Polymer nanocomposites on the basis of low density polyethylene and dressed kaolin

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Abstract. The influence of the organosilicon coupling agent — aminooxyethylaminopropyltrimethoxysilane — on the physicomechanical properties of nanocomposites based on a low density polyethylene and kaolin is considered. The kaolin nanoparticles with a size of 80-120 nm were obtained during the processing of the powdered mineral in a laboratory mill mark A-11 at a rotor speed of 30,000 rpm. The regularity of changes in the properties of the dressed polymer nanocomposites depending on the concentration of the filler and coupling agent is shown. For comparative analysis, composites with dressed and undressed filler were used. The results of the study showed that nanocomposites with dressed nanoparticles are characterized by relatively high values of ultimate tensile stress, elongation at break, and flexural strength. Only when the concentration of the filler is 20 wt.% and higher, there is a noticeable deterioration in strength and elongation at break of the composites. This is interpreted by the fact that in the process of crystallization and growth of spherulites most of the filler accumulates in the amorphous region which consists of a large number of “feed-through chains” determining the mechanism of formation of the “neck” under uniaxial tension. The increase in the proportion of filler particles in the inter-spherolite space is accompanied by the fact that the feed-through chains become “walled up” in amorphous space.

1. Introduction
One of the widely used methods for modifying the structure of a polymer matrix is the loading of various types of mineral fillers into its composition. In this case, it is possible not only to significantly reduce the cost of the composite, but also to improve a number of physical-mechanical characteristics. However, the use of this method of polymer modification does not always allow to achieve the desired results, since most of the fillers are not well wetted with a polymer matrix, which unconditionally affects the deterioration of their basic physical-chemical properties [1-4].

In this regard, the technique of loading silane coupling agents into composites, intended to targeted improve the adhesion interaction at the polymer-filler interface, is most widely used. Given the complexity of the mechanism of interaction of the coupling agents with the filler and the polymer matrix, in the literature constant attention is paid to the study of this problem [5]. The use of nanoparticles in polymer composites further enhances the interest in using coupling agents in this direction.

Based on the foregoing, the purpose of this work was to study the simultaneous influence of coupling agents and structure-forming agent on the basic operational properties of nanofilled composites.
2. Experimental part

As the object of study was used a low density polyethylene (LDPE) grade 10604-007. The melt flow index (MFI) of the LDPE is 0.72 g/10 min, ultimate tensile stress $\sigma_t = 14.3$ MPa, elongation at break 525%, flexural strength $\sigma_f = 11.6$ MPa, density 923 kg/m$^3$. Mineral filler was kaolin and coupling agent.

Kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) — white clay consisting of kaolinite mineral. As the coupling agent of kaolin nanoparticles were used: aminoethylaminopropyltrimethoxysilane $\text{NH}_2(\text{CH}_2)\text{NH}(\text{CH}_2)\text{Si(OCH}_3)\text{3}$ (AEPMOS) — light yellow liquid with a density 1024 kg/m$^3$. It is intended for dressing glass fiber fillers of composite materials and mineral fillers in order to increase their adhesion to polymer materials.

The kaolin nanoparticles with a size of 80-120 nm were obtained during the processing of the powdered mineral in an A-11 laboratory mill at a rotor speed of 30000 rpm.

2.1. Preparation of polymer composite

0.5-2.0% Aqueous solution of a coupling agent (AEPMOS) acidified with acetic acid to pH = 3.5 was mixed with dispersed particles of kaolin at a temperature of 25°C for 60 min. Varying the concentration of the filler particles and the coupling agent in the aqueous solution, it was possible to change its concentration on the surface of the filler particles within fairly wide limits from 0.5 to 3.0 wt.% of the weight of kaolin taken. After that, the solution was filtered and the filler impregnated with a coupling agent and vacuum dried at a temperature of 75-80°C.

Dressed kaolin nanoparticles were loaded into the LDPE melt at the rollers at a temperature of 160°C and stirred for 8-10 min until the components of the mixture were evenly dispersed.

To study the physical-mechanical properties, polymer nanocomposites were subjected to pressure at a temperature of 160-170°C. Samples for mechanical tests were cut down from the pressed plates.

Ultimate tensile stress and elongation at break were determined in accordance with Russian Standard GOST 11262-80. Flexural strength was determined in accordance with GOST 9550-81.

