Macromolecular Nanotechnology

Influence of carbon nanotubes functionalization on their dispersibility and properties of poly(styrene/methacrylate) nanocomposites

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ABSTRACT

Nanocomposites with polystyrene, poly(styrene-*co*-methyl methacrylate) and poly (styrene-*co*-octadecyl methacrylate) matrix and pristine or oxidized, methyl ester, dodecyl ester, ethyl benzene ester functionalized multiwall carbon nanotubes are prepared by *in situ* polymerization reaction. Performed preparation has revealed possibility of a direct synthesis of complex nanocomposites with volatile accomplishment of the distribution and dispersion of carbon nanotubes depending on their functionalization in relation to the host matrix. Calorimetric measurements show a glass transition temperature shift downwards in all composites while the opposite is obtained by dynamical mechanical analysis. However, it turned out that the contribution of added filler in the matrix depends on the particular type of functional groups introduced to the surface of the carbon nanotubes, so that shifts towards both higher and lower values of the mechanical moduli are recorded.

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1. Introduction

Polymer materials are among the most commonly-used materials. The interest in their application widening trough preparation of polymer composites has been present for many years and has been intensified lately. A large number of fillers are investigated wherein the particular role belongs to the carbon nanotubes (CNT's) due to their well-known extraordinary properties: high aspect ratio, light weight and excellent mechanical, thermal, electrical and magnetic properties. In that way, they earned a special place in the scientific and industrial community. However, apart from these excellent properties CNT's display a range of difficulties while working with them because of their inclination to form aggregated bundles caused by the strong van der Waals' attractive forces. The clusters and bundles of CNT's in polymer matrix tend to act as defect sites which affect negatively mechanical and electrical properties of nanocomposites. Therefore the biggest challenge is the effective dispersion of individual CNTs in the polymer matrices.

Three methods are commonly used for the composites fabrication: (a) solvent casting i.e. film casting of suspensions of CNTs in dissolved polymers; (b) *in-situ* polymerization of monomer in presence of CNTs; and (c) melt-mixing of CNTs with polymers. There are various opinions on the quality of each of them. The solution casting is often pointed out as the most valuable technique to form CNTs/polymer nanocomposites. However, its use is restricted to the soluble polymers and large amounts of solvents are wasted. The melt-mixing is the preferred method of polymer/CNTs composite preparation, which is

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mostly used for thermoplastics and most compatible with existing polymer processing technique such as industrial extruder and injection moulding machine. Finally, *in-situ* polymerization has advantages over other composite fabrication methods since the wetting of CNT by polymer phases is better during the formation of polymers composites. Although this kind of polymerization most often involves epoxy monomers, also composites based on aniline, pyrrole, olefin and vinyl monomers have been used [1–8]. Composites of CNTs and polystyrene [9–14], one of the most widely used commercial polymers, and its rubbers [15–18] are widely explored. Composites were prepared mainly from the solution of polystyrene [12] or by its coagulation in water [10], by emulsion polymerization [19] resulting with polystyrene grafted MWCNT or with polystyrene latex [9], dried and subsequently annealed in order to remove any remaining solvent or freeze dried and compression moulded. At the same time single and multiwall carbon nanotubes of various kinds of functionalization, (in)organic, (non)-covalent, respectively, were prepared and examined [10,13]. These attempts mainly aimed at use of carbon nanotubes as fillers in order to improve conductivity of polymeric materials.

