Preparation of Composite Materials Containing Polyethylene and Carbon Nanotubes by \textit{in situ} Ethylene Polymerization over Titanium-Magnesium Catalyst Fixed on the Surface of Carbon Nanotubes

A.A. Zdanovich\textsuperscript{1}, M.A. Matsko\textsuperscript{1}, A.V. Melezhik\textsuperscript{2}\textsuperscript{*}, A.G. Tkachev\textsuperscript{2}, V.A. Zakharov\textsuperscript{1}

\textsuperscript{1} Boreskov Institute of Catalysis SB RAS, Lavrentiev Ave. 5 (Prospekt Akademika Lavrentieva 5), Novosibirsk, 630090, Russia; \\
\textsuperscript{2} Tambov State Technical University, NanoTechCenter, 106, Sovetskaya St., Tambov, 392000, Russia

* Corresponding author. Tel.: +7 4752 63 92 93. E-mail address: nanocarbon@rambler.ru

Abstract

The data on the preparation of composite materials containing polyethylene and multi-walled carbon nanotubes (MWCNTs) of the Taunit brand are presented. To obtain these composites by \textit{in situ} polymerization, a catalytic system formed by the interaction of an organomagnesium compound and TiCl\textsubscript{4} on the surface of nanotubes was used. The catalyst fixed on the MWCNT surface has a high activity in ethylene polymerization and allows to obtain a polymer with different molecular weight. The data on the formation of a polymer on the MWCNT surface and the morphology of composites formed on various Taunit samples are presented.

Keywords

Carbon nanotubes; polyethylene; nanocomposites; polymerization filling method; \textit{in situ} polymerization.

Introduction

Recently, it has been of great interest to create new polymer-carbon nanocomposites due to their improved physical and mechanical properties compared to pure polymer. They are widely in demand in various fields of technology [1, 2]. Such composite materials have high strength, low density, and the introduction of conductive carbon nanomaterials into polymer structure makes it possible to control their electrophysical properties. Widespread methods for introducing fillers, based on the methods of mechanical mixing of polymer melts, have significant limitations due to the inhomogeneity of the obtained composite materials. To obtain polymer composites with a uniform and controlled distribution of the carbon component in the polymer matrix, the well-known \textit{in situ} polymerization method [3] seems to be promising. This method consists in anchoring catalysts of various compositions on the surface of carbon nanomaterial (CNM) and carrying out the olefin polymerization on an anchored catalyst.

A large number of studies have been performed on the preparation of polyolefin / CNM composite materials by \textit{in situ} polymerization using various types of catalytic systems: Ziegler – Natta [4–7], metallocenes [8–10], and post-metallocenes [11]. Among these catalytic systems, Ziegler-type catalysts are the easiest to obtain. Moreover, having high activity they allow to control the molecular structure of the resulting polymer over a wide range.

Earlier, we proposed 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 (MgR\textsubscript{2}) on structural defects of MWCNTs followed by the deposition of the active component (TiCl\textsubscript{4}) [12].

This work presents this method to fix a titanium-magnesium catalytic system on the surface of Taunit MWCNT samples that differ in morphology, structural characteristics, and degree of purity (residual content of the catalyst used in the synthesis of MWCNTs). The data on the composition of the catalytic system formed on the MWCNT surface and its activity in
ethylene polymerization were received. Composite materials using Taunit samples with different morphologies, varied content of MWCNTs, and varied molecular weight of polyethylene were obtained. The morphology of the polymer formed on the surface of various MWCNT samples was studied.

**Experiment**

**Starting materials**

Multi-walled carbon nanotubes manufactured by NanoTechCenter, Tambov were used. Nanotubes were grown in an industrial reactor from a propane-butane mixture on metal oxide catalysts, which were mixed oxides CoMoAlMgO or FeMoAlMgO. Moreover, an increase in the CVD synthesis time leads to an increase in the mass yields of CNTs, an increase in their length, and at the same time an increase in their degree of aggregation. In order to reveal the effect of these factors on the properties of polymer composites, several batches of CNTs were synthesized at different growth times.