MFI of LDPE composites was determined on IIRT instrument at a temperature of 190°C and a load of 5 kg.

3. Results and discussion

The loading of kaolin nanoparticles into the composition of the LDPE has basically two goals: to strengthen the polymer matrix and reduce the price of the nanocomposite. Depending on the highest priority tasks, a strategy of a scientific approach is being built for the formation of polymer composite. As a rule, the most optimal solution is the simultaneous execution of both tasks.

Finally, the use of AEPMOS pursues the main problem associated with improving the wettability of the surface of filler with polymer matrix. This effect is interpreted by the fact that part of the functional groups of the coupling agent interacts with oxides of the filler metals and its hydrocarbon part interacts with the polymer matrix. Both mechanisms make contributions to the formation of “monolayer” of the coupling agent in the boundary regions and as a result of it the maximum effect is achieved in improving the adhesion and wettability of the surface of filler particles with the polymer matrix.

Data on the physical-mechanical properties of nanocomposites based on LDPE and kaolin are presented in Table 1. From comparative analysis of this data, it can be established that the introduction of mentioned components leads to improvement of the properties of composites with the exception of elongation at break. For example, as the concentration of the coupling agent in the composition of the LDPE increases, maximum values of the ultimate tensile stress and flexural strength are achieved at 1.0 wt.%. However, there is a slight decrease in the elongation at break. A further increasing the concentration of AEPMOS leads to a certain increase in the MFI, which can be interpreted due to plasticizing effect. This effect is characteristic of polymer compositions occurred when they are mixed with viscous polar liquids, which is AEPMOS in our case [6,7].

Further, in the study of the separate effects of kaolin on LDPE, the expected result was achieved with a maximum breaking stress at 5.0 wt.% of its content. The fact is that kaolin is poorly wetted with
LDPE macrochains, which, ultimately, is manifested in a significant decrease in the elongation at break and ultimate tensile stress, especially at its high concentrations. Characteristically, the flexural strength continuously increases with increasing concentration of kaolin nanoparticles in the composite. All this is explained by the difference in the mechanism of destruction of the supermolecular structure of the composites under uniaxial tension and flexural. In other words, a decrease in the elongation at break and tensile strength of highly filled composites can apparently be interpreted only by the fact that in the process of cooling, crystallization and growth of spherulites most of the filler accumulates in the amorphous region which consists of a large number of “feed-through chains” that determine the mechanism of the formation of a “neck” under uniaxial tension. And as the share of filler particles increases in the inter-spherolite space, the feed-through chains become “walled up” in amorphous space. As a result, the conformational mobility of macrochains is deteriorating which undoubtedly affects the difficulty of the process of monobasic stretching of the samples and the deterioration of the ultimate tensile stress of the composites [8].

Table 1. Physical-mechanical properties of nanocomposites based on LDPE and kaolin

