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

Yasir A. Haleem, Daobin Liu, Wenxing Chen, Changda Wang, Caihao Hong, Zhen He, Jianwei Liu, Pin Song, Shuhong Yu, Li Song

PII: S1359-8368(15)00250-4

DOI: 10.1016/j.compositesb.2015.04.012

Reference: JCOMB 3543

To appear in: *Composites Part B*

Received Date: 22 October 2014

Revised Date: 7 April 2015

Accepted Date: 8 April 2015

Please cite this article as: Haleem YA, Liu D, Chen W, Wang C, Hong C, He Z, Liu J, Song P, Yu S, Song L, Surface functionalization and structure characterizations of nanodiamond and its epoxy based nanocomposites, *Composites Part B* (2015), doi: 10.1016/j.compositesb.2015.04.012.

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

Yasir A. Haleem[a], Daobin Liu[a], Wenxing Chen[a], Changda Wang[a], Caihao Hong[b], Zhen He[c], Jianwei Liu[c], Pin Song[c], Shuhong Yu[c], Li Song[a,*]

[a]*National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui, 230029, P. R. China*

[b]*Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100049, P.R. China*

[c]*Division of Nanomaterials & Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemistry, Hefei, Anhui, 230026, P. R. China.*

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

---

[*] Corresponding author.TEL:+86-551-63602102. EMAIL: song2012@ustc.edu.cn

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.

Keywords: A. Polymer-matrix composites (PMCs); B. Interface; B. Mechanical properties; D. Surface analysis; Nanodiamond

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]. Urmimala *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 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. Sobia *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 color 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 hours 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 hours. The orange color vapors 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 hours 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 92g of hardener is used into 100g 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 two minutes. The mixture was put into vacuum for five minutes to remove the air bubbles and then casted into the molds. 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-$\kappa_{\alpha1}$ (λ= 1.5406Å) radiation in the 2θ range of 20^o-80^o. 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 the 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 according to Holt *et al*. [31] and this graphitic shell (sp^2 carbon) is removed during acid functionalization and as a result the size of the primary particles of functionalized DND is smaller than that of the pristine DND as depicted in Figs. 2b and 2c.

The pristine and functionalized DND powders were examined by using TEM to affirm the DLS particle size distribution measurements of pristine and functionalized DND. We found that the pristine sample has DND aggregates around 315 nm whereas the functionalized sample has DND aggregates around 100 nm as depicted in Figs. 3a and 3c. Furthermore, it can be reasserted that the size of the primary particles in pristine sample is almost equal to 6 nm whereas in functionalized DND sample, it is less than 4 nm as shown in the Figs. 3b and 3d. TEM analysis shows a decrease in primary particle size after functionalization and this decrease in size is in consistent with the estimation based on XRD patterns analysis using Scherrer equation.

The presence of oxygen containing functional groups on the surface of DND is confirmed by the FTIR spectra of pristine and functionalized DND as shown in Fig. 4a. The FTIR spectrum of pristine DND does not have very prominent peaks while in functionalized DND spectrum the peaks can be seen very clearly which confirms the presence of hydroxyl and carboxyl functional groups on its surface. Absorption peaks around 3429 cm^{-1} and 1626 cm^{-1} can be assigned to stretching and bending vibrations of OH group respectively [7]. Another absorption peak observed around 1785 cm^{-1} can be assigned to the stretching vibrations of C═O group [32]. The absorption peak around 1275 cm^{-1} can be assigned to the stretching vibrations of C─O group [32] as depicted in Fig. 4a. XPS data were acquired to ascertain the presence of the carboxyl and hydroxyl groups on the surface of the functionalized DND. The Fig. 4b is attributed to the XPS spectra of pristine and functionalized DND. The peak around 284.8 eV can be assigned to carbon and the sharpness of the peak confirms that the most of the sample content consist of carbon [33,34]. It is very difficult with XPS data to differentiate between sp^3 and sp^2 carbon. However a decrease in the peak height in functionalized DND can be attributed to the removal of the sp^2 carbon and this is supported by the XRD and Raman data. The peak around 530 eV can be assigned to oxygen and indicates that the oxygen containing groups are present in the samples [33,34]. The peak around 399 eV can be assigned to nitrogen and clearly seen in pristine DND [33,34]. Since production of the DND involves nitrogen containing explosives so it gets contaminated in the process [3]. The nitrogen peak is not very prominent in functionalized DND which is a clear indication of the removal of the impurities due to functionalization. The elemental ratio obtained by the XPS is shown in the table 1. According to the data the atomic ratio of carbon has decreased in functionalized DND which can be related to the removal of sp^2

