Polymer composites based on functionalized carbon nanotubes

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Abstract. The present paper considers the efficiency of using carbon nanotubes (CNTs) functionalized by titanium stearate groups for modifying polyethylene and polypropylene. For this purpose, the strength characteristics, Shore hardness, thermal diffusivity and conductivity of the obtained nanocomposites were determined. The weak effect of the CNTs (0.01-1.5 wt.%) on the values of thermal conductivity coefficients and thermal diffusivity was revealed. It was found that compared to the unmodified matrix, nanocomposites containing 0.01-0.1 wt.% of the titanium stearate-functionalized CNTs demonstrate, an increase in the Shore hardness by 12.5-14.5%, a decrease in the weight wear by 54.2%, and the daily water absorption - to the values below the threshold of sensitivity of the standardized method of determination. The functionalization by the titanium stearate groups made it possible to reduce the CNTs mass fraction in the composition of polyethylene and polypropylene composites by more than 10 times compared with the pristine nanotubes.

1. Introduction

Covalent and non-covalent functionalization of carbon nanotubes (CNTs) is one of the generally accepted methods for solving the problem of their distribution in polymers and solvents [1]. In particular, CNTs with oxygen- [2-3] and nitrogen-containing [4] groups are successfully used for modifying epoxy binders. Functionalized CNTs possessing the affinity for non-polar matrices are suitable for employing in composites based on polyethylene (PE) polypropylene (PP). In particular, alkylated [5], fluorinated [6] and silanized [7] CNTs belong to efficient PE and PP modifiers. However, the implementation of the CNTs functionalization methods presented is technologically complex due to a large number of stages and the use of expensive and/or toxic reagents. In this paper, it is proposed to use a more environmentally friendly and economical way of functionalizing CNTs with titanium stearate groups.

The purpose of this work was to study the effectiveness of using functionalized CNTs for the PE and PP modification. In this regard, the strength characteristics, Shore hardness, thermal stability, thermal conductivity and thermal diffusivity of composites with technical carbon, pristine and functionalized nanotubes were determined at various modifier concentrations.

2. Materials and methods
“Taunit-M” CNTs (d = 8 ÷ 15 nm, length ≥ 2 µm, and specific surface area 300-320 m²/g) produced by "NanoTechCenter" Ltd. (Tambov, Russia) were used herein. For their functionalization, the nanotubes were first treated with concentrated nitric acid at 110 °C for 5 h, and then washed on the filter with distilled water to neutral pH. A 40-wt. % aqueous paste of CNTs, carboxylated with 1.0 mmol/g COOH-groups (according to titrimetry data), was obtained. 1.5 g of triethanolamine and 200 mL of distilled water were added to this paste, after which the mixture was mechanically stirred to form a homogeneous suspension, treated with ultrasound for 0.5 h and cooled. Then, with stirring, 100 mL of a solution containing 10 mmol of triethanolamine titanate (TEAT) and 150 mL of a solution containing 20 mmol of triethanolamine stearate (STEA) were added. The resulting mixture was stirred for 2 h. At the same time, carbon dioxide was passed into it at a rate of 1 L/min. The following chemical reactions took place:

\[
\begin{align*}
Ti[N(CH_2CH_2O)_3CH(CH_2CH_2OH) + 2(HOCH_2CH_2)_2NH(C_{17}H_{35}COO) + 3CO_2 + 3H_2O \rightarrow & \rightarrow N(CH_2CH_2O)_3CH(CH_2CH_2OH)Ti(C_{17}H_{35}COO)_2 + 3(HOCH_2CH_2)_2NH(HCO_3) ; \\
2COOH & + [N(CH_2CH_2O)_3CH(CH_2CH_2OH)Ti(C_{17}H_{35}COO)]_2 + H_2O + CO_2 \rightarrow \\
& \rightarrow (-COO) \_2 Ti(C_{17}H_{35}COO) + (HOCH_2CH_2)_3NH(HCO_3). 
\end{align*}
\]

The second reaction represents the interaction between the carboxyl groups on the CNTs surface and diethanolamine titanate distearate formed as a result of the TEAT-STEA interaction.

At the end of the process, the precipitate was washed on the filter with distilled water and dried in a vacuum oven at 80 °C until the weight loss stopped. As a result, the functionalized CNTs were obtained, with titanium distearate mass fraction of about 26 %. The transmission electron microscopy (TEM) images of the pristine and functionalized CNTs are shown in figures 1a and 1b, respectively. A modifying layer up to 2 nm thick can be identified on the CNTs surface.

![Figure 1. TEM images of the pristine (a) and titanium stearate-functionalized (b) CNTs.](image)
peak at 1697 cm\(^{-1}\) is assigned to the vibrations of the C=O bonds in carboxyl. According to [8], the peaks at 1415; 939 and 803 cm\(^{-1}\) characterize the vibrations of the Ti–O bonds.

