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Physical and Mechanical Properties of Nanocomposites Based on High-Density Polyethylene and Refuse Burnout of Household Waste

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Abstract—The article presents the results of studying the structure and properties of composites based on high-density polyethylene and refuse burnout of household waste. The filler was refuse burnout with different particle sizes: 75–110, 300–500, and 1200–2000 nm. It has been shown that nanocomposites with a particle size of 75–110 nm have comparatively high physical and mechanical properties. Properties such as breaking stress, elongation, heat resistance, and melt flow rate were investigated. A theoretical analysis of the obtained experimental data based on modern ideas about the association between structure and properties is given.

Keywords: composites, polymer matrix, refuse burnout, viscosity, melt fluidity

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INTRODUCTION

As the applications of industrial polymeric materials in various fields of mechanical engineering, shipbuilding, aircraft engineering, military and space technology, etc., have expanded, the problem of improving their quality and performance has become more acute [1, 2]. Various techniques have been undertaken to modify their structure and properties by introducing mineral and polymeric fillers, plasticizers, stabilizers, lubricants, polymer–polymer mixing, chemical cross-linking, etc. [3, 4]. It is obvious that the synthesis of polymer materials with given properties for various technical directions is not always useful and effective. Therefore, a purposeful change in properties is given to large-tonnage polymers already directly during their processing. This raises not only the problem of obtaining a polymer material of the right quality but also the problem of reducing its cost. In this respect, the use of industrial waste as a modifier of industrial polymers has always been the focus of specialists in the field of processing and application of composite materials [5–7]. The problem under consideration becomes even more relevant if nanosized particles of refuse burnout are used as filler. This problem is relatively new and little studied.

To this end, this work focuses on the study of a complex of physical, mechanical, and technological characteristics of nanocomposite materials based on high-density polyethylene and refuse burnout of household waste.

EXPERIMENTAL

Industrial samples of high-density polyethylene (HDPE), as well as refuse burnout of household waste, were used as the object of research.

HDPE has the following properties: breaking stress—31.4 MPa, elongation—475%, melt flow index (MFI)—1.25 g/10 min, melting point—128°C, heat resistance—124°C.

As filler, we used refuse burnout of household waste obtained at 1200°C in thermal ovens of the Balakhan waste processing plant in the city of Baku [8].

Refuse burnout nanoparticles were obtained on an A-11 analytical device at a rotor speed of 30000 rpm.

The particle size of the refuse burnout was determined using an STA PT1600 Linseiz instrument (Germany); it was 75–110 nm, 300–500 nm, 1200–2000 nm. Of the three millings obtained, nanoparticles were samples of refuse burnout with sizes of 75–110 nm.

Composites based on HDPE and refuse burnout were prepared by mixing on rollers at a temperature of 160–170°C. After the HDPE was melted on the rollers for 8 min, the refuse burnout was introduced in portions. On the basis of the obtained polymer composite, plates with a thickness of 2 mm were pressed at a temperature of 190°C; the holding time under pressure was 30 min. Under a pressure of 90 MPa, the temperature of the pressed plate was reduced to 90°C.

The melting point was determined on a Q-1500d derivatograph, and the heat resistance was determined by the Vicat method on an HDT-Vicat instrument,

Table 1. Influence of the concentration and size of refuse burnout particles on the main physical and mechanical properties of composite materials (HDPE)

No.	Composition of composites based on HDPE + refuse burnout (rb)	Particle size of refuse burnout, nm	Breaking stress, MPa	Elongation, %	Melt flow rate, g/10 min	Vicat temperature, °C
1	HDPE	–	31.4	475	1.25	124
2	5HDPE + 5 rb		36.7	125	1.54	125
3	90HDPE + 10 rb		33.2	85	1.46	128
4	80HDPE + 20 rb	75–110	26.3	45	1.33	130
5	70HDPE + 30 rb		23.5	35	1.01	130
6	60HDPE + 40 rb		21.7	30	0.82	135
7	95HDPE + 5 rb		31.3	95	1.42	125
8	90HDPE + 10 rb		32.7	65	1.05	126
9	80HDPE + 20 rb	300–500	25.1	30	0.93	128
10	70HDPE + 30 rb		22.0	25	0.97	129
11	60HDPE + 40 rb		19.1	20	0.68	131
12	95HDPE + 5 rb		28.8	55	1.45	125
13	90HDPE + 10 rb		28.4	35	0.94	126
14	80HDPE + 20 rb	1200–2000	23.3	20	0.88	126
15	70HDPE + 30 rb		19.6	20	0.87	127
16	60HDPE + 40 rb		17.2	15	0.55	128

which is characterized by a high measurement accuracy. The relative experimental error is 3–5%.

