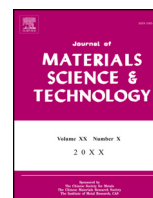




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## Promising commercial reinforcement to the nanodiamond/epoxy composite by grafting ammonium ions

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### ABSTRACT

A simple, economic, efficient and eco-friendly nanodiamond (ND) modifying method to reinforce the ND/epoxy composite for the industrialization of the high-performance ND/epoxy composite is always desired. In the present work, the ND was successfully modified only using aqueous ammonia through an easy-to-operate method by replacing the hydrogen atoms in the carboxyl group with ammonium ions. Ammonia, which is the only pollutant in the process, could be recycled. The modified ND/epoxy composite showed an overwhelming advantage over the neat epoxy or the ND/epoxy composite in storage modulus in their glassy state without any degradation of tensile strength, hardness and fracture toughness.

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### 1. Introduction

Diamond, the hardest material in nature, is not only loved by lovers. For the outstanding mechanical properties, thermal conductivity (4 times more than that of copper at room temperature) [1], and some other advantages in optics [2] and pressure resistance [3], it catches the eyes of scientists from every corner of the world. With the industrialization of the nanodiamond (ND) produced by the detonation method, the small size, rich chemistry of its carbon surface and low price make diamond an easy-to-operate and economically viable nanomaterial in both the academic and the industrial world.

Epoxy resins, with good stiffness, high specific strength, low cure shrinkage, strong adhesion, excellent weatherability and chemical resistance [4–6], are preferred by various engineering applications.

In 1960s, these two excellent materials were first combined together by researchers at “Altai” center in the former Union of Soviet Socialist Republics (USSR), and then more and more special advantages for this unique composite were discovered and attracted unstoppable interest all over the world [7]. Lightweight, strong, biocompatible and cheap ND/epoxy composite could show

great potential in applications in automotive industry, aerospace and medical field [8]. However, limited interfacial interaction between ND and epoxy, and the dispersion of ND are always regarded to be the two key obstacles to the fully manifestation of the advantages of the ND/epoxy composite [9]. Building chemical bonds between the amino groups attached nanofillers and epoxy resins is a successful solution to this problem for the carbon nanotube/epoxy composite [10], thus various methods were developed to modify the ND with amino groups. In 2011, this method was first applied to the ND/epoxy composite [11]. In 2014, Guo et al. [12] modified ND by refluxing ND with SOCl<sub>2</sub>, anhydrous DMF, and TETA, followed by washing with plenty of distilled water. In 2015, amino groups attached ND was obtained by treating the mixture of ND, acetone and oleylamine in an ultrasonic bath [13]. In 2016, a ND modifying work was carried out through a solvent-free gas-phase treatment with 1-aminopyrene, or 2-aminofluorene, or 1-octadecylamine under moderate vacuum, at temperatures of 150–180 °C [14]. Though various ND modifying methods were developed to reinforce the ND/epoxy composite, poisonous reagents and relatively complex processes, which terribly obstructing the industrialization of the composites [15], still seem not to be effectively controlled in the preparation of the amino groups attached nanofillers even now. In order to industrialize the ND/epoxy composites, a low-cost, easy-to-operate and eco-friendly process is always desired.

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In the present work, we give up the conventional covalent modification method to obtain amino groups attached ND, and modify ND by grafting ammonium ions to the ND surface to combine ND and epoxy together. Consequently, a simple, economic, efficient and eco-friendly ND modifying method is proposed to reinforce the mechanical performances of the ND/epoxy composite, which has the potential to be industrialized.

## 2. Experimental

### 2.1. Materials

ND powders (high-purity grade) were bought from Beijing Grish Hitech, China. Concentrated aqueous ammonia was supplied by Sinopharm Chemical Reagent Co., Ltd. And zy5401A epoxy and zy5401B curing agent were obtained from Nanjing Zhongying New Nanomaterials Co., Ltd.

### 2.2. Modification of ND

At first, the ND was treated in an aqueous ammonia solution overnight in a sealed container under continuous and vigorous stirring at room temperature. Then, the sealed container was opened and transferred to a vacuum oven holding at 333 K overnight. The excess ammonia gas was evaporated during this process and recovered by water through the air vent of the vacuum oven. The as-obtained sample is labeled as  $\text{NH}_4^+$ -ND.