**Taunit Co-40** – MWNTs of the Taunit-M type obtained on a cobalt catalyst with a growth time of 40 min. The content of the CoMoAlMgO catalyst is 4.1 %. The specific surface area is 379 m$^2$/g. The bulk density is 20 g/dm$^3$.

**Taunit Co-5** – MWNTs of the Taunit-M type obtained on a cobalt catalyst, but with a very short growth time (5 minutes). The content of the CoMoAlMgO catalyst is 12.0 %. The bulk density is 6 g/dm$^3$. The low bulk density may indicate that with a short growth time the nanotubes do not have time to agglomerate and form the very bulky mass.

**Taunit Fe** – MWNTs of the Taunit-M type obtained on an iron catalyst in an experimental flow reactor. The estimated contact time of growing nanotubes with a carbon source gas is about 30 minutes. In these nanotubes the content of the FeMoAlMgO catalyst is 9.4 %. The specific surface area is 467 m$^2$/g. The bulk density is 30 g/dm$^3$.

**Taunit Fe-15** – MWNTs of the Taunit-M type obtained on an iron catalyst with a growth time of 15 min. The content of the FeMoAlMgO catalyst is 7.3 %. The specific surface is 183 m$^2$/g. The bulk density is 10 g/dm$^3$. It can also be seen here that with the short growth time nanotubes with the low bulk density are obtained probably due to the weak aggregation of such nanotubes.

**Taunit Fe-15P** is a batch of short MWCNTs Taunit Fe-15 purified from the catalyst by treatment with hydrochloric acid. The residual catalyst content is less than 1 %.

The outer diameter of all nanotubes is in the range of 10–20 nm.

Commercial dibutyl magnesium (“Acros Organics”) in the form of a solution in heptane with a concentration of 0.5 M contains triethyaluminium, 1 wt. %, the molar ratio is Mg/Al = 8.2).

**Preparation of the catalytic system fixed on the MWCNT surface**

A 0.5-gram mass of MWCNTs was loaded into a glass reactor and dried in vacuum ($10^{-2}$ torr) at a temperature of 250 °C for 4 h. Then, the reactor was cooled to room temperature and filled with argon. Then, in a stream of argon, 50 ml of heptane was added to the dried MWCNTs. With vigorous stirring, a solution of the magnesium-aluminum complex (MgBu$_2\times$0.1 AlEt$_3$) in heptane was added at the ratio of 2 mmol MgBu$_2$ per g of MWCNTs. The resulting suspension was stirred for 30 minutes at room temperature, then the liquid phase was decanted, the precipitate was washed twice with pure heptane, and heptane was added to a total volume of 50 ml. Then, a solution of TiCl$_4$ in heptane was introduced with stirring at the ratio of 2 mmol TiCl$_4$/g of MWCNTs. The catalyst suspension was stirred for 30 minutes at room temperature, then the liquid phase was decanted, the precipitate was washed twice with heptane. Heptane was then added to a total volume of 250 ml.

The magnesium and titanium contents in the catalysts were determined by inductively coupled plasma atomic emission spectrometry (ICP AES) using a PerkinElmer Optima 4300 DV instrument.

**Preparation of MWCNT/PE composite by in situ polymerization**

Composites were prepared in a steel reactor with a volume of 1 liter. Before polymerization, the reactor was evacuated at 80 °C and residual pressure of $10^{-2}$ torr, then it was cooled to room temperature and filled with argon. Before polymerization, the catalyst suspension in heptanes was dispersed for 30 minutes in a Sapphire ultrasonic bath (volume 1.3 l, frequency 35 kHz, generator power 50 W). Then, a suspension containing MWCNTs with an anchored catalyst (0.1–0.2 g in 250 ml of heptane) was introduced in a stream of argon into a polymerization reactor. After that, a cocatalyst (triethyl aluminum, 3.8 mmol/l) was introduced with stirring into the reactor, then the reaction mixture was heated to a temperature of 80 °C. The reactor was feed by ethylene (1–2 bar). Hydrogen (1 bar) was used to control the molecular weight of the resulting polymer. The polymer yield was controlled by changing of the polymerization time.
Methods for studying the properties of composites

