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Nanoarchitectonics at surfaces using multifunctional initiators of surface-initiated radical polymerization for fabrication of the nanocomposites

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ABSTRACT

In this work, the nanoarchitectonics approach to synthesize a new functional material with certain configurations and hierarchical motifs of the multifunctional initiators of surface-initiated radical polymerization (MPIs) on surface of multi-wall carbon nanotubes (MWCNTs) was realized. The presence of covalently-linked MPIs on the surfaces of amine functionalized MWCNTs was confirmed by Raman spectroscopy and thermal analysis. Nanocomposites of polybutylene terephthalate – poly(tetramethylene oxide) – (PBT/PTMO) with modified nanotubes show higher values of Young's modulus, elongation at break, and crystallization temperature in comparison to non-modified ones.

1. Introduction

Nanoarchitectonics is a relatively new concept implying the methodology for construction of functional materials with certain configurations and hierarchical motifs at a nanoscale [1,2]. The concept, termed as nanoarchitectonics, was first proposed by Masakazu Aono and Katsuhiko Ariga and then summarized in numerous excellent works [3,4]. This concept is based on combination of nanotechnology methodology with various research trends, especially supramolecular chemistry [5,6]. Most prominent is an application of the principles of nanoarchtectonics to engineer surfaces of micro- and nanoparticles, nanotubes as well as live cells or organisms [6–15].

Application of multifunctional initiators of surface-initiated radical polymerization (MIs) in the nanoarchitectonics processes is new and prospective method to fabricate materials with high molecular organization. MIs are a class of the products with different chemical structure, which have at least two types of functional groups. The first type of functional groups are able to fabricate self-assembly on solid surfaces ("grafting to"), while second type of functional groups are able to initiate surface-grafted polymerization ("grafting from") [16–18]. The third type of the functional groups is responsible for special properties, such as pH-sensitivity, compatibility and biocompatibility etc. Main techniques of the surface-initiated radical polymerization using MIs are surface-initiated atom transfer radical polymerization, surface-initiated reversible addition fragmentation chain transfer polymerization, surface-initiated photoiniferter-mediated polymerization and surface-initiated polymerization using peroxide initiators or azoinitiators [16–18].

MIs were used for fabrication of the self-assembly on different microscale and macroscale substrates, such as silicon, glass, silica, boron nitride, halloysite or carbon nanotubes, and following fabrication of the grafted polymer brushes or nanocomposites [16–18]. Despite the strong suitability of using the MIs for realization of the nanoarchitectonics' approach, only few research groups seriously thought about it. Special attention was paid to the application of nanoarchitectonics using MIs to engineer the surfaces of the live cells. Pioneering work was done by Insung S. Choi [19] who developed a cytocompatible method of surface-initiated, activator regenerated by electron transfer, atom transfer radical polymerization for engineering cell surfaces with synthetic polymers.

Polymer nanocomposites are among the most promising materials for a number of applications. They often possess specific mechanical, physical, magnetic, optical, dielectric or electromagnetic properties not available in polymers alone [20–25]. Carbon nanotubes (CNTs) attract particular attention as the fillers used in such nanocomposites [26, 27]. A CNT is an allotropic form of carbon, which looks like a rolled sheet of graphene. They are shaped like tubes about some nm in diameter and one or some μm long. It was postulated [23–28] that CNTs exist in

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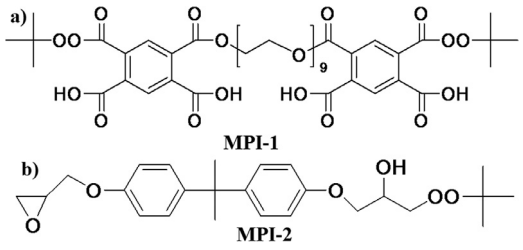

Fig. 1. MPIs with carboxyl (MPI-1) or epoxy (MPI-2) functional groups.

two dimensions simultaneously (microscale and nanoscale). The aspect ratios of length to diameter for CNTs are between 10^8 and 10^9, thus being much larger than for any other known filler [28].

