Vacuum 155 (2018) 178–184

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Dye diazonium-modified multiwalled carbon nanotubes: Light harvesters for elastomeric optothermal actuators

Asma Bensghaïer[a,b,c,*], Klaudia Forro[d], Mahamadou Seydou[b], Aazdine Lamouri[b], Matej Mičušik[d], Mária Omastová[d,***], Mohamed Beji[a], Mohamed M. Chehimi[b,c,**]

[a] Université de Tunis El Manar, Faculté des Sciences, Laboratoire de Chimie (Bio)Organique, Structurale et de Polymères (LR99ES14), Campus Universitaire, El Manar 2092, Tunisia
[b] Univ Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086, CNRS, F-75013 Paris, France
[c] Université Paris Est, ICMPE (UMR7182), CNRS, UPEC, F-94320 Thiais, France
[d] Polymer Institute, Slovak Academy of Sciences, 845 41 Bratislava, Slovakia

ARTICLE INFO

Keywords:
Diazonium salts
Dyes
Multiwalled carbon nanotubes
Ethylene vinyl acetate elastomer
Optothermal actuators

ABSTRACT

Novel elastomer/modified carbon nanotube nanocomposites were prepared by melt mixing ethylene vinyl acetate (EVA) matrix with dye-grafted multiwalled carbon nanotubes (MWCNTs, CNTs in short). The latter were prepared by spontaneous reactions of diazotized Azure A (AA-N_2^+), Neutral Red (NR-N_2^+) and Congo Red (CR-N_2^+) dyes with CNTs in water at RT. The dispersion of the dye-modified CNTs was facilitated with cholesteryl 1-pyrenecarboxylate (PyChol) surfactant. The EVA/modified CNT nanocomposites were employed as optothermal actuators. The photo-actuation measurements were performed on the un-stretched as well as the stretched strips of pristine EVA and EVA/CNT-dye nanocomposites using a dynamic mechanical analyzer (DMA) equipped with a red light emitting diode (red LED) at a wavelength of 627 nm illuminated either 10 s or 30 s. The concentration of modified dyes, the use of PyChol surfactant and the applied pre-strain were the parameters investigated in this work.

To sum up, the nanocomposites prepared so far could be regarded as promising optothermal actuators used for touch displays visually impaired people.

1. Introduction

Optothermal actuators (OTA) are new generation of actuators made from various materials such as liquid crystalline elastomers [1] and polymer-carbon nanotube nanocomposites [2,3]. As far as the latter are concerned, nanocomposites of CNT and ethylene vinylacetate (EVA, a synthetic rubber) were demonstrated to be potentially useful as OTA materials [4,5]. The team of Omastová [6] has benefited from the photoactuation ability of EVA/CNT nanocomposites to construct Braille microsystems in view of developing new types of visual-aid tablet for visually impaired people. In these smart materials, it is imperative to control the CNT-polymer interfaces in order to reach the following three main objectives:

(i) CNTs must adhere to the matrix to obtain nanocomposites without phase separation;
(ii) CNTs must be aligned within polymer matrix;
(iii) optothermal properties of CNTs must be transferred to the matrix via the matrix/CNT interface/interphase and matrix chains should be stretched and fixed.

These interfacial and adhesion aspects can be addressed using modified CNTs through covalent and non-covalent approaches in order to avoid the presence of CNT bundles within the matrix. To address this issue via a non-covalent route, cholesteryl 1-pyrenecarboxylate (PyChol), a non-ionic surfactant, was designed and employed to facilitate the dispersion of CNTs in EVA [6]. The rationale for using PyChol lies in the fact that this surfactant has two parts: an aromatic pyrene group which interacts with CNTs via π stacking and an aliphatic side which interacts with the elastomeric matrix. Elsewhere, it has been demonstrated that actuation of SU-8 was achieved by doping this matrix with Lilac or Yellow dyes [7]. Strong absorption of specific wavelength resulted in heating and expansion of the dye/Su-8 hybrid.

