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Influence of carbon nanotubes functionalization on the mechanical properties of polymethacrylate nanocomposites

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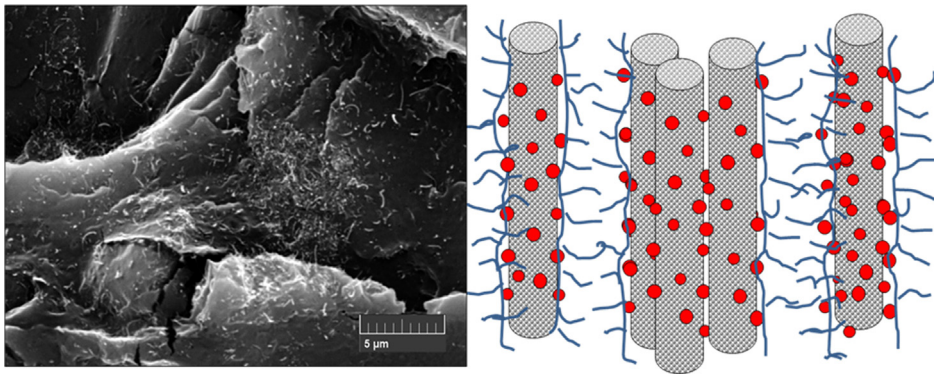
HIGHLIGHTS

- Polymethacrylate composites with carbon nanotubes were studied by microindentation.
- The influence of nanotubes functionalization on the mechanical properties was shown.
- Some assumptions about the structural peculiarities of the composites were made.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanocomposites based on poly (methyl methacrylate) (PMMA) and a copolymer of methyl methacrylate and hexyl methacrylate were investigated. The fillers were: multi walled carbon nanotubes (MWCNTs) and functionalized MWCNTs (oxidized). The samples were studied by the depth sensing indentation methods (DSI) based on measurement of load–displacement curves at a constant loading speed. The tests were performed on a dynamic ultra microhardness tester DUH-211S in accordance with ISO 14577-1. The dynamic hardness, Martens hardness, indentation hardness, indentation modulus and elastic part of the deformation work were measured. Classical Vickers hardness was also determined.

It was established that the mechanical properties of the polymer matrices have been improved by adding 1% of MWCNTs in spite of their being or not functionalized. The presence of functionalized nanotubes had a particular effect upon the different polymer composites. They improved the micromechanical characteristic for PMMA composites and worsened those of copolymer composites. The following assumptions about the structural peculiarities of the composites investigated have been proposed: the reason for the different effect of the modified carbon nanotubes are the length of the side chains and different interaction; the long hexyl groups spatially hinder the contact of the ester groups with functionalized MWCNTs and thus facilitate the agglomeration of the latter.

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1. Introduction

Despite having excellent mechanical properties, when carbon nanotubes are used as a filler of polymer nanocomposites, they cannot achieve their full potential and contribute to a significant

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improvement in the properties of the composite. The mechanical behavior of the nanocomposites depends on many factors [1]. The most important one in achieving effective load transfer across CNT/matrix is the interfacial interaction between a polymer matrix and CNTs [2–7].

The type of interaction could be the weak Van der Waals bonding between the reinforcement and the polymer molecules, which is the most common. Other interactions could be the micromechanical blocking as CNTs are strong and long enough to block the movement of the polymer chains [8,9]. The contribution of this mechanism is manifested at a relatively low CNTs content [9]. The third contact type could be caused by arising of chemical bonds between the nanofiller and matrix [10]. The latter type is not probable in many cases, especially of CNTs.

The interface bonding can be enhanced by surface modification of the carbon nanotubes, namely by oxidization [11–13], surface functionalization [14] or physical coating. Unfortunately, often such a surface treatment damages the structure of carbon nanotubes and worsens its mechanical properties.

Our working group have investigated CNTs nanocomposite based on polypropylene [15–17] and epoxy resin [18].

There are many publications that systematize known hitherto polymer nanocomposites with carbon nanotubes, their mechanical properties and the methods for increasing the efficiency of composite interfaces [19–23].

Conventional polymethacrylates are glassy amorphous polymers, with a glass transition temperature decreasing with the increasing side chains' length. Especially PMMA composites filled with carbon nanotubes have been the subject of numerous studies due to their diverse range of applications aimed at obtaining materials of improved strength and durability [24–27].

