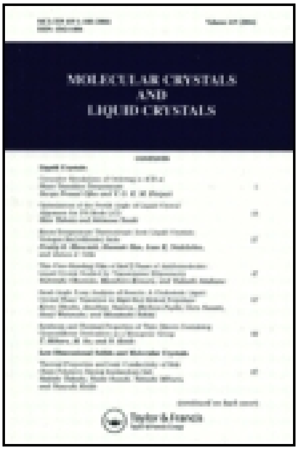

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FUNCTIONALIZATION OF MULTIWALL CARBON NANOTUBES: PROPERTIES OF NANOTUBES-EPOXY COMPOSITES

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Multiwall nanotubes were functionalized using plasma treatments, chemical oxidation, ball milling and thermal treatments. In optimized conditions, plasmas modify nanotubes surface chemistry with a great selectivity. Vickers microindentation and tension tests performed on epoxy resin loaded with multiwall nanotubes allow comparison of the influence of nanotubes surface chemistry and microtexture on loaded resin mechanical properties.

Keywords: multiwall nanotubes; plasma treatments; nanotubes-epoxy mixture; Vickers microindentation; tension tests

INTRODUCTION

Carbon nanotubes are expected to be good matrix reinforcing materials for the next generation of composites due to their intrinsic properties [1,2]. Good interfacial adhesion between nanotubes and polymer should be necessary to enhance the mechanical properties of epoxy resin loaded with nanotubes, especially the tensile strength. In this study, different kinds of catalytic multiwall nanotubes (MWNTs) were synthesized using acetylene as the carbon feedstock. Then, in order to improve the interaction between MWNTs and epoxy matrix, different kinds of treatments (plasma, chemical, thermal, ball-milling) were performed. Finally, the influence of MWNTs surface chemistry and/or microtexture (investigated by X-ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM)) on mechanical properties of MWNTs-epoxy mixture was examined by performing Vickers microindentation and tension tests.

EXPERIMENTAL

Pristine MWNTs were produced by catalytic decomposition of acetylene at 600°C, either on small Co particles (2.5 wt%) supported on zeolite NaY in using the method described in Ref [3], or on CoMgO solid solution [4]. This latter method allows in-situ formation of Co particles supported on MgO, and leads to higher MWNTs yields. Nanofilaments were also produced by decomposition of acetylene, but at 900°C on Co particles supported on silica [5]. Additional thermal treatments were performed at 1600°C allowing formation of a surface free of oxygenated groups, and at 2400°C to improve microtextural organization [6].

Three kinds of plasma treatments (Ar/NH_3, O_2 and Methyl Methacrylate (MMA)) were applied to nanotubes. These low pressure plasmas, generated by a radio-frequency discharge, allow introduction of either a specific polar functional groups or a coating on MWNTs surface with a thin polymer film. Chemical oxidation was obtained after reaction with a NaClO solution (12°Cl) at room temperature. Ball-milling was performed using a stainless steel cell, under air for three hours. After these treatments, MWNTs surface chemistry and microtexture were characterized by XPS (VG Escalab 250) and TEM (Phillips CM20) respectively. Mechanical tests performed on MWNTs-epoxy resin mixtures consisted of: (a) Vickers microindentation measurements made on plasma treated MWNTs-based epoxy resin. Since these MWNTs are available only in small amounts, tests which use very little material are necessary. In this case composites consist of pellets containing 10 wt% dispersed MWNTs in CIBA-GEYGI LY556/HT972 epoxy. Young's modulus was obtained from force/displacement curves. (b) Tension tests (DY22 Adamel Lhomargy apparatus) on dog-boned specimens (ASTM D 638) containing 6 wt% dispersed MWNTs in CIBA-GEYGI LY5052/HY5052 epoxy. Tensile strength and modulus were obtained from the resulting stress/strain curves.

RESULTS

Pristine Nanofilaments and MWNTs Microtexture

Nanofilaments microtexture (Fig. 1a) consists of wrinkled aromatic layers, slightly tilted relative to tube axis, which induces numerous edge planes on

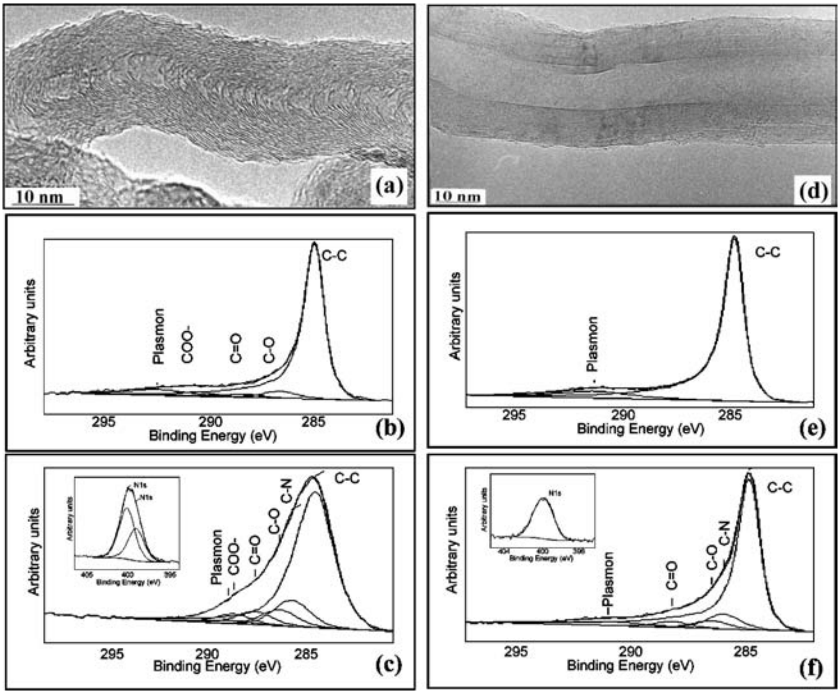

FIGURE 1 Nanofilaments characteristics before (a)-(b), and after (c)Ar/NH_3 plasma exposure. MWNTs characteristics before (d)-(e), and after (f)Ar/NH_3 plasma exposure.

the surface. Nanofilaments XPS data (Fig. 1b) give an atomic ratio $O/C_{at} = 4.10^{-2}$, where the oxidation is due to a purification step by HNO_3 [5].

