Increase the strength characteristics of polymer films by radiation graft polymerization

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Abstract. The possibility of increasing the strength characteristics of polymer films based on polyethylene and polyamide by radiation graft polymerization was investigated. Two methods of graft polymerization (direct method and the method of polymer mixtures cross-linking) on the PMMA films surface were studied. The possibility of increasing the strength and elasticity of polymeric films by radiation modification of polymethyl methacrylate was shown.

1. Introduction

The work is devoted to studying the radiation graft polymerization of polymethyl methacrylate polymer films used for the medical devices manufacture, in order to increase their strength characteristics. The studies were conducted with using of ionizing γ-radiation Co^{60} at the facility RHM - γ - 20.

The graft polymerization is one of the most promising methods of modern modifications of various polymers and polymeric materials. The principal difference between the graft polymerization from the conventional type polymerization is a reaction initiation nature. The initiation of graft polymerization is carried out by active sites generated one way or another in the starting polymer macromolecules and not to monomer molecules or specially introduced into the initiator system [1, 2].

The radiation graft polymerization is based on the generation of active sites radical and ionic nature in the various polymers under the ionizing radiation influence followed by graft polymerization of various monomers (acrylates, acrylamide, N-isopropylacrylamide, N-vinylpyrrolidone, etc.). The radiation graft polymerization solves the problem of obtaining modified materials with a predetermined set of processing and performance properties. The radiation output and the graft polymerization rate depends on both nature of the substrate and nature of the monomer. The radiation effects is affected by many factors such as the energy spectrum and intensity, exposure time during irradiation and thereafter, the temperature at which the irradiation and temperature, which arises in the material as a result of interaction with radiation, manufacturing technology of the samples and their subsequent treatment, the level of internal stress therein, the content and composition of impurity.

An advantage of radiation graft polymerization is its versatility, enabling to modify the polymers of virtually any nature, size and shape (film, fibers, powders, etc.). Each graft polymerization method involves processes, which are characterized by a variety state of polymer - monomer system [2-7].

The objects of study in this paper are selected polymeric films: polyamide film (nylon 6, h = 0,015 mm) and a polyethylene terephthalate film (PET, h = 0,012 mm) and high density polyethylene (HDPE, h = 0,06 mm).

Nylon is a synthetic polyamide obtained by polycondensation of adipic acid and hexamethylenediamine. It has properties such as heat resistance, flexibility, elasticity, high strength, dimensional stability and chemical agents. Nylon is cross-linked by radiation. Tendency to crosslink was shown under such changes, as a reduction in the solubility, increasing temperature resistance, etc. [8]. Nylon is not soluble in most organic

solvents, it does not give the effects of mild acids, alkalis and salt water, which allows its use in medical devices.

Polyethylene is a plastic physiologically neutral material. It has low vapor and gas permeability, does not react with alkali of any concentration and solutions of any salt, resistant to gasoline, water, oil. Different branching degree of the polymer chain polyethylenes of high (LDPE) and low pressure (HDPE) determines the difference between the properties of these materials. Exposure to radiation on polyethylene leads to increase its tensile strength at room temperature until the irradiation dose approximately equal 10 Mrad; with further increasing of the radiation dose on the tensile strength starts to decrease slowly. Elongation at break also increases slightly and then decreases sharply. Such decrease of the elongation at break due to increased crosslinking density are also found in many other polymers [9-11].

Polyethylene terephthalate is a polyester, formed by condensation of ethylene glycol and terephthalic acid. It is characterized by high strength, resistance to abrasion and multiple strains in tension and bending and are relatively resistant to the action of light, x-ray, gamma - rays [12, 13]. The predominant process during irradiation is stitching.

Solving the problem of the polymeric materials hardening is related to the search for ways to improve the performance of products based on them, and, above all, health care products.

1. Results and Discussion

In the first stage of the work we investigated the possibility of polymethyl methacrylate (PMMA) grafting on the films surface. PMMA is approved for use in products for implantation into the human body. As is known from the literature, PMMA grafting to polymer fibers (films) under certain conditions of synthesis leads to raising their strength characteristics [14-16].

Two methods of radiation graft polymerization was investigated in this work: method of polymer blends cross-linking and direct method of graft polymerization [17].

