Strengthening of polymer ropes based on polypropylene with carbon nanotubes

I V Zaporotskova¹, L S Elbakan* and D E Vilkea²

¹Volgograd State University, Universitetsky Ave., 100, 400062 Volgograd, Russia

*elbakyan@volsu.ru

Abstract. The issues of using carbon nanotubes as fillers to strengthen polymer ropes used in the mining industry, oil and gas production, metallurgy, power engineering, etc. are considered in the work. The method for producing a nanocomposite based on polypropylene doped with carbon nanotubes has been developed. Experimental studies of the most significant strength characteristics of the created prototypes of polymer composite materials have been carried out. To determine the mechanisms acting upon the introduction of nanotubes into the polymer matrix, DFT calculations of the interaction of propylene monomer with the surface of single-walled nanotubes of different diameters and chirality have been performed.

1. Introduction

Currently, the creation of composite structures based on nanomaterials is associated with many expectations in solving technological problems in various fields. Despite the large number of works devoted to the study of the structure and properties of nanostructured composites, circles, it is necessary to decide which can be attributed to nanocomposites, are very diverse and numerous.

Polymer materials have found wide application in the development of many industries and they can definitely be considered one of the main engines of technical progress. However, the problem of obtaining polymeric materials with increased strength properties is extremely urgent. At present, the most promising method for creating polymer materials is the using of nanofillers, that leads to the production of polymer nanocomposites. The object of our attention is carbon nanotubes (CNTs) with exceptional mechanical and electrical properties [1–2]. These make it possible to use them as nanofillers of polymeric materials to obtain a fundamentally new product with unique physical and mechanical properties and performance characteristics.

Previously, we studied copolymers based on methyl methacrylate, butyl methacrylate, and methacrylic acid, doped with carbon nanotubes in an amount of 0.05 wt%, and it was experimentally proved that these modified nanocomposites are significantly superior to polymers without CNT additions in terms of the investigated performance characteristics. Based on theoretical calculations performed using the DFT method, the adsorption activity of the structural units of the ternary copolymer of methyl methacrylate, butyl methacrylate and methacrylic acid in relation to single-walled carbon nanotubes used to modify the selected polymer was proved [3–4].

Another polymer, the scope of which is gradually expanding, is polypropylene. The world consumption of polypropylene is increasing every year. Its share in the production of goods in various fields is steadily growing. It gradually captures new market segments, displacing less technologically advanced polymers. So, a polypropylene cord is a universal thing in households and in production. It has gained such popularity thanks to a set of qualities. The cord does not sink in water, is not afraid of
high temperatures, acids and alkalis, and has good breaking characteristics. The main purpose of twisted polypropylene cords is to fasten securely various loads, fixtures, and equipment parts. Polypropylene cord is produced hollow, without a core, or with a solid central part. With a core, more durable products are obtained. They are used in a variety of industries such as: fishing fleet; yachting; agriculture; building; aviation industry, etc. That is why the production of polymeric materials based on polypropylene with improved operational properties is quite relevant today.

2. Technology of obtaining new composite polymer materials doped with carbon nanotubes

Carbon nanotubes have unique mechanical characteristics and are considered as an effective means for obtaining composite polymer materials with high strength properties [5-6]. There are many publications devoted to the study of such materials [7-12]. However, to realize this possibility, it is necessary to ensure the most uniform dispersion of carbon nanotubes in the polymer matrix. This will ensure efficient transfer of the load from the polymer material to the nanotube and, accordingly, increase the strength characteristics of the polymer while maintaining its plasticity. Otherwise, CNTs can deteriorate the strength properties of the material, causing its embrittlement.

A model of the device has been developed that allows the best possible achievement of the desired result. The claimed ultrasonic device for doping carbon nanotubes into a polymer matrix is quite simple to manufacture, versatile and economical.

