Investigation of mechanical properties of masterbatches and composites with small additions of CNTs

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Abstract. The present paper investigated physical and mechanical properties of the nanotube masterbatches and the polymer composites with low contents of carbon nanotubes (CNTs), which were obtained by diluting masterbatches. Ethylene-octene copolymer was used as the binder for the masterbatches, which provides the elasticity of the material at a content 20 wt% of CNT. Masterbatches were obtained with a 2-roller mixer, and their additive to polypropylene was carried out on a single screw injection molding machine. Strength properties of ethylene-octene copolymer increased when adding CNTs in an amount of 5-20 wt%. When the concentration of CNT in masterbatches is reduced to 0.01-0.1 wt% its strength characteristics increased up to 4-18%. The most effective strengthening of polypropylene was observed with the content of CNTs 0.1 wt%.

1. Introduction

Carbon nanotubes (CNTs) have a unique complex of physical and mechanical properties, which provides great perspectives of their use in the creation of functional and constructional materials [1-4]. The mechanical properties of CNTs are extremely high, but the problems associated with their dispersion into a polymer matrix are major challenges to realize these properties. Therefore the CNTs and CNTs-based composites are advanced materials for modern materials engineering. CNTs have been considered as a nanoreinforcing filler with a random orientation similar to conventional short fiber reinforced composites [5-8]. However, CNTs are characterized by an extremely high ratio of length to diameter, which contributes to tangling and significantly complicates the process of compounding makes it extremely difficult engineering challenge.

Many different dispersion methods have been applied for loading polymer matrices with CNTs. Sonication is the most commonly reported method [9-12]. It is a process where a transducer is used to agitate particles in solution with a high power ultrasound field with the cavities which implode with a violent and localized release of energy. In high viscosity systems, such as melt of thermoplastic sonication have many problems. Method of compounding on twin screw extruder was used usually for high-viscosity melt of thermoplastics [13, 14]. To improve the mechanical properties of the composites generally is enough small additions of CNTs, but the preparation of composites containing nano-dispersed fillers in an amount of less than 1 wt% is greatly complicated by the problem of effective compounding.
Highly filled systems based on CNTs and polyolefin binder with the high physical and mechanical characteristics can be used as heat or electrically conductive elastic composites, as well as a masterbatch of CNTs to modify with small additives the properties of polymer composites during processing in industrial plants.

A highly promising method of dispersing nanofillers in a polymeric binder, especially in materials with a wide processing temperature range, such as thermoplastic and amorphous modified of polyethylene is rolling. This method allows obtaining highly filled systems with a good distribution of the CNTs for different applications for modern materials engineering. Therefore in this paper we present investigation of the properties of CNTs masterbatch obtained by rolling and evaluated their effectiveness in improving the mechanical properties of thermoplastics.

2. Materials and methods

The objects of study were chosen MWCNTs brand “Taunite-M”, carbon black (CB) “Printex PX-2” and polygraph produced by Ltd. «NanoTechCenter», Tambov, Russia. For obtaining masterbatches we used ethylene-1-octene copolymer Lucene™ LC370 (by LG Chem. Ltd.) as polymer matrix. To synthesize the polymer-nanotube masterbatch was used 2-roller mixer (UB-6175), at a processing temperature of 120±3 °C with a time of treatment of nearly 30 min, to prepare composite samples for mechanical tests we used polypropylene (PP) brand PPG 1120-16, Russia. Obtaining of composites based on masterbatches was carried with Injection Molding Machine Haitian SA 900 with the parameters shown in Table 1. The choice of processing parameters and the formation of a polymer composite was based on the recommendations of the manufacturer for this brand (PPG 1120-16) polymer binder.

| Table 1. Parameters of obtaining PP samples for mechanical testing |
|---------------------------------------------------------------|
| Parameter | Parameter Value |
| Mark of binder | PPG 1120-16 |
| Zone temperature of the material cylinder, °C | 215/220/225/230/230 |
| I / II / III / IV / nozzle |
| Mold temperature, °C | 60±5 |
| Screw speed, % | 60 |
| Rate of injection/ molding pressure, c.u./% | 35/35 |
| Shrinkage pressure, c.u. | 43 |
| Forming time, s | 35±5 |
| Cooling time, s | 20±5 |

Breaking bending stress was determined according to ISO 178:210. The impact strength was determined according to ISO 179-1:2000. Tensile stress at break and elongation at break were determined in accordance with ISO 527-1.

