The structure and physicomechanical properties of composite materials based on linear polyethylene and nanosized carbides

V.P. Gordienko, A.V. Kasperskii, and G.N. Kovaleva

1Institute of Natural Technical Systems, Russian Academy of Sciences
2M.P. Dragomanov National State Pedagogical University, Kiev, Ukraine

SELECTED FROM INTERNATIONAL POLYMER SCIENCE AND TECHNOLOGY, 42, NO. 5, 2015, REFERENCE PM 14/9-10/07; TRANSL. SERIAL NO. 17431

SUMMARY

An investigation was made of the structure at different levels of its organisation and the physicomechanical properties of linear polyethylene under the action of nanosized silicon, titanium, and molybdenum carbides. It was established that the change in the thermomechanical characteristics of the nanocomposites and the increase in hardness and softening point of the materials are due to modification of the molecular and crystal structure of the polymer by nanosized carbides.

Earlier it was shown [1–4] that the introduction of nanosized additions of sulphides and oxides into polyethylene leads to a considerable change in the molecular and supermolecular structure of the material, and also to an increase in its physicomechanical characteristics. Here, the main factor improving the properties of the thermoplastic material is the chemical interaction between the organic macromolecules and the surface of the inorganic nanosized additions, which occurs under thermomechanical action and UV irradiation of the composite [1, 4]. It is of interest to use nanosized carbides as additives modifying the structure and properties of thermoplastic materials, given their high affinity for polymeric hydrocarbons. At the same time, there have been practically no studies of thermoplastic material–nanosized carbide systems.

This work was devoted to an investigation of the effect of nanosized carbides on the structure of a typical hydrocarbon polymer (polyethylene) and the physicomechanical properties of the nanocomposites obtained.

The investigation was conducted on a large-tonnage polymer – linear polyethylene (PE) with a viscosity-average molecular weight of $9.5 \times 10^4$ and a degree of crystallinity of 54%. As nanodisperse additives, use was made of silicon, titanium, and molybdenum carbides (SiC, TiC, MoC). The characteristics of the nanosized carbides are given in Table 1.

<table>
<thead>
<tr>
<th>Parameters of particles</th>
<th>SiC</th>
<th>TiC</th>
<th>MoC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (nm)</td>
<td>20–40</td>
<td>50–70</td>
<td>30–50</td>
</tr>
<tr>
<td>Specific surface (m$^2$/g)</td>
<td>60–80</td>
<td>10–30</td>
<td>45–65</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>3.22</td>
<td>4.92</td>
<td>8.40</td>
</tr>
<tr>
<td>Shape</td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
</tbody>
</table>

Nanosized carbides were introduced into PE in a quantity of 0.2–7.0 vol%. From the composites produced by homogenising the polymer melt with additions of nanosized carbides in a Brabender plastograph (40 min at 453 K), specimens of 1 ± 0.05 mm and 3 ± 0.1 mm thickness were manufactured by hot pressing (pressure 35 MPa at a temperature of 443 K for 20 min). A polymer not containing nanosized carbides was treated by a similar regime. The content of gel fraction (crosslinked macromolecules) and the amount of graft polymer on particles of nanosized carbides were determined by extraction of unbound macromolecules of PE and free nanosized particles of carbides with boiling toluene to constant weight of the residue, just as in Gordienko et al. [4]. X-ray diffraction analysis of the crystal structure of PE specimens (degree of crystallinity and fold height of the
crystallites) was carried out on a DRON-3 diffractometer.

Thermomechanical analysis (TMA) of materials was conducted by the Kargin–Sogolova method [5] with a heating rate of 1 K/min and a periodic load of 0.5 MPa for 10 s. The dependence of the compressive strain of specimens on temperature was investigated on a thermomechanograph similar to that described by Regeta et al. [6]. From the thermomechanical curves, the temperature of the start of high-elastic strain and its magnitude were estimated [5]. As physicomechanical properties of composites of PE with nanosized carbides, the Brinell hardness (GOST 4870-91 standard) and Vicat softening point under 1 kg load were determined on an indentor of 1 mm² area with a heating rate of 2 K/min [7]. For calculation of the physicomechanical characteristics of the PE composites, the values of seven parallel specimens were used.