The ultrasonic device for doping carbon nanotubes into a polymer matrix works as follows:
1. Dispersion of nanotubes in a solvent (e.g., ethanol). The dispersion process is carried out in an ultrasonic bath with water for 20-30 minutes. It is important to observe the temperature regime (the temperature of water in the bath should not exceed 24-25 °C). Further, the solvent used is distilled off in such a way as to avoid the process of coagulation of carbon nanotubes (for this, bubbles should not appear in the liquid during evaporation).
2. Granular polymer material (polypropylene) is pre-cleaned and degreased.
3. Dried granular polypropylene is treated with an adhesive primer for painting polymer coatings of various nature (in this case, polypropylene). All actions are performed at room temperature.
4. In 20-30 minutes after applying the primer, the required amount of nanotubes is added to the polymer material, which is accompanied by mechanical stirring.
5. The process of drying the polymer nanocomposite at room temperature.

A technology has been developed for introducing multi-walled CNTs into a polymer matrix when creating a protective coating for construction ropes. For reinforcement, nanotubes manufactured by OOO Taunit (Tambov) were used. The introduction of CNTs was carried out in the process of creating a coating based on PRO700 polymer material (modified polypropylene) on the equipment of SEVERSTAL LLC - a twin-screw extruder. Samples of coated polymer ropes with different percentages of nanotubes were obtained, which were then tested for rupture to determine the quality of the coating. We have made new polymer composite materials in the form of ropes based on the selected polymer with different content of carbon nanotubes.

Figure 1 shows samples of polypropylene with and without CNTs in granular form.

Figure 1. Polymeric material based on polypropylene before the polymerization process: a) pure polypropylene (without CNTs); b) polypropylene modified with CNT.
3. Experimental studies of the strength characteristics of the obtained samples of polymer nanocomposite materials

We have carried out experimental studies of the strength characteristics of polymer ropes. Various samples of ropes with polymer cores have been obtained at the factory. The diameter of the core of the obtained ropes is 6.0 mm, the diameter of the rope itself (the core with a polymer coating) is 8.3 mm. For the study, some series of samples of a nanocomposite polymer material doped with carbon nanotubes in an amount from 0.05% to 0.2 wt% are prepared, as well as a reference sample - a polymer material without CNTs. The length of each sample is 15 cm. The study has been carried out on a universal tensile electromechanical machine REM-50-1. The principle of the machine is based on the transformation of the kinetic energy generated by the servo drive into a load force applied to the test sample. For research, the main test conditions are introduced: the shape of the sample is a cylinder (indicating the diameter and length), the working speed of the moving crosshead is 0.1 mm / min, the limit of the relative error of maintaining the loading rate of the device is ± 1%, the limit of the permissible relative error of movement ± 1%, the test lasts until the destruction of the sample with the initial value of the load applied to the sample - 0.05 kN. The maximum load of the installation is 50kN.

It has been found that polymers modified with CNTs are significantly superior to polymers without the addition of CNTs in terms of the investigated performance characteristics. Table 1 shows the results of tests to determine the maximum permissible load for a polymer material without CNTs and a polymer nanocomposite material with an optimal CNT content.

Table 1. Values of the maximum permissible load of samples with the optimal content of carbon nanotubes (CNT).

| Sample, No. | Content of samples | Maximum permissible load F, kN |
|-------------|--------------------|-------------------------------|
| 1           | PP without CNT     | 3.495                         |
| 2           | PP + CNT (0.1 wt. %) | 4.437                       |
| 3           | PP + CNT (0.2 wt. %) | 3.525                       |

After rupture, the coating on sample 3 fractured brittle (figure 2b), the fracture of the coating was almost even. Moreover, when this sample is bent, the coating easily breaks with the formation of the same even fracture. Consequently, the addition of 0.2% CNTs leads to increased brittleness of the polymer.

The coating of sample 2 retained its flexural plasticity. At rupture, the maximum load leading to destruction of the coating increased by 26.95% in comparison with sample 1 (coating without CNTs).

![Figure 2. Prototypes with the optimal content of CNTs and without CNTs: a) before testing; b) after tensile test.](image-url)
The coating of sample 2 retained its flexural plasticity. At rupture, the maximum load leading to destruction of the coating increased by 26.95% in comparison with sample 1 (coating without CNTs).

