STUDY OF MECHANICAL PROPERTIES OF THE COMPOSITION BASED ON LOW-DENSITY POLYETHYLENE MODIFIED WITH CARBON NANOTUBES

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Abstract

The composition and concentration of carbon nanotubes leading to a significant improvement in the electro-physical properties of low-density polyethylene (LDPE) of 10803-020 grade have been experimentally determined. Modified multi-wall carbon nanotubes (MWCN) were used as modifying additives. The difference of developed LDPE nanocomposite was that for the first time a small amount of carbon nanotubes was introduced into the LDPE, which varied within the range of 0.01–0.1 % wt. It was found that the content of 0.05 % wt. of carbon nanotubes in the composition of low-density polyethylene (LDPE + 0.05 % wt. of NC) significantly increased its electric strength.

The temperature dependences of dielectric loss tangent (tg σ), specific volumetric resistivity (ρ V) and permittivity (ϵ), as well as the kinetics of physical and mechanical changes in them under the influence of electric discharges in the air and UV irradiation were studied. Specific volumetric resistivity significantly increases in the optimal LDPE nanocomposite and dielectric loss tangent is reduced, i.e. a good correlation is observed between these characteristics. It is shown that the addition of carbon nanotubes in an amount of 0.05 % wt. significantly increases its resistance to the effects of electric discharges and UV irradiation.

Based on the experiments, it was concluded that the observed improvement in the dielectric properties of the LDPE film after the introduction of 0.05 % wt. of carbon nanotubes into its composition is associated with a change in the supramolecular structure of the LDPE.

Keywords: LDPE, carbon nanotubes, permittivity, UV irradiation, specific volumetric resistivity

I. Introduction

The development of science and technology requires the creation of new materials, which is one of the most important areas of modern physics [1-6]. In recent decades, the use of various types of nanomaterials has opened up new opportunities in many industries, with the oil industry being particularly noteworthy [7-10]. Polymer nanocomposites, due to their high characteristics, low weight, low cost and ease of processing, can be used as structural and insulating materials, as sealants, thermal insulation, binders in temperature-regulating coatings, seals, and reinforcing materials. Currently, polyolefin-based nanocomposites are used in the aviation and shipbuilding industries, as well as in mechanical engineering, energy, electronics, electrical engineering, radio engineering, transport, construction and other industries [11-13]. Various methods are known for creating compact, cheaper and light devices using polymer composites based on carbon nanotubes.

Reducing the filler size to the nano-range allows significantly decreasing its content in the polymer volume, and at the same time to achieve a significant improvement in operational characteristics due to the appearance of additional mechanisms of interaction of the polymer matrix with nanoparticles. Polyethylene differs from other thermoplastics by a very valuable set of properties.

Polyethylene products have high strength, resistance to aggressive environments and radiation, they are non-toxic, and have good mechanical and dielectric properties. Polyethylene is processed by all known methods for thermoplastics [14, 15].

It is known [16-18] that the effect of partial discharges in the air on polymers at room temperature is accompanied by the processes of oxidation, destruction and cross-linking of macromolecules, an increase in dielectric losses, a decrease in breakdown voltage, electrical and mechanical durability, as well as erosion of the polymer surface.

By using fillers based on various types of nanoparticles, it is possible to obtain polymers that combine traditional and new quality characteristics that at first glance seem mutually exclusive. This is extremely useful in cases when it is necessary to simultaneously provide transparency and flexibility of the material, a certain degree of impact resistance and rigidity, physical, insulating characteristics and conductivity.

The aim of this study is to develop a polymer nanocomposite based on LDPE with the additives of carbon nanotubes to obtain materials and products with the improved dielectric and mechanical properties, good heat resistance, as well as to minimize the rate of film ageing during operation.

II. Materials and experimental methods

Low-density polyethylene (LDPE) of 10803 grade was chosen as the object of the study, and modified multi-wall carbon nanotubes (MWCNT) were used as additives. Additives in the amount of 0.01-0.1% wt. were introduced into the original raw LDPE by mechanical melt-blending, which is widespread due to its obvious simplicity and ease of industrial development. To prepare films by hot pressing from blanks obtained in a casting machine, a manual electrically heated hydraulic press PG-60 was used. The calculated amount of MWCNTs was loaded into a polished flat mold in the form of 0.1-mm thick gasket. A fluoroplastic film (foil) was used to prevent adhesion. The mold was heated to 140-150°C. After reaching the required temperature, the mold was compressed under a pressure of 150 atm. After cooling the mold, the films were removed. Samples were made from the resulting 60-80 μ m thick films to determine the physical, mechanical, electrical and optical properties.