The intrinsic viscosity ($\eta$) of the polymer component of MWCNT/PE composites was measured in decalin at 135 °C on a Ubbelode viscometer. The viscosity average molecular weight was calculated by the Margolies formula (1):

$$M_v = 5.37 \times 10^4 \times [\eta]^{1.49}.$$

The molecular weight distribution (MWD) of the polymer component of MWCNT/PE composites was determined on a PL-220 high-temperature liquid gel permeation chromatograph at a temperature of 160 °C in an eluent of 1,2,4-trichlorobenzene, at a flow rate of 1 cm$^3$/min. To separate the polymers, a PL Gel Olexis column kit was used. To construct the calibration curves, polyethylene and polystyrene standards were used in a wide range of molecular weights ($MW$) (750–13200000 g/mol).

Electron microscopic images of MWCNTs and MWCNT/PE composites were obtained using a scanning electron microscope (JSM6460LV, Jeol). To do the research, the samples were fixed on a copper holder using carbon tape. To prevent recharging of the studied MWNT/PE samples, a thin layer of gold (coating thickness 10-15 nm) was preliminarily applied (sprayed).

The uniformity of the MWCNT distribution in the polymer matrix was evaluated using optical microscopy (a ZEISS Stemi 2000-C microscope equipped with a CMOS camera, magnification ratio from 64 to 100). The preparation of thin films of the samples was carried out by hot pressing at a temperature of 160°C and a pressure of 400 kg/cm$^2$.

Results and discussion

The formation of a catalytic system for ethylene polymerization on the MWCNT TAUNIT surface

The most effective Ziegler–Natta catalysts for ethylene polymerization are supported systems that contain highly dispersed magnesium dichloride as a support and titanium chlorides as an active component (titanium-magnesium catalysts – TMC).

In the present work, we used the MgBu$_2$ $\times$ $\times$ 0.1 AlEt$_3$ complex dissolved in heptane as the initial organomagnesium compound to form a catalyst on the surface of MWCNTs.

Table 1 presents data on the chemical composition of the catalytic systems formed on the surface of the MWCNT Taunit.

| Experiment number | CNT Taunit type | Catalyst composition |
|-------------------|-----------------|----------------------|
| 1                 | Co-40           | Mg, mmol/g Ti, mmol/g Mg/Ti |
| 2                 | Co-5            | 0.9                   | 0.8                  | 1.8 |
| 3                 | Fe              | 1.0                   | 0.7                  | 1.4 |
| 4                 | Fe-15           | 1.0                   | 0.9                  | 1.1 |
| 5                 | Fe-15 P         | 0.8                   | 1.1                  | 0.7 |

In all cases (Table 1), a close amount of the organomagnesium compound 0.8–1.0 mmol/g is fixed on the surface of Taunit samples of various modifications, which leads to a rather high Mg content (1.9–2.4 wt. %). After treating the suspension of MWNT/MgBu$_2$ with a TiCl$_4$ solution, the amount of anchored titanium was 0.7–1.1 mmol/g (3.7–5.3 wt. % Ti). The molar ratio Ti/Mg is close to MWCNTs of various modifications; it is within the range 1.9–2.2. These results correspond to the data obtained earlier in the study of the catalyst formation on the MWCNT surface obtained on the Fe–Co catalyst [12].

It was shown in [12] that the formation of an active catalyst on the MWCNT surface occurs as a result of anchoring MgBu$_2$ on the surface defects of MWCNTs. The subsequent treatment of MgBu$_2$ with a TiCl$_4$ solution leads to the formation of a polymerization catalyst containing complexes of titanium and magnesium on the MWCNT surface.