![IR-spectra of the titanium stearate-functionalized CNTs.](image)

**Figure 2.** IR-spectra of the titanium stearate-functionalized CNTs.

Heat-resistant PE (PE-RT SP 988, LG Chem, South Korea) and PP (Polykom LLC, Russia) were subjected to modification. The concentration of the filler (pristine CNTs, functionalized CNTs, and carbon black - CB) was 0.01-1.5 wt. %. The modifying additives were mixed with the granular polymer (PE, PP) in melt in a Brabender rotary mixer. Samples with the required geometric parameters were obtained by injection molding.

The studies on the hardness of composites according to Shore (scale D) were carried out on a 5069 UHL 4.2 IT model device (self-made). Strength characteristics were evaluated on a DBBMTCL-500 kg polymer testing machine (Testometric, UK). The measurement error on this instrument was ±5 %.

The study on the tribological characteristics was performed on a friction machine (Korvet-41, Russia) by determining the weight wear. Cylindrical samples with a diameter of 35 mm and a height of 6.5 mm were fixed with a screw in the center of the friction machine table. The abrasive mesh P150 (75-106 µm) was used as a counterbody, the diameter of its working area was 120 mm. The weight wear was determined by changing the sample mass before and after testing. The time of the experiment was 20 min, the load on the sample was set with a force of 0.5 kg with a shoulder of 200 mm from the axis of the mechanism for lowering the cartridge, and was controlled by spring weights throughout the experiment. The counter body rotation frequency was 12.5 rpm. The measurement error on this instrument was ±5 %.

The daily water absorption of composites was evaluated by increasing the mass of the standard composite sample after exposure to distilled water for 1 day. The measurement error on this instrument was ±2 %.

The studies on the thermal conductivity and thermal diffusivity were carried out using the information-measuring system of thermophysical properties of solid materials (self-made), which was previously calibrated on the reference materials (polymethylmethacrylate). The cylindrical sample with a diameter of 35 mm was placed on a laboratory table, a measuring probe was placed on top. After 10 min of temperature control, the thermal conductivity was measured. The time between experiments was 15 min. The measurement error on this instrument was ±5 %.

The thermal stability of the composites was estimated on the basis of the analysis of the TG/DSC curves obtained on the STA 449 F3 Jupiter synchronous thermal analysis device (Netzsch, Germany). During the measurements, the furnace was filled with air at a flow rate of 30 mL/min. The temperature
program included holding at 30 °C for 10 min, heating from 30 to 900 °C at a rate of 10 °C/min, and cooling the samples to room temperature at a rate of 15 °C/min.

3. Results and discussion

The results of mechanical tests of the PE composites modified with various types of carbon nanomaterials (CB, pristine and functionalized CNTs) are presented in table 1.

The introduction of both carbon black and CNTs, as a rule, contributes to the improvement of the studied physical and mechanical properties of polyethylene. An increase in Shore hardness can reach 3.5 and 7 units in the presence of CB and CNTs, respectively. However, this indicator is observed at 1.5% concentration of the initial CNTs in the composite. To achieve the same effect, only 0.1 % of the functionalized CNTs is required, i.e. 15 times less. The maximum hardness jump is observed at the lowest content of the modifier, and then it stabilizes. The weight wear resistance also increases markedly in the presence of even 0.01-% carbon materials. And the most effective ones are the functionalized CNTs with a minimum concentration.

Table 1. Physical and mechanical properties of the PE composites.

| Modifier       | Mass fraction (%) | Shore hardness | Weight wear (g) | Maximum load under cutting (N / mm²) | Maximum load under bending (N / mm²) |
|----------------|-------------------|----------------|-----------------|--------------------------------------|--------------------------------------|
| -              | -                 | 56             | 0.0409          | 17.1                                 | 37.9                                 |
| 0.01           | CB                | 58.0           | 0.0356          | 17.2                                 | 38.9                                 |
| 0.10           |                   | 57.5           | 0.0321          | 16.6                                 | 41.5                                 |
| 0.50           |                   | 57.5           | 0.0289          | 17.1                                 | 37.1                                 |
| 1.00           |                   | 59.5           | 0.0336          | 18.2                                 | 42.5                                 |
| 1.50           |                   | 59.5           | 0.0347          | 17.1                                 | 42.2                                 |
| 0.01           | 0.10              | 60.0           | 0.0293          | 17.2                                 | 38.4                                 |
| 0.10           |                   | 61.0           | 0.0261          | 17.2                                 | 37.7                                 |
| Pristine CNTs  | 0.50              | 61.0           | 0.0241          | 17.5                                 | 38.0                                 |
| 1.00           |                   | 62.0           | 0.0238          | 17.5                                 | 37.5                                 |
| 1.50           |                   | 63.0           | 0.0248          | 17.5                                 | 38.0                                 |
| 0.01           | 0.10              | 63.0           | 0.0187          | 18.5                                 | 38.9                                 |
| Functionalized CNTs | 0.50      | 63.0           | 0.0191          | 17.3                                 | 41.5                                 |
| 1.00           |                   | 62.5           | 0.0219          | 17.5                                 | 37.1                                 |
| 1.50           |                   | 62.0           | 0.0227          | 16.5                                 | 42.5                                 |

The parameters of the maximum PE load for bending and cutting under the action of carbon modifiers do not change so unequivocally. At some concentrations of CB, the initial and functionalized CNT, these properties may deteriorate. At best, it is possible to achieve an increase in the maximum stress in a cutting condition of 8.2% in the presence of 0.01 wt. % functionalized CNTs, in a bending condition of 12.1 % in the presence of 1 % CB or functionalized CNTs.
Figure 3. The effect of the concentration of the CB (1), pristine (2), and functionalized (3) CNTs on the daily water absorption of the PE composites.