carbon whereas the decrease in atomic ratio of nitrogen can be related to the removal of impurities. On the other hand the increase in the atomic ratio of oxygen supports the claim that after functionalization the presence of carboxyl and hydroxyl groups on the surface of the functionalized DND is significantly enhanced which is in concordance with the FTIR spectra of pristine and functionalized DND as shown in Fig. 4a.

To further explore the structure and surface modification, XANES study was carried out on the DND samples due to their sensitivity to the electronic evolution and the variation of their local structure as shown in Fig. 5. In comparison, the peak around 290 eV (1s-σ*) confirms the presence of sp^3 carbon in functionalized DND but this peak is absent in pristine DND because of dominant presence of sp^2 carbon attributed to peaks at 285.6 eV (1s-π*) and 292.9 eV (1s-σ*) [35]. The small peak at 285.6 eV as compared with same peak in pristine DND can be seen in functionalized DND spectrum which shows that it still has nominal sp^2 carbon [35]. Another peak around 287.4 eV is an important signature of oxygen containing surface functional groups [22,35] which reasserts the FTIR and XPS analysis. Therefore, it is clear from all of the results that the surface modification of pristine DND not only decreases the sp^2 carbon but also helps to introduce oxygen containing functional groups on the surface of functionalized DND. It is perspective that the functionalized DND can be a good reinforcement in making of nanocomposites using epoxy resin as a matrix because of small in size and oxygen containing surface functional groups which are able to interact efficiently with the epoxy molecular network. Hence, the interaction of these functional groups with the epoxy molecular network is remarkably strong and as a result the mechanical properties of epoxy resin can be enhanced considerably.

Herein, nanocomposites were prepared using pristine and functionalized DND as reinforcement in epoxy matrix. The different concentrations that were prepared are 1, 10, 20, and 30 wt% of epoxy. The Young's modulus and tensile strength are illustrated by bar graphs in Fig. 6. The Fig. 6a shows the Young's modulus of nanocomposites. The Young's modulus of neat epoxy is around 2900 MPa whereas the average maximum value of Young's modulus observed is around 6550 MPa in 30 wt% functionalized DND/epoxy nanocomposite. The highest value of Young's modulus observed is around 7250 MPa which is 2.5 times higher than that of neat epoxy. The Fig. 6b shows the tensile strength of nanocomposites. The tensile strength of neat epoxy is around 61 MPa. The highest tensile strength of 91 MPa is observed at 1 wt% functionalized DND concentration. The enhancement in tensile strength is almost 1.5 times higher than that of neat epoxy. To rationalize the enhancement in tensile properties the neat epoxy, 10 wt% pristine and functionalized DND/epoxy nanocomposite samples were examined with SEM and micrographs are shown in Figs. 7 and 8. It is clear from the SEM micrographs that the surface of the neat epoxy is relatively smooth (as shown in Figs. 7a and 8a) while the surface roughness has been increased after the addition of DND particles as shown in Figs. 7b and 7c. The hackles can be seen clearly on the surface of the nanocomposites which emphasize on the presence of strong interface among DND and epoxy. It can also be seen that pristine DND has large aggregates [36] than that of functionalized DND (as shown in Figs. 8b and 8c), agreeing with TEM analysis.