If dispersion of CNTs is an important parameter to control when one

* Corresponding author. Université Paris Est, ICMPE (UMR7182), CNRS, UPEC, F-94320 Thiais, France.
** Corresponding author. Université Paris Est, ICMPE (UMR7182), CNRS, UPEC, F-94320 Thiais, France.
*** Corresponding author. Polymer Institute, Slovak Academy of Sciences, 845 41 Bratislava, Slovakia.
E-mail addresses: souma-souma1@hotmail.fr (A. Bensghaïer), maria.omastova@savba.sk (M. Omastová), chehimi@icmpe.cnrs.fr (M.M. Chehimi).

https://doi.org/10.1016/j.vacuum.2018.06.018
Received 18 December 2017; Received in revised form 15 May 2018; Accepted 5 June 2018
Available online 06 June 2018

tackles CNT-polymer nanocomposites, still for OTAs application the interaction of materials with light dictates the end optothermal properties. We have thus reasoned that one could bridge previously reported strategies on the dispersion of CNTs using surfactants [4] and the doping of polymeric matrices with dyes [7] in view of making new OTA materials. Towards this end, CNTs should not only be dispersed but also be conjugated with dyes in order to achieve optimal OTA properties. However, it is required that the CNTs (which impart remarkable mechanical properties) and the dyes (they harvest the light) remain linked. For example, there should be no displacement of the dye by any surfactant molecule used to disperse CNTs. One mean of achieving this goal is to conduct covalent modification of the CNTs with dyes.

With this motivation in hand, this work aims at modifying CNTs with diazonium derivatives of commercially available, low cost dyes, namely Azure A (AA), Neutral Red (NR) and Congo Red (CR). The three selected dyes have an aromatic amine which can be diazotized to yield a diazonium salt which is known to react spontaneously with sp^2 C materials such as CNTs to form strong covalent CNT-aryl bonds with high aryl grafting density [8,9]. Actually, one of the most important features of diazonium surface chemistry is that it permits to rapidly provide functional multicomponent systems with robust interfaces owing to the covalent bonds between the said adhering components [10]. The surface modification of CNTs was carried out with AA-N_2^+, NR-N_2^+ and CR-N_2^+ dye diazonium compounds. The CNT-dye hybrids were mixed with ethylene vinyl acetate (EVA) and the photoactuation properties of the resulting nanocomposites were determined. To do so, the CNT-dye/EVA nanocomposites were subjected to mechanical stresses under illumination cycles.

2. Experimental

2.1. Materials

Azure A, Neutral Red and Congo Red (all Alfa Aesar products) were used as received. MWCNTs (diameter 1–10 nm, length 60–100 nm, purity > 90%) were Nanocyl 7000 products. Ether and acetone (Aldrich, spectrophotometric grade) were used as received. Deonized water was used for various cleaning and dilution processes. Ethylene-vinyl acetate copolymer (EVA, EVATANE 28-25, Arkema, France) containing 28 wt% vinyl acetate (VA) was employed as the polymeric matrix. MWCNTs were Nanocyl® - 7000 type purchased from Nanocyl S.A., Belgium. The MWCNT characteristics are the following: 90% purity, metal oxide impurity of 10%, the average diameter is around 9.5 nm, the average length is 1.5 μm, and surface area is 250–300 m^2/g (as determined by BET). Cholesteryl 1-pyrenecarboxylate (PyChol) was employed as the compatibilizer and was synthesized as reported in Ref. [5], and chloroform ($CHCl_3$ p. a., Mikrochem, Slovakia) was employed as the solvent.

2.2. Grafting of carbon nanotubes with dye diazonium compounds

The synthesis and NMR characterization of the three diazotized dyes AA-N_2^+, NR-N_2^+ and CR-N_2^+ dye diazonium compounds were reported in Ref. [11]. MWCNTs were first sonicated for 20 min in distilled water (using Bioblock model S-Line, effective US power 75 W, 37 kHz) and reacted with 3 samples of dye diazonium compounds as follows: 40 mg (3.33 mmol) of ultrasonically dispersed MWCNTs were added to an aqueous solution of 200 mg of diazonium salt (in 100 ml) and the mixture was left under vigorous stirring at RT for 20 min. For each dye, acetone was added to the resulting suspension of CNT-Dye hybrid and the mixture was centrifuged for 30 min at 8000. The precipitate was thoroughly washed with ethanol and the cycle was repeated until the washings were clear and colorless. In a final step, the CNT-Dye hybrids were ultrasonicated in deionized water to ensure that only grafted aryl groups remained at the CNT sidewalls. The grafted CNTs were dried at 60 °C overnight.

