Materials Chemistry and Physics 216 (2018) 223–229

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Microhardness of poly(methyl methacrylate)-multiwalled carbon nanotubes composites: Effect of ultraviolet irradiation

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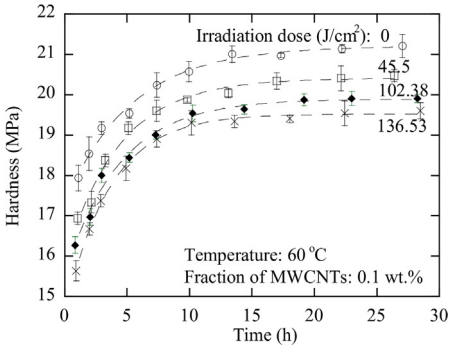
HIGHLIGHTS

- Hardness of the PMMA composite is analyzed by first-order kinetic process.
- Hardness of the PMMA composite increases with heating temperature and time.
- Hardness of the PMMA composite increases with weight fraction of MWCNTs.
- Hardness of the PMMA composite decreases with increasing UV dose.
- Hardness of the PMMA composite at equilibrium follows the van't Hoff relation.

GRAPHICAL ABSTRACT

Temporal evolution of the hardness of UV-irradiated PMMA-MWCNT composite with different irradiation doses.



ARTICLE INFO

Keywords:
Microhardness
Poly(methyl methacrylate)
Multiwalled carbon nanotubes
Ultraviolet light

ABSTRACT

Understanding the mechanical behavior of polymer matrix composites under the service conditions is of practical importance to improve structural durability and reliability. In this work, we study the microhardness of poly(methyl methacrylate)-multiwalled carbon nanotubes (PMMA-MWCNTs) composite as a function of the fraction of MWCNTs and the irradiation of ultraviolet (UV) light in a temperature range of 50–80 °C. Increasing temperature, heating time, and the weight fraction of MWCNTs causes the increase of the microhardness of the PMMA-MWCNT composite, while increasing the UV-irradiation dose causes the decrease of the microhardness of the PMMA-MWCNT composite. A first-order kinetic process is proposed to analyze the variation of the microhardness of the PMMA-MWCNT composite with time. The activation energy for the first-order kinetic process increases with increasing the weight fraction of MWCNTs, and decreases with increasing the UV-irradiation dose. The temperature dependence of the microhardness of the PMMA-MWCNT composite at equilibrium state follows the van't Hoff relation.

1. Introduction

Polymers matrix composites (PMCs) reinforced by carbon nanotubes (CNTs) have become important materials in a variety of engineering areas, including automotive, aerospace, electronics, etc. It has been demonstrated that CNTs incorporated in a polymer matrix can enhance the mechanical strength of PMCs, which are based on the excellent mechanical properties of carbon nanotubes.

In the last decade, there are extensive reports on the manufacturing [1–3] and mechanical characterization of CNT-reinforced PMCs [4–6]. Ali et al. [7] studied the dependence of the mechanical properties of natural rubber nanocomposites on multiwalled carbon nanotubes

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https://doi.org/10.1016/j.matchemphys.2018.06.010
Received 7 March 2018; Accepted 4 June 2018
Available online 05 June 2018
0254-0584/

(MWCNTs) grafted by poly(methyl methacrylate) (PMMA), and found the improvement of the mechanical properties of the natural rubber nanocomposites. Bisht et al. [8] compared the effect of graphene-nanoplateles (Gr) and MWCNT on the enhancement of the mechanical and thermomechanical behavior of epoxy, and found that the improvement in the epoxy-CNT composite is better than the epoxy-Gr composite for the weight percentage larger than 0.2%. Mammeri et al. [8] investigated the effect of surface chemistry of MWCNTs on the mechanical properties of MWCNT–PMMA based hybrid coatings, and observed that the MWCNTs with functional groups on surface increased the indentation hardness of the coatings. Choong et al. [9] revealed that the processing history has little effect on the hardness of melt-compounded polycarbonate-MWCNT nanocomposites.

The structural durability of PMCs in service environments has determined the short- and long-term performances of PMC-based structures. It is important to investigate the variation of the deformation behavior of PMC-based structures under the service conditions since the deformation behavior is dependent on the degree of environmental degradation. There are reports about the irradiation effect of ultraviolet (UV) light on the mechanical behavior of polymer, which has been attributed to the UV-induced changes of structures of polymer [10]. Eve and Mohr [11] suggested that the UV irradiation caused the loss of ductility and the decrease of the strength and strain at rupture of PMMA, and found that the hardness of PMMA decreased with the increase of the irradiation dose. Similar behavior has been observed in PS, LDPE and epoxy [12–14]. Qu et al. [15] studied the effect of UV irradiation on the elastic modulus of polyimide films, and found that increasing the irradiation dose causes the increase of surface damages and the decrease of elastic modulus. There is little study on the effect of UV irradiation on the contact deformation of polymers matrix composites.

The structural integrity of CNT-reinforced PMCs in service environments plays an important role in determining engineering applications. It is the purpose of this work to investigate the microhardness of poly(methyl methacrylate)-multiwalled carbon nanotubes (PMMA-MWCNT) composite after exposure to UV irradiation. The mechanism controlling the variation of the microhardness of the PMMA-MWCNT composite is discussed.

