INFLUENCE OF UV IRRADIATION AND BIOFILLERS ON THE IR SPECTRUM OF LDPE

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The paper presents the results of a study of the IR spectra of high-pressure polyethylene (LDPE), modified with fish bone (*FR*) composites *LDPE*+xvol. % FB taken on a Fourier spectrometer, in the frequency range of $4000-400cm^{-1}$. It was found that the introduction of fishbone modifiers into HDPE in the optimal amount does not contribute to the appearance of new intense absorption bands, i.e., does not change the overall structure of the composites. This means that the fishbone modifier is process compatible with *LDPE*. The introduction of fish bone filler into LDPE promotes a noticeable change in the intensity of the formation of C=O groups (1720 cm^{-1}), which is a measure of the oxidative degradation of polymer chains. The results show that the introduction of fish bones into low-density polyethylene structures contributes to the formation of an optimal and stable structure, which, in turn, prevents the intense development of the photooxidative process caused by ultraviolet irradiation.

Keywords: UV irradiation, biofillers, LDPE, IR spectra, fish bone

INTRODUCTION

At present, in many areas, ranging from household appliances to special-purpose equipment, electret microphones, dosimeters, pressure sensors, air filters, electromechanical converters, etc. Polymer composite materials are widely used [1,2]. The scope of application of modified polymeric materials with a certain combination of properties inherent in a particular material is expanding. As a rule, modifiers change the supramolecular structure, which largely determines the physicochemical and mechanical properties of the polymer and composites based on them. The nature of the influence of additives on the supramolecular structure and properties of the polymer is determined simultaneously by the amorphous and crystalline phases. It is known that the nature of structure formation in composites also depends on the external conditions in which the formation of supramolecular structures occurs. Fillers play the role of artificial crystallization nuclei, which leads to a change in the properties of the material. Thus, by changing the type of fillers, it is possible to control the properties of polymer-based composites.

The main reason for supramolecular formation is the superiority of intramolecular interaction forces between groups of atoms that make up a polymer macromolecule over intermolecular interaction forces and the high flexibility of macromolecules. Based on the above material and the role of the filler in the study of composites, we chose fish bones as a filler, which have stable physical parameters [3], which have a huge raw material base in nature. We assume that these distinctive properties of this material should be reflected in the properties of biopolymer composites.

In recent years, much attention has been paid to obtaining new composite materials modified with additives of biological origin [4]. In this direction, we and foreign researchers have obtained and studied biocomposites with various modifiers [5,6]. The study of the resistance of composite materials to external influences plays an important role in solving practical problems. External influences adversely affect the appearance, structure, and properties of materials and lead to significant material damage. Examples of environmental influences include solar radiation (ultraviolet radiation, visible light and x-rays). As you know, the sun's rays in one way or another negatively affect polymeric materials. Under the influence of radiation, the structure and interatomic bonds of polymers are destroyed, and these effects on macromolecules cause oxidation of the material, which, in turn, changes color and worsens mechanical and physical properties. In addition, other factors such as temperature changes, humidity, excess oxygen, and ultraviolet radiation further exacerbate the effects.

However, the ultraviolet rays contained in the sun's rays are more likely to affect the absorption of the material. Most polymers used in industry and in everyday life are subject to drastic changes under the influence of ultraviolet light; color changes; loses the brightness of its surface; cracks on surfaces; sometimes the material is completely destroyed. The rate of dissipation increases with the duration and intensity of the sun's rays. This effect is called ultraviolet aging of the material and refers to one of the types of polymer aging. [7, 8]. It is known that IR spectroscopy is widely used in structural analysis. The IR spectrum is used as a source of primary information about a compound of a known nature, while only individual features of the structure are revealed, which make it possible to outline a rational plan for further research. Infrared spectroscopy is currently used by organic physicists most often due to its versatility, the possibility of direct and independent determination of a number of important functional groups and structural fragments in small amounts of the studied substance in any of its state of aggregation and without any significant limitation of physical and chemical properties.

In the light of the foregoing, this work is devoted to obtaining new composite materials with fillers of biological origin and studying the effect of ultraviolet radiation on their structure.

EXPERIMENTAL TECHNIQUE

To obtain biocomposites, high-pressure polyethylene (LDPE) grade M-158 was used as a matrix, and fish bone (FB) was used as a filler. To obtain filler powders, at the beginning, the fish bones were thoroughly cleaned and dried by gradually increasing the temperature from room temperature to 50° C, keeping at this temperature for 24 hours, then the fish bones dried in this way were ground into powder in a special mill. The content of the biofiller in the composites ranged from 1 to 7 vol.%. Composites were obtained from a homogeneous mixture of powders of matrix components and filler using a heated press at a temperature of 420K and a pressure of 15*MPa*. Hardening crystallization mode-rapid cooling of samples in a water-ice mixture.