The nature of interaction of PE macromolecules with the surface of nanosized carbides is shown fairly fully by the amount of graft polymer and the content of gel fraction in specimens of thermoplastic material as a function of the concentration of nanosized additions (Table 2). After burning off of the gel fraction at a temperature of 873 K, it was established that the amount of graft polymer increases with increase in the concentration of nanosized carbides, reaching 25–31%, depending on their nature, with a 7% content of additions. A similar tendency is observed for the PE gel fraction content in these composites. Here, the PE gel fraction content in all cases is lower than the amount of graft polymer on the nanosized carbide particles, and the effectiveness of these processes falls in the order SiC > TiC > MoC.

The maximum values of graft polymer and gel fraction (P = 31%, G = 25%) are observed for PE containing 7% SiC. Such values of graft polymer and gel fraction content are achieved only in the case of the introduction of nanosized silicon dioxide into the PE and UV irradiation of the composite for 120 h [4].

On the basis of the data in Table 2 and the experiment conducted by Gordienko et al. [4], it can be assumed that some PE macromolecules, after thermomechanical action in a polymer melt with nanosized carbide particles, are chemically grafted on the surface of these particles. The nanosized carbide particles are evidently bound with the three-dimensional network of the polymer. The difference in the effect of the investigated additions of nanosized carbides on the molecular structure of the PE is probably due to parameters of the particles of these carbides (Table 1).

In an early work [8] it was assumed that the crystallisation of linear PE may begin with macromolecules chemically bound with the surface of solid disperse particles, in particular titanium dioxide. In Gordienko et al. [4], this assumption was substantiated during the crystallisation of linear PE with nanosized silicon dioxide particles. In this work, the effect of nanosized carbides on the parameters of the crystal structure of PE is given in Table 3.

It can be seen that, during the crystallisation of PE in the presence of additions of nanosized silicon, titanium,
and molybdenum carbides, simultaneous increases in the degree of crystallinity of the polymer and in the fold height of its crystallites occur. The most effective increase in the parameters of the crystal structure of PE is observed with 0.5% additions of carbides in the polymer. Increase in the content of nanosized carbides lowers the effect of these particles on the crystal structure of the PE. In terms of their effect on the crystal structure of polyethylene, the nanosized carbides can be placed in the order SiC > TiC > MoC, which correlates with the degree of grafting of PE macromolecules on the surface of particles of the additives and with the content of polymer gel fraction (cf. Tables 2 and 3). Thus, the maximum increase in the degree of crystallinity (by 11%) and the maximum increase in the fold height of the crystallites (by 4 nm) occur in specimens of PE containing 0.5% nanosized SiC. The particles of nanosized carbides seem to act as PE crystallisation initiators only in the case of the chemical grafting of macromolecules on the surface of particles of the additives. Crystallisation initiators promote the formation of a more thermodynamically equilibrium and ideal crystal structure of the polymer. It must also be taken into account that nanosized SiC particles are commensurate with the fold height of the PE crystallites. This should have a significant effect on the kinetics and thermodynamics of crystallisation of the polymer and on its supermolecular structure. Increase in the content in the polymer of gel fraction (crosslinked macromolecules) localised in amorphous regions of the PE should hamper the crystallisation of the thermoplastic material, which is observed with increase in the concentration of nanosized carbides in the polymer (Tables 2 and 3).

An important characteristic of thermoplastic materials is the magnitude of strain under low compressive loads, determined in a wide temperature range [5]. Figure 1 shows this dependence in the temperature range 370–490 K. It can be seen that strain of the initial PE begins to appear at 373 K and reaches 91% at 392 K.