It should be noted that the purification of the Taunit Fe-15 MWCNTs (containing 7.3 % FeMoAlMgO) from the catalyst has little effect on the amount of magnesium and titanium compounds to be anchored. A higher amount of the fixed active component in the Taunit MWCNTs can be noted in comparison with the data of [12], which can probably be explained by a higher content of defects on the Taunit MWCNT surface.

Using the polymerization filling method, composites based on various types of MWN Ts and polyethylene were obtained. Tables 2 and 3 show data on the effect of the MWNT Taunit type on the catalyst activity fixed on their surface in ethylene polymerization and the properties of the obtained composites. Kinetic curves of ethylene polymerization on Taunit/MgBu$_2$/TiCl$_4$ systems are shown in Figs. 1 and 2.
Table 2

The effect of the MWCNT Taunit type on the activity of the catalyst fixed on their surface in ethylene polymerization and molecular weight distribution of the obtained composites

| Experiment number | MWCNT type       | τ, min | Yield, g PE/g MWCNT | MWCNT, wt. % | Activity, kg PE/[mole Ti time bar] | \(M_w\), kg/mol | \(M_w/M_n\) |
|-------------------|------------------|--------|---------------------|--------------|-----------------------------------|----------------|-------------|
| 1                 | Taunit Co-40     | 38     | 140                 | 0.7          | 138                               | –              | –           |
| 2                 | Taunit Co-5      | 0.85   | 11                  | 8.3          | 323                               | –              | –           |
| 3                 | Taunit Co-5      | 5      | 50                  | 2.0          | 420                               | 82             | 5.1         |
| 4                 | Taunit Co-5      | 28     | 232                 | 0.4          | 360                               | 100            | 5.3         |
| 5                 | Taunit Fe        | 2      | 3                   | 23           | 169                               | –              | –           |
| 6                 | Taunit Fe        | 20     | 46                  | 2.1          | 100                               | –              | –           |
| 7                 | Taunit Fe        | 64     | 124                 | 0.8          | 51                                | –              | –           |
| 8                 | Taunit Fe-15     | 2      | 5                   | 8.1          | 266                               | –              | –           |
| 9                 | Taunit Fe-15     | 23     | 180                 | 0.5          | 264                               | 130            | 4.8         |
| 10                | Taunit Fe-15 (Och) | 11     | 84                 | 1.2          | 214                               | –              | –           |

Polymerization conditions: 80 °C, 2 bar C\(_2\)H\(_4\), 1 bar H\(_2\), [AlEt\(_3\)] = 3.8 mmol/l.

Table 3

The activity of the TMC catalyst anchored on the Taunit Co-5 surface at ethylene polymerization in the absence of hydrogen and the molecular weight of the obtained ultra-high molecular weight polyethylene

| Experiment number | τ, min | Yield, g PE/g MWCNT | MWCNT, wt. % | Activity, kg PE/[mole Ti time bar] | \(M_w\), kg/mol |
|-------------------|--------|---------------------|--------------|-----------------------------------|----------------|
| 11                | 13     | 100                 | 1.0          | 421                               | 2 600          |

Polymerization conditions: 40 °C, 1 bar C\(_2\)H\(_4\), [AlEt\(_3\)] = 3.8 mmol/l.

---

**Fig. 1.** Kinetic curves of ethylene polymerization on the Taunit-Co/MgBu\(_2\)/TiCl\(_4\) catalyst system (experiment numbers correspond to those given in Table 2)

**Fig. 2.** Kinetic curves of ethylene polymerization on the Taunit-Fe/MgBu\(_2\)/TiCl\(_4\) catalyst system (experiment numbers correspond to those given in Table 2)
It can be noted that shorter nanotube samples (Taunit Co-5, Taunit Fe-15 and Taunit Fe-15P) show a higher activity in ethylene polymerization in comparison with long nanotubes (Taunit Co-40 and Taunit Fe). Apparently, due to the short growth time, Taunit Co-5, Taunit Fe-15 and Taunit Fe-15P are the least aggregated and the lightest. The higher activity of the catalytic systems formed on their surface is probably associated with a looser morphology of short tubes and, as a consequence, a greater availability of active sites for the monomer. Kinetic curves of ethylene polymerization shown in Fig. 1 and 2 are relatively stationary, which makes it possible to obtain composites with the required MWCNT content by varying the reaction time.

