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Comparative study of the ball milling and acid treatment of functionalized nanodiamond composites

Muhammad Khan[a,*], Li Tiehu[a], Ting Kai Zhao[a], A.A. Khurram[c], Imran Khan[b], Azeem Ullah[b], Asif Hayat[c], Amjad L. Lone[c], Farman Ali[d], Sundas Iqbal[a]

[a] State Key Laboratory of Solidification Processing, Shaanxi Engineering Laboratory for Graphene New Carbon Materials and Applications, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, PR China
[b] Fujian Institute of Research on the Structure of Matter, CAS, Fuzhou, Fujian 350002, China
[c] Laboratory for Advanced Materials Processing, NCP Complex, Islamabad, Pakistan
[d] Department of Chemistry, Hazara University, Mansehra, K.P.K., Pakistan

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ABSTRACT

Diamond nanoparticles (DNPs) have been strongly integrated into diverse technological applications due to its nano-size, good chemical stability, super hardness, thermal conductivity and biocompatibility. Agglomeration and non-uniform distribution of DNPs in different matrices are the two main concern problems which limits its wide spread applications. Herein, our present research work demonstrated a comparative study of ball milling and acid treatments of functionalization DNPs through surface modification with carboxylic acid and amid functional groups. The dispersion measurement showed that ball mill treated DNPs is uniform and homogeneously dispersed in dimethyl-sulfoxide (DMSO) rather than as-received and acid treated DNPs. Furthermore, the use of various weight percentages of acid and ball mill functionalized DNPs in epoxy resin showed that 0.2 wt % is the optimum amount which revealed the highest ultimate tensile strength, flexural strength, Young's modulus and energy to break values of the nanocomposites. The comparative analysis showed that ball mill treatment of functionalization significantly enhanced the mechanical performances of epoxy resin more effectively than acid treatment thus demonstrated the importance of ball milling technique.

1. Introduction

Diamond is well known for its remarkable properties like optical transparency, thermal conductivity, stability, resistance to corrosion and hardness which make it one of the promising reinforcement in the modern research era [1]. It covers a wide range of application in electronic, mechanical and medicinal industries [2,3]. One dimensional (1-D) diamond nanorods and 2D nanoplates are the well-known morphological forms of the diamond [8]. In addition, ultrnanocrystalline diamond (UNCD) with particle size in the range of 1–10 nm is recently synthesized, extensively used in many technological applications. The literature survey shows a verity of method used for the preparation of DNPs, such as chemical vapor deposition, Irradiation of carbon with electrons, ion irradiation of graphite, gas phase nucleation at ambient pressure. The most economical way is the detonation process which is commercially in practice [9]. High surface energy and the presence of metal impurities on the surface of DNPs result in agglomerates, incorporate poor dispersion consequently limits its application. To overcome this hitch, researchers normally introduce some functional groups attachment to the surface of DNPs [10].

Osawa and co-worker prepared stable aqueous suspension of DNPs and studied the structure and properties of single ultra-nanocrystalline diamond [11]. The behavior, effects of agglomeration of DNPs and work on the deaggregation were studied by Xue. Q.J et al. [12]. Similarly; Kruger and colleagues reported that wet-stirred-media-milling in water is effective technique to break aggregates with simultaneous dispersing in water [13]. Sobia et al. worked on the functionalization and mechanical performances of acid and UV/Ozone treated nanodiamond in epoxy matrix. They observed that flexural strength, modulus, and toughness of epoxy nanocomposites loaded by 0.1 wt% functionalized DNPs have been enhanced up to 85%, 57%, and 39%, respectively as compared to non-functionalized DNPs [4]. The use of salt for the breakage of DNPs agglomerates as an excellent milling media source has also been reported in the literature [13].

Herein, an effort has been made to nurture some functional groups on the surface of DNPs in the shape of carboxylic acid and amide functional groups using acid treatment and ball-milling method of functionalization. The comparative effects of functional groups on the

* Corresponding author.
E-mail address: mkhanchemistry@yahoo.com (M. Khan).

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dispersion, deaggregation and different mechanical aspects of DNPs composites have been investigated and reported.

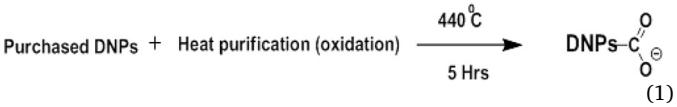
2. Experimental

2.1. Materials

The DNPs having 99% purity, gray color and 5–7 nm in diameter were provided by Hengqiu Nanotechnology incorporation China. Whereas, sulfuric acid, nitric acid, ammonium bicarbonate, acetone and ethanol were purchased from sigma Aldrich, while tri-ethylene tetra amine (TETA) which is also known as hardener from huntsman advanced materials USA was used. Moreover, Araldite (5052) epoxy resin was used as polymer matrix in this work.

2.2. Heat purification of nanoparticles

As received DNPs were heat purified at 440 °C for 5 h (h) to remove the non-carbonaceous impurities which were attached on the DNPs surface during its synthesis [9]. Whereas, the metal impurities were oxidized into metal oxides during this heat treatment which were usually removed through acid treatment.



