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Architectural and mechanical performances of carbon nanotube agglomerates characterized by compaction response

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ABSTRACT

Compaction responses have been carried out to characterize the architectural and mechanical performance of carbon nanotube (CNT) agglomerates efficiently. The agglomerate density, agglomerate strength and internal pressure were obtained quantitatively, and the relationships between them were discussed. Agglomerates were classified into soft and hard agglomerates by strength. Hard agglomerates and soft agglomerates dominated double walled CNTs and aligned multi-walled CNT arrays respectively while both hard and soft agglomerates dominated conventional multi-walled CNTs. The microstructures and interaction between CNTs were discussed to explain the different agglomerate behaviors.

1. Introduction

One dimensional nanomaterial (e.g. nanotubes, nanowires and nanorods) has been the focus of nanoscience and nanotechnology due to high surface area and large aspect ratio. Some pristine properties of these nanomaterials disappeared due to unavoidable agglomeration. It is usually bad for further applications in advanced composites due to poor dispersion in matrix. Whereas, we can also make use of the agglomeration behaviors such as in nano agglomerate fluidization of carbon nanotubes (CNTs) [1–3] and yarn drawn from CNT arrays [4,5]. Good cushion performance is also found for CNT agglomerates [6]. However, few attentions have been paid to the agglomerate properties except some reports based on the scanning electron microscopy, transmission electron microscopy observation [7,8], a most direct way but a limited eyeshot. Dynamic laser scattering [9,10] is used to characterize the aspect ratio of one dimensional nanostructure, while small angle X-ray and neutron scattering [11,12] are used to characterize the alignment of arrays, however they are not efficient to characterize the structures of irregular agglomerates. Essentially, mechanical performance of the agglomerates, crucial to the dispersion and further application, is not easily obtained from the above methods.

Compaction response has been used to characterize the submicron size alumina powder structure by Bruch [13]. When the green density is plotted against the logarithmic pressing pressure for agglomerated powder, two straight line segments would appear. The break point in the curve was interpreted as the onset of the breakage of agglomerates. The pressing pressure at the break point was ascribed as the intrinsic strength of agglomerates by Niesz [14]. Ge [15] used the ratio of the slopes of these two straight lines to characterize the relative density of agglomerates. In this article, compaction response is employed to characterize the structural and mechanical performance of CNT agglomerates.

2. Experimental

Multi-walled CNTs (MWCNTs) prepared in nano agglomerate fluidized bed reactor (A-MWCNTs) [1–3], crushed A-MWCNTs (C-MWCNTs), long aligned MWCNT arrays (L-MWCNTs) [16,17] and double-walled CNTs (DWCNTs) [18] were used. DWCNTs were purified by hydrochloric acid to remove MgO support before drying in oven with a carbon content over 99%. Metal catalyst contained in A-MWCNTs was not removed in order to maintain the agglomerate structures of A-MWCNTs. However, when crushed by airstream, parts of catalyst can be separated from the C-MWCNTs due to segregation. The impurity contents are lower than 2% for L-WNCNTs and C-MWCNTs, while it is not more than 7% for A-MWCNTs.

Hydrostatic pressure was applied through an oil jack [19] to push the sample upward relative the punch so that CNT samples were

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compressed (Fig. 2a), during which the displacement and pressure were measured by micrometer caliper and pressure gauge for calculating the bulk density of the compacted sample. To monitor the pore size evolution during compression, parallel samples were compressed under different pressures and taken out of the die cavity followed by Hg penetration measurement or other tests [6].

3. Results and discussion

3.1. Architecture and compaction response of CNT agglomerates

Agglomerate morphologies of MWCNTs were observed (Fig. 1), consistent with the multi-stage model by Yu [2]. Primary agglomerates formed when MWCNTs grown from the catalyst nucleus, which were composed by the strong chemical bond with the catalyst and entanglement between MWCNTs. Secondary agglomerates were structured by the weak interactions between primary agglomerates, such as van der Waals force, static electrical force, or conglutination. The primary agglomerates, combined by chemical bond and entanglement, have a high strength and can be considered as hard agglomerates, while the secondary agglomerates joined by weak physical interaction are considered as soft agglomerates.

Linear relationship was founded between the compact density and the logarithmic pressing pressure with several break points for one-dimensional CNT fibers (Fig. 2b). Typically, there are four straight line segments in the compaction curve of A-MWCNTs. So there might be three stage agglomerates in A-MWCNTs, while the breakdowns near 0.1,1 and 25 MPa were interpreted as the breakage of the agglomerates.