The breaking stress and elongation of the nanocomposites were determined from the results of analytical data (out of five measurements) in accordance with GOST 11262-80. The relative experimental error is 3–5%.

The MFI of polymeric materials was determined using a capillary rheometer CEAST MF50 Melt Flow Tester (Instron, Italy) at a temperature of 190°C and a load of 5 kg. The relative experimental error is 5%.

RESULTS AND DISCUSSION

When assessing the physicomechanical characteristics of polymer composites, it was important to identify what properties are the most sensitive to changes depending on the concentration of refuse burnout. In this case, it seems possible to most clearly trace the regularity of these changes and thereby give an appropriate interpretation to the processes affecting the mechanism of the formation of supramolecular structural formations in the polymer matrix. Considering that for the first time nanodispersed refuse burnout is used as a filler, it should be clear how important it is to clarify the role of the size factor in changing properties.

Table 1 shows the results of the investigation of the effect of the concentration of refuse burnout and the size of the particles on the nature of the change in properties. By comparing the data presented in this table, it can be determined that the particle size of the filler has a significant effect on the physical and mechanical properties. From the comparative analysis of the presented data, it can be seen that samples obtained from refuse burnout nanoparticles with a size of 75–110 nm are characterized by relatively high values of strength and heat resistance. It is characteristic that, with an increase in the size of filler particles, there is a general tendency to worsen the properties of composites. At the same time, the most sensitive to changes in the concentration and particle size of refuse burnout are such indicators as relative elongation, breaking stress, and heat resistance.

It is known that the introduction of filler particles into the composition of a polymer matrix is always accompanied by the formation of heterogeneous nucleation centers, which, as a rule, have a tangible effect not only on the mechanism of the crystallization process but also on the size of spherulite formations [9–11]. In the melt of the polymer matrix in the absence of a filler, homogeneous nucleation centers are mainly formed, which are an accumulation of macrosegments oriented to each other. The strength of bonds between oriented macro-segments of HDPE mainly depends on the van der Waals interaction. Therefore, these structures in the melt are less resistant to thermomechanical action, and therefore the process of their decomposition and reduction is based on the establishment of a thermodynamic equilibrium state. The introduction of filler particles promotes the adsorption of macrochains on their surface with the additional formation of heterogeneous structural units, nuclei of crystallization. Thus, in filled systems, homogeneous and heterogeneous nucleation centers are simultaneously formed, and the more developed the surface of particles and the higher their concentration, the higher the probability of orientation of macrosegments on them. In this case, the strength of the physical bond of macrosegments with particles is based not only on the van der Waals bond but also on the adhesive bond. Therefore, heterogeneous structures are more resistant to thermal effects; i.e., they are more likely to form stable microcrystalline formations. As the temperature decreases and the melt solidifies, macrosegments crystallize at these centers with the formation of small-spherolite supramolecular structures, which always contribute to an increase in the strength of the samples. However, the concentration and size of filler particles have an ambiguous effect on the properties of composites. As can be seen from Table 1, if the highest value of the breaking stress for nanocomposites appears at a concentration of 5.0 wt %, then for composites with relatively large particle sizes, the maximum strength is formed for samples with a thermal ash content of up to 10 wt % inclusive. One gram of nanosized refuse burnout contains a much larger number of particles than 1 g of a conventional dispersed filler. That is why the introduction of a minimum amount (5.0 wt %) of nanosized refuse burnout is sufficient for a significant increase in the strength of the nanocomposite.