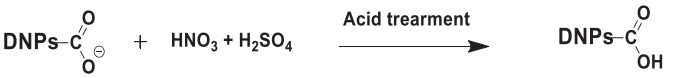
(1)

2.3. Functionalization of nanoparticles

In this research work two types of surface functionalization were performed i.e. acid treatment and ball milling method for the deaggregation and uniform dispersion of DNPs.

(I) Acid treatment of functionalization

In this method the heat purified DNPs were refluxed with mixture of HNO_3 and H_2SO_4 with (1:9) at 280 °C for 24 h in a round bottom flask to attach carboxylic acid functional groups on the surface of DNPs as well as to remove the traces of metal oxide impurities if still remaining on the DNPs surface after the heat purification process [8]. During heating an orange color vapours are produced which were back condensed to the flask by the condenser. After the reflux process, acidic solution containing DNPs was rinsed with deionized water up to a neutral pH. Finally, wet DNPs having neutral pH were dried and characterized for the functionalization of carboxylic acid group.

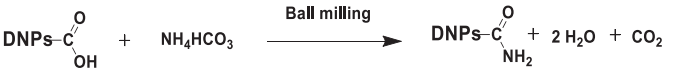


(2)

(II) Ball milling method of functionalization

In this method the acid treated DNPs were further treated for the in-situ functionalization of amide functional groups on the DNPs surface as well as for the disintegration of large DNP clusters into individual particles. We, first, optimized milling time as 2 h after conducting a series of experiments. Non-toxic and easily available milling media such as sodium chloride was selected for this experimental work. The grains of NaCl are helpful for the de-agglomeration of DNPs [23]. Ammonium bicarbonate and sodium chloride were chosen in spherical shapes to increase the collision impact on the particles and to reduce the area of collision as well as to improve the effectiveness of ball milling technique. The mechanism of ball milling technique is, basically, the centrifugal force in the planetary ball milling together with milling media creating an impact force on powder particles [3]. Since, ball milling was adopted for de-agglomeration and functionalization purposes, therefore, DNPs to milling media (Ammonium bicarbonate and sodium chloride) ratio was also adjusted 1:4:4 to get the optimum results and, all experiments were conducted at this optimized ratio. The DNPs and milling media were milled for 2 (h) at 500 rpm in the milling jars containing mixture of stainless steel balls of 2, 3 and 5 mm diameter having 58 number of each size balls.

After milling, the sample was placed in vacuum furnace under 0.7 MPa for 10 h at 100 °C to remove the moisture from the mixture. During this process, NH_4HCO_3 was dissociated and hydroxylated DNPs were converted into amide functionalized DNPs by the substitution of hydroxyl to amine functional groups on the surface of DNPs. Eq. (3) shows the amide functionalization of the carboxylated DNPs.



(3)

2.4. Fabrication of nanoparticles

Functionalized DNPs were measured according to the samples preparation and dispersed in ethanol solution. The dispersion of these solutions was done in a sonication machine for 40 min to make sure the deaggregation and uniform distribution of DNPs in 5052 epoxy matrix. First, the both methods functionalized DNPs were ultrasonically dispersed in epoxy resin, by varying the loading of DNPs i.e., 0.1, 0.2 and 0.4 wt%. Total seven samples along with blank epoxy were prepared. After 60 minute sonication, the mixture was degassed for 5–7 min to remove the trapped air bubbles. Afterwards, 10 pph of hardener (curing agent) was mixed through mechanical stirring with the help of a glass rod for 10 min. After well mixing, the mixture was poured into mould, which was already prepared. For easy separation, the surface of the moulds was wet by using silicon grease. Before casting, all the nanocomposite samples were left over night at room temperature to evaporate ethanol. Moreover, the samples were cured at 100 °C in an electric furnace for 4 h. After the curing samples were separated from the moulds and subjected to various characterizations.

3. Results and discussion

3.1. Characterization

In this study the microstructure and morphology of the samples were characterized by using (Hitachi H-600) transmission electron microscopy (TEM) and (XL30) Scanning electron microscopy (SEM). By using SEM analysis, EDX was also performed for the detection of elemental composition of functionalized DNPs. The crystallite structural information was obtained by using an (D/Max 2500 V PC-1, Cu-Kα radiation) having 2/min scan rate, X-ray diffractometer (XRD). The particle size distribution (PSD) of DNPs in the solvent/matrix is measured by using Malvern Zetasizer Nano ZS (Malvern Instruments Ltd., UK) equipped with a 10 mW He-Ne laser (633 nm) and an MPT-2 autotitrator at 20 °C in back scatter configuration using a dynamic light scattering (DLS) method. BX Fourier transformed infra-red spectrometer with attenuated total reflectance (ATR) attachment was used for the measurements of various functional groups attached on the surface of DNPs during functionalizations. The flexural, tensile, young's modulus and energy to break of the nanocomposites were characterized by using a universal testing machine at room temperature having 50 ± 5% relative humidity, using a crosshead speed of 10 mm min^{-1} and a load cell of 100 N. Five samples for each nanocomposite were tested to ensure the reproducibility of the measurements. Moreover, for the above measurements, the nanocomposites plates were cut into rectangular specimens according to the ASTM standards of D7264 for flexural measurement while D3039 was followed for the rest of analysis.