



Microstructure changes of polyurethane by inclusion of chemically modified carbon nanotubes at low filler contents

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ARTICLE INFO

Article history:

Received 11 October 2011

Received in revised form 10 February 2012

Accepted 12 February 2012

Available online 1 March 2012

Keywords:

A. Carbon nanotubes

A. Nanocomposites

B. Mechanical properties

D. Atomic force microscopy (AFM)

D. Transmission electron microscopy (TEM)

ABSTRACT

The surface of multi-walled carbon nanotubes (MWCNTs) was modified to introduce acidic groups in either covalent or van der Waals interaction bonding environments to establish cross-linking sites with a host polymer. Nanocomposites based on a polyurethane matrix (PU) containing chemically functionalised multi-walled carbon nanotubes (MWCNTs) have been shown to alter its mechanical performance depending on the nature of the surface functional groups on MWCNTs, which correlates to the type of bonding interaction of the surface group and also the dispersibility of MWCNTs and their influence on the domain structure of polyurethane. The stress at break for nanocomposites containing 0.25 wt% of acid-oxidised MWCNTs (MWCNT-ox), bearing covalently attached carboxylic, lactone and phenolic groups, was twice that of the native PU and Young's Modulus for the nanocomposites increased by four times. Whereas when hemin, which contains carboxylic functionality, was immobilised to the surface of pure MWCNTs, the improvement in Young's Modulus was only around twice that of pure PU. Differences in the disaggregation of MWCNTs into PU were observed between the samples as well as variation of the native domain structure of PU. The results also infer that the purification of MWCNTs from acid-oxidative lattice fragments (fulvic acids) is vital prior to conducting surface chemistry and polymerisation in order to ensure maximum mechanical performance enhancement in their reinforcement of the host polymer.

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1. Introduction

Carbon nanotubes (CNTs) represent an intriguing nanoscale system that exhibits high tensile strength and elastic moduli that is linked to the number of walls, the helical wrapping vector of the cylindrical graphene layers and its crystallinity or number of structural defects [1]. Furthermore, their high aspect ratio leads to percolation at low filler contents, which enables conductivity, and their large interfacial area implies greater load transfer over longer lengths. It has been demonstrated that arc-discharge CNTs have a higher Young's Modulus than those grown by chemical vapour deposition (CVD), yet CVD-CNTs are produced in higher purities and yields and are therefore attractive to the researcher [2].

Whilst a macroscale composite of carbon nanotubes has yet to reflect their individual mechanical properties, their incorporation as a filler to strengthen a polymer matrix is warranted. An extensive study of nanocomposites based on polymers containing CNTs

reveals that the mechanical performance of the host matrix can be substantially increased [3,4], depending on the type of CNT used and mixing method. This underlines the importance of the nature of interaction between the CNT and the host polymer, the degree of filler dispersion and how it affects the polymerisation (e.g. chain length) and polymer–polymer interactions, which can influence energy transfer [5]. Moreover, functionalisation of CNTs can enhance interaction with the polymer matrix groups through use of targeted chemistry leading to improved mechanical performance for covalently bonded systems.

In the direct mixing of pure CNTs into a host matrix, it is often difficult to separate agglomerated CNTs, due to their intrinsic hydrophobic surface leading to van der Waals interactions, to obtain a reasonable dispersion, although aligned CNTs in polymers have demonstrated superior mechanical performance. Therein, the outer surface of the CNT presents a π -bond network that tends to promote CNT–CNT interactions to minimise the available surface energy, however it also allows for van der Waals interactions with polycyclic aromatic hydrocarbon-based (PAH) systems. Whether incorporated directly into the polymer matrix or using PAHs to facilitate graft-to or graft-from reactions [6], the underlying CNT structure is unaffected (in a mechanical sense) by the

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attachment of polymer chains, thus maintaining the integral strength of the carbon nanotube. A second strategy is to prevent re-agglomeration of CNT by introducing surfactants [7]. Whilst this can decrease the storage modulus of the composite, there is evidence to show improvements in the interaction between the MWCNT filler and host matrix [8].

A third approach is to chemically functionalise the outer walls of the CNT, whereby disruption to the graphene cylinders introduces functional groups that allow covalent bonding of a polymer directly to the nanotube framework as well as potentially improving the interface between the filler and the polymer chains [9]. The change in surface properties of the CNT has an advantage in rendering the system less hydrophobic and improving interaction with other matrices. However, extensive acid oxidation of CNTs also renders the filler mechanically weaker [10] where the mechanical reinforcement that exists by virtue of the concentric arrangement of cylinders is degraded through lattice erosion and the exposed CNT shells can facilitate slippage.