The homogeneity of the film was determined by measuring the film thickness over the entire area. The film thickness was determined using an N3B-2 optical thickness gauge and a micrometer. The arithmetic mean of 10 measurements was taken as the sample thickness.

The results of multiple experimental studies of the mechanical, dielectric, optical characteristics and structural properties of the developed nanocomposite confirm the homogeneity of the MWCNT dispersion in the LDPE matrix.

Installation for the determination of the short-term electrical strength $E\pi p$ and lifetime τE , i.e. the time elapsed from the moment of application of an electric field to the sample until its breakdown, at different values of the voltage E was used.

The impact of electric discharges on polymer dielectrics was carried out in a test cell of asymmetric type. The cell is a system of metal electrodes, between which the studied polymer film was placed. A smooth stainless steel plate measuring 180x130 mm (the plate surface was nickel-plated on one side) was taken as the bottom electrode. The studied polymer film, before and after preliminary stretching according to the applied method, was tightly stretched onto this plate, which served as a grounded electrode. To obtain an air gap of constant thickness between the upper electrode and the polymer film, 1.5-mm thick glass spacers were placed along the edges. High voltage of industrial frequency from the AII-70 device was applied to the cell electrodes.

UV radiation was supplied by a DRSh-500 lamp. The DRSh-500 mercury-quartz lamp is a spherical flask made of quartz glass. The DRSh-500 lamp is a powerful, concentrated source of radiation in the visible and ultraviolet parts of the spectrum. The lamp operates in a limited volume (casing), provided that the dimensions of the casing and its ventilation conditions are such that the air temperature at a distance of 60 mm from the walls does not exceed 2500C

A 50 μ m thick sample, attached to a duralumin frame with a holder, is fixed on a tripod. UV rays are directed to the center. The distance from the source to the sample is 250 mm. A distance of 250 - 200 mm increases the effect of UV irradiation (ageing).

UV rays hit the sample at a right angle. The experiment was conducted at room temperature (200C). The experiment mode is as follows: the lamp is clamped using an inductor with a sparking distance 15-20 mm. The nominal voltage on the lamp is 70 V, the current - 7.5 A. In this case, the resulting nominal luminous flux is 22500 lm. The duration of the sample' irradiation is 15 and 30 hours.

III. Results and discussion

Fig. 1 shows the dependence of the short-term electrical strength of LDPE on the content of MWCNTs: LDPE + 0.05 % wt. MWCNTs, LDPE + 0.07 % wt. MWCNTs and LDPE + 0.1% wt. MWCNTs at room temperature.



Figure 1: Change in the electrical strength of the LDPE nanocomposite depending on the mass percentage of the MWCNT additive

It is evident from fig. 1 that with an increase in the weight % of MWCNT, electrical strength of polymer increases, and the maximum value of *E*pr is achieved with the introduction of 0.05 % wt. of

MWCNT into the composition of LDPE. With a further increase in the MWCNT content to 0.1 weight %, a sharp decrease in electrical strength is observed. Experiments have shown that with the introduction of the optimal (0.05 % wt.) content of MWCNT into the composition of LDPE, its electrical strength increases from $14 \cdot 10^{-7}$ to $16 \cdot 10^{-7}$ V • m⁻¹, i.e. by an order of 20%.

A good correlation is observed when studying the dependence of the specific volumetric resistivity (ρ_v), dielectric loss tangent (tg σ) and permittivity (ϵ) on the nanocarbon content at room temperature, which is shown in the table 1. Values of the electrophysical properties of LDPE and its nanocomposites are given in table 1.

It is evident from the table that ρ_v , tg σ and ε of LDPE are also sensitive to the introduction of the MWCNT additive, and the content of MWCNT - 0.05 % wt. is also optimal here, since it ensures the greatest stability of electrical properties in comparison with both the original LDPE and LDPE with other additive content.