2. Experimental details

Methyl methacrylate monomers (MMAs) (Sigma-Aldrich, St. Louis, MO), MWCNTs (Legend Star International Co., New Taipei City, Taiwan), radical initiator of 2-azobisisobutylnitrile (AIBN) (Aencore Chemical Co., Victoria, Australia), and polyethylene glycol octylphenyl (Triton X-100) (Acros Organics, Geel, Belgium) were used to synthesize PMMA-MWCNT composite. Table 1 lists the physical properties of the materials.

Polymerization was used to prepare PMMA-MWCNT composites consisting of MWCNTs of 0.1, 0.5 and 0.7 wt.%, respectively. Note that it is difficult to form uniform suspension due to the formation of the aggregates of CNTs for the concentration of MWCNTs larger than 0.7 wt.%. MMA monomer of 40 g and MWCNTs were mixed in a glass vessel, which was sonicated in a water bath at 50 °C for 2 h to form a suspension. After the sonication, Triton X-100 (polyethylene glycol octylphenyl) as surfactant was then dripped into the PMMA/MWCNT suspension, and the mixture was sonicated at 50 °C for 1.5 h. Finally, AIBN of 0.05 wt.% was added to the suspension under continuous sonication at 50 °C to form a suspension.

Table 1
Physical properties of MMA, MWCNT, and AIBN.

MMA	molecular formula	$C_5H_8O_2$
	density	0.94 g/cm^3
	melting point	−48 °C
	boiling point	101 °C
	molar mass	100.12 g/mol
MWCNT	outer diameter	20–30 nm
	inner diameter	5–10 nm
	length	10–30 μm
	purity	> 95%
	specific surface area	110 m^2/g
AIBN	molecular formula	$C_8H_{12}N_4$
	density	1.1 g/cm^3
	melting point	102 °C
	molar mass	164.21 g/mol

The suspension with AIBN was then placed in a Pyrex plate, which was covered with aluminum foil during the heat treatment in a water bath at 80 °C for 30 min to form a viscous liquid. The viscous liquid was then heat-treated at 40 °C for one day to achieve full polymerization and the formation of the PMMA-MWCNT composite. The PMMA-MWCNT composite was washed subsequently by acetone and deionized water to remove residual reactants, and dried at 80 °C in a vacuum oven to vaporize the un-reacted MMA monomers.

The PMMA-MWCNT composites was UV-irradiated in a UV curing machine in, which the UV light emitted from a mercury lamp of 1 kW (KINGO Electrical Enterprise Co., Tainan, Taiwan). The intensity of the UV light was measured as 1.58 mW/cm^2 by a power meter (G&R Labs) (Santa Clara, California). The specimen temperature was maintained at 38 °C by using an IR cut filter to inhibit the infrared irradiation of the UV light from the specimen. The other filter prevented the specimens from the irradiation of UV light with wavelength greater than 300 nm. The irradiation doses were 45.50, 102.38 and 136.51 J/cm^2, corresponding to the irradiation time of 8, 18 and 24 h, respectively.

The microhardness tests of the PMMA-MWCNT composites were performed on a Micro-Vickers hardness tester (MVK-G1, Mitutoyo, Kanagawa, Japan). A normal load of 100 g was applied to the indenter for 25 s. The specimens of PMMA and the PMMA-MWCNT composites in the dimension of 20×15×2 mm^3, which were cut from un-irradiated plates by a laser cutting machine, were mechanically ground on SiC papers and polished with alumina suspension of ~1 μm alumina particles. The polished specimens were heat-treated at 90 °C in air for 24 h to remove residual stresses, and was then furnace-cooled down to room temperature.

After exposing annealed specimens to UV light for different times, the UV-irradiated specimens were placed in an oven at preset temperatures (50, 60, 70 and 80 °C) before performing the hardness test. The hardness test of the UV-irradiated specimens was conducted as quickly as possible after taking the specimens out of the oven, and the specimens were placed back into the oven immediately after the test. At least three hardness measurements were conducted for each condition.

3. Results

Fig. 1a shows temporal evolution of the hardness of un-irradiated PMMA, which were maintained at different temperatures. Increasing heating time and temperature caused the increase of the hardness of the un-irradiated PMMA, which is different from the trend of the hardness of metals. Such behavior suggests that there exist rearrangements of polymer chains and/or chemical reactions in the PMMA, leading to the hardening (crosslink) of the PMMA. This phenomenon is different from metals, in which the hardness is contributed by the motion of dislocations and the annihilation of dislocations increases with the increase of annealing temperature. The higher the temperature, the faster is the hardening.

The temporal evolution of the hardness of UV-irradiated PMMA with different irradiation doses at 50 °C is depicted in Fig. 1b. Similar to the un-irradiated PMMA, the hardness of the UV-irradiated PMMA increases with the increase of the heating time. The UV irradiation causes the decrease of the hardness of the PMMA. The larger the irradiation dose, the smaller is the hardness for the same period of heat treatment. The UV-irradiation likely causes structural degradation (scission of polymer chains) of the PMMA.

Fig. 1c shows temporal evolution of the hardness of un-irradiated