5. Discussion and analysis

The increase in Young's modulus has a direct relation with the DND content incorporated in epoxy resin as depicted in Fig. 6a. The both types of DND enhance the Young's modulus of epoxy but as expected, the enhancement in functionalized DND based nanocomposite is more pronounced compared to the pristine DND based nanocomposite. The higher Young's modulus of functionalized DND/epoxy nanocomposite reasserts that the functionalized DND is a better choice than that of pristine DND. On the other side, the tensile strength increases until 1 wt% of DND content and then starts decreasing with the further increase in DND content. In pristine DND/epoxy nanocomposite the tensile strength at higher concentrations gets even lesser than that of neat epoxy. Same trend in tensile strength is observed in functionalized DND/epoxy nanocomposite as well but it is still higher than that of neat epoxy. This contrast is essentially due to the small size and effective role of surface functional groups. The size reduction increases surface to volume ratio which results in large surface area for the attachment of functional groups. The oxygen containing surface functional groups hinder the agglomeration and enhance the interaction of functionalized DND with the epoxy molecular network. The agglomeration in pristine DND is due to high aspect ratio of DND particles whereas in case of functionalized DND this effect has been subdued by the surface functional groups. Interestingly, it can be noted that the dispersion of functionalized DND is quite homogeneous in epoxy resin matrix in contrast to pristine DND (as shown in Fig. 8c). The DND particles within epoxy network act as stress concentrators [37] and as their dispersion is uniform so they form a homogeneous stress field. But if the stress field is not homogeneous then it may initiate cracks which ultimately lead to failure. The size, reactive surface area, and uniform dispersion of DND in an epoxy network determine a positive role of DND in the enhancement of tensile properties of the nanocomposites. It is easy to anticipate that the functionalized DND which is small in size and rich in oxygen containing functional groups strongly interacts with the epoxy network by forming a strong interface. As known, the DND particles tend to agglomerate because of large surface area and the gradual increase in concentration further increases the size of the agglomerates which is happening in pristine DND. On the other hand gradual increase in concentrations, decrease the distance between the DND particles which lead to the formation of interface network due to the overlapping of the interfaces [38]. This interface network act as a bridge in transforming the load from epoxy matrix to reinforcement phase, the DND, and consequently enhance the Young's modulus as depicted in Fig. 6a. It is worth mentioning that the maximum amount of the DND which could be used for the making of nanocomposites is 30wt% of epoxy. At concentrations higher than 30wt% the agglomeration becomes so strong that it restricts the formation of nanocomposite by making it brittle. We suggest that the brittleness increases because at higher concentrations the interactions within the DND particles overcome the interactions between the DND and epoxy network. The surface functional groups tend to reduce the agglomeration but their effectiveness is subdued by high concentration of DND. These agglomerates act as a crack initiator [39] and consequently decrease the tensile strength of nanocomposites as shown in Fig. 6b. Hence, the brittleness increases while the tensile strength decreases with the gradually increase in DND concentration.

6. Conclusions

In summary, we used a wet chemical method to successfully functionalize pristine DND. The subsequent characterizations confirm the removal of sp^2 carbon and impurities from the pristine DND during acid functionalization process. It was observed that the functionalization process could not only reduce the size of the DND aggregates from 300 nm to 100 nm but also decreases the diameter of primary DND particles from around 6 nm to less than 4 nm, as well as this process introduce carboxyl and hydroxyl functional groups on the surface of DND particles. Herein, the pristine and functionalized DND were added into epoxy resin for making of nanocomposites. The size and surface modification of DND was found to play a key role in enhancement of tensile properties of nanocomposites. On increasing the quantity of the DND content in epoxy resin tensile properties enhanced because the oxygen containing surface functional groups can efficiently interact with the epoxy molecular network. These interactions are suggested to act as a bridge between the matrix and the reinforcement which efficiently transfers the load from matrix to reinforcement phase consequently improving the tensile properties of the nanocomposites. The maximum enhancement in Young’s Modulus is 2.5 times than that of neat epoxy in functionalized DND/Epoxy nanocomposites at 30 wt% concentration. The maximum enhancement in tensile strength observed is about 1.5 times in functionalized DND/Epoxy nanocomposites at 1 wt% concentration. We anticipate that the results may provide useful insights for engineering of DND’s surface and offer a way to create nanocomposite with high performances.