By dynamic mechanical studies on a nanocomposites based on poly (methyl methacrylate), A.C. Comer et al. have established a dual glass transition behavior [28]. The first (T_g) is close to (T_g) for the unfilled polymer, and a second, higher-temperature transition is attributed to relaxation of polymer chain segments constrained owing to their proximity to the filler particles. The position and intensity of the higher-temperature transition depends on filler content. Dielectric measurements, however, indicate no variation in the relaxation characteristics with increasing MWCNTs content.

Using a melt processing method for preparing of PMMA/MWNT composites Jin et al. have investigated the influence of MWNTs content on the dynamic mechanical behavior of the composites [29]. The storage modulus has been observed to increase as the MWCNTs loading increases due to the stiffening effect of the nanotubes. A slight increase in (T_g) has been indicated with increasing nanotube content because nanotubes hinder the segmental relaxation of the PMMA chains.

Efficient load transfer of multiwalled carbon nanotubes in polymer composites has been reported by Hwang et al. [30]. They have used a combination of PMMA and nanotubes with grafted to their surface PMMA chains and observed a physical interaction between them which reveals macroscopically a ten-fold increase in the modulus at a loading of 20 of wt% nanotubes.

In [31] the authors described preparation of three components reinforced composition by melt blending of: PMMA- poly (vinylidene fluoride) (PVDF) – carbon nanotubes. PVDF applied as a compatibilizer contributes to the significant improvement in the thermal and mechanical properties (decomposition temperature, elastic modulus) because CNTs incorporated into the PMMA/PVDF/CNT nanocomposites act as physical cross-linkers.

Other authors report on nanocomposites prepared by bulk polymerization of MMA in the presence of different amounts of MWCNT [32]. They have established that the glass transition temperature (T_g) of PMMA increases after MWCNTs incorporation. The obtained nanocomposites show a trend of molecular weight increasing with an increase in the quantity of MWCNT whereas it decreases at a higher initiator concentration.

In [33] the authors have established the independence of T_g, the storage modulus, the position of the tanδ peak and the dielectric relaxation mechanisms of the PMMA matrix by the addition of CNTs. This is explained by the weak polymer–filler interactions in the nanocomposites.

Microhardness and tribological behavior of MWCNT/PMMA have been an investigation objective in [34]. Nanocomposites show effective microhardness increasing, higher wear resistance and also a lower friction coefficient.

The aim of this article is to study how carbon nanotubes and their functionalization influence many mechanical properties for two polymethacrylate composites: poly (methyl methacrylate) (PMMA) and the copolymer of PMMA and poly (hexyl methacrylate). On the basis of microindentation methods [35] and taking into account recent achievements in the area of dynamic mechanical thermal analyses and positron annihilation for polymethacrilates, a structural explanation of the mechanical behavior of the samples would be searched for.

2. Experimental

2.1. Materials

The nanocomposites studied consisted of two types of polymer matrices:

- Poly(methyl methacrylate) (PMMA);
- A copolymer containing 10% mol. of methyl methacrylate and 90% mol. of hexyl methacrylate.

The nonfunctionalized and functionalized multiwall carbon nanotubes (MWCNTs) were used as a filler with the fallowing characteristics:

- Nonfunctionalized MWCNTs: purity >85%; length ~20 μm; external diameter >50 nm (Timesano, Chengdu, China);
- Functionalized MWCNTs (oxidized): purity >90%; containing —COOH groups; diameter 10–30 nm, length 10–30 μm and COOH content 1.55 wt.% (share of surface carbon atom: 8–10 mol%) (MWCNTs-COOH) (Chengdu Organic Chem. Co., Chinese Academy of Sciences).

The six samples subjected to investigation were:

1 - PMMA;
2 - PMMA + 1%MWCNT;
3 - PMMA + 1% MWCNT-COOH;
4 - Copolymer (10%PMMA + 90%PHMA);
5 - Copolymer + 1%MWCNT;
6 - Copolymer + 1%MWCNT-COOH

Multiwalled carbon nanotubes were added to monomer(s) and mixed in a ultrasound bath for 10 min. Afterwards, the mixture was placed into a preheated reactor and agitated additionally with an ultrasound probe (3 times for 30 s).

Solution of initiator Trigonox 21 ® (1 wt.% with respect to the mass of the monomer) was placed into a funnel and added in four intervals of 15 min, whereat the first one was after the mixture was heated to 90 °C. Finally, after the whole initiator was added, the reaction was allowed to proceed for 1 h in a nitrogen atmosphere, thus the total reaction time was 2 h.

The obtained polymers were cast into molds and drayed in an oven at 50 °C for 2 days and afterwards at room temperature until

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