film, PA/PE in the range from 400 - 4500 cm\(^{-1}\) before and after electrons irradiation with 18 kGy.

The infrared spectrum from 400 to 4500 cm\(^{-1}\) are characteristic basic intense absorption bands (see figure 1.) to the PE-layer related to the stretching (2820-2980 cm\(^{-1}\)) and the deformation (1480 cm\(^{-1}\), 725-740 cm\(^{-1}\)) fluctuations -CH\(_2\)- groups. Absorption bands related to deformation vibrations of -CH\(_3\) 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\(^{-1}\) [2].

### Table 2. Characteristic absorption in IR spectra of the sample PA/PE.

| Functional group | Characteristic absorption frequency, cm\(^{-1}\) |
|------------------|------------------------------------------|
|                  | PE-layers | PA-layers | PA/PE |
| Stretching vibrations |          |          |       |
| -C-C-             | 580 (sr.) | 928 (sr.) |
| -CH\(_2\)-        | 2820-2980 (s.) |
| -C=O              | 1623-1680 (s.) | 2020 (sl.) |
| -C-O-C-           | 1120 (s.) | 1257-1275 (s.) |
| -COO-             | 2340 (sl.) |
| -CH-              | 3268-3338 (s.) |
| Deformation vibrations |          |          |       |
| -CH\(_2\)-        | 1480 (s.) | 718-733 (s.) |
|                  | 725-740 (s.) |
| -CH\(_3\)         | 1380-1371 (s.) | 1170 (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
The 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 |
|-----------------------|------------------|-----------------------------------|
| Dose 0 kGy            |                  |                                   |
| 584                   | -C-C-            | 0.36                              |
| 1371-1366             | -CH₃             | 0.09                              |
| 2340                  | -COO-            | 0.75                              |
| 3085                  | -NH-             | 0.16                              |
| Dose 18 kGy           |                  |                                   |
| 584                   | -C-C-            | 0.36                              |
| 1371-1366             | -CH₃             | 0.10                              |
| 2340                  | -COO-            | 0.77                              |
| 3085                  | -NH-             | 0.18                              |

On the basis of the obtained results have been constructed the intensity of absorption bands in the sample PA/PE on electron irradiation at different dose. These dependences are shown in figure 2. and figure 3.

**Figure 2.** The dependence of the bands intensity of functional groups (-COO-; -CH₃; -C-C-) of different doses of fast electrons irradiation.

**Figure 3.** The dependence of the bands intensity of functional groups (-COO-; -NH; -C-C-) of different doses of fast electrons irradiation.

According to the curve of functional groups -NH and -C-C- the number of groups are reduction with growth of irradiation dose, but groups -COO- are increase. The functional groups -NH and -COO- are decreased at sample irradiation dose 18 kGy (see figure 3).

Thus, during irradiation of the sample of PA/PE film with 3 kGy in the PA-layer is degradation, and in PE-layer is cross-linking between molecules with the formation of oxygen bridges. With increasing doses of irradiation up to 20 kGy is noted the degradation in the PA-layer and the reduction of the ultimate methyl groups in PE-layer. Analysis of IR spectra show, that there a slight change in the structure of the sample, which can result in changing its barrier properties.

We obtained the dependence of the parameter wetting contact angle from the doses of irradiation with fast electrons from the inner (figure 4) and external (figure 5) layers. From figure 4 it is seen that the wetting angle of the irradiated sample is not in PE-layer (inner) is 80° and begins to decrease starting from 15 kGy 18 kGy and when the wetting angle is 70°. Therefore, the hydrophilicity of the PE-layer increases due to the increase in oxygen in the PE-layer.

In the PA-layer before irradiation is 73° and after radiation dose of 18 kGy – 76°, hence the parameter wetting contact angle practically does not change [9].
Thus, minor changes in the structure with increasing radiation doses cause changes in the properties of the polymer material, and therefore significantly affect the shelf life of agricultural products.

Figure 4. Dependence of the contact angle of PA/PE sample on the irradiation dose by fast electrons of the PE side.

Figure 5. Dependence of the contact angle of the PA/PE sample on the irradiation dose by fast electrons of the PA side.

4. Conclusion

In studying the structure of the polymer packaging PA/PE as a percentage of 20:80 film before and after irradiation by 5 MeV electrons doses of 3 to 20 kGy significant changes in the samples does not occur (there is little change in the structure of the material). Infrared spectroscopy showed that the irradiated sample PA/PE fast electrons in the PA-layer degradation occurs, and PE-layer is cross-linking between molecules with the formation of oxygen bridges. This is confirmed by the study of wetting contact angle where there is an increase in hydrophilicity of PE-layer. The values of the wetting contact angle in the PA-layer have practically not changed. Hence the degradation is insignificant. However, the findings are preliminary and require accumulation statistics.

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