Acknowledgement

This work is financially supported by the National Basic Research Program of China (2012CB825800 and 2014CB848900), the National Natural Science Foundation of China (U1232131) and the Fundamental Research Funds for the Central Universities (WK2310000035). Li Song thanks the recruitment program of global experts and the CAS Hundred Talent Program of China. Yasir A. Haleem acknowledges the CAS-TWAS president’s fellowship for financial support. Yasir A. Haleem also thanks Sobia A. R. for her technical guidance and Rafi Ullah for his critical comments and revisions on manuscript.

References

[1] Raty JY, Galli G. Ultradispersity of diamond at the nanoscale. Nat Mater 2003;2:792–5. doi:10.1038/nmat1018.

[2] Badziag P, Verwoerd WS, Ellis WP, Greiner NR. Nanometre-sized diamonds are more stable than graphite. Nature 1990;343:244–5.

[3] Kvit AV, Zhirnov V V, Tyler T, Hren JJ. Aging effect and nitrogen distribution in diamond nanoparticles. Compos Part B Eng 2004;35:163–6. doi:10.1016/j.compositesb.2003.08.003.

[4] Kulakova II. Surface Chemistry of Nanodiamonds. Phys Solid State 2004;46:621–8.

[5] Krueger A, Kataoka F, Ozawa M, Fujino T, Suzuki Y, Aleksenskii AE, et al. Unusually tight aggregation in detonation nanodiamond: Identification and disintegration. Carbon 2005;43:1722–30. doi:10.1016/j.carbon.2005.02.020.

[6] Abdul Khalil HPS, Fizree HM, Bhat AH, Jawaid M, Abdullah CK. Development and characterization of epoxy nanocomposites based on nano-structured oil palm ash. Compos Part B Eng 2013;53:324–33. doi:10.1016/j.compositesb.2013.04.013.

[7] Morimune S, Kotera M, Nishino T, Goto K, Hata K. Poly (vinyl alcohol) Nanocomposites with Nanodiamond. Macromolecules 2011;44:4415–21. doi:dx.doi.org/10.1021/ma200176r.

[8] Kinloch AJ, Mohammed RD, Taylor AC, Eger C, Sprenger S, Egan D. The effect of silica nano particles and rubber particles on the toughness of multiphase thermosetting epoxy polymers. J Mater Sci 2005;40:5083–6. doi:10.1007/s10853-005-7261-1.

[9] Shen XJ, Pei XQ, Liu Y, Fu SY. Tribological performance of carbon nanotube-graphene oxide hybrid/epoxy composites. Compos Part B Eng 2014;57:120–5. doi:10.1016/j.compositesb.2013.09.050.

[10] Chan M, Lau K, Wong T, Ho M, Hui D. Mechanism of reinforcement in a nanoclay/polymer composite. Compos Part B Eng 2011;42:1708–12. doi:10.1016/j.compositesb.2011.03.011.

[11] Krueger A, Lang D. Functionality is Key□: Recent Progress in the Surface Modification of Nanodiamond. Adv Funct Mater 2012;22:890–906. doi:10.1002/adfm.201102670.

[12] Krueger A, Ozawa M, Jarre G, Liang Y, Stegk J, Lu L. Deagglomeration and functionalisation of detonation diamond. Phys Status Solidi 2007;204:2881–7. doi:10.1002/pssa.200776330.

[13] Krueger A. The structure and reactivity of nanoscale diamond. J Mater Chem 2008;18:1485–92. doi:10.1039/b716673g.