| No | Composition of material*, wt.% | Ultimate tensile stress, MPa | Elongation at break, % | Flexural strength, MPa | Melt flow index, g/10 min |
|----|--------------------------------|-------------------------------|------------------------|------------------------|---------------------------|
| 1  | LDPE                           | 14.3                          | 525                    | 11.6                   | 1.03                      |
| 2  | LDPE+0.5C                       | 14.5                          | 495                    | 12.0                   | 1.05                      |
| 3  | LDPE+1.0C                       | 14.9                          | 465                    | 12.2                   | 0.99                      |
| 4  | LDPE+2.0C                       | 13.0                          | 470                    | 12.2                   | 1.12                      |
| 5  | LDPE+3.0C                       | 12.2                          | 310                    | 10.5                   | 1.53                      |
| 6  | LDPE+5K                         | 15.4                          | 435                    | 13.2                   | 1.41                      |
| 7  | LDPE+10K                        | 16.3                          | 110                    | 14.8                   | 2.18                      |
| 8  | LDPE+20K                        | 14.0                          | 55                     | 15.9                   | 2.63                      |
| 9  | LDPE+30K                        | 12.2                          | 25                     | 16.7                   | 1.96                      |
| 10 | LDPE+40K                        | 11.6                          | 15                     | 17.0                   | 1.32                      |
| 11 | LDPE+5K+0.5C                    | 15.9                          | 430                    | 13.4                   | 1.51                      |
| 12 | LDPE+5K+1.0C                    | 17.2                          | 450                    | 13.8                   | 1.64                      |
| 13 | LDPE+5K+2.0C                    | 16.6                          | 375                    | 13.8                   | 1.82                      |
| 14 | LDPE+5K+3.0C                    | 13.8                          | 275                    | 12.9                   | 1.86                      |
| 15 | LDPE+10K+0.5C                   | 16.7                          | 105                    | 15.2                   | 2.35                      |
| 16 | LDPE+10K+1.0C                   | 18.0                          | 120                    | 15.6                   | 2.42                      |
| 17 | LDPE+10K+2.0C                   | 18.5                          | 95                     | 16.2                   | 2.57                      |
| 18 | LDPE+10K+3.0C                   | 15.3                          | 100                    | 16.0                   | 2.73                      |
| 19 | LDPE+20K+0.5C                   | 15.2                          | 60                     | 16.5                   | 2.71                      |
| 20 | LDPE+20K+1.0C                   | 16.0                          | 75                     | 17.0                   | 2.77                      |
| 21 | LDPE+20K+2.0C                   | 18.2                          | 55                     | 17.3                   | 2.92                      |
| 22 | LDPE+20K+3.0C                   | 15.8                          | 55                     | 16.9                   | 2.88                      |
| 23 | LDPE+30K+0.5C                   | 13.6                          | 30                     | 17.0                   | 2.25                      |
| 24 | LDPE+30K+1.0C                   | 14.6                          | 40                     | 18.4                   | 2.24                      |
| 25 | LDPE+30K+2.0C                   | 15.7                          | 25                     | 18.5                   | 2.05                      |
| 26 | LDPE+30K+3.0C                   | 14.1                          | 25                     | 18.0                   | 2.18                      |
| 27 | LDPE+40K+0.5C                   | 12.8                          | 25                     | 17.4                   | 1.33                      |
| 28 | LDPE+40K+1.0C                   | 13.0                          | 25                     | 18.2                   | 1.42                      |
| 29 | LDPE+40K+2.0C                   | 13.3                          | 20                     | 18.7                   | 1.74                      |
| 30 | LDPE+40K+3.0C                   | 14.1                          | 15                     | 18.9                   | 1.59                      |

* K — kaolin, C — coupling agent.
It should be noted that we recorded some improvement in the MFI of the samples in the process of loading kaolin. This is interpreted by the fact that the kaolinite or nanoclay contained kaolin in the composition has a layered structure which has a positive effect on the improvement of the MFR of the samples.

According to the data presented in Table 1, simultaneous loading of a filler and a coupling agent into the composition of the LDPE ambiguously affects the change in its properties. For example, it has been shown that the maximum effect in improving properties can be achieved by varying the concentration of the coupling agent and the filler. When the concentration of kaolin in the composite is 5 wt.%, the maximum ultimate tensile stress and flexural strength are achieved at AEPMOS content of 1.0 wt.%, when kaolin content is 10, 20, and 30 wt.% — at 2.0% AEPMOS, and with 40 wt.% kaolin — at 3.0% AEPMOS from the weight of filler. It becomes obvious that with increasing kaolin concentration a relatively larger amount of AEPMOS is required to achieve the maximum effect in improving the physical-mechanical properties.

The process of dressing kaolin should be carried out taking into account the peculiarities of the structure of polymer matrix sufficient melt flow ability, its compatibility with foreign particles, and the ability to form heterogeneous structures. The optimum ratios of the components of the mixture should be appropriately selected, at which the maximum effect is achieved in improving the basic physical-mechanical characteristics and their negative impact on the rheological features of the polymer composites is minimized. Such approach to analysis and study of dressed polymer composites opens up promising possibilities for obtaining qualitatively new types of polymer composite materials with predetermined properties.

4. Conclusions

It has been established that the loading of kaolin dressed with organosilicone compound into the composition of the LDPE leads to a significant improvement in the physical-mechanical characteristics of nanocomposites.

The higher concentration of the filler in the nanocomposite structure, the greater a required coupling agent on the nanoparticles surface to maintain the strength properties at a satisfactory level. The loading of kaolin leads to some increase in the MFI of nanocomposites thereby contributing the improvement of technological features of their processing.

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