

Derivatografic Analysis And Thermophysical Properties Of Composites With Fillers Of Biological Origin

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Abstract—In the presented work, using fillers of biological origin - fish bone and 1% Al_2O_3 nanoparticles, bionanocomposites of the LDPE + x vol% FB + 1% Al_2O_3 type were obtained on the low-density polyethylene matrix. From a homogeneous mixture of LDPE powder, fish bone and aluminum nanoparticles, using a manually heated press at a temperature of 120°C and a pressure of 15MPa. Samples were subjected to differential thermogravimetric analysis. The study was conducted on the "Perkin Elmer" STA 6000 and NETSCHE DSC 204 F1 Phoenix derivatographs. The samples were heated in the temperature range 60-1800C in a platinum crucible at a rate of 10 deg / min. The LDPE + x vol% FB composites and nanocomposites of the LDPE + x vol% FB + 1 vol% Al_2O_3 type were studied, where, x = 3; 5; 7 vol.%. Based on the results of differential thermal and derivatographic analysis, the active parameters of composites with fillers of biological origin were determined: changes in entropy, enthalpy, Gibbs energy, thermal melting energy, degree of crystallinity. It was found that with increasing volume content of the filler, enthalpy, activation and Gibbs energies, degree of crystallinity decrease. With a change in the content of the filler, the regular change in entropy is disturbed; composite with a filler of 5% FB has the highest entropy. The degree of crystallization of LDPE + x vol% FB composites was determined, and it was revealed that the degree of crystallization decreases by 33% with an increase in the volume content of the filler from 3% to 7%. It is shown that dispersed particles of fish bone affect all levels of organization of the LDPE structure and thus lead to complex character of

the kinetics of changes in the thermophysical properties of the filled material.

Keywords— *thermogravimetric and differential-thermal analysis, nanocomposites LDPE + x vol.% FB+ 1vol.% Al_2O_3 , low density melting temperature, heat of formation, activation energy, change of entropy, enthalpy, Gibbs energy, the degree of crystallinity, composites LDPE + x vol.% FB.*

I INTRODUCTION

The rapid development of electronic technology require enhanced functionality already known solid materials, including insulators, and more in-depth research to identify new opportunities for their practical use. Progress in this field is defined by the special, including dielectrical properties of used materials. In this aspect the work aimed at improving the functionality of electronic devices and the search for new solutions in the practical field of information technology and converter equipment, in particular, to devices using active dielectric materials – composites. Obtaining the composites is accomplished by introducing into the polymer matrix the fillers of different origin [1-6]. The main advantage of the composite materials is that the materials and structures are created simultaneously and properties controlled by composition variation of material by the content of filler and matrix. The properties of composite depend on the filler material. In modern literature there are many works devoted to obtain and research of composite materials with various fillers [7-9]. Therefore, for obtaining new types of composite materials as filler are used materials of biological origin. Fillers of biological origin have several advantages: have a stable physical and chemical parameters have unlimited natural resources and their use should have a positive impact to the ecology of the planet. Properties and practical value of composites depends essentially from selecting of the filler. The objects of biological origin, such as bones, scales and skin of fish, 80% of which are composed of collagen,

already successfully used in food industry, medicine, cosmetics and other industries [10-12]. Expediency of use of the collagen is not in doubt, as by its nature of collagen - a protein of connective tissue. The unique physical and chemical characteristics inherent proteins that allow using collagen in different areas of human activity. From the collagen material can produce the membranes, monolayers and multilayer structures. In [13] shows how effectively can use piezoelectric properties of the scales and the bones of the carp fish, attaching to them the gold contacts, get a miniature generator alternative energy, which can be used for implantation of electronic monitoring devices and instruments of the body that control delivery of drugs into the body.

This paper is devoted to obtaining differential thermal gravimetric analysis and determination of physico-chemical parameters of composite materials in the matrix of low density polyethylene with fillers of biological origin - fish bone (FB) and aluminum nanoparticles.

II EXPERIMENTAL PART.