Uses of CNTs as fillers for polymers to improve their mechanical, physical and electrical properties have been reported in numerous publications [26, 29–31]. The most important application of these nanotubes is based on their mechanical properties as reinforcement in composite materials [32–35]. As in any composites containing fillers, the ability of the filler to disperse in a matrix, as well as the character of the interfacial interaction between the filler surface and the matrix are essential. This is especially important for nanocomposites, in which the interfacial surface is very large. Needless to say, the nature of the interfacial layer then determines the properties of the composite.

An effective way to improve the dispersion of nanotubes and their adhesion to the polymer matrix is a surface modification of CNTs. In previous works, non-chemical modification methods including mixing in a solvent [36,37] or a melt [38], encapsulation in a polymer shell [39] as well as polymer adsorption [40] were described. Polymerization of monomers "in situ" in the presence of CNTs [41,42] is convenient and straightforward in execution, but does not provide a sufficiently effective interaction between CNTs and the polymer matrix [42]. Another method of improving the compatibility is based on formation of reactive functional groups on the surfaces of CNTs, which are able to form chemical bonds with macromolecules of a polymer matrix [43–47]. Formation of such bonds by the method "grafting to" [48–51] or “grafting from” [52–54] improves both disaggregation of CNTs and their compatibility with polymer matrix. In addition, novel approach is connected with the creation of “brush like” hybrid fillers, which combine micro- and nanoscale carbon structures and consist of CNTs attached to the surfaces of the carbon microfibers [55]. In such case, nanotubes cannot agglomerate and are fairly uniformly distributed in the polymer matrix.

In previous studies [56–58], a method of attaching multi-wall carbon nanotubes (MWCNTs) to the polyethylene (PE) matrix was discribed. In the presence of a peroxide initiator, PE forms macroradicals, which can bind with the sp^2-hybridcarbon atoms on the surfaces of CNTs, thus providing covalent bonds between the CNTs and PE macromolecules.

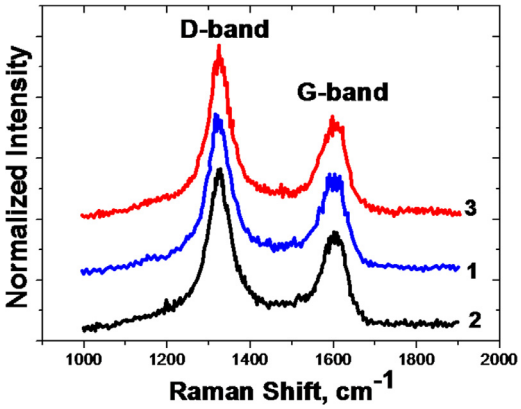

Fig. 3. Raman spectra of non modified NH_2-MWCNTs (1), modified with 1 wt. % MPI-2 (2), and modified with 1 wt. % MPI-1 (3) showing higher ratio of I_D/I_G as a result of the chemical modification.

Motivated by development of nanoarchitectonics, the present work is focused on implementation of a new approach towards bonding a polymer matrix with CNT surfaces. Amino-functionalized MWCNTs (NH_2-MWCNTs) were modified were modified by multifunctional peroxide initiators of the radical polymerization (MPIs), which are able to form covalent bonds with CNTs and contain peroxide groups for formation of free radicals to bond macromolecules of polymer matrix via the chain transfer reaction. Predictable interaction between amino groups of NH_2-MWCNTs and functional groups (carboxyl or epoxy) of the MPIs allows to synthesize new functional materials with certain configurations and hierarchical motifs of the MPIs on MWCNTs. Modified MWCNTs were used for fabrication of new nanocomposites that were studied in details using a differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and tensile testing.

2. Experimental section

2.1. Materials

NH_2-MWCNTs (Nanocyl NC3152) were purchased from Nanocyl S.A., Belgium. The inner diameter of MWCNTs is ≈ 4.0 nm. The outer mean diameter of the MWCNTs was about 10-15 nm with the length in the range of 0.5-1 μm. Amount of the NH_2 groups are ≤0.6%.