The introduction of nanosized carbides slightly reduces the values of the start of strain of the PE up to a temperature of 395 K, converting the polymer into the high-elastic state. The presence in carbide-containing PE of a three-dimensional network (gel fraction) and graft macromolecules on the surface of the nanosized particles (Table 2) leads to the polymer, after a temperature of 415 K, exhibiting high elasticity (Figure 1). The values of high-elastic strain of PE in the temperature range 415–490 K are different, depending on the nature of the nanosized carbides introduced. The highest value of high-elastic strain (23–28%) is possessed by a polymer containing 7% MoC, and the lowest (9–14%) by PE containing 7% SiC. A polymer with 7% TiC occupies an intermediate position (16–21%). Comparing the data in Table 2 and Figure 1, it can be asserted that the results of thermomechanical analysis and the changes in the molecular structure of thermoplastic systems of polyethylene and nanosized carbides are in good agreement. The changes in the molecular structure of the polymer nanocomposites are clearly reflected in the thermomechanical properties of these materials.

The changes in the molecular and crystal structure of PE that occur under thermomechanical action in the presence of nanosized carbides were likewise reflected in the change in hardness and softening point of the thermoplastic materials.

It can be seen (Figure 2) that the hardness of the thermoplastic materials with a carbide content of up to 0.5% increases sharply, in particular for SiC – by 24 MPa, which is due to the higher parameters of the crystal structure of PE. Further increase in the carbide content in the polymer to 7% increases the hardness value of the thermoplastic materials negligibly – by 3–6 MPa, in spite of a certain reduction in the parameters of the crystal structure of PE (Table 3). Such an effect is most likely due to the fact that, with increase in the carbide content in the polymer, the presence of crosslinked macromolecules chemically grafted on the surface of the nanosized particles, which are concentrated in amorphous areas of the crystallising thermoplastic, shows up in an increase in hardness of the composite materials. This contribution to increase in the hardness of the thermoplastic materials proves to be more significant than the limited reduction in the parameters of the crystal structure of the PE, because it is connected with the reinforcing effect of amorphous areas of the crystallising polymers.

The change in the softening point of the thermoplastic materials as a function of the content of nanosized carbides is similar in nature to the change in hardness of these materials (Figure 2). Nanosized silicon carbide has the greatest influence on increase in the softening point of PE: the introduction of 0.5% SiC increases the softening point by 20 K, and in the range 0.5–0.7% by only 13 K. The same softening point of 390 K can be achieved by introducing 0.5% SiC or 7.0% MoC.

![Figure 1. The temperature dependence of compressive strain (εc) of the initial PE (1) and of PE containing 7% SiC (2), 7% TiC (3), and 7% MoC (4)](image-url)
into the PE. Increase in the softening point of linear polyethylene when the investigated nanosized carbides are introduced chiefly correlates with change in the molecular and crystal structure of the polymer.

From the data given above it follows that the introduction of nanosized silicon, titanium, and molybdenum carbides makes it possible to alter the molecular and crystal structure of a typical thermoplastic polymer (linear polyethylene) in a way that is necessary to achieve an increase in the hardness and softening point of the composite materials. Maximum increases in hardness by 30 MPa and in softening point by 33 K are observed when 7% SiC is introduced into the polymer melt. The primary factor determining increase in the hardness and softening point of thermoplastic nanocomposites is the formation of chemical bonds between the components of the system: between polymer macromolecules and nanosized carbides. Such bonds arose under thermomechanical action when nanoadditives were introduced into the polymer melt. In this connection, crystallisation of the chemically grafted macromolecules is initiated at a higher temperature than in the initial PE and ends with the formation of a more ideal crystal structure of the polymer. Here, intermolecular crosslinks and a three-dimensional network are also formed in the polyethylene. Such transformations in the structure of the crystallising thermoplastic are accompanied with an increase in the hardness and softening point of the composite materials.

The results of this work could be used in the production of polymer nanocomposites based on crystallising thermoplastics to increase their hardness and softening point. It can be assumed that the introduction into polyolefins of nanosized carbides in greater quantity and range will lead to the production of materials with unique properties.

REFERENCES