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Strong and ultra-flexible polymer-derived silicon carbonitride nanocomposites by aligned carbon nanotubes

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ABSTRACT

We report the synthesis of flexible ceramic composites with a high tensile strength (536.33 ± 7.23 MPa) using carbon nanotube sheet aligned by mechanically stretching process. The process is based on the infiltration and pyrolysis of liquid ceramic precursor into aligned carbon nanotube sheet. Mechanical properties and microstructure of the resultant composites are investigated. The resultant nanocomposites maintain well-aligned carbon nanotube morphology with high volume fraction (60%) and long pullout (15 μm), contributing to a high degree of load-transfer efficiency and toughening. Flexibility test reveals that such ceramic nanocomposites retain the original mechanical properties and microstructures after one thousand repetitions of 75% bending deformation, showing excellent compliance and durability. Applications requiring materials with high flexibility and mechanical properties can benefit from this research.

1. Introduction

Ceramic composites represent a novel technology with multiple desired properties for applications such as jet engines and lightweight cars [1]. The ability to deform flexibly in ceramic materials is of profound interest for advanced specific applications, such as thermal protection system and battery materials [2–4]. However, strong ionic/covalent bonding makes conventional ceramic composites own high mechanical properties while suffer from low flexibility [5,6]. Minuscule ceramic objects have been created which demonstrate the ability to deform to large strains recoverably [7]. Large-sized flexible ceramics materials are also needed for macro-applications. A common method is derived from the embedding of ceramics powders in a polymer phase [4,8]. However, since this method is built on the presence of a polymer phase, the effective temperature of such flexible ceramic materials is restricted to a mild temperatures range (200 °C or less) [5].

As carbon nanotubes (CNTs) are exceptionally stiff and strong and can be bent to large angles without breaking, a new notion of flexible ceramic nanocomposites originates from the integration of carbon nanotubes with brittle ceramics. Since their discovery, carbon nanotubes have been predicted as one of the most promising candidates for novel reinforcement materials owing to their remarkable intrinsic mechanical, electrical and thermal properties [9–13]. However, owing to challenges such as fully dispersing individual nanotubes into the matrix [14–16], the properties of carbon nanotube reinforced nanocomposites are far below theoretical predictions. Macroscopic assembly of carbon nanotubes is needed to overcome these obstacles and to demonstrate the unique CNTs properties [17]. Carbon nanotube sheet with random structure can be prepared by vacuum filtration, layer-by-layer assembly and solution spraying [18–20]. Random carbon nanotube sheet can also be obtained directly by collecting gases flowing through a hot furnace, which contain carbon source and floating catalyst particles [21]. To utilize carbon nanotube's anisotropic properties along the longitude axis, in the past decades, a number of studies focus on producing assemblies of aligned carbon nanotubes [22–24]. Some methods involve dispersing carbon nanotubes in a solvent and using outer field force such as magnetic field and electrical field in a liquid polymer matrix [15,17,22,25]. Other researchers drew aligned carbon nanotube sheet or fiber directly from carbon nanotube forest synthesized by chemical vapor deposition (CVD) [21,26].

In this work, a novel technical method is presented to fabricate flexible ceramic nanocomposites by using aligned carbon nanotube sheet. Aligned carbon nanotube sheet is obtained by mechanically stretching of random carbon nanotube sheet in our previous research [27]. The existing methods, based on mixing carbon nanotubes in ceramic powders or ceramic polymeric precursor directly, have a limited volume fraction of carbon

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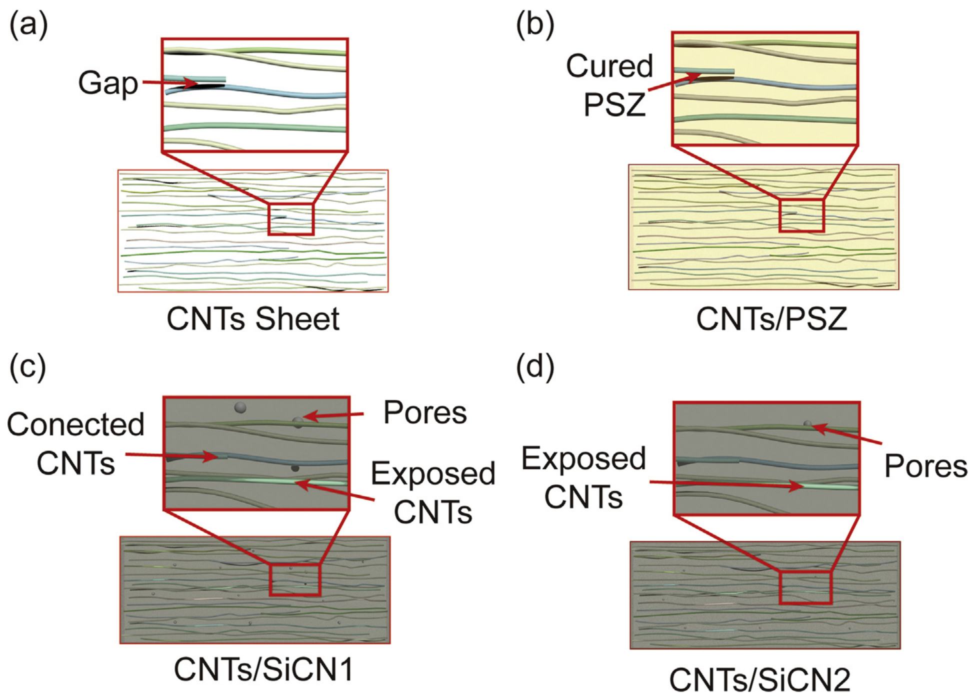