[14] Shenderova O, Tyler T, Cunningham G, Ray M, Walsh J, Casulli M, et al. Nanodiamond and onion-like carbon polymer nanocomposites. Diam Relat Mater 2007;16:1213–7. doi:10.1016/j.diamond.2006.11.086.

[15] Maitra U, Prasad KE, Ramamurty U, Rao CNR. Mechanical properties of nanodiamond-reinforced polymer-matrix composites. Solid State Commun 2009;149:1693–7. doi:10.1016/j.ssc.2009.06.017.

[16] Monteiro SN, De-Menezes GW, Bobrovnitchii GS, Skury ALD, Rodriguez RJS, D’Almeida JRM. Structure and mechanical properties of composites with diamond particles dispersed into modified epoxy matrix. Diam Relat Mater 2007;16:974–7. doi:10.1016/j.diamond.2006.12.003.

[17] Ayatollahi MR, Alishahi E, Shadlou S. Mechanical behavior of nanodiamond/epoxy nanocomposites. Int J Fract 2011;170:95–100. doi:10.1007/s10704-011-9600-3.

[18] Ayatollahi MR, Alishahi E, Doagou-R S, Shadlou S. Tribological and mechanical properties of low content nanodiamond / epoxy nanocomposites. Compos Part B Eng 2012;43:3425–30. doi:10.1016/j.compositesb.2012.01.022.

[19] Mochalin VN, Neitzel I, Etzold BJM, Peterson A, Palmese GR, Gogotsi Y. Covalent Incorporation of Aminated Nanodiamond into an Epoxy Polymer Network. ACS Nano 2011;5:7494–502.

[20] Rakha SA, Ali N, Haleem YA, Alam F, Khurram AA, Munir A. Comparison of Mechanical Properties of Acid and UV Ozone Treated Nanodiamond Epoxy Nanocomposites. J Mater Sci Technol 2014;30:753–8. doi:10.1016/j.jmst.2013.12.011.

[21] Zhao YQ, Lau KT, Kim JK, Xu CL, Zhao DD, Li HL. Nanodiamond/poly (lactic acid) nanocomposites: Effect of nanodiamond on structure and properties of poly (lactic acid). Compos Part B Eng 2010;41:646–53. doi:10.1016/j.compositesb.2010.09.003.

[22] Osswald S, Yushin G, Mochalin VN, Kucheyev SO, Gogotsi Y. Control of sp2/sp3 Carbon Ratio and Surface Chemistry of Nanodiamond Powders by Selective Oxidation in Air. J Am Chem Soc 2006;128:11635–42.

[23] Osswald S, Havel M, Mochalin VN, Yushin G, Gogotsi Y. Increase of nanodiamond crystal size by selective oxidation. Diam Relat Mater 2008;17:1122–6. doi:10.1016/j.diamond.2008.01.102.

[24] Palmese GR, McCullough RL. Effect of Epoxy-Amine Stoichiometry on Cured Resin Material Properties. J Appl Polym Sci 1992;46:1863–73.

[25] Blackman BRK, Kinloch AJ, Lee JS, Taylor AC, Agarwal R, Schueneman G, et al. The fracture and fatigue behaviour of nano-modified epoxy polymers. J Mater Sci 2007;42:7049–51. doi:10.1007/s10853-007-1768-6.

[26] D638-03. Standard test method for tensile properties of plastics, Annual Book of ASTM Standards (American Society of Testing and Materials). West Conshohocken: 2004.

[27] Chen P, Huang F, Yun S. Characterization of the condensed carbon in detonation soot. Carbon 2003;41:2093–9.

[28] Lee J-Y, Lim D-P, Lim D-S. Tribological behavior of PTFE nanocomposite films reinforced with carbon nanoparticles. Compos Part B Eng 2007;38:810–6. doi:10.1016/j.compositesb.2006.12.006.