As the polymer matrix used low density polyethylene (LDPE) brands 15803-020, average molecular weight - 80,000, a melting temperature - 120°C, density - 932 kg/m³, the degree of crystallinity - 49,2%. The active particles of the filler used shredded fish bone. To produce filler - fish bones are cleaned and rinsed thoroughly with clean water, heated to a temperature of 50°C, kept at this temperature for 10 minutes to an hour depending on the size of the bones. After that bones are crushed to a size of 100 microns. Volumetric content of the filler biological origin in the studied composites ranged from 3 to 7%, and volume content of Al₂O₃ nanoparticles was 1%. Composites were obtained from a homogeneous mixture of filler powder and LDPE using a hand press heated at a temperature of 120°C and a pressure of 15 MPa. The crystallization mode - quenching-cooling of the sample in an ice-water mixture. Thus obtained film samples were approximately 200 microns thick. Differential Thermal Analysis (DTA) were carried out on derivatograph "Perkin Elmer" STA 6000 and NETSCHE DSC 204 F1 Phoenix. The samples were heated in the temperature range 60-180°C in a platinum crucible with rate of 10 K / min. Melting heat of composites was determined by the melting of area of original crystalline phase LDPE. The degree of crystallinity (K) was determined by the method of dividing the heat of fusion of studied composites on a heat of fusion LDPE, assuming the heat of fusion LDPE is $\Delta H = 286.7 \text{ kJ / kg}$ [14]. Changes in entropy and Gibbs free energy were determined from the experimental data of the specific heat and enthalpy change of composites according to the method described in [15].

III RESULTS AND DISCUSSION

The results of the thermogravimetric (TG) and differential thermal analysis (DTA) of the studied composites LDPE / FB presented in figures 1-2.

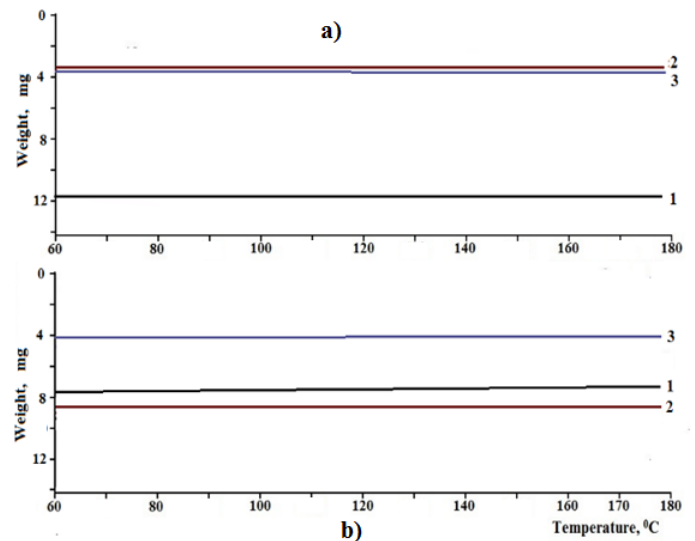


Figure 1. The thermogravimetric (TG) curves of composites LDPE+xvol.%FB (a) and LDPE+xvol.%FB +1vol.% Al₂O₃

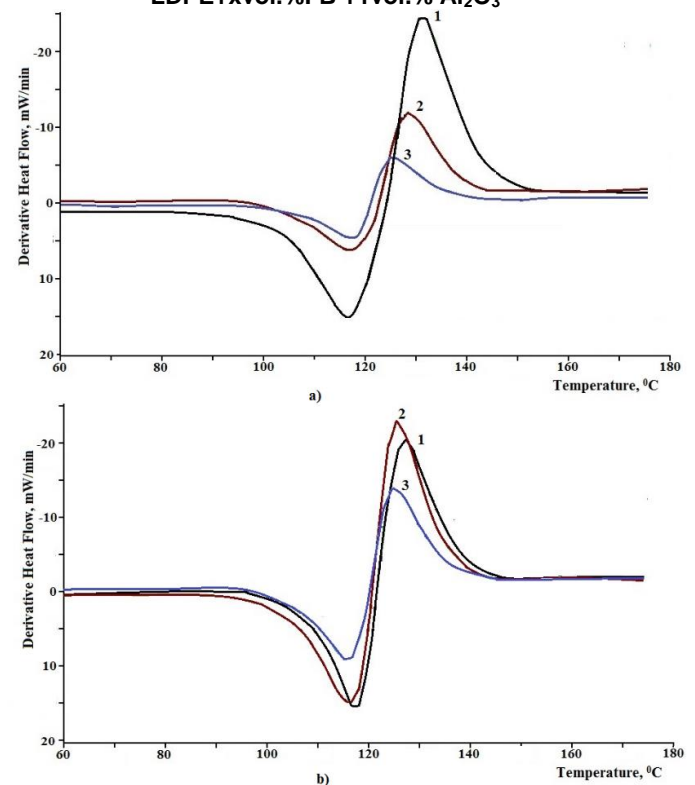


Figure 2. The differential thermal analysis (DTA) curves of composites LDPE+xvol.%FB (a) and LDPE+xvol.%FB +1vol.% Al₂O₃ (b)