Figure 4. The effect of adding the CB (1), pristine (2), and functionalized (3) CNTs on the Shore hardness of the PP.

The dependence of daily water absorption of the polyethylene composite on the concentration of the carbon modifier is shown in figure 3. The introduction of CB and CNTs contributes to the hydrophobization of the material. Moreover, the dependence of the index of water absorption of the composite on the concentration of the filler may be different. In the presence of the CB, it passes through a minimum at 0.1 wt.%. When the non-functionalized CNTs are added, the minimum water absorption of the composite is observed at 0.1 wt. %. The dependence of this parameter on the concentration of functionalized CNTs is variable. The first minimum of water absorption (0%) is observed at 0.01% modifier content, then, there is a slight increase to 0.06%, and at 1 and 1.5 % content of functionalized CNTs, a zero indicator is again observed.

A number of positive effects of using CNTs in the composition of PP-based composites are noted. At the functionalized CNTs content of 0.1 %, the Shore hardness increases up to 10 units (from 69.5 to 79.5). The use of the initial CNTs and CB at the same and higher concentrations does not allow achieving the same indicators (figure 4). This indicates a high affinity of the functionalized CNT to the PP matrix and good dispersibility within it.

Figure 5. Changes in the coefficients of thermal conductivity $\lambda$ (a) and thermal diffusivity $\alpha$ (b) of the PE in the presence of the CB (1) and functionalized CNTs (2).

According to the data presented in figure 5, the thermophysical characteristics of the PE when modifying with both the technical carbon and functionalized nanotubes change slightly. Instead of the expected increase in the coefficient of thermal conductivity ($\lambda$) in most cases, with the introduction of
CB or CNTs, there is a slight decrease (figure 5a). The thermal diffusivity (\(\alpha\)) of the material increases by about 34% in the presence of 1% functionalized nanotubes (figure 5b).

Analyzing the TG / DSC curves of the composites “PE-functionalized CNTs”, it can be observed that their thermal stability is high. The material is melted at 140-150°C. This significantly exceeds the temperature range of PE-RT SP 988 PE products.

Thus, the carbon materials contribute to the improvement of a number of physical-mechanical parameters of the PE and PP. However, the performance parameters depend on the type of the carbon modifier being used, its concentration and chemical pretreatment (functionalization).

As compared to the CB from the standpoint of improved mechanical properties, the higher efficiency of the CNTs is due to their structure and unique properties. The functionalized CNTs have a higher chemical affinity to the modifiable matrix, so that to achieve the required performance of the composites, consumption is required, an order of magnitude and more reduced compared to the initial CNTs [9]. It should be noted that in earlier published works [10], in order to increase hardness and resistance to wear, up to 5-10 wt.% of carbon nanotubes were introduced into polyethylene-based composites.

Another positive point in the application of the functionalized CNTs in the composition of polyethylene and polypropylene composites is the possibility of increasing resistance to moisture. Already with a minimum content of carbon nanotubes with titanium stearate groups (0.01 wt.%). The daily moisture absorption can be reduced to zero. This may be due to both more uniform dispersion of the functionalized CNTs in the polymer matrix, and their higher hydrophobic properties. For comparison, in [11], in order to make the polyethylene resistant to moisture, 1.5 wt.% of the CNTs is introduced into it.

The weak influence of the carbon modifiers used in the work on the thermophysical characteristics of the composites can be explained by two reasons. First, this is a high agglomeration of CB and the original CNTs. In the case of the use of functionalized CNTs, in addition to this reason, an enhanced interaction with the matrix can have an effect, as a result of which the CNTs no longer come into contact with each other, being separated by layers of a less conductive polymer. However, given that too high thermal conductivity of the material may contribute to heat loss to the environment when using polyethylene, for example, for the manufacture of hot water pipes, low thermal conductivity is rather an advantage than a disadvantage.

Summary
The functionalization of the CNTs with titanium stearate groups contributes to their adaptation to a PE-based polymer matrix and effective use in composites with increased hardness, wear resistance and moisture. These effects are quite pronounced at the functionalized CNTs concentrations equal to 0.01-0.1 wt.%.

Similar results with the initial (non-functionalized) CNTs can be achieved at concentrations that are an order of magnitude higher than those indicated herein.

Thus, the use of the functionalized CNTs to modify PE and PP is appropriate and contributes to the improvement of the performance characteristics of products on their basis.

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