### 2.3. Preparation of nanocomposites

The weight ratio between nanofiller and epoxy for the preparation of nanocomposites was 1:100. A ball milling technique was used to disperse ND or  $\text{NH}_4^+$ -ND into the epoxy. The planetary ball mill used was equipped with two 250 mL agate vessels and 280 agate balls (6 mm) for each vessel. The planetary ball mill was set at 40 Hz (515.6 r/min for rotation, 257.8 r/min for revolution) for 2 h. After milling, the curing agent was added with a zy5401A to zy5401B weight ratio of 5:1.38. After the mixture was uniformly stirred and degassed, it was poured into stainless molds and cured at 60 °C for 2 h and then 100 °C for 2 h. Finally, the samples were cooled to room temperature naturally. The samples without adding nanofillers were also fabricated with the same procedures.

### 2.4. Characterizations

The X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250 XPS system with a monochromatized Al K $\alpha$  X-ray source (1486.6 eV). SEM images were taken on FEI nano-450 after the fracture surface was coated by Pt. Tensile tests were carried out with an SANS CMT5205 mechanical testing machine at room temperature following GB/T 2567-2008. Micro-hardness was measured using a microhardness tester Qness Q-10A+ with a testing force of 490 mN. Dynamic mechanical analysis (DMA) was performed in the single-cantilever blending mode using NETZSCH DMA 242 E from 30 to 250 °C. The heating rate was set at 3 °C/min and the frequency used was 1 Hz.

The fracture toughness was measured on single-edge notch-bend (SENB) specimens according to ASTM D5045-14 using SHIMADZU AG-X (10 kN). The sample dimensions were 5 mm × 10 mm × 44 mm. A 5-mm-deep sharp notch was prepared by machining for every specimen. Then, fracture tests were carried out on the notched specimens via three-point bending at room temperature. The loading rate was 10 mm/min until the specimens were loaded to failure. Then the mode-I critical-stress intensity factor ( $K_{Ic}$ ) were calculated based on Eq. (1).

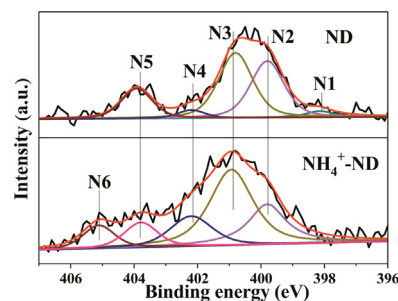


Fig. 1. N 1s XPS spectra of ND and  $\text{NH}_4^+$ -ND (The intensities are not in the same scale).

$K_{Ic}$  in units of  $\text{MPa m}^{1/2}$  is defined as follows:

$$K_{Ic} = \left( \frac{P_Q}{BW^{3/2}} \right) f(x) \quad (1)$$

where  $P_Q$  is the fracture load,  $B$  is the specimen thickness,  $W$  is the specimen width.  $f(x)$  is defined as:

$$f(x) = 6x^{3/2} \frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{(1+2x)(1-x)^{3/2}} \quad (2)$$

where  $x = a/W$  and  $a$  is the crack length.

For every mechanical test, at least 5 specimens were tested to make sure the accuracies of results.

## 3. Results and discussion

The ND used, as we indicated before [16], with a sphere-like morphology and a uniform particle size of about 5–8 nm, owns an as high as 9.7 at.% O content, and most of which is O=C–O species (a sum of carboxyl, anhydride, lactone, and ester groups). The anhydride, lactone, and ester groups could easily turn into the carboxyl group by hydrolysis. Then, the carboxyl group could react with adsorbed ammonia to form ammonium carboxylate species [17]. When the epoxy meets the ND modified by the above mentioned method, the epoxy group may react with the ammonium carboxylate species during the curing process. This idea is expected to reinforce the ND/epoxy composite by building strong and widely existing interfacial interactions between ND and epoxy.

### 3.1. A promising commercial ND modifying method

Aqueous ammonia, a cheap and common reagent in both laboratories and factories, was used to modify the ND. A room-temperature treatment was designed for the hydrolysis reaction of the surface O=C–O species to carboxyl group, and the following reaction between the carboxyl group and the adsorbed ammonia. Then, the treatment in oven could promote the reactions to the greatest extent possible, and easily remove the excess aqueous ammonia by evaporation at the same time. The evaporated ammonia was then collected by water to recover the aqueous ammonia, which could be recycled in this method.

After modified by aqueous ammonia, a 33% increase of the N content could be found from ND (1.2 at.%) to  $\text{NH}_4^+$ -ND (1.6 at.%), which means that the nitrogen contained group is successfully located on the ND surface. XPS is also a powerful method to give out both qualitative and semiquantitative analyses to elements in different chemical states. After the deconvolution of the N 1s spectra of ND and  $\text{NH}_4^+$ -ND, different N species can be seen (Fig. 1). For the low nitrogen content resulted in low intensity of N 1s XPS spectra, the relative contents of the different N species from the deconvolution may not be accurate enough. However, after modified, an obvious

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