Morphology evolution of A-MWCNTs after pressing under different pressures was compared (Fig. 3). The primary agglomerates were not affected by compacting below 3 MPa, however when above 30 MPa, a little larger than the strength (25 MPa) of primary agglomerate, the agglomerates were broken, and the sub-micrometer sized pores disappeared.

Ex-situ Hg penetration provided detailed evolution of pores during the break of CNT agglomerates (Fig. 2c). The multi-peaks in crude sample may be related to multi-stage agglomerates. After pressing under 0.4, 2.5 and 31 MPa, the pores larger than 3000 nm, 500 nm and 30 nm disappeared respectively, indicating the breakdown of several different agglomerates. When extruded from the die cavity, the sample pressed under 275 MPa would expand [6] with a pore volume from nearly zero (not more than 0.05 ml/g) to 1.4 ml/g, only a little smaller than that under 31 MPa (1.7 ml/g) as shown in Fig. 2c. The similar pore size distributions and pore volumes after pressing under 31 MPa and 275 MPa, good recovery and cushioning performance [6] may be derived from the fact that all instable agglomerates have been destroyed above 31 MPa, consistent with the primary agglomerate strength of 25 MPa.

When dispersed in water by ultrasonic, the different size distributions of CNT provide another indirect proof of CNT agglomerate breakage. For CNT samples compressed under 0, 0.4 and 2.5 MPa, the size distribution changed only a little. However, for samples compressed under 31 MPa and 275 MPa, there was an increase of volume fraction in the range of smaller size (Fig. 2d). Although the size of CNT dispersed in water is different from the CNT agglomerate size, it can still be concluded that the CNTs compressed over 31 MPa are more easily to be dispersed, which may be due to the agglomerate breakage.

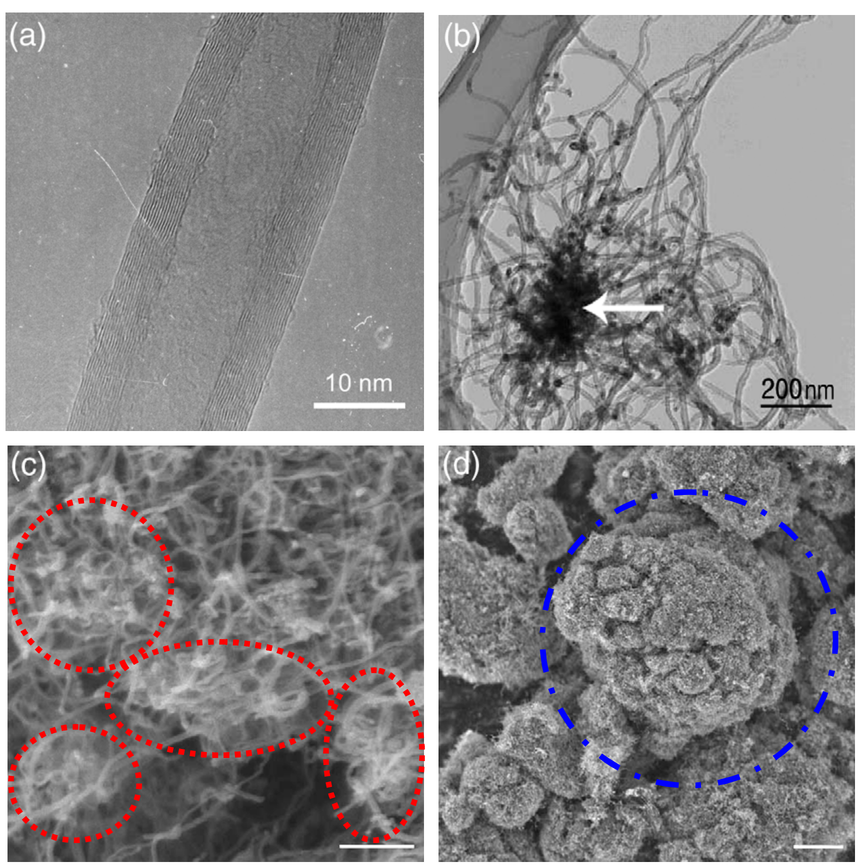

Fig. 1. Multi-stage agglomerate morphologies in A-MWCNTs: (a) single MWCNT; (b) primary agglomerate with catalyst nucleus; (c) primary agglomerates, scale: 300 nm; (d) secondary and larger agglomerates, scale: 3 μm. (Reprinted with permission from [6].)