2.2. Synthesis and characterization of multifunctional peroxide initiators of the radical polymerization (MPIs)

MPIs with carboxyl (MPI-1) or epoxy (MPI-2) functional groups, (see Fig. 1 in Section 3.1) were used for modification of the NH_2-MWCNTs.

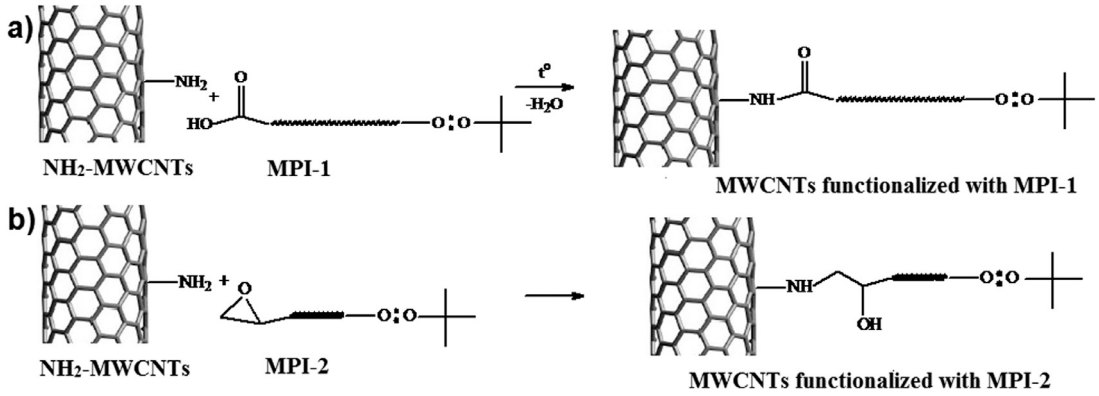

Fig. 2. Modification of the NH_2-MWCNTs by interaction between the carboxyl groups of MPI-1 (a) or epoxy groups of MPI-2 (b) with NH_2-MWCNTs.

MPI-1 was obtained from pyromellitic dianhydride, polyethylene glycol (PEG-9) and *tert*-butyl hydroperoxide following our previously described method [59]. Mr=900g/mol, the acid number (A.N.)=223 mg KOH/g, the content of active oxygen ($O_{act.}$)=2.9% (calculated: Mr=1030 g/mol, A.N.=218 mg KOH/g, $O_{act.}$=3.1%). MPI-2 was synthesized by the interaction of Bisphenol A diglycidyl ether with *tert*-butyl hydroperoxide according to the method reported by Bratychak et al. [60]. M=420 g/mol, E.N.=9.0%,$O_{act.}$=2.9% (calc.: M=430 g/mol, E.N.=10.0%,$O_{act.}$=3.7%).

2.3. Modification of the NH_2-MWCNTs with MPIs

In a flask with 100 g of 2-butanone, 0.05 g MPI was added. After dilution, 5 g of NH_2-MWCNTs were added and ultra-sonicated for 10 minutes. The suspension was stirred with a magnetic stirrer for 24 hours, filtered through a "Millipore" membrane filter and washed with acetone to remove the excess of MPI. Modified MWCNTs were dried at 50°C to constant mass.

2.4. Preparation of nanocomposites

To prepare the nanocomposite, copolymer polybutylene terephthalate - polytetramethylene oxide (PBT/PTMO) was used as matrix; it contains 45 wt.% PBT and 55 wt. % PTMO with Mr between 2500 and 3000 g/mol. 0.3 wt. % of NH_2-MWCNTs or MPIs modified NH_2-MWCNTs were added in the copolymer melt and dispersed using ultrasound sonification as described in [61].

2.5. Analytical techniques

2.5.1. Raman spectroscopy

Raman spectra were recorded using a “Horiba JobinYvonLabRam HR800” Raman spectrometer with a laser wavelength 633 nm and mesh of 600 lines per mm. The exposition time was 30 seconds.

2.5.2. Scanning electron microscopy (SEM)

A Leo FE-SEM 1530 scanning electron microscopy (SEM) (operating at different voltages) was used to examine the morphology of NH_2-MWCNTs and nanocomposites.

2.5.3. Differential scanning calorimetry (DSC)

The thermal characterization of polymeric materials was performed by means of differential scanning calorimetry. The standard procedure performed was: samples of about 15 mg were heated from -50 to + 260°C at a scan rate of 10°C/min and held for 10 min in order to eliminate any thermal history of the material. Subsequently, the samples were cooled to 50°C using scan rates of 10°C/min. In order to observe, the melting peak after crystallization, the samples were reheated to +260°C at a heating rate of 10°C/min under a N_2 flow. Thermal analysis was performed using a NETZSCH 204 F1 Phoenix differential scanning calorimeter.

2.5.4. Thermogravimetric analysis (TGA)

To investigate the thermal stability of non-modified and modified NH_2-MWCNTs, TGA in an atmosphere of nitrogen as well as in synthetic air were performed. First, NH_2-MWCNTs sample were heated in a nitrogen atmosphere to burn amorphous carbon and surface functional groups. Then the heating was continued in synthetic air. Thermogravimetric analysis was performed using TGA T Q500.

2.5.5. Tensile testing

Tensile testing of nanocomposites was performed using Zwick BTC-FR2.5TH.P05 machine, Germany, at temperature 23±2°C. The speed of elongation was 25 mm/min, the initial distance between the clamps was about 30 mm. Five measurements for each sample were made and averages values were calculated. Young’s modulus values were calculated for the elongation range from 0.05 to 0.25%.

Table 1
Raman spectral analysis of non-modified and modified MWCNTs.

Type of CNTs	D-band	G-band	I_D/I_G
Non modified NH_2-MWCNTs	1.51	1.0	1.51
MWCNTs modified with 1 wt. % MPI-2	1.54	1.0	1.54
MWCNTs with 1 wt. % MPI-1	1.63	1.0	1.63

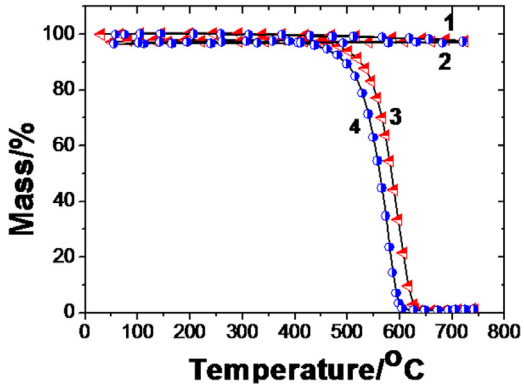

Fig. 4. Thermogravimetric curves of non-modified (1 and 3) and MPI-2 modified MWCNTs (2 and 4) in nitrogen (1 and 2) and synthetic air (3 and 4).

3. Results and discussion

In our previous works, boron nitride nanotubes functionalized with MPIs were fabricated and characterizated in details [62–64]. In turn, amino-functionalized MWCNTs (Nanocyl NC3152) with uniformly distributed amino groups on the surface were used in this work to synthesize a new functional material with certain configurations and hierarchical motifs of the MPIs on MWCNTs. The synthesis of MPIs functionalized MWCNTs and fabrication of the nanocomposites are depicted in Figs 2 and 5. The chemical composition and morphology of the resulting functionalized MWCNTs were analyzed using Raman spectroscopy, TGA and SEM, respectively, and are described in Section 3.1. In turn, the impact of the MPIs functionalized MWCNTs on properties of the nanocomposites was analyzed by DSC, TGA and tensile testing and is presented in Section 3.2.

3.1. Modification and characterization of MWCNTs (Raman spectroscopy, TGA and SEM)

To modify the amino functionalized MWCNTs, the MPIs with carboxyl (MPI-1) [59] or epoxy (MPI-2) [60] functional groups were used. Both of these functinal groups are able to react effectively with primary amino groups of the amino functionalized MWCNTs. Their chemical structures are presented in Fig. 1.

The interaction between the carboxyl or epoxy groups (from the MPI molecules) and amino groups (from the NH_2-MWCNTs) resulted in covalent binding of MPIs to nanotubes. Reaction between substances with carboxylic groups and amino groups is called as amidation. Water molecules are eliminated from the reaction and amide bonds are formed from the remaining pieces of the carboxylic acid and the amine. In turn, the reaction of the primary amines with an epoxy groups creates both a secondary amines and secondary alcohols. Modification of NH_2-MWCNTs with MPIs is presented in Fig. 2.

As was shown in literature [65], an efficient method to study the chemical structure of MWCNTs surfaces is Raman spectroscopy. Raman spectrum of NH_2-MWCNTs presented in Fig. 3 demonstrates two intense peaks at 1360 and 1580 cm^{-1}, known as D and G-bands, respectively. The D-band is caused by defects in the CNTs structure. At this time, G-band is assigned to C-C vibrations. The ratio between their intensities depends from the chemical structure on surface of CNTs and is changing

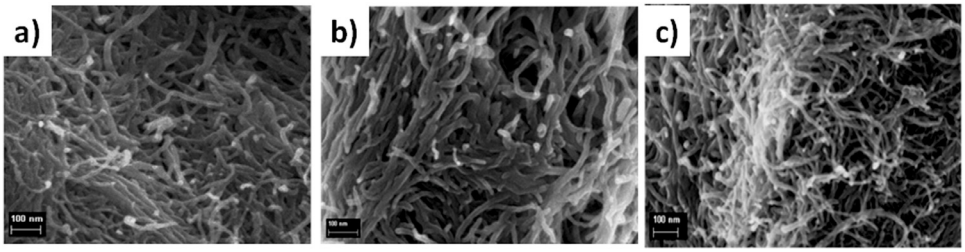

Fig. 5. SEM micrographs of non-modified NH_2-MWCNTs (a), modified with 1 wt. % MPI-1 (b) and modified with 1% MPI-2 (c).

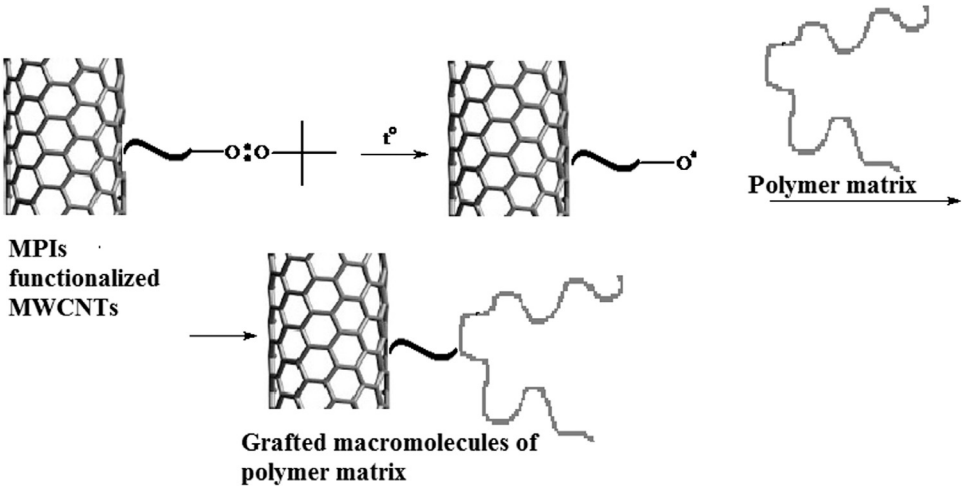

Fig. 6. Grafting of the macromolecules of the polymer matrix to the MPIs functionalized NH_2-MWCNTs via chain transfer mechanism.

after its modification. One can see from the Table 1 that the intensity ratio of D/G bands (I_D/I_G) for modified nanotubes is higher than for non-modified ones. Apparently, the surface of the CNTs contains more defects caused by the presence of the additional surface groups resulting from modification process.