4. Theoretical studies of polypropylene with CNTs (6, 6), (6, 0), (7, 1) adsorption process

We have carried out theoretical studies of the adsorption activity of polypropylene with respect to carbon nanotubes (6, 0), (7, 1), (6, 6) used to modify the monomer and create a new composite polymer material. The choice of such CNTs is due to the fact that they belong to different types of chirality and, as a consequence, have different physical properties [13]. To study the adsorption capacity of polypropylene, molecular clusters of single-walled carbon nanotubes, the boundaries of which were closed by pseudo-hydrogen atoms, were considered. The main dimensional characteristics of clusters are presented in Table 2.

| CNT size | Chirality type | Number of atoms | Cluster length, Å | Diameter, Å | CNT radius, Å |
|----------|----------------|-----------------|------------------|-------------|--------------|
| (6, 0)   | «zigzag»       | 117             | 15.42            | 4.70        | 2.35         |
| (7, 1)   | «chiral»       | 237             | 28.60            | 5.91        | 2.96         |
| (6, 6)   | «armchair»     | 190             | 16.62            | 8.1         | 4.05         |

The adsorption process has been simulated by step-by-step approach of polypropylene to the outer surface of the clusters, along the normal drawn to the surface carbon atom located in the center of the cluster. The geometry of the system was optimized at every step. The choice of the place of adsorption in the center of the molecular cluster makes it possible to avoid the edge effects of the influence on the process of pseudoatoms that close the boundaries of the cluster. In the structure of the monomer, an active center has been chosen that is capable to provide a stable bond of the monomer under consideration with the CNT surface - a hydrogen atom. The calculations have been performed within the DFT design scheme. The calculations had been done and the energy indicators of the system at each step were obtained that allowed us to construct curves of the interaction energy dependence on the distance between the selected monomer (polypropylene) and CNT. The obtained values have been normalized according to the formula (1),

\[ E = E_{\text{calc}} - (E_{\text{sub}} + E_{\text{PP}}) \]  

\( E_{\text{calc}} \) – energy of the adsorption complex, obtained as a result of calculations, \( E_{\text{sub}} \) – energy only CNT, \( E_{\text{PP}} \) – polypropylene energy.

It is established that each curve has a minimum corresponding to the established interaction at certain distances. Figure 3 shows the potential energy profiles of the of carbon nanotubes of the type (6, 0), (6, 6) and (7, 1) with polypropylene. The analysis of the obtained curves established the following results:

1. In all the cases under consideration, a minimum of energy is observed in the negative region. This confirms the realization process of the adsorption interaction of propylene with carbon clusters of the considered types of nanotubes.

2. This interaction, carried out at a distance of 3.1-3.3 Å between CNTs and polypropylene monomer, corresponds to the case of physical adsorption.
Figure 3. The graph of the dependence of the interaction energy on the distance between the propylene monomer and CNTs of the type (6, 0), (6,6), (7,1).

Table 3. The main electronic-energy characteristics of the adsorption process of polypropylene atoms on the outer surface of carbon nanotubes of the types "arm-chair", "chiral" and "zig-zag", where Ead is the adsorption energy; Rad - adsorption distance.

| Chirality and nanotube size               | Physical adsorption |
|------------------------------------------|---------------------|
|                                          | Rad, Å              | Rad, Å              |
| (6, 0) «zig-zag»                         | 3.1                 | -0.148              |
| (7, 1) «chiral»                          | 3.1                 | -0.188              |
| (6, 6) «arm-chair»                       | 3.3                 | -0.379              |

The results obtained prove the possibility of obtaining stable polymer complexes doped with carbon nanotubes.

5. Conclusions
We have investigated the possibility of interaction of polypropylene with the surface of carbon nanotubes. The results obtained theoretically confirm the possibility of creating polymer composite materials based on polypropylene doped with CNTs. The technology of introducing carbon nanotubes into the polymer matrix has been worked out and recommendations have been formulated for determining the conditions for creating a composite material and its use. The optimal amount of carbon nanotubes (in percentage-mass equivalent) for obtaining a composite mixture with the best characteristics, ensuring the improvement of the operational properties of the material, has been determined.

6. References
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