3. Results and discussions

In this work we were investigated the mechanical properties of highly filled composites based on two modifications of CNT. Also PP materials were obtained with additions of these nanotubes in an amount of 0.01-0.1 wt%.

The results of investigating the mechanical properties of the highly filled systems based on the thermoplastic polymer matrix LC370 are presented in Table 2. Rigidity of obtained material, which
was evaluated by the elastic modulus, regularly increases with increasing of filler content, wherein the properties of material based on CB Printex PX-2 inferior to those of materials based on the CNT at the same concentrations.

**Table 2. Mechanical Properties of highly filled systems based on LC370**

| Composition                  | Modulus of elasticity, MPa | Stress at break, MPa |
|------------------------------|----------------------------|----------------------|
|                              | along the direction of rolling | transversely to the direction of rolling | average over all | along the direction of rolling | transversely to the direction of rolling | average over all |
| LC370                        | 14 | 14 | 14 | 8 | 8 | 8 |
| LC370 + CNTs, 5 wt%          | 21 | 19 | 20 | 9 | 9 | 9 |
| LC370 + CNTs, 10 wt%         | 37 | 31 | 34 | 9 | 10 | 10 |
| LC370 + CNTs, 20 wt%         | 25 | 70 | 47 | 12 | 12 | 12 |
| CB Printex PX-2              | 32 | 29 | 30 | 8 | 9 | 8 |

Stress at break slightly higher for the samples to which the application of a load carried in the direction perpendicular to the linear displacement of the material on the rollers. There is also an increase in the stress at break when increasing the concentration of CNTs.

Investigation of mechanical characteristics of highly filled systems based on PP matrix with small additions of CNTs is presented in Table 3.

**Table 3. The mechanical properties of PP with small additions of CNTs**

| Composition                  | Stress at break, MPa | Elongation at break, % | Modulus of elasticity, MPa | Charpy impact strength notched kJ/m² |
|------------------------------|----------------------|------------------------|---------------------------|------------------------------------|
| PP+LC370                     | 18.1±0.5             | 551±8                  | 1138±24                   | 5.6±0.3                            |
| 0.01 wt% of Taunite-M (masterbatch with 10 wt% of CNTs) | 18.9±0.5             | 568±8                  | 1314±24                   | 5.8±0.3                            |
| 0.1 wt% of Taunite-M (masterbatch with 10 wt% of CNTs) | 20.4±0.5             | 566±8                  | 1348±24                   | 6.1±0.3                            |
| 0.01 wt% of Taunite-M (masterbatch with 5 wt% of CNTs) | 18.4±0.5             | 569±8                  | 1318±24                   | 6.0±0.3                            |
| 0.01 wt% of CB Printex PX-2 (masterbatch with 10 wt% of carbon black) | 19.1±0.5             | 539±8                  | 1307±24                   | 5.7±0.3                            |
| 0.1 wt% of CB Printex-PX2 (masterbatch with 10 wt% of carbon black) | 17.3±0.5             | 530±8                  | 1279±24                   | 6.2±0.3                            |

Adding CNT masterbatches at extremely low concentrations enhances the stress at break by 13% and the modulus of elasticity of 18% for composites containing 0.1 wt% of Taunite-M with 10 wt% of CNT. Addition of the CNT in an amount of 0.01 wt% irrespective of the masterbatch types provides increased strength properties not more than 4-15% compared with the pure PP. The introduction of CB increases lower of mechanical properties compared to introduction of the CNTs. The concentration dependences in the case of introducing carbon black are the same as in the case introduction of CNTs.
4. Conclusions

Were investigated the physical and mechanical properties of highly filled systems based on CNTs and polyolefin binders (masterbatches) and polymer composites with low contents of CNTs obtained by dilution it with a screw injection molding machine.

It is found that by using ethylene-octene copolymers as a binder can be obtained the elastic materials even when CNT content of 20 wt%. When adding CNTs to ethylene-octene copolymer observed increase in its strength properties, which could allow using it as a final product, such as creating conductive articles.

When adding CNT masterbatches in polypropylene, with a final CNT concentration of 0.01-0.1 wt%, was an increase in the strength properties of up to 18%. The most efficient hardening is observed at CNT content of 0.1 wt%. The addition of CB under similar conditions provides a smaller increase strength properties, and in some cases, their decline.

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