Irradiation of the samples with UV rays was carried out using a DRSh-500 illuminator. The main parts of the illuminator are a spherical mercury-quartz ultrahigh-pressure lamp of the DRSh-500M type and a hemispherical consul. Mercury-quartz lamp DRSH-500 is a powerful, concentrated source of radiation in the visible and ultraviolet parts of the spectrum. The lamp operates in a limited volume (casing), the dimensions of the casing and the conditions for its ventilation are such that the air temperature at a distance of 6cm from the walls does not exceed 523K. Samples with a thickness of $40\mu m$ are attached to a duralumin frame using a holder fixed to a tripod. UV rays are directed towards the center of the film. The distance from the source to the sample is 25cm. UV rays hit the sample at a right angle. The experiment was carried out at room temperature with water cooling. The mode of the experiment is as follows: the lamp is ignited using an inductor with a spark length of 15-20mm. Rated voltage on the lamp 70V, current 7.5A. In this case, the resulting nominal luminous flux is 22500lm. The brightness in the center of the column is 150Mnt. The duration of the irradiation of the sample is 15 hours.

To study structural changes in biocomposites, we used the IR spectroscopy technique based on measuring the transmission spectra of translucent films. The spectra were taken on a Varian 640 *FT-IR IR*-Fourier spectrometer in the wavelength range $4000-400cm^{-1}$. Samples for research were obtained in the form of thin films $1-10\mu m$ thick and $8x30mm^2$ in size by step-by-step pressing under a pressure of $6\cdot10^4 N/m^2$ at room temperature using a special Varian mold.

RESULTS AND DISCUSSION

In fig.1. *IR* spectra of pure low-density polyethylene are given. As follows from fig.1. on the IR spectrum at 700, 1367, 1500 and $2900cm^{-1}$ clearly defined maxima are observed, and at 2150 and $2380cm^{-1}$ there are clear minima.



Fig.1. IR spectrum of pure low density polyethylene



Fig.2. IR spectra of biocomposites LDPE + x vol% FB; (where: I - x = 3, 2 - x = 5, 3 - x = 7) in the frequency range $4000 - 400 \text{ cm}^{-1}$

The results of the study of the *IR* spectra of composites modified with fish bone are shown in fig. 2.a. The studies were carried out in composites with fillers 3; 5; 7vol% *RK*. As follows from fig. 2. maxima appear on the *IR* spectrum of biocomposites at 719, 728, 1367, 1467 and $2900cm^{-1}$. With an increase in the volume content of the filler, additional maxima appear in the *IR* spectrum at 2330 and $560cm^{-1}$.

The IR spectra of the same biocomposites irradiated with UV rays for 15 hours were studied. As follows from fig. 3, no significant changes are observed in the IR spectrum of biocomposites after irradiation, only at $3960cm^{-1}$ a noticeable maximum appears, while the remaining maxima are preserved.

A comparison of the *IR* spectra of films and composites based on *LDPE* shows that the added amounts of fillers do not contribute to the appearance of new absorption bands; practically do not change the shape of their IR spectra. This gives us reason to assume that these modifiers in the proposed amount

are technologically compatible with *LDPE*, i.e., they mainly affect the physical structure of *LDPE*.

In all studied composites of LDPE+x vol% FB with a frequency range of $1460-1466cm^{-1}$, bands are clearly defined, which, in combination with unresolved weak bands at frequencies of 1644- $1367 cm^{-1}$, are a characteristic feature of the aromatic ring. The assumption of the presence of an aromatic ring is confirmed by strong absorption in the frequency range of $3000-2800cm^{-1}$, the region of stretching vibrations of hydrogen sp² with hybrid carbon atoms. The compound also contains alkyl radicals (side chains on the aromatic ring), as evidenced by strong absorption in the range of 2800- $3000cm^{-1}$, as well as bands of corresponding bending vibrations at $1467-1362cm^{-1}$. In the region of 2000- $1800cm^{-1}$, there are weak absorption bands, which are important for determining the number and position of substituents.



Fig.3. IR spectra of biocomposites LDPE+x vol% FB; (where: 1-x=3, 2-x=5, 3-x=7) in the frequency range 4000- $400cm^{-1}$ irradiated with UV rays for 15 hours.

A very strong band of out-of-plane bending vibrations of aromatic hydrogen at $730cm^{-1}$ is also characteristic of ortho-substituted benzene derivatives.

The spectrum does not show characteristic bands of hydrogen-containing functional groups OH, NH, SH.

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