MWNTs, produced on zeolite NaY then annealed at 1600°C (Fig. 1d) have their walls made of continuous and straight aromatic layers parallel to the axis. Hence this material is less reactive than previous MWNTs. In XPS data, (Fig. 1e) the C1s core level is narrower in comparison with nanofilaments (Fig. 1b) having better aromatic layers organization which improves conduction. Moreover, the annealing removes carbon/oxygen bonds.

For MWNTs produced on a CoMgO solid solution, higher yields are obtained and MWNTs are more entangled. The microtexture is similar to Figure 1d and the XPS data to Figure 1e.

Plasma Treated Nanofilaments and MWNTS

After Ar/NH_3 plasma treatment, XPS analysis (Fig. 1c) gives N/C_{at} as high as 18.10^{-2} for "herring-bone" nanofilaments, due to numerous edges planes on their outer surfaces. For 1600°C annealed MWNTs, N/C_{at} is only 8.10^{-2} (Fig. 1f), due to the continuous aromatic layers, less defects and edges planes accessibility. However, despite a secondary vacuum inside the reactor before plasma discharge, oxygen is also present in great amount; therefore this treatment is non-selective.

Oxygen plasma treatments were tested on 2400°C annealed nanotubes, i.e. totally devoid of oxygen surface groups, because this is the best way to functionalize such organized materials. XPS data show a rapid O/C_{at} increase, then a saturation after 5 min exposure time leading to an $O/C_{at} = 10.10^{-2}$ regardless of the plasma parameters. The advantage of such treatment is the selective grafting of carbon-oxygen bonds (in great majority C=O). Oxygen radicals present in the plasma favor the formation of the more stable carbonyl bond.

In the case of Methyl Methacrylate plasma, a very thin highly cross-linked film coats the nanotubes surface as O/C_{at} in the polymer film reaches 20.10^{-2}, without etching of the nanotube surface.

Other Treatments

For tensile tests, needing large amounts of MWNTs, classical treatments such as chemical oxidation, ball milling and thermal treatments were performed on CoMgO nanotubes. After oxidation, similar O/C_{at} are obtained for both chemical (NaClO) or plasma oxidation, i.e. $O/C_{at} = 10.10^{-2}$. However, in the case of plasma oxidation, shorter time is necessary (20 min instead of 6 hours) and better selectivity is obtained. After ball milling, a strong agglomeration of the nanotubes without any oxygen grafting results. After thermal treatment at 2400°C, MWNTS having well organized aromatic layers without surface groups are obtained.

Vickers Microindentation

Microindentation techniques are usually focused on carbon fiber indentation in a composite, in order to study the interlaminar shear strength of the interface. In this study, it was used as a way to compare the effect of plasma treatments on the interface quality between nanotubes and epoxy resin. The comparison of Young modulus data (Table 1) shows the positive but small effect of plasma treatments, while the highest values (increase of a factor 1.2) are obtained for oxygen plasma-treated MWNTs. Nevertheless, due to the fact that a local probe is used, a high dispersion of E values is obtained.

These results also show that improving the hydrophilic behavior of the nanotubes favors the resin infiltration process and MWNT dispersion. Hence, more nanotubes are involved in the matrix reinforcement.

TABLE 1 Young's Modulus of Reinforced Epoxy Resins, Related to MWNT Plasma Treatments

MWNTs 10 wt% in pellets	E (GPa)	Standard deviation (%)
Unreinforced epoxy	4.2	1
After Ar/NH_3 plasma	4.29	3.5
Pristine	4.32	3.7
After MMA plasma	4.68	3.4
After O_2 plasma	5.07	2.8

TABLE 2 Tensile Properties of Epoxy Resins Loaded with MWNTs. (S.D.: Standard Deviation)

MWNTs 6 wt% in specimens	E (GPa)	S. D. (%)	σ (MPa)	S. D. (%)	ε (%)	S. D. (%)
Unreinforced epoxy	3.1	4	72	4	4.8	13
Ball milled	2.9	4	44	11	1.5	15
Pristine	3.6	0.8	64	4	2.9	9
Oxidized	4.1	0.5	56	8	2	10
Annealed	4.7	1.4	52	2	1.7	2

Tensile Tests

In order to get more global data, macroscopic mechanical tests were performed on dog-boned MWNT-epoxy specimens, using on heat treated, chemically oxidized and ball-milled MWNTs.

Table 2 shows that loading epoxy resin with MWNTs leads to brittle composites. Indeed, the fracture strength and strain are reduced for all MWNTs. However, it is possible to increase the tensile modulus by 52% by using heat treated nanotubes due to the fact that annealing improved the intrinsic mechanical properties of the nanotubes. For oxidized nanotubes, the reinforcing effect is improved due to a better dispersion of the nanotubes in the epoxy resin; however, the strong interface observed in the fracture surfaces is responsible for increased brittleness.

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