The effect of the type of carbon nanotubes on the molecular weight characteristics of the polymers obtained on the MWCNT/MgBu2/TiCl4 catalyst system was studied. The method of gel permeation chromatography was used to analyze the polymer components of the composites obtained under identical conditions on the MgBu2/TiCl4 system immobilized on Taunit Co-5 and Taunit Fe-15. The results presented in Table 2 show that the catalytic system anchored to the samples of MWCNT Taunit of various modifications produces a polymer with close molecular weight (82–130 kg/mol) and close molecular weight distribution (MW/Mn = 4.8 – 5.3).

On the Taunit Co-5/MgBu2/TiCl4 catalyst system, a polymer composite with ultra-high molecular weight polyethylene (UHMWPE) was obtained (Table 3). The polymer part of the composite, obtained at 40 °C and an ethylene pressure of 1 bar, is characterized by a viscosity of 13.6 dL/g, which corresponds to a molecular weight of 2600 kg/mol. It should be noted that the high activity of the catalytic system is maintained even at a low polymerization temperature (40 °C) upon receipt of UHMMPF (Table 3).

To sum it up, it can be noted: the high activity of the catalytic system in a wide temperature range (40–80 °C) which allows to obtain a high polymer yield under mild conditions (C2 = 2 bar); the stability of the kinetic curve which allows to obtain composites with the required MWCNT content, varying the reaction time, as well as the weak dependence of the molecular weight characteristics of the polymer part on the type of support (carbon nanomaterial).

**Studying the morphology of polyethylene formed during ethylene polymerization on the TAUNIT/TMC system**

Using the method of scanning electron microscopy, the influence of the MWCNT morphology (Taunit Co-40 and Co-5, Taunit Fe and Fe-15) on the morphology of MWCNT/PE composites obtained by in situ polymerization (see Figs. 3 and 4) was studied. It can be seen that all the presented samples of MWCNT powders at the macro level are agglomerates (macro particles) in the form of elongated curved sheets (“lamellas”) of various sizes (from 30 to 300 μm; Fig. 3a, d and Fig. 4a, d). With a scaling-up one can notice that these “lamellas” are quite loose and consist of entangled nanotubes (Fig. 3b–c, e–f, Fig. 4b–c, e–f).

In order to study the peculiarities of the formation process of Taunit/PE MWCNT composites depending on the MWCNT type, composites with low yields were obtained: 3 g PE/g Taunit Fe-15, 5 g PE/g Taunit Fe and 11 g PE/g Taunit Co-5 (see Fig. 5–7). Figs. 5–7 show microphotographs of composites based on MWCNT Taunit in comparison with microphotographs of the corresponding nanotubes.

During the growth of polyethylene on the Taunit Fe/TMC sample (sample 5, the yield of 3 g PE/g MWCNTs) shows that there is a partial destruction of MWCNT agglomerates (Fig. 5d–e) and the formation of polymer microparticles in the form of disks (diameters from 120 to 300 nm) on MWNT fibers (Fig. 5f).

During the polymerization on TMC on the Taunit Fe-15 MWCNTs (composite 8, yield 5 g PE/g MWCNTs), more complete destruction of “the lamellas” occurs (Fig. 6d), and the formation of loose agglomerates consisting of round particles of 200–500 nm in size is observed (Fig. 6e). Polymeric disks are characterized by a diameter of 100–600 nm (Fig. 6f).

Fig. 7 shows photographs of sample 2 with the yield of 11 g PE/g MWCNT obtained on the Taunit Co-5/TMC catalyst system. Compared with the initial Taunit Co-5 agglomerates (Fig. 7a), Fig. 7d shows that in situ polymerization completely destroys “the lamellas” of the initial nanotubes with the formation of loose aggregates larger than 50 μm in size, consisting of round particles. In Fig. 7f, smooth fibers with a diameter of 60–90 nm can be seen. These are probably nanotubes coated with a thin layer of polymer. Also, the formation of a large number of individual circular particles of polymer diameters of 400–600 nm is visible.