The graft polymerization process was performed in two stages: in the first stage polymer film was placed in a 1% solution of polymethyl methacrylate in methyl methacrylate (MMA) for 20 minutes, then extracted, dried from monomer and exposed γ-irradiation Co^{60} in an inert atmosphere with absorbed dose 25 - 157 kGy at 40 ° C. After irradiation, the film was washed in MMA and dried. The film tensile strength (σ, MPa) and elongation at puncture (deformability - ε, %) was determined on a tensile testing machine RFI - 30.

The calculation of the deformation-strength characteristics was conducted by the formulas:

$$\sigma = k_\sigma \frac{p}{hd}, \text{ MPa} \quad (1)$$

$$\varepsilon = k_\varepsilon \frac{l}{d} \times 100, \% \quad (2)$$

where: k_σ = 1,1 and k_ε = 2,2 – normalization coefficients, depending on the diameter of the indenter (lancing device); P - load at which the sample breaks, kg / cm^2; h - sample thickness, in millimeters; d - diameter of the working area (4 mm); l - elongation to break (puncture), mm.

The PMMA re-polymerization was carried out at once grafted films. 7 steps PMMA grafting were performed for each film. The test results of radiation-modified PMMA (by the method of crosslinking polymer blends) the polymer films are shown in Figures 1 and 2.

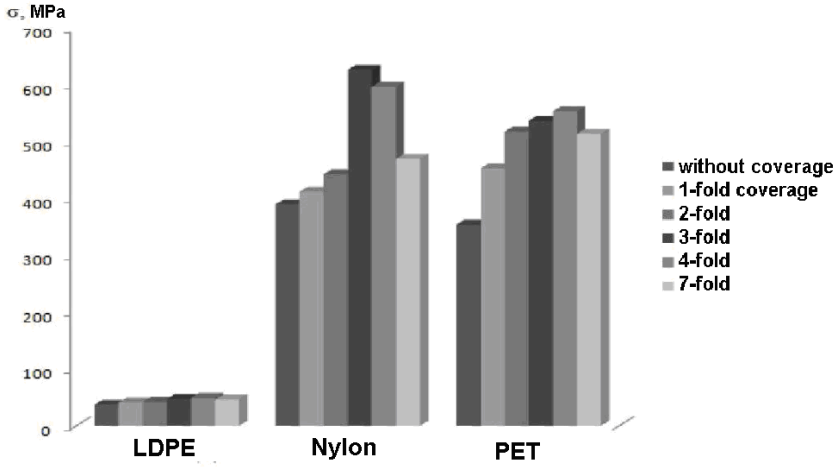

Figure 1. Tensile Strength of polymer films, modified by radiation crosslinking PMMA polymer blends at break when tested at a puncture.

The results show increase film strength in selected conditions of modifying. As it is seen in Figure 1, with triple vaccination PMMA polyamide film on its tensile strength increased by over 50%. The same increase was also noted for the strength of the PET film but quadruple grafting. Changes in film strength of LDPE under these conditions of the grafting polymerization insignificant. Increasing the multiplicity of the covering to 7 reduces the strength characteristics of the films, which may be related:

1 – with increasing thickness of the grafted PMMA layer, properties which at some point begin to dominate vaccination properties of the film itself;

2 – a polymethylmethacrylate destruction at high doses (PMMA polymer is advantageously degraded);

3 – with an increase in crosslink density in the substrate under the action of radiation which is to "overcure" stage leads to structural changes in the film itself.

Change in the deformability of the films studied by grafting PMMA by crosslinking polymer blends is shown in Figure 2.

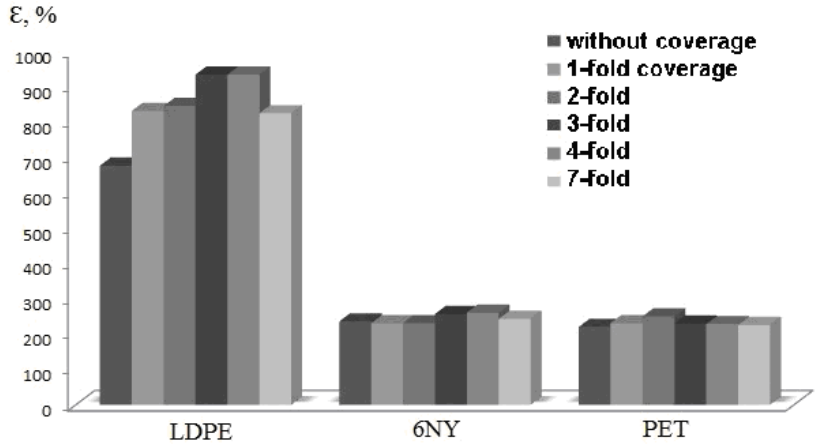

Figure 2. The deformability of polymer films modified PMMA by radiation crosslinking polymer blends during the test to rupture at a puncture.

