Reinforcing of polyethylene with carbon nanofibers: an approach to improve CNF distribution via pre-coating of CNF surface by PE

E S Petukhova¹, A L Fedorov¹, Yu I Bauman², A A Zdanovich², I V Mishakov² and M A Matsko²

¹Institute of Oil and Gas Problems of the Siberian Branch of the RAS - Division of Federal Research Centre “The Yakut Scientific Centre of the Siberian Branch of the Russian Academy of Sciences”, Avtodorozhnaya str. 20, Yakutsk, 677007, Russia
²Boreskov Institute of Catalysis of the Siberian Branch of the RAS, Lavrentieva 5, Novosibirsk, 630090, Russia

E-mail: evgspar@rambler.ru

Abstract. The article describes a method of the synthesis of carbon nanofibers (CNFs) and a technique for obtaining masterbatches, which are represented by CNFs with a layer of pre-synthesized polyethylene (PE) on their surface. Using scanning electron microscopy, it was shown that in-situ ethylene polymerization over the catalyst anchored on the CNF surface allow to evenly cover CNFs surface by PE. Pristine and pre-coated CNFs were introduced to commercial PE matrix. It has been found that the reinforcing of PE with CNFs leads to improved mechanical properties and two times higher resistance to abrasive wear. The application of the proposed approach makes it possible to reduce significantly the carbon filler's effective concentration and distribute uniformly the filler throughout the composite.

1. Introduction

It is known [1] that polymer composite materials' properties significantly depend on the uniformity of the filler distribution and the features of the interaction at the filler/polymer matrix interface. Among the methods for improving the adhesive interaction at the phase interface, the following are most known: mechanochemical treatment of fillers and polymers [2, 3], functionalization of filler surfaces [4, 5], adding compatibilizers [6, 7], etc. Carbon nanofibers (CNFs) have found a wide application in producing polymer composite materials with high mechanical properties, wear resistance, and other unique properties [8, 9]. However, there are two main problems during composites' production: the agglomeration of CNF particles and their nonuniform distribution. To solve the emerging issues, Mainikova et al. [10] used an ultrasonic mixer and a concentrate based on oligoxypropylene glycol as CNFs. In [11], to increase CNFs' adhesion to a polymer matrix based on polyethylene (PE), the filler was treated by cold plasma. As a result, the authors have achieved an increase in adhesion and a better distribution of fibers in the polymer matrix. The well-known in situ polymerization method effectively obtains polymer masterbatches with a uniform and controlled distribution of the carbon component in the polymer matrix [12]. This method consists of anchoring catalysts of various compositions on the surface of carbon nanomaterial and carrying out olefin polymerization on the anchoring catalyst. Zdanovich et al. [13] suggested a simple and effective method for the formation of a titanium-
magnesium catalytic system on the surface of carbon nanotubes by fixing hydrocarbon-soluble magnesium dialkyls (MgR₂) on structural defects of nanotubes followed by deposition of the active component (TiCl₄) [13]. In this work, we have offered to synthesize a PE layer on the CNF surface to obtain PE composites with CNFs for improving the adhesion between the nanofiller and the polymer matrix. It has been shown that the previously developed technique of the formation of a catalytic system for ethylene polymerization [13] can be successfully applied for CNFs.

2. Research subjects
We used PE grade PE2NT11 (PJSC Kazanorgsintez, Russia) as a polymer matrix. CNFs synthesized in the laboratory of investigation of nanostructured catalysts and sorbents of Boreskov Institute of Catalysis SB RAS (BIC SB RAS, Novosibirsk, Russia) were used as a filler. A PE layer was synthesized on the CNF surface by the catalytic polymerization laboratory of the BIC SB RAS to improve the adhesive interaction in the polymer/filler system.

3. Methods for the synthesis of CNF and a PE layer on their surface. Technology for obtaining PE nanocomposites
Sample of CNFs were obtained by catalytic decomposition of a propane-butane mixture on Ni-Cu/Al₂O₃ catalyst at 650°C. CNF synthesis was carried out in a Brother XD-1200NT horizontal tube furnace (China) equipped with a quartz reactor. Before the experiment, 0.5 g of the catalyst were uniformly distributed over the surface of a quartz plate, which was then placed into a reactor and heated in an argon flow up to 650°C at 10°C/min. After reaching the temperature regime, the C₃-C₄ mixture was supplied to the catalyst for 1 hr. The reactor was also cooled to room temperature in an inert atmosphere. The yield of the carbon product was 48.6 g per 1 g of catalyst, and the bulk density was 0.076 g/cm³.