TGA curves of non-modified and MPI-2 modified NH_2-MWCNTs obtained in nitrogen and synthetic air are presented in Fig. 4. The weights of non-modified NH_2-MWCNTs do not change significantly during the heating under a N_2 flow. This indicates a low content of amorphous carbon in the MWCNTs. Meanwhile, modified MWCNTs lose part of their weight, again showing the efficiency of the modification process. In general, TGA curves obtained from "native" and MPIs functionalized NH_2-MWCNTs are very similar, but some differences in their character indicate successful modification process. The thermal decomposition process of the non-modified NH_2-MWCNTs in synthetic air starts at around 490°C and ends around 630°C. At this time, start of the decomposition of MPI-2 modified NH_2-MWCNTs is around 460°C and finish is at 600°C. Unfortunately, but TGA don't allow to determine amount of the grafted MPI-2 suggesting on their low concentration on the surface.

Morphological structures of non-modified and MPIs modified NH_2-MWCNTs were observed by SEM. Results are shown in Fig. 5.

Comparison of SEM micrographs of non-modified NH_2-MWCNTs (Fig. 5a) and MPIs modified MWCNTs (Figs. 5b and c) suggests that the size of CNTs changed only slightly in the process of modification; even more importantly, the modification does not increase the agglomeration of carbon nanotubes.

3.2. Fabrication and properties of the nanocomposites with MPI functionalized NH_2-MWCNTs (DSC, TGA and tensile testing)

Polymer nanocomposites with special fillers, such as CNTs, are promising materials which have improved properties in comparison to polymer composites with conventional fillers. Of critical importance for nanocomposites is the ability of the filler to disperse in a polymer matrix

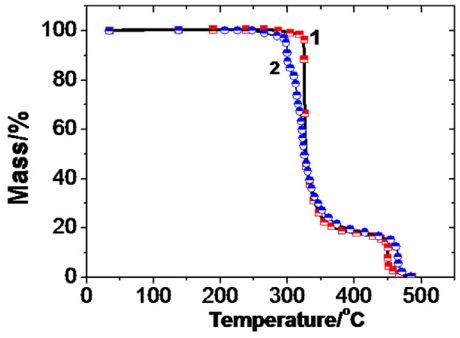

Fig. 7. Thermogravimetric curves of copolymer PBT/PTMO (1) and its nanocomposites with MPI-2 functionalized NH_2-MWCNTs (2).

which is defined by the character of the interfacial interaction between the filler surface and the polymer matrix. In our work, we proposed an effective nanoarchitectonics approach to improve the dispersion of nanotubes and their adhesion to the polymer matrix using MPIs functionalized MWCNTs. At heating, peroxide fragments generate free radicals, which enable grafting of polymer macromolecules to the surfaces of CNTs that is likely to occur due to the chain transfer mechanism (Fig. 6).

The thermal properties of the composites were paid attentions in numerous works [66–68]. In works [67,68] were studied the thermal properties of surface-modified expanded perlite/paraffin and capric acid/intercalated diatomite. The TGA curves of copolymer PBT/PTMO and PBT/PTMO nanocomposites with MPI-2 functionalized MWCNTs are shown in Fig. 7. Nanocomposites with modified CNTs begin to lose mass at a lower temperature than those with non-modified CNTs because of degradation and removal of low molecular products of MPI-2 destruction. The mass loss of copolymer PBT/PTMO starts at around 324°C and ends around 470°C, while the starting temperature of nanocomposites

Table 2
The results derived from the DSC studies of the PBT/PTMO nanocomposites.

Sample	10°C/min 2nd heating T_m,[°C]	ΔH_m,[J/g]	X_c, [%]	2nd cooling T_c,[°C]
PBT/PTMO	188	13.6	9.7	146
PBT/PTMO +0.3wt. % NH_2-MWCNTs	187	12.1	8.7	158
PBT/PTMO + 0.3wt. % NH_2-MWCNTs/MPI-1	188	14.8	10.5	156
PBT/PTMO + 0.3wt. % NH_2-MWCNTs/MPI-2	189	15.6	11.1	159

Table 3
Results of tensile testing of PBT/PTMO nanocomposites.