Styrene based rubbers used as matrices for composites prepared with different CNT concentrations seem to attract even more attention [15–18,20–23]. Thus, styrene-acrylonitrile copolymer (SAN)/CNTs nanocomposites were manufactured by applying the latex concept [17], styrene-isoprene copolymer by emulsion and miniemulsion polymerization in the presence of SWNTs, as well as by mixing dispersed SWNTs with styrene-isoprene copolymer latex after polymerization [18]. Styrene-butadiene rubber (SBR)/CNTs nanocomposites were prepared by the melt mixing process [17] while a novel technology to prepare (SBR)/CNTs composites was developed by combining a spray drying method and a subsequent mechanical mixing process [17]. Nitrile-butadiene-rubber (NBR), emulsion styrene-butadiene-rubber (e-SBR) with random segment distribution, and solution styrene-butadiene-rubber (s-SBR) were used as elastomer matrix where the preparation of composites by a masterbatch process was compared to the direct melt-mixing process using two different types of multiwalled CNT [20]. Newly, styrene–ethylene–butylene–styrene (SEBS)/CNT composites were prepared via a sequential process of (electrostatic adsorption assisted dispersion)-plus-(melt mixing) [21]. Also, thermoplastic tri-block copolymer elastomer s tyrene–butadiene–styrene/CNT composites [22,23] prepared by extrusion and solution casting were studied. However, papers that describe polystyrene/CNTs composite prepared *in situ* are scarce despite the fact that by this method better results should be expected due to a more uniform distribution of nanotubes in a starting low-viscosity liquid phase that leads to a more uniform mixing with monomer and consequently polymer. Furthermore, although according to the theoretical predictions one can expect strong noncovalent interaction between PS and CNTs [24], the experimental findings did not support it [25]. Consequently, there is intense endeavour to improve contact surface area of carbon nanotubes with polymer matrix via chemical modification of nanotubes' surfaces, though such a procedure creates defects in the CNTs lattice, which can diminish the electrical and thermal conductivity of CNTs and deteriorate their mechanical properties [20,26]. The objective of this research was to determine how chemical modification of multiwall carbon nanotubes' surfaces with functional groups: methyl ester, dodecyl ester and ethyl benzene ester can influence their dispersion in styrene and two styrene-alkyl methacrylate copolymer matrices (styrene-*co*-methyl methacrylate and styrene-*co*-octadecyl methacrylate matrices). Also, oxidized and pristine multiwall carbon nanotubes were used for preparation of composites with the same matrices. The share of alkyl methacrylate in copolymer was 10 mol.% since even that small amount changes interactions and consequently properties like glass transition temperature of polystyrene significantly (T_g: polystyrene, 100 °C; poly(octadecyl methacrylate), −100 °C) [27].

2. Experimental part

2.1. Materials

Multiwall carbon nanotubes, MWCNT (C) (Chengdu Organic Chem. Co., Chinese Academy of Sciences), were used as received. The characteristics of used MWCNT are: diameter > 50 nm, purity > 85%, length $\geqslant$ 20 μm. *Oxidized multiwall carbon nanotubes*, MWCNT-COOH (CO) (Chengdu Organic Chem. Co., Chinese Academy of Sciences), were used as received. The characteristics of used oxidized CNT are: diameter from 10 to 30 nm, purity > 90%, length from 10 to 30 μm and COOH content 1.55 wt.% (share of surface carbon atom: 8–10 mol.%). *Functionalized multiwall carbon nanotubes*, MWCNT-COOCH$_3$ (CM), MWCNT-COOC$_{12}$H$_{25}$ (CD), MWCNT-COOCH$_2$-CH$_2$-C$_6$H$_5$ (CE), prepared in our laboratory and characterized according to the procedure described in detail previously [28,29] were used for preparation of composites. Oxidized multiwall CNT (MWCNT-COOH 1.55 wt.% COOH) are suspended in SOCl$_2$, mixed in ultrasonic bath and further mixed and heated under inert nitrogen for 24 h. Multiwall carbon nanotubes functionalized by acyl chloride are isolated after removal of nonreacted SOCl$_2$. Afterwards, they are added to required alcohol (anhydrous methanol CH$_3$OH or 98% dodecanol C$_{12}$H$_{25}$OH) and heated under reflux or to 110 °C. The reaction is allowed to proceed for 48 h. Finally, the alcohol surplus is removed by vacuum filtration, yielding alkyl-ester functionalized nanotubes, MWCNT-COOCH$_3$ or MWCNT-COOC$_{12}$H$_{25}$, which are dried in a vacuum oven 24 h at 50 °C. In case of the modification reaction of oxidized nanotubes into MWCNT-COOCH$_2$-CH$_2$-C$_6$H$_5$ the following procedure was performed: water solution of sodium hydroxide is added to oxidized multiwall carbon nanotubes (CNT-COOH, 1.55 wt.% COOH) aided with an additional mixing in ultrasonic bath (30 min, 40 kHz, max. 160 W). Afterwards, NaOH solution with (2-bromoethyl)benzene and hexadecyltrimethylammonium bromide were added and the reaction is allowed to proceed for 20 h, partially at the reflux temperature. Functionalized MWCNT-COOCH$_2$-CH$_2$-C$_6$H$_5$ are separated by vacuum filtration, washed with chloroform, methanol and demineralized water, and finally dried in a vacuum oven 48 h at 50 °C.