[29] Lequan XC, Kang WP, Davidson JL, Guo M, Choi BK. Micro-Raman , SEM , XPS , and electron fi eld emission characterizations of nitrogen-induced shallow defects on nanodiamond films fabricated with different growth parameters. Diam Relat Mater 2009;18:191–5. doi:10.1016/j.diamond.2008.12.003.

[30] Patterson AL. The Scherrer Formula for X-Ray Particle Size Determination. Phys Rev 1939;56:978–82.

[31] Holt KB. Diamond at the nanoscale: applications of diamond nanoparticles from cellular biomarkers to quantum computing. Philos Trans R Soc A 2007;365:2845–61. doi:10.1098/rsta.2007.0005.

[32] Sileverstein RM, Webster FX, Kiemle DJ. Spectrometric Identification of Organic Compunds. 7th ed. John Wiley & Sons, INC; 2005.

[33] Petit T, Arnault JC, Girard HA, Sennour M, Bergonzo P. Early stages of surface graphitization on nanodiamond probed by x-ray photoelectron spectroscopy. Phys Rev B 2011;84:1–5. doi:10.1103/PhysRevB.84.233407.

[34] Liu Y, Gu Z, Margrave JL, Khabashesku VN. Functionalization of Nanoscale Diamond Powder□: Fluoro-, Alkyl-, Amino-, and Amino Acid-Nanodiamond Derivatives. Chem Mater 2004;16:3924–30.

[35] Chang IP, Hwang KC, Ho JA, Lin CC, Hwu RJ, Horng JC. Facile Surface Functionalization of Nanodiamonds. Langmuir 2010;26:3685–9. doi:10.1021/la903162v.

[36] Lam CK, Cheung HY, Lau KT, Zhou LM, Ho MW, Hui D. Cluster size effect in hardness of nanoclay/epoxy composites. Compos Part B Eng 2005;36:263–9. doi:10.1016/j.compositesb.2004.09.006.

[37] Ma J, Mo MS, Du XS, Rosso P, Friedrich K, Kuan HC. Effect of inorganic nanoparticles on mechanical property, fracture toughness and toughening mechanism of two epoxy systems. Polymer 2008;49:3510–23. doi:10.1016/j.polymer.2008.05.043.

[38] Zhang H, Tang LC, Zhang Z, Friedrich K, Sprenger S. Fracture behaviours of in situ silica nanoparticle-filled epoxy at different temperatures. Polymer 2008;49:3816–25. doi:10.1016/j.polymer.2008.06.040.

[39] Ash BJ, Siegel RW, Schadler LS. Mechanical Behavior of Alumina/Poly(methyl methacrylate) Nanocomposites. Macromolecules 2004;37:1358–69. doi:10.1021/ma0354400.

Legends:

Fig. 1. (a) XRD patterns (b) Raman spectra of pristine and functionalized DND

Fig. 2. (a) DLS particle size distribution curves of pristine and functionalized DND; the corresponding schematic models for single dispersed (b) pristine and (c) functionalized DND

Fig. 3. TEM nanographs of pristine and functionalized DND at low magnification, scale bar 100nm (a) & (c) and high magnifications, scale bar 5nm (b) & (d) respectively

Fig. 4. (a) FTIR spectra and (b) XPS spectra of pristine and functionalized DND

Fig. 5. XANES spectra of pristine and functionalized DND

Fig. 6. (a) Young's modulus and (b) tensile strength of pristine and functionalized DND/epoxy nanocomposites and error bars are indicating standard error and calculated by standard deviation values of 5 samples