We used a MgBu₂/TiCl₄ catalytic system to synthesize the polymer layer on the CNF surface. The fiber was dried in a vacuum using a three-necked glass reactor (10⁻² Torr, 250°C, 4 hr). Then, after cooling to room temperature, 50 ml of heptane were added and, with vigorous stirring, a solution of the magnesium-aluminum complex (MgBu₂*0.1AlEt₃) in heptane at 1.5 mmol of MgBu₂ per 1 g of CNFs. After stirring for 30 minutes, the liquid phase was decanted. The precipitate was washed twice with heptane, and heptane was added to a total volume of 50 ml. A TiCl₄ solution in heptane was added at 1 mmol TiCl₄/g of CNFs treated with MgBu₂. After stirring for 30 minutes, the liquid phase was decanted. Heptane was added to the washed precipitate up to 250 ml in total. The reaction mixture was kept for 30 minutes in a «Sapphire» ultrasonic bath (1.3 L, frequency 35 kHz, generator power 50 W). The magnesium and titanium content in the catalysts was determined by inductively coupled plasma atomic emission spectrometry at a Perkin Elmer Optima 4300 DV. The obtained catalyst contained 0.30 mmol Mg/g of CNFs and 0.45 mmol Ti/g of CNFs.

The production of CNFs with a pre-synthesized PE layer was carried out in a steel reactor with a 1 L volume. Before polymerization, the reactor was evacuated at 80°C and a residual pressure of 10⁻² Torr for 1.5 hr to remove oxygen and traces of moisture; then, it was cooled to room temperature and filled with argon. The prepared suspension containing CNFs with an anchored catalyst (1 g in 250 ml of heptane) was added in an argon flow into the polymerization reactor. After that, with stirring, a cocatalyst (triethylaluminum, 3.8 mmol/L) was added into the reactor, the reaction mixture was heated up to 80°C, and ethylene was supplied to the required pressure (2 bar). Hydrogen (1 bar) was used to control the molecular weight of the resulting polymer. Throughout the reaction, the mixture was vigorously stirred, the temperature in the reactor was maintained constant. An automated system maintained the ethylene pressure and recorded its consumption during the reaction, calculating the polymerization rate. The reaction was carried out until a predetermined amount of PE was obtained, which provided the polymer's required concentration of CNFs.

Polyethylene composites were produced using a laboratory plasticorder Brabender PL2200 (Germany). For this, the PE was smelt at 180°C and a roll rotation speed of 30 rpm in a rotary mixer of the plasticorder. 0.1, 0.5, and 1.0 wt.% of fillers were gradually added into the molten mass. The
resulting mixture was mechanically crushed, and tapes with 2-2.5 cm wide and 2-2.5 mm thick were obtained by extrusion (180°C, 10-15 rpm).

The study of the mechanical properties of materials was carried out on a universal testing machine UTS-2 (Germany) according to GOST 11262-2017 and 9550-81 [14, 15]. Abrasive wear tests were carried out on an AR-40 machine according to the procedure described in GOST 11012-2017 [16]. Electron microscopic studies were carried out using a JEOL JSM-6480LV electron microscope (Japan).

4. Results and discussion

Figure 1 shows electron micrographs of initial sample of CNFs and sample of CNFs, on the surface of which a PE layer is synthesized. The carbon product morphology is represented mainly by fibers, the diameter of which does not exceed 0.5 µm (figure 1a). It should be noted that since the growth of CNFs occurs on a nickel-copper catalyst, metal particles are incorporated into the structure of the filaments. Since these particles show high activity in the reaction of ethylene hydrogenation, the carbon material was preliminarily washed from the catalyst particles with a hydrochloric acid solution.

One can see that the sample obtained by polymerizing ethylene on the CNF/MgBu₂/TiCl₄ catalyst (figure 1b) is uniformly covered with a polymer layer. The diameter of the polymer-coated fibers increased significantly and ranged from 500 to 1300 nm. In general, the polymer follows the shape of the original nanofibers.

The kinetic curve of ethylene polymerization shown in figure 2 is relatively stationary, which makes it possible to obtain masterbatches with the required CNF content by varying the reaction time. During 10 minutes of the reaction, 15.7 g of the masterbatch were obtained (activity 78 kg PE/[mol Ti hr*bar]). The resulting material contained 6.7 wt% of CNFs; the rest was synthesized PE.

![Figure 1. Electron micrographs: a. initial CNFs; b. CNFs modified by PE.](image1)

![Figure 2. Kinetic curve of ethylene polymerization on the CNF/MgBu₂/TiCl₄ catalytic system.](image2)
Table 1 presents the study results of the mechanical characteristics and density of PE composites containing modified and unmodified CNFs.