Sample	Curve	Young's modulus, [MPa]	Tension at break, [MPa]	Elongation at break, [%]
PBT/PTMO	1	79	31.1	588
PBT/PTMO + 0.3 wt. % NH_2-MWCNTs	2	84	31.2	717
PBT/PTMO + 0.3 wt. % NH_2-MWCNTs/MPI-1	3	92	32.9	805
PBT/PTMO + 0.3 wt. % NH_2-MWCNTs/MPI-2	4	93	32.7	698

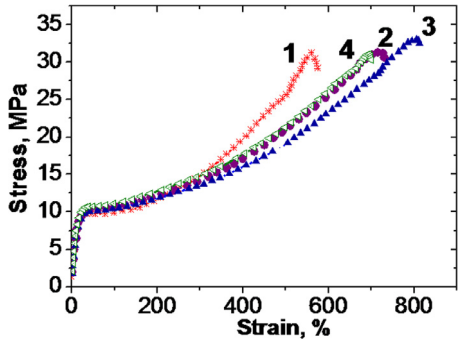

Fig. 8. Stress-strain curves for unfilled PBT/PTMO (1) and nanocomposites with 0.3 wt.% non-modified NH_2-MWCNTs (2) and 0.3 wt. % NH_2-MWCNTs/MPI-1 (3) and 0.3 wt. % NH_2-MWCNTs/MPI-2 (4).

with MPI-2 functionalized NH_2-MWCNTs are 294°C and the ending temperature is almost same as for copolymer PBT/PTMO. For both samples, the TGA curves showed a two-step thermal degradation.

Analysis of the results presented in Table 2 shows higher values of specific enthalpy (ΔH_m) for the composites fabricated using MPIs functionalized MWCNTs in comparison to PBT/PTMO or nanocomposites with "pure" MWCNTs. At this time, substantial growth of the crystallization temperature to the values of up to 156-158°C was caused by introduction of the non-modified as well as modified MWCNTs.

Results of tensile testing PBT/PTMO nanocomposites are shown in Fig. 8 and Table 3.

Mechanical properties of the polymer composites are important characteristics allowing not only to predict possibilities of their applications but also integration into various industrial processes [68,69] As was described previously [70,71], CNTs have many superior properties such as high aspect ratio, elastic moduli in the TPa range, and high fracture strain. Nanometric reinforcements of the composite materials are based on interactions at molecular level, increasing synergic effects between matrix and nanostructures, thus only small quantities of CNTs can increase drastically the mechanical properties of nanocomposites. The effectiveness of CNTs in fabrication of the reinforced polymer composite strongly depends on the ability to disperse the CNTs uniformly throughout the matrix without reducing their aspect ratio. Due to the van der Waals attraction, nanotubes are held together as ropes and bundles. In addition, they have very low solubility in solvents to remain as entangled agglomerates and as such there is a lack of interfacial bonding between the CNTs and the polymer chains that limits stress transfer. To solve the difficulty of dispersion, chemical modification through functionalization was used in this research.

It can be clearly seen that the introduction of MWCNTs leads to the increase in both Young's modulus and elongation at break of nanocomposites (Table 3). The highest elongation at break was observed for MWCNTs modified with MPI-1. This is likely to be due to the larger length and flexibility of oligomeric chains in MPI-1 molecules, compared to the MPI-2 one. We conclude that the tensile elongation at break is inversely proportional to brittleness.

4. Conclusions

In this work, the nanoarchitectonics approach to synthesize a new functional material with certain configurations and hierarchical motifs of the MPIs on surface of MWCNTs was realized. The NH_2-MWCNTs modified with MPIs easily dispersed in a thermoplastic elastomers matrix and improved the mechanical properties of nanocomposites in comparison with non-modified fillers. Plausible explanation is covalent binding of polymer matrix macromolecules with NH_2-MWCNTs surface. Apparently, MPI-1 including the carboxyl groups should be considered the most effective modifier. It provides not only a significant increase in tensile strength, but also improves elasticity of nanocomposites. We also noted that the modification of MWCNTs practically does not worsen the thermal properties of the composites.

Declaration of Competing Interest

All authors declare no conflict of interest.

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