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Surface functionalization and structure characterizations of nanodiamond and its epoxy based nanocomposites

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ABSTRACT

The aim of this study is the potential use of nanodiamond to make the lightweight and strong nanocomposites. Here, effects of size and surface modification of detonation nanodiamond (DND) on mechanical performance of epoxy based nanocomposites is presented. Our characterizations reveal that the process of functionalization not only removes the non-diamond content and impurities by significantly reducing DND's size but also introduces oxygen containing functional groups on its surface. The average size of functionalized DND aggregations could be decreased from 300 to 100 nm in contrast to pristine DND, which greatly benefits its homogeneous dispersion in epoxy matrix. In addition, strong chemical bonding among functionalized DND and epoxy resin due to functional groups leads to the formation of efficient interface. These interfaces overlap at high concentrations making a network which in turn significantly enhances the tensile properties. The enhancement in Young's modulus can reach up to 2.5 times higher than that of neat epoxy whereas the enhancement in tensile strength is about 1.5 times in functionalized DND/epoxy nanocomposites.

1. Introduction

Carbon nanostructure materials are potentially useful due to their unique structural, thermal and mechanical properties. Among them, detonation nanodiamond (DND) with sp^3 carbon–carbon bond is one of the most promising candidates for making ultra-strong nanocomposites. Meteorites, protoplanetary nebulae, and interstellar dust naturally contain nanodiamond (ND) particles [1]. It can be produced commercially at mass scale by detonation of carbon-containing explosives such as trinitrotoluene and hexogen in a steel chamber [2]. The DND is composed of mainly carbon with 10–20% oxygen and 2–3% nitrogen [2,3]. The shape of DND particle is spherical having a diamond (sp^3 carbon) core which is surrounded by a shell of amorphous graphite (sp^2 carbon) [4,5]. The size of primary particles of DND is less than 10 nm and it is in powder form [2]. Due to its highly interactive surface DND exists in the form of clusters having diameters in the range of 100–500 nm [6]. These clusters are tightly packed and difficult to disintegrate [7]. Mechanical and thermal properties of DND make it a good choice for using it as reinforcement in polymer matrix for the fabrication of nanocomposites [7]. Epoxy resin is a good choice to use it as a matrix material because it is highly cross linked material [8,9]. The mechanical properties of the nanocomposites not only depend on the size but also on the interaction of the DND with epoxy molecular network [10]. The highly tailor-able surface [11–13] of the DND is an advantage to strengthen this interaction by introducing some functional groups on its surface [14]. Maitra et al. [15] synthesized polymer-matrix composite with low ND content up to 0.6 weight percent (wt%) having better mechanical properties. Increasing the ND content increases the crystallinity of the poly-vinyl alcohol (PVA) owing to the strong interaction between ND and PVA matrix. Morimune et al. [7] used a simple casting method from aqueous medium and prepared PVA and ND composite. They reported a 2.5 times increase in Young's modulus with only 1 wt% of the ND content as compared to simple PVA film having high transparency even with the inclusion of ND. Monteiro et al. [16] produced stronger and tougher composite using DND as

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reinforcement with 17% of hardener with respect to epoxy resin and proposed that the incorporated diamond particles play a dual role in the epoxy matrix. Diamond particles restrict the epoxy molecular network and as a result impairing the mobility of epoxy molecules which increased the dynamic mechanical stored energy. The low interfacial stress between the epoxy matrix and diamond particle sharp edges decreases the quasi-static tensile strength [16]. Ayatollahi et al. [17,18] investigated mechanical properties of ND epoxy based composites and found improvement in Young's modulus and tensile strength of nanocomposite with the addition of 0.1 wt% of ND as compared to pure epoxy. Mochalin et al. [19] covalently linked ethylenediamine to the surface carboxyl groups through amide bonds and then the functionalized diamond nanoparticles were covalently incorporated into epoxy resin for polymer nanocomposite fabrication. The nanocomposite having covalent linkage between ND and epoxy resin showed a three times higher hardness, 50% higher Young's modulus and two times lower creep as compared to those having no covalent linkage between ND and epoxy resin. Rakha et al. [20] functionalized DND by exposing to UV/O_3 and fabricated nanocomposites using activated DND and epoxy. They reported that flexural strength, modulus, and toughness have been increased up to 85, 57, and 39% respectively. They also reported that optimal amount of DND for the fabrication of nanocomposite is 0.1 wt% and higher concentrations lead to decrease in mechanical properties. However, it is still a challenge to control DND's dispersion [21], various surface functional groups and the interface inside polymer matrix. Herein, we demonstrate a study on functionalized DND and its epoxy based nanocomposite. This work has been done by keeping in mind the need of cheap, strong and lightweight nanocomposites not only to use in automotive and aerospace industry but also in medical field because of the biocompatibility of nanodiamond.