2.3. Preparation of EVA/CNT nanocomposites

Different types of EVA nanocomposites filled with 0.1 or 3 wt% modified MWCNT (the samples are abbreviated CNT-AA, CNT-NR and CNT-CR), were prepared by casting from solution. The required quantity of the CNT-Dye and cholesteryl pyrenecarboxylate (PyChol) compatibilizer were dispersed in chloroform using a CNT-Dye/PyChol ratio of 1/5, which is the optimal ratio previously reported [12]. The solution was vigorously stirred for 1 h under sonication using a Hielscher 400 S sonicator at amplitude of 20% (35 μm, 60 W/cm^2) and a duty cycle of 100% (see Supplementary Material SM1). After sonication, EVA was added and the CNT dispersion and the whole mixture was further stirred for 3 h at 1200 rpm. The solution was subsequently poured into a Teflon-coated Petri dish and dried at RT for 12 h (see SM2). After drying, the flexible elastomer film filled with modified CNTs was placed in an oven and gradually heated to 40, 60, and 70 °C overnight. Additional drying was performed in a vacuum oven for 6 h at 70 °C. The flexible composite film was prepared by compression moulding in a laboratory press (Fontijne SRA-100, The Netherlands) for 15 min at 80 °C, under a pressure of 2.4 MPa. The composite samples were cut (length 30 mm, width 5 mm, thickness 0.3 mm) and stretched with 50 and 100% deformation at 40–50 °C. Then the stretched samples were quenched in cold water to freeze the alignment of the nanotubes [4] (See SM3, SM4).

2.4. Characterization

Transmission Electron Microscope (TEM) images were recorded using a FEI Tecnai F20 microscope operating at 200 kV. The samples were prepared by dispersing a small amount of nano-composite samples in ethanol and an ultrasonication of 1 min. Then a drop of the suspension was spread on a 400 mesh cupper grid covered with a holey carbon film. Then ethanol was evaporated and the sample observed in the TEM.

UV–Vis was recorded using an amplitude cca 35 μm (20% of max. Amplitude), Acoustic power density cca 60 W/cm^2) and measured in thin cuvette (light path 1 mm).

The photo-actuation measurements were performed by Dynamic Mechanical Analysis (DMA) (Q 800 machine, TA Instruments, USA) of the different nanocomposites using the tensile iso-strain method, a preload of 0.04 N and a pre-strain 0.05% were maintained at a constant temperature of 25 °C. As a light source, red light emitted diode (LED) with $\lambda = 627$ nm (Luxeon Rebell, Philips, The Netherlands) was used.

2.5. DFT Quantum chemical calculations

DFT Calculations were performed with the Vienna Ab-Initio Simulation Package (VASP 5.4.1) [13]. Electron-ion interactions were described by the projector-augmented wave (PAW) method [14]. Convergence of the plane-wave expansion was obtained with a cut-off of 500 eV. The generalized gradient approximation (GGA) was used with the Perdew-Burke-Ernzerhof (PBE) functional [14]. Sampling in the Brillouin zone was performed on a grid of $(3 \times 1 \times 1)$ k-points for the geometry optimizations. Dispersion effect is taken into account using the recent Grimme D3 method [15].

3. Results and discussion

3.1. General preparation of flexible EVA/CNT-Dye nanocomposite films

The CNT-dye hybrids were prepared as previously reported and the CNT modification was confirmed by a range of complementary analytical techniques (IR, TEM, Raman, TGA and XPS) [11]. Although grafting density can be tuned [11], only the highest extent of dye grafting was considered in order to maximize the effect of illumination on photoactuation. As detailed in the Experimental section, the CNT-