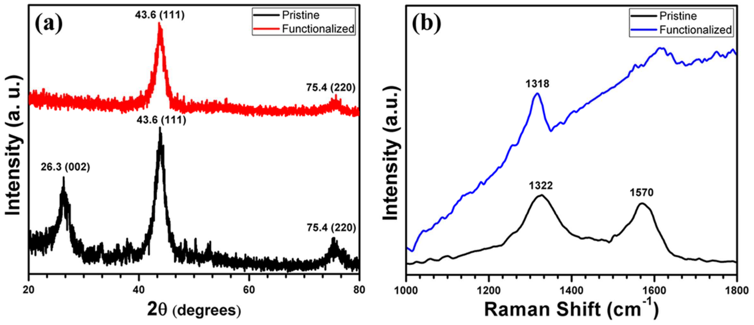
Fig. 7. SEM micrographs of (a) Neat Epoxy, 10 wt% (b) pristine and (c) functionalized DND/epoxy nanocomposites at low resolution

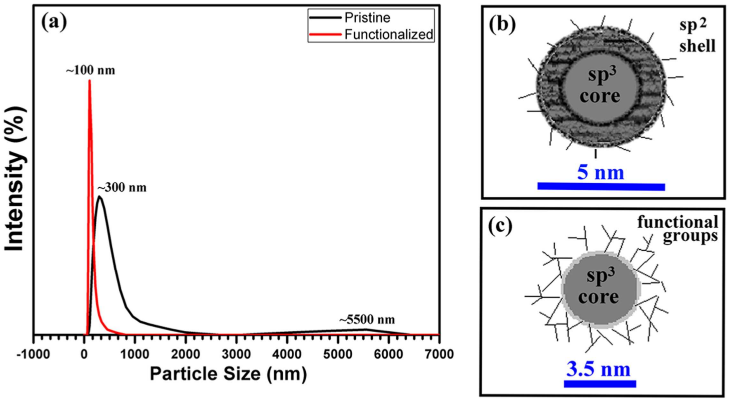
Fig. 8. SEM micrographs of (a) Neat Epoxy, 10 wt% (b) pristine and (c) functionalized DND/epoxy nanocomposites at high resolution

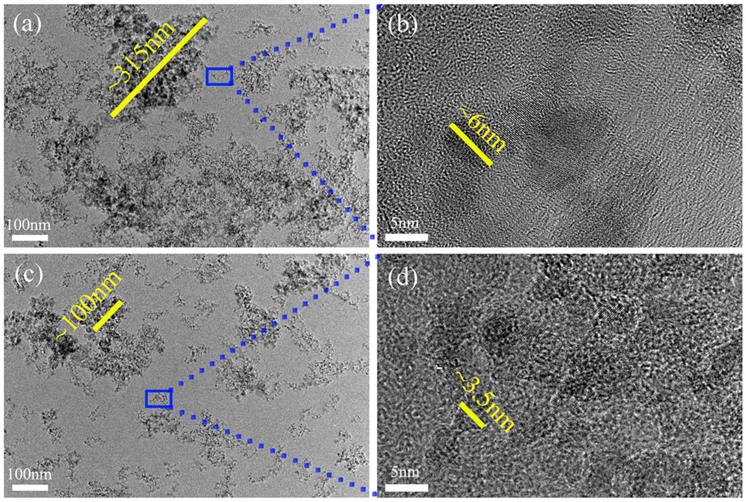
Table 1: XPS elemental data of pristine and functionalized DND

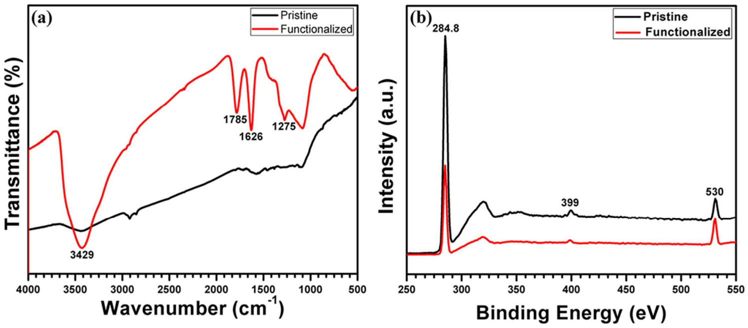
Table 1: XPS elemental data of pristine and functionalized DND