Whilst this has been explored in a cursory sense [3], the direct performance comparison of CNTs that are mixed in a pure state with polyurethane, those that are functionalised through van der Waals interactions with an intermediate bridge to the polymer and those that are covalently linked to the polymer has not been made. Such a study is compounded by a problem where the acid-oxidation, as a traditional means of chemically functionalising CNTs, generates lattice oxidative fragments that behave similar to fulvic acids, in that these species are hydrophobic in acid conditions and therefore their creation promotes immediate interaction with the surface of CNTs. Such fulvic acids are extensively functionalised with acidic groups that also facilitate chemical reactions, in graft-to and graft-from polymerisation approaches, and can account for up to 50% of the total number of acidic groups in a CNT-ox system [11,12]. Their removal will leave purely covalent sites for target synthesis, however, a number of reports involving covalent cross-linking in CNT-polymer composites, which utilise CNT-ox, have neglected to include a fulvic acid removal strategy and therefore raises questions about the mixture of covalent and van der Waals bonding environments to the final mechanical strength of the composite.

Polyurethane (PU) is an important polymer in skin patches, coatings and catheter applications [13], where intra- and inter-chain hydrogen bonding interactions generate hard and soft domains [14] and is therefore an attractive material to be used as polymer matrix for nanocomposites as it immediately highlights changes in its properties at the inclusion of different types of filler. The investigation of nanocomposites based on a PU matrix containing CNTs has been previously reported [4,15,16]. Herein, we investigate the mechanical performance of PU composites containing CNTs with group-specific functionalisation of the CNT surface as well as exploring covalent and non-covalent interactions between the filler and polymer. CNTs, which possess acidic groups through PAH functionalisation (immobilised through van der Waals forces) and through acid-oxidation covalently bound to the CNT lattice, were used at low content levels to elucidate changes to the microstructure of PU.

2. Materials and methods

2.1. Carbon nanotube pretreatment

Multi-walled carbon nanotubes (MWCNTs) were purchased from TMSpetsmash (Ukraine), which were grown using the CVD technique. Pure MWCNTs (pMWCNTs) were prepared from raw CNT samples through low temperature oxidation to remove surface amorphous carbon and then refluxed in hydrochloric acid

(HCl) to remove any residual metal catalytic particles. Samples were then washed extensively in water and dried at 100 °C.

2.2. Hemin coated MWCNTs

Hemin coated MWCNTs (MWCNT~hemin) were prepared by sonicating pMWCNTs in a solution of excess hemin dissolved in tetrahydrofuran (THF). The mixture was adjusted to pH 1–2 with the addition of HCl (2 M) and left for 8 h. MWCNTs were separated from solution by centrifugation and washing with acidified methanol (MeOH)-THF mixture until no further colouration of the supernatant was observed (confirmed using UV-Vis), then washed with MeOH and dried at 100 °C.

2.3. Acid-oxidised MWCNTs

Acid-oxidised MWCNTs (MWCNT-ox) were prepared by refluxing MWCNTs in nitric acid (HNO₃, 70%, 6 h) and then washed with water until pH neutral. Samples were then refluxed in sodium hydroxide (NaOH, 2 M, 1 h) to remove surface immobilised fulvic acids, then washed in NaOH solution until no further colouration was obtained (confirmed using UV-Vis). The covalent surface groups were regenerated by refluxing in HCl (2 M, 10 min). Samples were finally washed in water till pH neutral and dried at 100 °C.

2.4. Reduction of acidic groups

MWCNT-hemin and MWCNT-ox samples (100 mg) were sonicated in dry THF (50 ml) to obtain a good dispersion. Lithium aluminium hydride (LiAlH₄) in THF (1 M, 10 ml) was added under nitrogen and the mixture refluxed for 4 h. After cooling, excess LiAlH₄ was decomposed with careful addition of MeOH. Reduced samples (MWCNT~hemin-red and MWCNT-red respectively) were stirred in HCl to remove trace decomposition products and then washed thoroughly in water and dried at 100 °C. Samples were checked for the generation of additional fulvic acids through the reduction step, but none were detected.

2.5. Surface group analysis

All samples were titrated according to the Boehm method [11,17]. MWCNT samples (50 mg) were sonicated in sodium bicarbonate (NaHCO₃), sodium carbonate (Na₂CO₃) and NaOH solution (0.01 M, 20 ml, with 0.1 M NaCl) and stirred for 8 h. Samples were separated through centrifugation and the supernatant filtered through 0.2 µm PTFE filters to ensure all MWCNTs were removed. Aliquots (5 ml) were titrated against HCl (0.01 M, with 0.1 M NaCl) using a pH metre to monitor the reaction. Titration analysis was repeated three times. Solutions were stored under nitrogen and were checked to ensure that atmospheric carbon dioxide had not affected the titration [18].

2.6. Polyurethane nanocomposite preparation

The polyurethane based on poly(oxypropylene)glycol with $M_w = 2000 \text{ g mol}^{-1}$, trimethylol propane and toluylene diisocyanate was used as a matrix for nanocomposites synthesis. To prepare the nanocomposites, MWCNTs (0.01, 0.1 and 0.25 wt%) were sonicated with the monomer prior to polyurethane synthesis.

2.7. Atomic force microscopy

Surface topography and phase images were obtained using a multimode Nanoscope IIIa atomic force microscope. Tapping mode

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