Attention should also be paid to the fact that the introduction of thermal ash into the HDPE composition contributes to a significant decrease in the relative elongation of the composites. This decrease in elongation is typical of filled polymer systems. This is interpreted by the fact that, during the cooling of the samples and their crystallization, part of the filler particles are displaced by growing crystalline formations into the interspherolite amorphous space, which, as is known, is characterized by the presence of passage macrochains. The more filler particles accumulate in the amorphous region, the less the conformational mobility of the anchoring chains becomes, which, upon uniaxial deformation, first of all undergo rupture, accompanied by a decrease in the relative elongation [12–15].

Figure 1 shows an electronic image of the filled composites, from where it can be seen that the introduction of filler particles results in uniform dispersion of particles in the polymer matrix. According to this pattern, the filler particles are preferably distributed in the inter-spherulitic space.

Another important technological indicator is the heat resistance of composite materials. As can be seen from Table 1, with an increase in the concentration of refuse burnout, regardless of the size of its particles, an increase in the heat resistance of the composites is observed. The only difference is that, with an increase in the particle size of the refuse burnout, the effect of increasing the heat resistance of the samples decreases. For example, if an increase in the concentration of nanoparticles from 5 to 40 wt % is accompanied by an increase in heat resistance by 10°C (from 125 to 135°C), then in samples with a particle size of 300–500 nm this increase is 6°C, and in samples with a particle size of 1200–2000 nm it increases by only 3°C. The latter is important because it can be argued that the addition of refuse burnout to HDPE contributes, on one hand, to an increase in the bonding strength of the macrochains on the surface of its particles, and on the other hand, the formed reinforced small-spherulitic supramolecular structure increases its resistance to thermofluctuational decay.

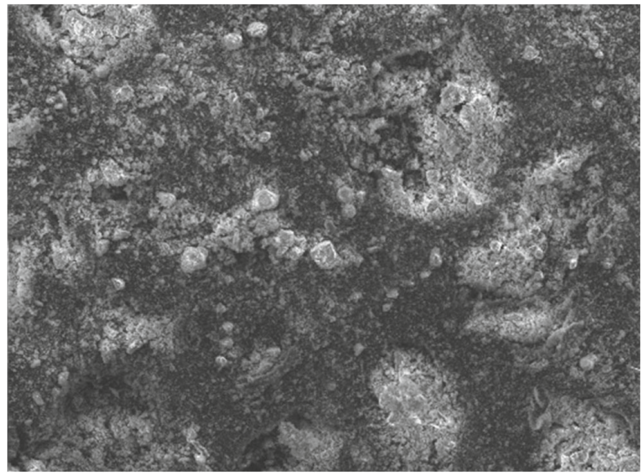

Fig. 1. Electronic image of filled composites HDPE + 20 wt % refuse burnout.

Analyzing the data presented in Table 1, one can note that the introduction of up to 20 wt % nanoparticles (experiments 2–4) of the refuse burnout initially promotes a slight increase in such a technological indicator as the MFI. A further increase in the content of nanoparticles is accompanied by a slight decrease in the MFI to 0.82 g/10 min. Such an increase in the MFI in experiments 2–4 is explained by the fact that various types of carbon black, including graphite, are formed in the composition of the refuse burnout as a result of heat treatment in furnaces at 1200°C. We believe that, owing to its layered structure, graphite contributes to an increase in the MFI of composites. A further increase in the concentration of refuse burnout over 20 wt % (experiments 5, 6) already leads to a slight decrease in the value of this indicator. It is possible that, at high concentrations of refuse burnout nanoparticles, other components present in its composition contribute to an increase in the viscosity of the melt and, accordingly, to a decrease in MFI.

It should be noted that, in contrast to nanoparticles, the introduction of 10 wt % dispersed particles of the refuse burnout into the HDPE composition leads to some decrease in the melt fluidity. All these circumstances are important, since they allow us to assert that refuse burnout, unlike other minerals, contributes to the retention of the melt flow of composites even at its 40 wt % content in HDPE. In other words, it is possible to process the obtained polymer composite materials by standard injection molding and extrusion methods. Thus, it can be stated that, among the composites filled with refuse burnout, nanocomposites have comparatively better physicomechanical and technological characteristics. Even at high filler concentrations, the composites retain the ability to be processed on standard equipment.

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