Nº	Materials	Properties			
		Ed 10-7,	tgδ	Qv (Ohm∙m)	ε
		V ⁻ m ⁻¹	f=kHs, t=20°C	t=20 °C	
1	LDPE-108 (original)	14	4,5.10-4	1.1015	2.4
2	LDPE-108+0.05% wt. of MWCN	16	3.10.4	1.1016	2.1
3	LDPE-108+0.07% wt. of MWCN	10	4.10-4	1.1012	2.3
4	LDPE-108+0.1 % wt. of MWCN	5	5.10-4	1.108	2.6

Table 1

Thus, the detected increase in the electrical strength and stability of the LDPE nanocomposite can be related to the structural features of the specified additive, which ensures dense packing of macromolecules during film formation [19, 20].

It is known that in order to determine the possibility of using a polymer as insulation and to obtain information about the thermal motion and molecular structure of the polymer, it is necessary to know not only the value of the dielectric characteristics (tg σ , ρ_v and ε), but also the nature and quantitative characteristics of their dependence on temperature, electric field, UV irradiation and other factors [21-23].

Figure 2 shows the temperature dependences of the dielectric loss tangent ($tg\sigma$) of LDPE (without additives) and nanocomposites on its base before and after electrical ageing under the influence of discharges in air.



Figure 2: Temperature dependences of the dielectric loss tangent of the initial LDPE film and its optimal nanocomposite before and after electrical ageing under the action of discharges in air at $U_{age} = 7$ kV and $t_{age} = 5$ hrs on the electric field strength: 1.2 - LDPE + 0.05 % wt. MWCNT before (1) and after (2) ageing; 3.4 - LDPE before (3) and after (4) ageing

From the obtained experimental data (fig. 2) it is evident that in all temperature ranges of the test the introduction of the MWCNT additive in the amount of 0.05% wt. into LDPE leads to a decrease in the dielectric loss tangent (curve 1) comparing to LDPE without additive (curve 3). From the temperature dependence of the dielectric loss tangent it follows that under the action of discharges on LDPE films without the additive there is a significant increase in the maximum of dipole-segmental losses (in the region of 323-353K) (curve 4). At the same time, the introduction of the proposed MWCNT additive in the specified amount into LDPE prevents processes leading to its electrical ageing, and thus reduces the maximum of dielectric losses in this temperature range [curve 2].

It is known that under the influence of electric discharges in the air, oxidative destruction occurs [22]. As a rule, oxidative destruction in polymers is usually accompanied by the formation of polar groups in them, which is an independent movement of chain segments. The maximum value of $tg\sigma$ is determined by the number of monomer links (segments) and polar groups formed in the polymer [24, 25].

In the temperature dependence of $tg\sigma$ of the LDPE film and its nanocomposite after UV irradiation in air, the experimental data of which are shown in fig. 3, an insignificant change in the value of dielectric losses in the original LDPE film is observed (curve 2).



Figure 3: Temperature dependences of the dielectric loss tangent of the LDPE film and its optimal nanocomposite before and after UV irradiation n air at t_{irr} = 15 hrs. 1, 2 - LDPE before (1) and after (2) irradiation; 3, 4 - LDPE + 0.05 % wt. of % NC before (3) and after (4) irradiation

However, when introducing the optimal amount of nanocarbon into the LDPE composition, the value of $tg\sigma$ after UV irradiation remains practically unchanged (curve 2). The experimental results allow us to assume that the addition of MWCNT reduces the change in $tg\sigma$ of the LDPE film under the influence of electrical discharges and UV irradiation [26]

For real polymeric materials used as dielectrics for electrical and radio insulation, the specific volumetric resistivity depends on their composition, as well as on molecular structure and supramolecular structure of the polymers. Temperature, electric field, the effect of ionizing radiation and various additives also have a significant effect on the specific volumetric resistivity of polymeric dielectrics.

Figure 4 shows the results of study of the temperature dependence of the specific volumetric resistivity of the LDPE film and its optimal modification before and after electrical ageing under the influence of discharges in air.



Figure 4: Temperature dependence of logarithm of the specific volumetric resistivity of the LDPE film and its optimal modification before and after electrical ageing under the influence of discharges in air at $V_{age} = 7 \text{ kV}$, $t_{age} = 5 \text{ hrs. } 1, 2 - LDPE + 0.05 \%$ wt. of NC before (1) and after (2) ageing; 3, 4 – LDPE before (3) and after (4) ageing

As can be seen from fig. 4, ϱ_v of the original sample of LDPE film decreases monotonously with temperature increase. After the introduction of the specified additive, ϱ_v value of the LDPE film increases (curve 1).

After the impact of electric discharges in air, the dependence $lg \rho_v = f(T)$ undergoes significant changes for both the original LDPE and the nanocomposite. However, the addition of MWCNT in an optimal amount (0.05 % wt.) significantly slows down the intensity of their decrease during electrical ageing (curve 2) more than for the initial LDPE (curve 4).

Fig. 5 shows temperature dependence of the specific volumetric resistivity of the LDPE film and its optimal nanocomposite before and after UV irradiation.

As can be seen from Fig. 5, the specific volumetric resistivity ρ_v of the modified LDPE after UV irradiation changes in the same way as before irradiation.



Figure 5: Temperature dependence of logarithm of the specific volumetric resistivity of the LDPE film and its optimal modification before and after UV irradiation in air at $t_{irr} = 15$ hrs. 1, 2 - LDPE +0.05 % wt. of NC before (1) and after (2) of the irradiation; 3, 4 – LDPE before (3) and after (4) the irradiation

However, as can be seen from Fig. 5, as well as from the dielectric loss tangent, with prolonged exposure to UV irradiation, the specific volumetric resistivity of the LDPE-based nanocomposite decreases slightly (curve 2), while for the LDPE without additives it decreases significantly (curve 4).

Probably, the temperature trend of electrical resistance and the dielectric loss tangent before and after electrical ageing and UV irradiation in the air, chemically active substances (ozone, nitrogen oxides, etc.) interacting with macromolecules cause the appearance of a number of new low-molecular groups and compounds, aldehydes, acids, alcohols, ethers, etc. According to [26], these groups can diffuse into the volume of the sample and thereby contribute to the improvement of the dielectric characteristics of the polymer material.

Thus, the improvement of ρ_v and $tg\sigma$ established by us before and after electrical ageing and UV irradiation with the introduction of the proposed MWCNT additive in the optimal amount is the result of formation of optimal structures in the polymer.

In the same samples, the temperature dependences of the dielectric permittivity (ϵ) were studied, the results of which are shown in Fig. 6.

The results of the studies showed that in the entire studied temperature range (283-373k), the dielectric permittivity of LDPE and its nanocomposite (LDPE + 0.05 % wt.) practically does not change with temperature change. From Fig. 6 it is evident that ε increases approximately equally in the entire studied temperature range, therefore, to clarify the dependence on the test time, it is sufficient to study the change in ε at only one temperature (300 K).



Figure 6: Temperature dependence of dielectric permittivity (ϵ) of LDPE film and its optimal nanocomposite. 1 – PE (without additive), 2 - LDPE + 0.05 % wt. of MWCNT

Thus, the detected increase in the dielectric properties and stability of LDPE can be associated with the structural features of said nano-additive, which ensures dense packing of macromolecules during film formation [26]. Dense packing of macromolecules in the structure of the developed nanocomposition leads to increased intermolecular interactions, which contribute to a significant slowdown in the rate of oxidation-destructive processes during electrical ageing and UV irradiation.

IV. Conclusion

The possibility of obtaining a nanocomposite for electrical insulation purposes based on the low-density polyethylene of grade 108 03 - 020 with MWCNT additives was established experimentally. The range of change in the filler's amount was experimentally substantiated, i.e. the optimal composition of the studied nanocomposite for improving operational characteristics was determined. The developed LDPE nanocomposite is distinguished by the fact that for the first time a significantly small amount of carbon nanotube additives was introduced into the LDPE composition, which varied within the range of 0.01-0.1 % wt. It was found that with an increase of MWCNT additives content in the LDPE composition, the electrical strength significantly decreases, and a positive effect is observed only at 0.05 % wt. of the said additives. It was established that the developed LDPE nanocomposite has a relatively increased resistance to the effects of electrical discharges and UV radiation, which opens up wide areas of application in various industries, especially in the oil industry.

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