**Table 1.** Mechanical characteristics and density of PE composite materials containing modified and unmodified CNFs.

| №  | Material        | CNFs, wt% | σ<sub>a</sub>, MPa | σ<sub>y</sub>, MPa | ε<sub>ε</sub>, % | E<sub>d</sub>, MPa |
|----|-----------------|-----------|-------------------|-------------------|----------------|-----------------|
| 1  | PE2NT11         | -         | 28.6              | 21.5              | 744.5          | 1090.3          |
| 2  | PE2NT11 + 0.1% CNFs | 0.1       | 22.5 – 30.2       | 21.7              | 709.5          | 1110.1          |
| 3  | PE2NT11 + 0.5% CNFs | 0.5       | 26.5              | 21.5              | 717.2          | 1108.5          |
| 4  | PE2NT11 + 1.0% CNFs | 1.0       | 22.5              | 22.1              | 611.0          | 1138.2          |
| 5  | PE2NT11 + 0.1% modCNFs | 0.007     | 29.9              | 22.1              | 738.2          | 1125.8          |
| 6  | PE2NT11 + 0.5% modCNFs | 0.033     | 30.1              | 21.7              | 768.7          | 1132.5          |
| 7  | PE2NT11 + 1.0% modCNFs | 0.067     | 30.5              | 21.4              | 774.0          | 1107.3          |

<sup>a</sup> σ<sub>a</sub> – strength at rupture.

<sup>b</sup> σ<sub>y</sub> – yield strength.

<sup>c</sup> ε<sub>ε</sub> – elongation at rupture.

<sup>d</sup> E – elastic modulus.

It was found that adding unmodified fibers into the PE composition leads to a decrease in the elongation at rupture. The strength at rupture with the addition of 0.1 wt% of CNFs varies over a wide range, indicating the agglomeration of nanofibers in the polymer matrix. With an increase in CNF concentration, the strength at rupture gradually decreases. Combined with a decrease in the elongation at rupture, it indicates the accumulation of inhomogeneities in the composite material. However, adding modified CNFs (masterbatches) into the polymer composition improves the deformation characteristics of the composite; with an increase in the filler concentration, there is a tendency to increase the elastic modulus and strength at rupture. It should be noted that the elastic modulus of a composite containing 1.0 wt% of modified CNFs is lower than the ones containing 0.1 and 0.5 wt% of a similar filler. The obtained result can be associated with the plasticizing effect of PE applied on the CNF surface; it leads to a decrease in the whole material’s rigidity. The rest of all studied materials’ characteristics are at the same level as the base PE grade.

Table 2 shows the study results of abrasive wear of the composites.

**Table 2.** Abrasive wear of PE nanocomposites.

| №  | Material              | CNFs, wt% | Abrasive wear, mg |
|----|-----------------------|-----------|------------------|
| 1  | PE2NT11               | -         | 10.8±1.0         |
| 2  | PE2NT11 + 0.1% CNFs   | 0.1       | 12.8±2.0         |
| 3  | PE2NT11 + 0.5% CNFs   | 0.5       | 11.5±1.3         |
| 4  | PE2NT11 + 1.0% CNFs   | 1.0       | 9.9±0.4          |
| 5  | PE2NT11 + 0.1% modCNFs| 0.007     | 6.0±0.1          |
| 6  | PE2NT11 + 0.5% modCNFs| 0.033     | 5.5±0.8          |
| 7  | PE2NT11 + 1.0% modCNFs| 0.067     | 5.5±0.4          |

It can be seen that the abrasive wear of composites containing unmodified CNFs is slightly higher than the one of the base PE grade, which proves that composites with this type of filler have an inhomogeneous structure. The abrasive wear of composites with masterbatches is almost two times lower than ones of the base grade. We can observe a similar effect in forming a homogeneous fine-spherulite ordered structure [17]; it also could explain this case.
5. Conclusion
Thus, the paper describes a method for synthesizing CNFs using a nickel-copper catalyst, which provides a high yield of carbon material. We present methods for synthesizing a PE layer on the CNF surface and a catalytic system for carrying out this reaction. It is shown that the suggested approach allows the reaction to proceed in a stationary mode, to produce CNFs with a uniform PE layer on the surface and regulate the CNF concentration in the masterbatch. Studies of the mechanical properties, density, and abrasive wear of PE composite materials have shown that the pre-synthesis of a PE layer on the CNF surface allows obtaining a material with a stable set of strength characteristics and improved wear resistance, which indicates a uniform distribution of the filler in the polymer material and the formation of a small-spherulite supramolecular structure. It is noteworthy that the content of CNFs in composites with modified fibers (masterbatches) is 15 times lower, with the same concentration of the added initial and modified CNFs. It shows that the method of synthesizing a PE layer on the surface of CNFs significantly increases their efficiency as a dispersion-reinforcing filler. However, it should be taken into account that an increase in the concentration of modified CNFs can lead to a significant increase in the proportion of pre-synthesized PE, which can negatively affect the final composite properties. To overcome these limitations, one can choose proper polymerization conditions during obtaining masterbatches. Hence, the PE layer's molecular structure (molecular weight distribution, microstructure) maybe tuned to the characteristics of the PE matrix (grade) into which these masterbatches are introduced.

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