

# Effects of plasma surface modification on interfacial behaviors and mechanical properties of carbon nanotube- $\text{Al}_2\text{O}_3$ nanocomposites

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(Received 5 June 2007; accepted 26 November 2007; published online 26 December 2007)

The effects of plasma surface modification on interfacial behaviors in carbon nanotube (CNT) reinforced alumina ( $\text{Al}_2\text{O}_3$ ) nanocomposites were studied. A unique plasma polymerization method was used to modify the surfaces of CNTs and  $\text{Al}_2\text{O}_3$  nanoparticles. The CNT- $\text{Al}_2\text{O}_3$  nanocomposites were processed by both ambient pressure and hot-press sintering. The electron microscopy results showed ultrathin polymer coating on the surfaces of CNTs and  $\text{Al}_2\text{O}_3$  nanoparticles. A distinctive stress-strain curve difference related to the structural interfaces and plasma coating was observed from the nanocomposites. The mechanical performance and thermal stability of CNT- $\text{Al}_2\text{O}_3$  nanocomposites were found to be significantly enhanced by the plasma-polymerized coating.

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Carbon nanotubes (CNTs) have been widely used as additives to reinforce strength of polymer composite materials, such as epoxy,<sup>1</sup> petroleum pitch,<sup>2</sup> and poly(methyl methacrylate),<sup>3</sup> due to their extraordinary mechanical properties.<sup>4–6</sup> Only recently, exciting progress in using CNTs as reinforcing additives to ceramic composites has been reported.<sup>7–10</sup> However, a great challenge still remains in using CNTs as reinforcing agents in ceramic composites mainly associated with high temperature process, in which the oxidation process occurs and CNTs are damaged due to high temperature ( $>1500^\circ\text{C}$ ). Even at  $1500^\circ\text{C}$ , the CNT-reinforced  $\text{Al}_2\text{O}_3$  composite is not well sintered, leading to low mechanical performance.<sup>8</sup>

Additionally, the effective utilization of nanotubes in composite applications depends strongly on the ability to disperse CNTs sufficiently throughout the matrix. Furthermore, good interfacial bonding is required to achieve load transfer across the CNT-matrix interface, a condition necessary for improving the mechanical properties of ceramic composites. Considerable progress on dispersing CNTs in ceramic matrices<sup>10–14</sup> have been reported and toughened alumina has been achieved by addition of nanosize second phases and the

spark plasma sintering.<sup>14,15</sup> However, the critical issues on CNT dispersion and high temperature oxidation are yet to be addressed. Furthermore, it is of fundamental importance to develop a process that can modify the surfaces of the nanoparticles and nanotubes in high density CNT- $\text{Al}_2\text{O}_3$  composites and understand the effects of interfaces on the mechanical behaviors and physical properties. Recently, we have developed a plasma polymerization method to modify the surface of CNTs.<sup>16–20</sup> In this letter, we present the experimental results on the plasma surface modified carbon nanotubes and alumina nanoparticles and their effects on the structural interface behaviors. The mechanical property data are reported for the CNT- $\text{Al}_2\text{O}_3$  composites with and without surface modifications.

The CNT- $\text{Al}_2\text{O}_3$  composite powders were prepared by the molecular level mixing with well dispersed CNTs in the  $\text{Al}_2\text{O}_3$  matrix.<sup>21</sup> The single-wall carbon nanotubes were provided by Helix Material Solutions, Inc., TX, having dimensions of 1.3 nm in diameter and  $0.5\sim 3\ \mu\text{m}$  in length. The alumina nanoparticles with the average diameter of 47 nm were purchased from Nanophase Tech. Co., IL. The single-wall CNT and alumina (CNT- $\text{Al}_2\text{O}_3$ ) powders were mixed in an ethanol solution and dispersed ultrasonically. The CNT- $\text{Al}_2\text{O}_3$  gel was dried and ground into a fine powder. The volume fraction of CNTs was 9 wt % in this study. The

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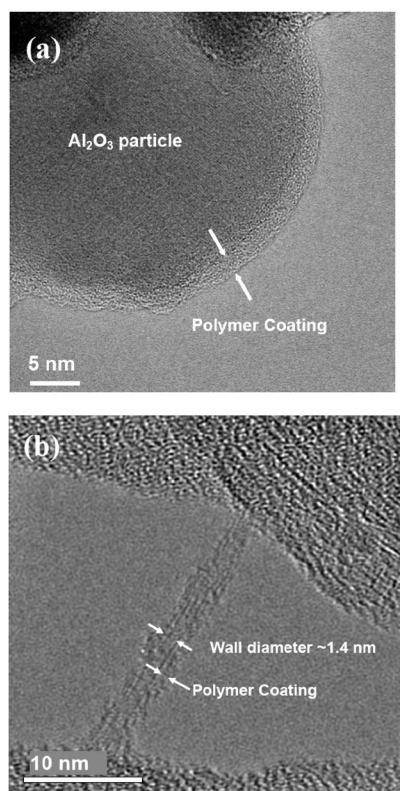


FIG. 1. (a) Bright-field TEM image of plasma-polymerized pyrrole coated  $\text{Al}_2\text{O}_3$  nanoparticles and (b) HRTEM image of polymerized pyrrole coated CNTs.

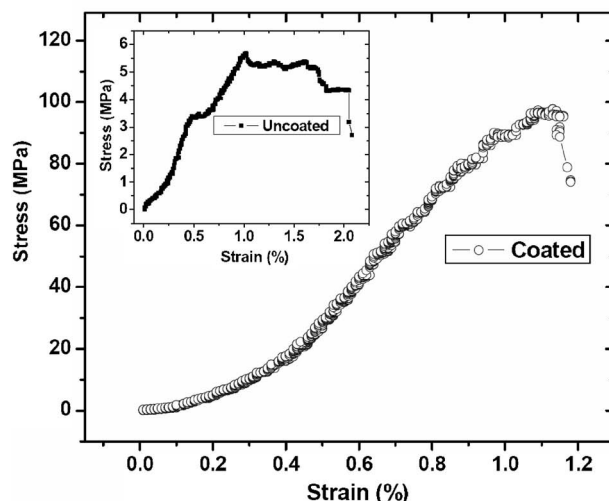
CNTs and  $\text{Al}_2\text{O}_3$  nanoparticles were coated with ultrathin films by plasma polymerization using pyrrole as monomer. The details of plasma polymerization process can be found in Refs. 16 and 20.

The CNT- $\text{Al}_2\text{O}_3$  nanocomposites were sintered by two different methods, namely, ambient sintering at 1000 °C and hot-press sintering (HPS) at 1200 °C. For ambient sintering, the consolidated CNT- $\text{Al}_2\text{O}_3$  were placed in a tube furnace and sintered at 1000 °C for 12 h under reduced pressure in a flowing gas mixture of 5 vol % of  $\text{H}_2$  and 95 vol % of  $\text{N}_2$ . For hot-press sintering, the CNT- $\text{Al}_2\text{O}_3$  mixed powder was loaded into a graphite die and compacted into a solid sample using direct current induced hot-press (dc hot-press) technique. A pressure of 120 MPa was used at a temperature of 1200 °C and held for 2 min.

The surface and interface morphology of nanoparticles and ceramic matrix was studied by the Philips XL-30 field emission scanning electron microscopy (SEM). The microstructures of CNT- $\text{Al}_2\text{O}_3$  powders and sintered nanocomposites were studied by JEOL 2010F transmission electron microscopy (TEM) and the mechanical properties of the nanocomposites were characterized by using the mechanical characterization loading stage system (Ernest F. Fullam, Inc., NY), with a compression loading stage and strain-gauge acquisition system. The compressive strength and elastic modulus were determined.

Figure 1 shows the HRTEM images of the polymerized pyrrole coated  $\text{Al}_2\text{O}_3$  nanoparticles and carbon nanotubes by plasma treatment. As can be seen in Fig. 1(a), the  $\text{Al}_2\text{O}_3$  nanoparticles exhibit spherical shape. A thin pyrrole coating of 3 nm is uniformly deposited on the surfaces of the nanoparticles. The lattice image of alumina can also be clearly seen in sharp contrast to the amorphous coating. Figure 1(b)

(a) CNT-Alumina by ambient sintering at 1000 °C



(b) CNT-Alumina by hot-press sintering at 1200 °C

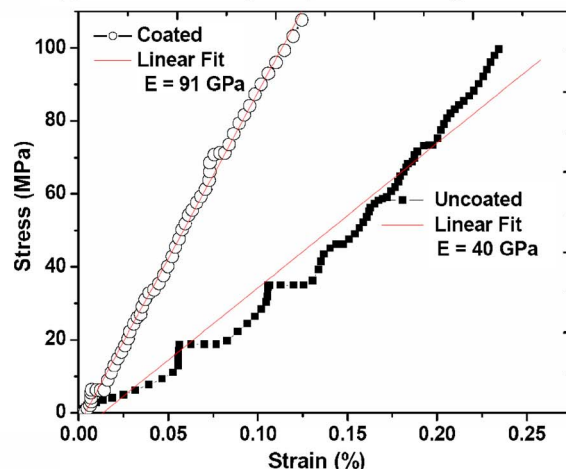


FIG. 2. (Color online) Stress-strain curves of the coated and uncoated CNT- $\text{Al}_2\text{O}_3$  nanocomposites obtained from the mechanical characterization loading stage system, (a) after ambient sintering at 1000 °C, and (b) after dc hot-press sintering at 1200 °C.

is the bright field HRTEM image of the pyrrole coated single-wall CNT. The single-wall CNT, a few nanometers in diameter, is also coated with the uniform polymerized pyrrole film.

The stress-strain curves for the coated and uncoated CNT- $\text{Al}_2\text{O}_3$  composites by both ambient and hot-press sintering are plotted in the Fig. 2, respectively. Figure 2(a) shows the results of the CNT- $\text{Al}_2\text{O}_3$  composite by ambient sintering at 1000 °C. We found that a distinctive yielding is observed in the uncoated sample [inset of Fig. 3(a)] at the low stress level, which corresponds to the initial movement of the CNTs. However, the CNTs network still participate in stress bearing as they are entangled in the matrix. Therefore, the strain-stress curve experiences a rapid increase after first yielding, indicating certain interfacial bonding between the CNTs and alumina grains. As stress further increases, a second yielding is observed at a much higher stress level. This second yielding relates to the slippage and debonding of the CNTs, responsible for the large amount of nonlinear deformation up to fracture.

In contrast, the coated sample in Fig. 2(a) exhibits much improved rigidity and fracture strength with an initial nonlinear portion of the stress-strain curve. As a result of poly-

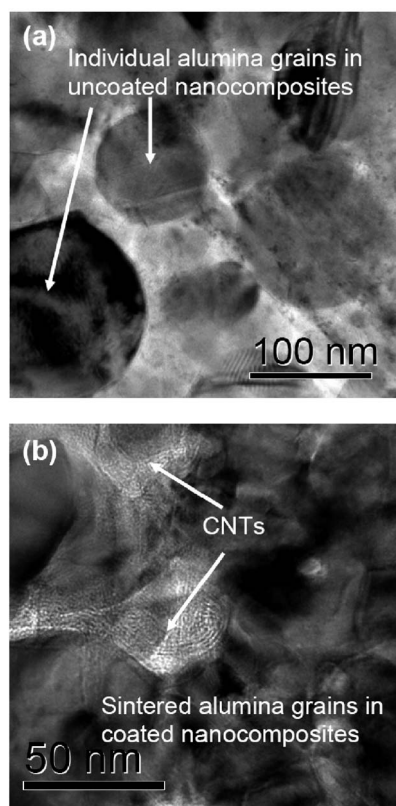


FIG. 3. TEM images of CNT- $\text{Al}_2\text{O}_3$  nanocomposites after hot-press sintering (a) uncoated nanocomposites only have individual alumina grains, and (b) in coated nanocomposites, CNTs are well preserved and surrounding the alumina grains.

mer coating, the stress-strain curve of the coated sample continues to increase while yielding takes place at a low stress level for the uncoated sample. This behavior suggests a well strengthened interfacial bonding for the plasma coated sample. The strong interfacial bonding persists until final fracture is reached. The strength of the composite sample has increased from 4.3 MPa (uncoated) to 97.8 MPa (coated); more than 20 times higher. Consistently, the modulus has increased from 7.10 GPa (uncoated) to 9.85 GPa (coated). The rapid increase clearly indicates much stronger interfacial bonding achieved in the composites due to surface coating. These results clearly demonstrate the effects of the plasma polymerization on the interfacial behaviors of the CNT- $\text{Al}_2\text{O}_3$  nanocomposites at low sintering temperatures.

Figure 2(b) shows the stress-strain curves of the CNT- $\text{Al}_2\text{O}_3$  composite by the dc-hot-press sintering. As can be seen in this figure, the stress-strain curves all exhibit quite linear behaviors that are typical of ceramics. Comparing to the results of the low-temperature sintered samples, it is quite consistent that the uncoated sample exhibits a relatively lower modulus as compared to that of the coated one. The modulus is significantly improved up to 91 GPa for the coated sample. However, the corresponding value of the compressive force has reached the maximum (4000 N) of the mechanical characterization loading stage system without fracturing the sample. Therefore, the maximum strength of the sample is not determined. Nonetheless, the improvement of the modulus is at least a factor of 2, indicating a great potential in further enhancing the mechanical properties.

The TEM study further reveals the micro structural differences between the uncoated and coated samples after hot-

press sintering. As shown in Fig. 3(a), only individual alumina grain is observed while the CNTs appear to be mostly decomposed in uncoated nanocomposites. In contrast, as shown in Fig. 3(b), CNTs are well preserved and surrounding the alumina grains in coated nanocomposites. The lattice structures of CNTs are also well defined indicating improved thermal stability at such high sintering temperature. Although, at 1200 °C, the polymer coating on the CNTs is assumed to be entirely burned out, residuals of carbon from the coating could have considerably enhanced their stabilities at the sintering temperature. As a result of this thermal stability, the coated nanocomposites exhibit considerable improvement in modulus.

In conclusion, we have developed a plasma polymerization method to modify the interfaces of the CNT- $\text{Al}_2\text{O}_3$  nanocomposites. Ultrathin pyrrole coating ( $\sim 3$  nm) was deposited on the surfaces of CNTs and  $\text{Al}_2\text{O}_3$  nanoparticles by plasma polymerization. Significant effects on interfacial structural and related mechanical behaviors were observed through both electron microscopy and mechanical characterization. The enhanced CNTs dispersion is found to be closely associated with the polymer thin films deposited on the surfaces of CNTs and  $\text{Al}_2\text{O}_3$  nanoparticles. Due to surface modification, the CNTs are well preserved and bonded to the alumina nanoparticles, therefore responsible for the enhanced mechanical properties.

The authors at University of Cincinnati are grateful to Chemat Technologies and US Air Force for the support under a SBIR grant. The hot-press sintering experiments performed at Boston College were supported by NSF NIRT 0304506.

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