Investigations were carried out on composites LDPE + x% vol.FB, where x = 3; 5; 7. As well as for the nanocomposites of LDPE + x% vol.FB + 1 vol.% Al₂O₃. According to TG analysis of a composite curve in the temperature range 60-180°C not observed weight loss, i.e. composite thermo-stable in the

temperature range 60-180°C. Similar studies were carried out for nanocomposites with fillers 3; 5 and 7 vol. % FB and nanoparticles 1% Al₂O₃. Note that for these composites in the temperature range 60-180°C weight loss is observed i.e. sample thermostable. (b).

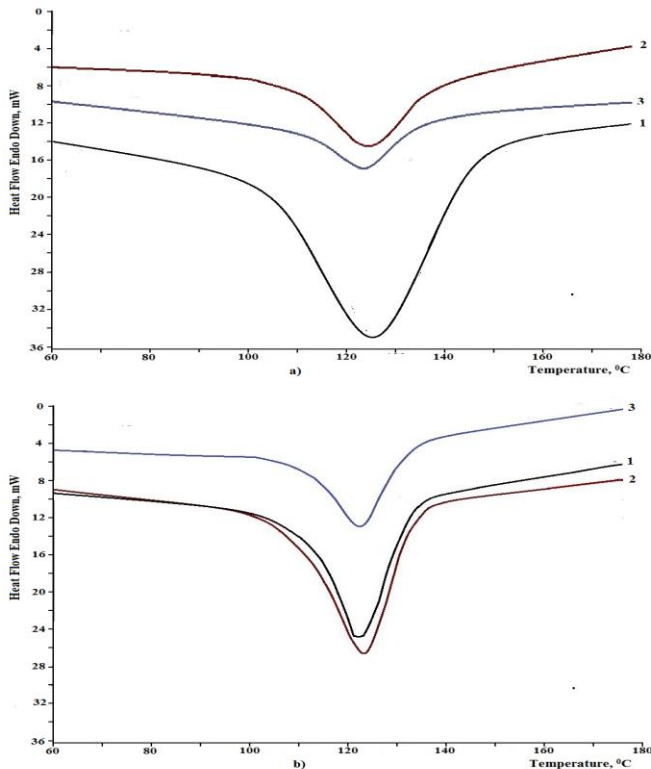


Figure 3. The differential scan calorimetry analysis (DSC) curves of composites LDPE+xvol.%FB (a) and LDPE+xvol.%FB +1vol.% Al₂O₃ (b).

As can be seen from Figure 2 (curve 1.), the DTA curve of composite with a filler 3 vol. FB% endo and exothermic effect are in 118°C and 134°C, and a single endoeffect detected in the DSC curve at 126,29°C (Figure 3a,curve 1). As follows for the DTA curve of composite 5 vol.%FB endo and exothermic effects are observed at temperatures of 118.8 and 131,6°C, (Figure 2.curve 2) and the only endothermic effect on the DSC curve (figure 3 a. curve 2) is observed at 126,81°C. In the DTA curve of composite

LDPE+7vol.%FB endothermic and exothermic effects are observed at 119.1 and 128,9°C, (Figure 2. curve 3) respectively, and the endothermic effect on the DSC curve at 123,98°C (figure 3.a,curve 3).