2. Research outline

The disintegration of the DND clusters and size reduction of the primary DND particles was done by using chemical functionalization. In particular, pristine DND is treated with acids and as a result of this treatment not only the oxygen containing functional groups are generated on the surface of functionalized DND but a decrease in size is observed as well and this claim is supported by a number of characterizations. The reduction of the size of primary particles gives more room to attach functional groups on the surface. These functional groups not only enhance the interactions of the primary particles with epoxy molecular network but also hinders the aggregation of the primary particles. In addition, the functionalized DND is used as one of the promising reinforcement agents to significantly enhance the mechanical properties of epoxy nanocomposite due to its homogeneous dispersion and excellent interaction with epoxy matrix.

3. Experimental work

The DND powder was purchased from Henan Union Abrasives Corporation, China having phase purity around 50%. The colour of the Pristine DND powder is Black and size of the DND clusters is below 500 nm as per the supplier's specifications. Pristine DND powder was oxidized at 435 °C for 5 h to remove the impurities [20,22]. These impurities include traces of metals and non-diamond (amorphous and graphitic) carbon content [23]. The oxidized DND was refluxed with the solution of sulphuric acid and nitric acid [15]. A condenser was attached at the opening of round bottom flask and the whole assembly was put on a heating mantle at the boiling temperature about 280 °C continuously stirring for 24 h. The orange colour vapours produced during the heating were condensed back to the flask by the condenser. The multiple refluxes were made to obtain the desired amount of the acid functionalized DND powder. After the completion of reflux period the acid/DND solution was washed with de-ionized water to obtain neutral pH using centrifuge machine. The solution of water and functionalized DND was dried at 80 °C for 24 h to get the functionalized DND powder. The pristine and functionalized DND powders were characterized by Raman spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), dynamic light scattering (DLS), X-ray absorption near edge spectroscopy (XANES), Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). The nanocomposites were formed by using pristine and functionalized DNDs with epoxy as a matrix. The epoxy matrix used is DiGlycidyl Ether of Bisphenol-A (DGEBA) and hardener used for curing is MethylHexaHydroPhthalic Anhydride (MHHPA). For best mechanical properties the 92 g of hardener is used into 100 g of epoxy [24]. First of all epoxy was degassed for half an hour using ultrasonicator. Then predetermined amount of DND was added into epoxy followed by the ultrasonication for an hour at 50 °C. Afterwards MHHPA was mixed with the mixture of DND/epoxy through mechanical mixing machine for 2 min. The mixture was put into vacuum for 5 min to remove the air bubbles and then casted into the moulds. Standard curing process was adopted for the curing of the nanocomposite samples [25]. Nanocomposite samples were examined by scanning electron microscopy (SEM) and tested according to ASTM D638 [26] standard for tensile properties.

4. Experimental results

The XRD patterns were acquired using Cu-$\kappa_{\alpha 1}$ (λ = 1.5406 Å) radiation in the 2θ range of 20°–80°. The XRD pattern of pristine DND shows the presence of the sp^3 as well as sp^2 carbon, while the XRD pattern of functionalized DND only shows the presence of sp^3 carbon as shown in Fig. 1a. The peaks around 43.6° (111) and 75.4° (220) are referred to sp^3 carbon while peak around 26.3° (002) is referred to sp^2 carbon [27] and this peak is absent in functionalized DND which corroborate the removal of sp^2 carbon content significantly due to surface functionalization. The Raman spectroscopy was further used to differentiate between the sp^3 and sp^2 carbon in the spectrum range of 1000–1800 cm^{-1} acquired using laser of wavelength 532 nm as shown in Fig. 1b. According to the spectrum of pristine DND the peak around 1322 cm^{-1} [28] is a characteristic diamond peak while the peak around 1570 cm^{-1} [28] is a characteristic graphite peak but in the spectrum of functionalized DND only diamond peak at 1318 cm^{-1} is present and no prominent graphite peak is observed [29] which confirms that sp^2 carbon has been removed successfully from pristine DND.

The DLS particle size distribution curves of pristine and functionalized DND in de-ionized water suspension solutions are shown in Fig. 2a. According to DLS measurements the pristine sample has average DND aggregates around 300 nm and some aggregates are even larger having particle size around 5000 nm whereas the functionalized sample has average DND aggregates around 100 nm. The presence of oxygen containing functional groups on the surface of functionalized DND hinders the interaction within DND particles and further these groups tend to interact with the solvent molecular network and by considering this reason the average aggregate size of functionalized DND is smaller than that of the average aggregate size of pristine DND. Furthermore, using the Scherrer equation [30] according to the full width at half maximum of XRD patterns shown in Fig. 1a the size of the pristine DND is estimated to be approximately 5 nm and the size of the functionalized DND is estimated to be approximately 3.5 nm. The diamond core in pristine sample is surrounded by amorphous graphitic shell