Fig. 1. Illustration of polymer impregnation and pyrolysis process to prepare aligned carbon nanotube reinforced silicon carbonitride nanocomposites. (a) CNTs sheet, (b) CNTs/PSZ, (c) CNTs/SiCN1, and (d) CNTs/SiCN2.

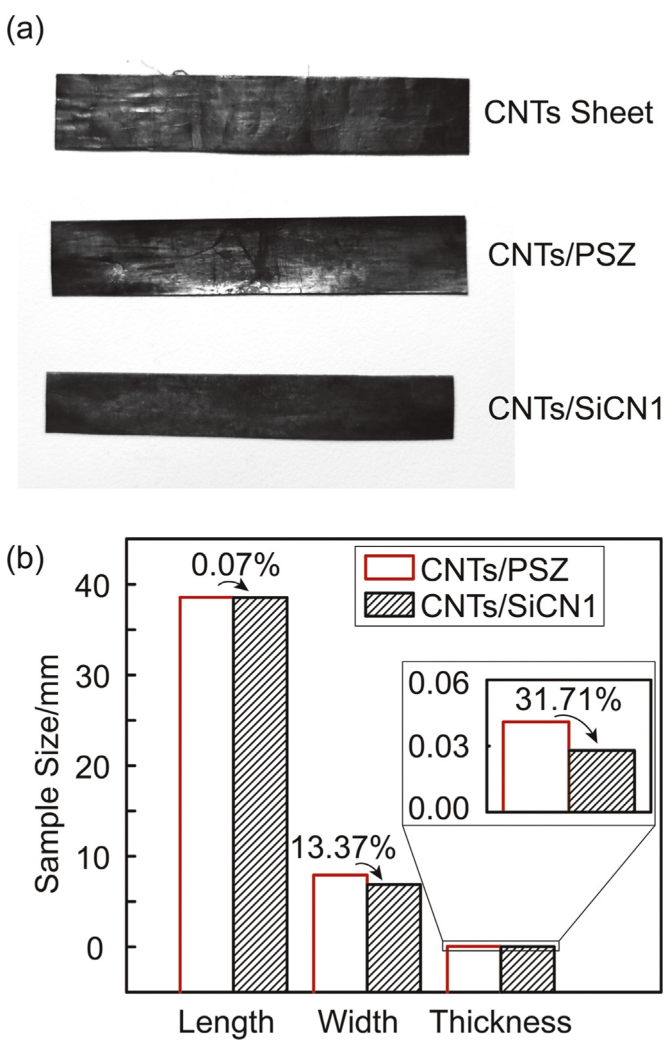

Fig. 2. (a) Optical images of the three samples (CNTs sheet, CNTs/PSZ and CNTs/SiCN1). (b) Sample size change in length, width and thickness from CNTs/PSZ to CNTs/SiCN1.

nanotubes in ceramic matrix [28–33]. Our approach is to impregnate liquid polysilazane (PSZ), most commonly as the polymeric precursor of silicon carbonitride (SiCN), into the aligned carbon nanotube thin sheet with high volume fraction. This process is based on the wet infiltration of liquid ceramic polymeric precursors, which is called polymer impregnation and pyrolysis (PIP) process to fabricate carbon fiber reinforced ceramic nanocomposites [34]. Flexibility, mechanical properties and microstructure of our ceramic nanocomposites are characterized and studied. The toughening mechanism of carbon nanotubes in ceramic matrix composites is also studied in our material system.

2. Experimental procedure

2.1. Starting materials and preparation

Aligned carbon nanotube sheets were prepared by mechanical-stretching method from random carbon nanotube sheets (Nanocomp Technologies, Inc.), comprising of multi-walled carbon nanotubes (diameter as 6–8 nm and length around 1 mm). The random carbon nanotube sheets were mechanically stretched to a specified strain. The details are provided in our previous work [27,35]. The elongation percentage or strain was monitored and the machine was stopped at a specific amount of strain. In this research, the elongation percentage was controlled to 35%. After mechanical stretching, aligned carbon nanotube sheet with 8 mm width and 0.041 mm thickness was obtained. The aligned carbon nanotubes sheet was cut into 38 mm in length for this research. Polysilazane (KiON Defense Technologies, Inc.), a liquid thermosetting resin with repeat units in which silicon and nitrogen atoms are bonded in an alternating sequence, was used as the liquid preceramic precursor of silicon carbonitride in our experiment and 4 wt% dicumyl peroxide (Sigma-Aldrich Co.) was used as the thermal initiator [36].

The integration of aligned carbon nanotube sheet with polysilazane precursor to prepare flexible ceramic nanocomposites was illustrated in Fig. 1. There were four stages illustrated: