BIOFUNCTIONAL COMPOSITES "POLYMER/CARBON NANOTUBES"

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Introduction

Development of medicine, especially for rehabilitation, is connected with searching for new materials to produce and substitute an organism's parts damaged due to illness. Presently there are vast possibilities to create artificial prosthetic appliances of practically any organ. So the problem is to develop (to create) new materials which would have biomechanical characteristics similar to natural ones. Due to the unique structure and combination of high durability, electro- and thermoconductivity, carbon nanotubes (CNT) are prospective fillings for creation of new composite materials [1]. In this work, structural features, physical and mechanical characteristics were studied of nanocomposites on the base of polytetrafluoroethylene (PTFE), isotactic polypropylene (PP), butadiene-nitrile, and fluorinated rubbers with CNT as filler. Also some biocompatibility properties were studied in experiments *in vivo.*

Experimental

The method of obtaining multi-walled carbon nanotubes (MWCNT) and their characterization are described in [2]. The average diameter of nanotubes was 10–20 nm, specific surface area determined by argon desorption was 200–400 m^2/g, and bulk density was within 20–40 g/dm^3. According to TEM, X-ray diffraction, Raman spectroscopy data, the noticeable amount of amorphous carbon presence was not detected. Four types of nanocomposites based on polymeric matrices – polytetrafluoroethylene (PTFE), polypropylene (PP), and two types of rubbers – were studied. The composites based on PTFE were obtained by methods of mixing PTFE powder (F4-PN20) with CNT in the presence of liquids and following coagulation of PTFE aqueous dispersion with CNT. The dried powdered mixtures were molded by hot-pressing. The samples of composites with different CNT contents (5, 10, 15, and 20 wt%) were tested for uniaxial compression by using *2167-P50* recording device with automatic record of deformation diagrams. Thus conventional yield strength at compression ($\sigma0.2$) and compression elasticity modulus (Ec) were determined. The surface of initial PTFE and PTFE–15% CNT nanocomposite was studied using a *NanoScope IIIa* atomic-force microscope (Veeco corp.). The data obtained were processed with the help of *GWIDDION* software. Samples' surfaces were also studied by AFM tip loaded with antibodies, immunoglobulin type G (IgG) obtained from the animal blood serum. Nanocomposites on the base of polypropylene (PP) 21060 with content of CNT within 0.05–5.0 wt% were obtained by stirring a mixture of molten PP and CNT in an extruder at 50 rpm. Primary samples were got as granules and processed further by hot-pressing.

The samples of rubber filled with CNT were obtained by rolling the raw rubber. Nanocomposites of PP−MWCNT with CNT content of 0.05, 1.0, 3.0, and 5.0 wt%, PTFE−MWCNT with CNT content of 15 wt%, and initial polymer matrices were chosen for experiments *in vivo*.

Results and discussion

According to obtained data the characteristics of the melting temperature were slightly sensitive to the presence of filler and its concentration. At the same time, the beginning of crystallization temperature and other temperature characteristics were significantly influenced by CNT and changed in non-monotone mode with increasing CNT concentration in the polymer matrix. Thus, the lowest temperature for melting to begin in the system PP−MWCNT was observed at 0.05 wt% CNT. This concentration meets the maximum temperature process range, which decreases both at increasing and decreasing CNT concentration. For the crystallization process, there is monotonous, but non-linear temperature dependence of characteristic with increasing concentration of CNT in the studied range. The data obtained agree well with the results [3] for the system PP+0.8% of single-walled carbon nanotubes (SWCNT) when compared with PP+1.0% CNT; the crystallization temperature of PP+CNT is higher as compared with pure PP (Fig. 1).

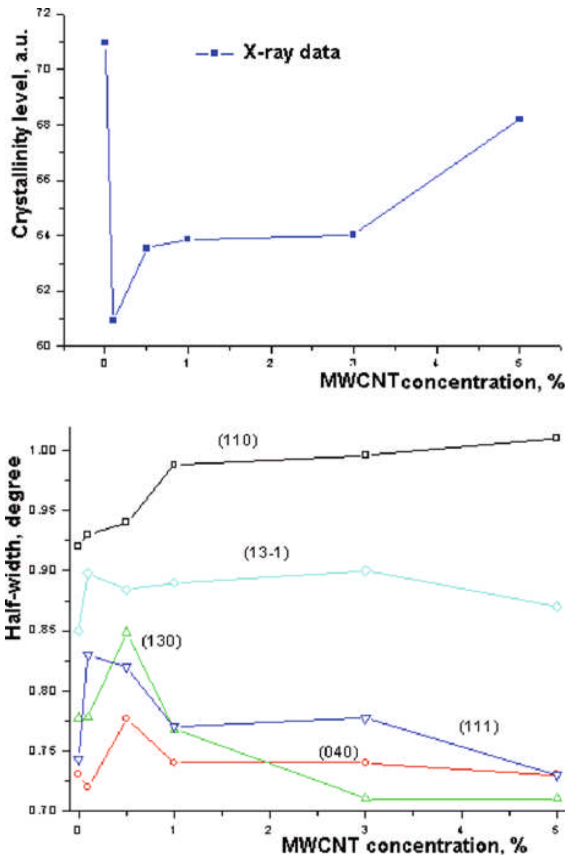
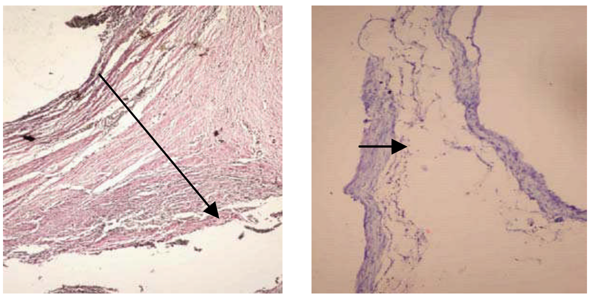


Fig. 1 Dependence of crystallinity level and half-width of diffraction peaks of PP−CNT nanocomposite on MWCNT concentration.

In works was suggested [4, 5] to determine the compatibility of artificial materials with living body by the thickness of fibrous-connective capsule (pocket) that formed around foreign body. Testing of materials was carried out by implantation of the preformed samples into the muscle “pouch” on the back of experimental animals. In order to decrease the number of animals in study and to receive the unbiased results by comparison of the body reaction to different material types the samples were implanted on one animal in different parts of the back. The two types of samples implanted per animal were (a) initial PTFE and (b) PTFE filled with 15 wt% CNT. In the case of PP−CNT the samples with different contents of CNT (0.05, 0.1, 3, and 5 wt%) were implanted along both back’s sides. Four weeks after operation, the samples with surrounding tissue were excised for further histological study and for investigation of the samples’ surface. The level of body reaction was determined by measuring the thickness of fibrous-connective capsule which formed around the sample. According to the histological data the insertion of 15 wt% CNT into PTFE matrix essentially influences the fibrous-connective formation around the sample. Histological slides (Fig. 2) have shown that the capsule thickness around initial PTFE was appreciably larger.



PTFE **PTFE-CNT**

Fig. 2 Thickness of fibrous-connective tissue around PTFE and PTFE+15 wt% MWCNT.

The surface triggers the mechanism of foreign body recognition by immunoglobulin type G adhesion (IgG) [5, 6]. To measure the adherent IgG forces to surface is possible with the use of AFM. The scheme of measuring is represented in Fig. 3.

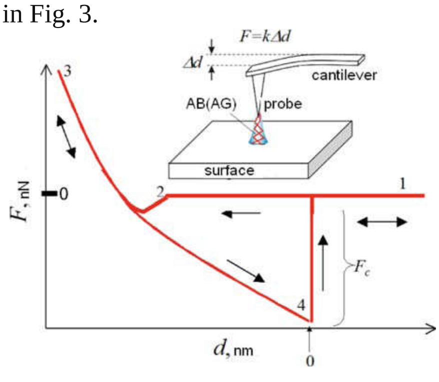


Fig. 3 Scheme of pull-off forces evaluation Fc by ACS method. Bioadhesion force (retention) was determined by evaluation of tip cantilever compliance Δd as $F = k\Delta d$, where k is cantilever elastic constant.

In all studies standard silicon nitride AFM tip was used (*DNP-20*, Veeco corp.) with nominal cantilever flexibility of 0.06 N/m. The force of interaction of modified AFM tip with initial matrix surface was higher than with nanocomposite. It means that the initial PTFE matrix is recognized by living organism as foreign material which triggers bodies’ protective reaction. The interaction of PTFE−CNT system and modified AFM tip is lower and it means that body’s protective reaction would be lower. The data obtained agree with histological results which unambiguously show that PTFE−CNT composites cause the least fibrous-connective capsule formation around them. In other words, presence of MWNT in matrix improves biocompatibility.

Conclusions

Carbon nanotubes (CNT) are prospective fillers for polymer materials due to their unique structure and outstanding combination of strength, electrical and thermal properties of CNT. Reinforcement of polymers including elastomers with infinite CNT net results in change of both three-dimensional material parameters and surface properties. In the systems PTFE−CNT, PP-CNT, and rubber elastomers−CNT, increase of mechanical parameters was observed such as yield strength, elasticity modulus, breaking strength, wearing resistance, as well as chemical stability and electrical conductivity. Filling of polymers with CNT changes their surface properties and improves biocompatibility. This was demonstrated by experiments in vivo with PTFE-CNT and PP-CNT systems. Filling of polymers with CNT leads to decreasing of interaction forces between AFM tip modified with antibody and nanocomposite surface. This effect can be used as a method for measuring artificial implants’ biocompatibility. At low CNT concentration (below percolation threshold) the structure peculiarities were observed due to the presence of disordered phase. This phase probably appears around nanopores, and its existence correlates with other characteristics of the system. Polymer-CNT composites are prospective materials for manufacturing medical endoprosthesis.

References

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