Results derivatografic and differential thermal analysis nanocomposites LDPE+x.vol.%FB+1 vol.% Al₂O₃ are shown in Figure 1b and 2b. As it follows from Figure 2b, on the DTA curve of nanocomposite LDPE+5vol.FB+1%vol. Al₂O₃ (curve 1),LDPE+5vol. FB+1%vol.Al₂O₃(curve2) and LDPE+7vol.%FB+1vol.% Al₂O₃ (curve 3) endothermic effects are observed at 118.8; 119.2; 119.3°C respectively, and the exothermic effects of these nanocomposites also observed at 129; 128.4; 129.1°C, respectively.On the DSC (Figure 3b.) depending observed a single endothermic effect at 124.73 °C for composite 3 vol.% FB (curve 1), while in the composite 5 vol.% FB the same effect was seen in 125,7°C (curve 2). For composite 7 vol.% FB on a DSC endothermic effect was observed at 124.86 °C (curve 3). As a result of differential thermal and derivatografic analysis were indirectly defined such active parameters as heat capacity, enthalpy change, energy, heat of fusion, the activation energy of composites with fillers of biological origin. The entropy change, Gibbs energy determined by the experimental data with the formulas:

$$\Delta S = \int \frac{C_p}{T} dT ; \Delta G_T = \Delta H_T - T\Delta S$$

Where, ΔS - The entropy change, ΔG_T - Gibbs energy ΔH_T - given entalpy change, T – temperature. The results of calculations are shown in Table. As shown in Table, with increasing volume fraction of the filler decreases the enthalpy, activation and Gibbs energies, degree of crystallinity. With the change of the filler content the regular change in entropy is broken, that is, composite filled 5 vol.% FB has the highest entropy. At the nanocomposites LDPE + x vol.% FB + 1vol.% Al₂O₃ parameters change as follows: with the increase of the filler content volume of fish bones the entropy and energy of activation increases.

Table. Thermal and physical parameters of composites LDPE+xvol.%FB and LDPE+xvol.%FB +1vol.% Al₂O₃.

Composites	The melting temperature, °C	Heat quantity, mC	Change of enthalpy, C/kg	Energy of activation, kC/mol	Heat capacity C/ kg°C	Changes in entropy, C/mol°C	Gibbs energy, C/mol°C	The degree of crystallization, %
3 vol.% FB	126.29	2070	174,948	0.1749	2,762	1914.473	-66830	61
5vol.% FB	126.81	585	149,394	0.1494	14,463	6702.197	-700512	52
7 vol.% FB	123.98	453	118,220	0.1182	11,093	5331.138	-542734	41
3vol.% FB +1vol.%Al ₂ O ₃	124.73	945	122,955	0.1230	5,378	2327.943	-167409	42
5 vol.% FB +1vol.%Al ₂ O ₃	125.70	1073	123,958	0.1240	11,231	5785.807	-603318	43
7 vol.% FB +1vol.%Al ₂ O ₃	124.86	569	136,518	0.1365	2,789	1307.244	-26704	47

Determined the degree of crystallization of composites LDPE+xvol%FB and it revealed that an increase in the

volume of the filler content from 3 to 7%, degree of crystallization be reduced by the 33%. And in the nanocomposites of LDPE + x vol.FB + 1% vol.% Al₂O₃ with the increase in volume filler content there is a slight increase in their crystallinity. In this case, occurs the amorphization crystalline phase of matrix whereby the melting point of composites decreases. In general, composites LDPE / FB with the increase in volume fraction of the filler occurs amorphization of the crystalline phase of the matrix. Analysis of the results thermophysical performance compositions LDPE with additive fishbone showed that these processes are due to structural changes in the matrix at the molecular and supermolecular levels occurring under the influence of various additives particle dispersion degree depending on the concentration of biological filler.

It should be noted that the thermal properties of composite LDPE+ 5 vol.%FB differ significantly from others. This is apparently due to the chemical addition of macromolecules to the surface of the fish bone particles. Such changes caused by the action of the solid particulate additives as artificial embryos structuring occurs when administered in a polymeric matrix of inorganic nature other additives.

Analysis of the results shows that the dispersed particles fishbone affect all levels of the organization structure of LDPE and thus lead to the complex nature of the kinetics of change of thermal properties of compounded material. The most significant effect on the properties of the particles have a fishbone in an amount of 5 vol.%, Which is probably due to the favourable conditions of the addition of polymer crystallization of macromolecules in the particles of additive and the formation of a partial netted structure of LDPE.

Conclusion

By the using experimental results of differential thermal and derivatografic analyses defined thermal parameters composites of biological origin, and revealed that with increasing volume fraction of filler of composites LDPE + x vol.% FB crystallinity is reduced and the degree of crystallinity of nanocomposites LDPE+x vol.% FB+1vol.% Al₂O₃ on the contrary increases.

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