Fig. 8 shows microphotographs of composite 3 characterized by a higher yield of PE on the Taunit Co-5 MWCNTs (50 g PE/g MWCNTs). Photographs on Figs. 8a, b show that the destruction of large aggregates of the size that were previously observed in Fig. 7d occurs for a sample with a lower yield (11 g PE/g MWCNTs). Fig. 8c, d show that the polymer grows on the MWCNT surface in the form of polymer disks, with a disk thickness of about 10–20 nm. In Fig. 8d, at maximum magnification, one can notice a separate nanotube coated with an inhomogeneous polymer layer.
Fig. 3. SEM photographs of the starting samples of MWCNT Taunit obtained on a Co catalyst

Fig. 4. SEM photographs of the starting samples of MWCNT Taunit obtained on a Fe catalyst
Fig. 5. SEM photographs of the starting sample of MWCNT Taunit Fe and composite PE/Taunit Fe (3 g PE/g MWCNT, Sample 5 in Table 2)

Fig. 6. SEM photographs of the starting sample of MWCNT Taunit Fe-15 and composite PE/Taunit Fe-15 (5 g PE/g MWCNTs, Sample 8 in Table 2)
Fig. 7. SEM photographs of the starting sample of MWCNT Taunit Co-5 and composite PE/Taunit Co-5 (11 r PE/g MWCNTs, Sample 2 in Table 2)

Fig. 8. SEM photographs of the composite 50 g PE/Taunit Co-5 (Sample 3 in Table 2)
The obtained samples of Taunit/PE MWCNT composites are homogeneous gray powders, a typical form of which is shown in Fig. 9. No formation of separate white particles of pure PE, as well as individual black particles of MWCNT agglomerates, was observed, indicating a uniform coating of MWCNTs with polyethylene particles. Thin films of MWCNT/PE composites (thickness ~ 100 μm) were obtained by hot pressing and studied by optical microscopy (Fig. 10). Fig. 10 shows that the size of the residual MWCNT agglomerates in the film samples, as a rule, does not exceed 50 μm. Based on the results obtained, it can be concluded that MWCNTs are fairly evenly distributed in the polymer matrix of composites and the developed method is promising for producing composites with different content of MWCNTs, both masterbatch and finished composites based on MWCNTs of various types and polyethylene.

**Conclusion**

This work shows the possibility of the formation of the MgR₂/TiCl₄ catalytic system for ethylene polymerization on the surface of various types of Taunit multi-walled carbon nanotubes. It was found out that 0.8–1.0 mmol Mg/g MWCNTs and 0.5–1.1 mmol Ti/g MWCNTs are fixed on the MWCNT surface. The formed catalyst system exhibits high activity (up to ~ 400 kg PE/[mol Ti hour bar]) in a wide temperature range (from 40 to 80 °C). The stationary profile of the kinetic curves of ethylene polymerization allows to obtain composites with the required MWCNT content by varying the reaction time.
Using scanning electron microscopy, it was shown that during in situ polymerization, the MWCNT agglomerates are destroyed. The polymer grows on the MWCNT surface in the form of disks and, with an increase in the yield, uniformly covers the surface of the nanotube. The optical microscopy in thin films of composites obtained by hot pressing shows that the size of residual MWCNT agglomerates, as a rule, does not exceed 50 μm. Based on the results obtained, it can be concluded that MWCNTs are fairly evenly distributed in the polymer matrix of composites and the developed method is promising for producing both masterbatch and finished composites based on MWCNTs of various types and polyethylene. At the same time, the developed approach allows to vary widely both the MWCNT content in composites (23–0.5 % and less) and the molecular weight of the obtained polyethylene (from 82–130 up to 2600 kg/mol).