With this method of grafting a polyethylene film for an increase in elasticity of up to 38% at 4.3 times of the coating. For polyamide and polyethylene terephthalate films elasticity remains virtually unchanged.

Modifying polyamide film "Nylon 6" and PET film held by direct graft polymerization method using an excess of methyl methacrylate monomer (MMA). LDPE film is unstable in MMA under the influence of

ionizing γ - radiation. The test film images were exposed in MMA monomer at 40 ° C at a total absorbed dose of radiation 18 kGy, with the suppression of the homopolymerization process. After reaction, the samples gain (ΔP, %) and the strength characteristics of the films was measured. The test results obtained films grafted "Nylon 6" and PET are shown in Table 1.

Table 1. Changes in the weight and strength of "Nylon 6" films and PET modified by the direct method of radiation graft polymerization.

Film	Absorbed Dose, kGy (Mrad)	Film weight gain ΔP, %	σ,MPa	ε,%	Δ σ, %	Δ ε,%
	0.0	-	449±31	286±39	-	-
Nylon 6	18 (1.8)	4	699±54	347±82	56	21
	0,0	-	387±57	330±1	-	-
PET	18 (1.8)	2.5	475±23	275±1	22	-15

The data in Table 1 shows that carrying out a direct reaction in the monomer graft polymerization at an absorbed dose of 18 kGy results in increased strength both test films. The most significant hardening obtained for the film "Nylon 6" (vaccinated 4% PMMA). Formability increases with rising the strength for the polyimide film, while the PET film strength decreases with increasing the elasticity. In addition, the increase in strength to PET is almost twice less than that of the polyamide film 6NY. This can be explained by the fact that the graft to polyethylene terephthalate require higher absorbed doses than for grafting to the polyamide. This is due to the dissipation of radiation energy polyester benzene ring. A further increase of the absorbed radiation dose in the system of a polymer film - the monomer leads to deformation of the film due to the strong growth of the grafting to the surface layer of PMMA films.

Modification of study PMMA polymer films in the process of radiation grafting confirmed changes in the IR - spectra: in the area of 1730 cm-1 band appears, characteristic of an ester group of methyl methacrylate [18]. As an example of Figure 3 shows the spectra of LDPE film precursor film and the film with a single or double coated PMMA polymer blends by crosslinking.

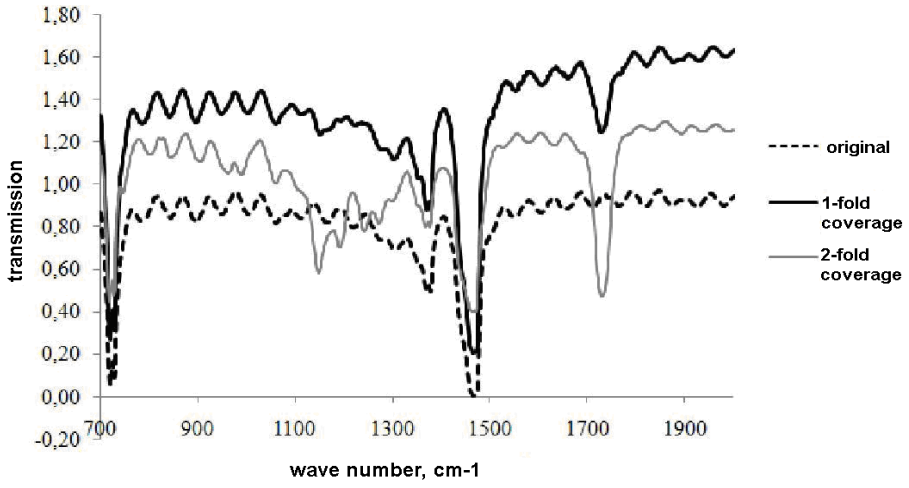

Figure 3. IR spectra of LDPE films, original and modified by PMMA.

2. Conclusion

Comparing the results obtained in this study during the radiation-chemical grafting to the polymer PMMA film, it can be concluded that the method for crosslinking polymer blends of polymeric materials studied most versatile and effective in terms of increasing their strength properties. In addition, each substrate requires an individual approach when choosing a radiation graft polymerization conditions.

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