Acknowledgments

The authors are grateful to A.N. Serkova and N.A. Rudina for receiving microphotographs of the studied images. The studies were conducted using the equipment of the Center for Collective Use “National Center of Catalyst Research”. This work was carried out within the framework of the budget project for Boreskov Institute of Catalysis.

References

1. Tong X., Liu C., Cheng H., Zhao H., Yang F., Zhang X. Surface Modification of Single-Walled Carbon Nanotubes with Polyethylene via In Situ Ziegler. Natta Polymerization, Appl. Polym. Sci. 2004, 92, 3697-3700. https://doi.org/10.1002/app.20306
2. Spitalsky Z., Tasis D., Papagelis K., Galiotis C. Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties. Prog. Polym. Sci. 2010, 35, 57-401. https://doi.org/10.1016/j.progpolymsci.2009.09.003
3. D’yachkovskii F.S., Novokshonova L.A. The Synthesis and Properties of Polymerisation-filled Polyalkenes. Russ. Chem. Rev. 1984, 53, 117-131. https://doi.org/10.1070/RC1984v053n02ABEH003031
4. Park H.J., Kim J., Seo Y., Shim J., Sung M.Y., Kwak S. Wear behavior of in situ polymerized carbon nanotube/ultra high molecular weight polyethylene composites. Macromol. Res. 2013, 21, 965-970. https://doi.org/10.1007/s13233-013-1130-6
5. Wang N., Qin Y., Huang Y., Niu H., Dong J.Y., Wang Y. Functionalized multi-walled carbon nanotubes with stereospecific Ziegler-Natta catalyst species: Towards facile in situ preparation of polypropylene nanocomposites. Appl. Catal. A Gen. 2012, 435-436, 107-114. https://doi.org/10.1016/j.apcata.2012.05.041
6. Amoli B.M., Ramazani S.A.A., Izadi H. Preparation of ultrahigh-molecular-weight polyethylene/carbon nanotube nanocomposites with a Ziegler-Natta catalytic system and investigation of their thermal and mechanical properties. J. Appl. Polym. Sci. 2012, 125, E453-E461. https://doi.org/10.1002/app.36368
7. Liu Z., Yu M., Wang J., Li F., Cheng L., Guo J., Huang Q., Zhou Y., Zhu B., Yi J., Liu Y., Yang W. Preparation and characterization of novel polyethylene/carbon nanotubes nanocomposites with core-shell structure. J. Ind. Eng. Chem. 2014, 20, 1804-1811. https://doi.org/10.1016/j.jiec.2013.08.034
8. Funck A., Kaminsky W. Polypropylene carbon nanotube composites by in situ polymerization. Compos. Sci. Technol. 2007, 67, 906-915. https://doi.org/10.1016/j.compscitech.2006.01.034
9. Li S., Chen H., Cui D., Li J., Zhang Z., Wang Y., Tang T. Structure and properties of multi-walled carbon nanotubes/polyethylene nanocomposites synthesized by in situ polymerization with supported Cp2ZrCl2 catalyst. Polym. Compos. 2009, 31, 507-515. https://doi.org/10.1002/pc.20831
10. Al-Harthi M.A. Mechanical Properties of Polyethylene-Carbon Nanotube Composites Synthesized by In Situ Polymerization Using Metallocene Catalysts. 2018 https://doi.org/10.1155/2018/4057282
11. Zhang L., Castillojos E., Serp P., Sun W.-H., Durand J. Enhanced ethylene polymerization of Ni(II) complexes supported on carbon nanotubes. Catal. Today. 2014, 235, 33-40. https://doi.org/10.1016/j.cattod.2014.03.067
12. Zdanovich A.A., Semikolenova N.V., Kuznetsov V.L., Matsko M.A., Moseenko S.I., Zakharov V.A. Formation of Ziegler-type catalytic systems on the surface of multi-walled carbon nanotubes for the production of composite materials by in situ polymerization. J. Appl. Polym. Sci. 2019, 136, 48212. https://doi.org/10.1002/app.48212