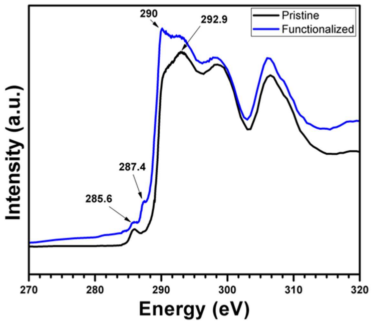
Samples	Carbon (at.%)	Oxygen (at.%)	Nitrogen (at.%)
Pristine DND	93.51	3.29	3.2
Functionalized DND	86.13	11.94	1.92

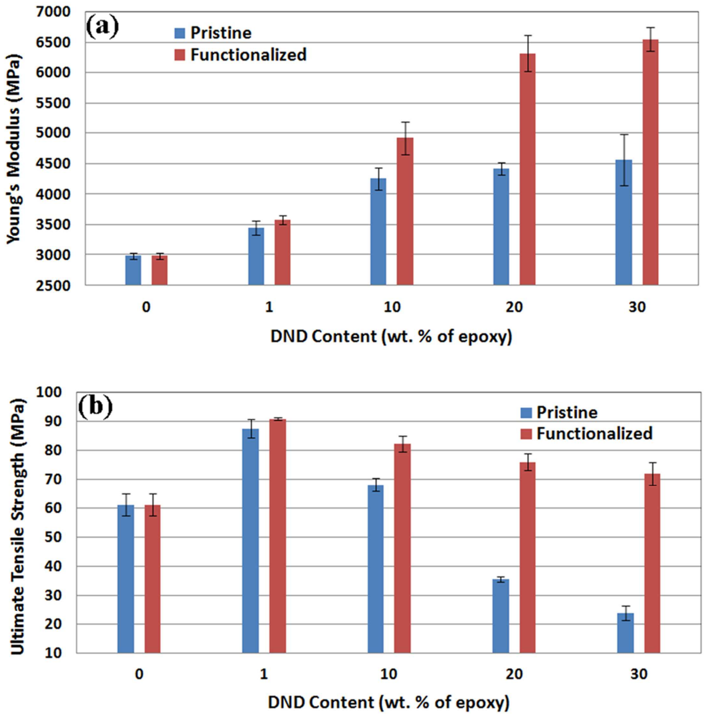

(a)
Pristine
Functionalized
43.6 (111)
75.4 (220)
43.6 (111)
26.3 (002)
75.4 (220)
Intensity (a. u.)
20
40
60
80
2θ (degrees)
(b)
Pristine
Functionalized
1318
1322
1570
Intensity (a.u.)
1000
1200
1400
1600
1800
Raman Shift (cm-1)

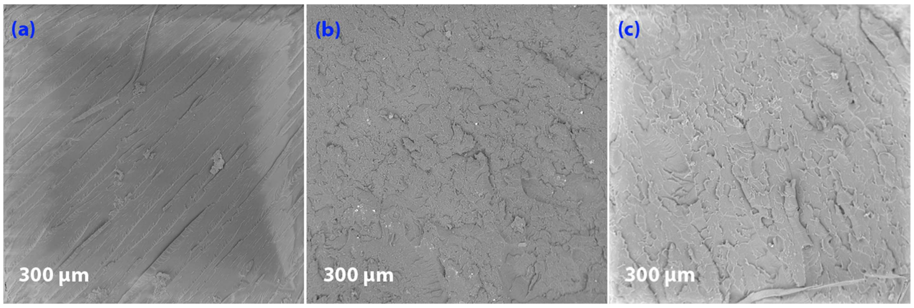

(a)
Pristine
Functionalized
~100 nm
~300 nm
~5500 nm
Intensity (%)
-1000
0
1000
2000
3000
4000
5000
6000
7000
Particle Size (nm)
(b)
sp2 shell
sp3 core
5 nm
(c)
functional groups
sp3 core
3.5 nm

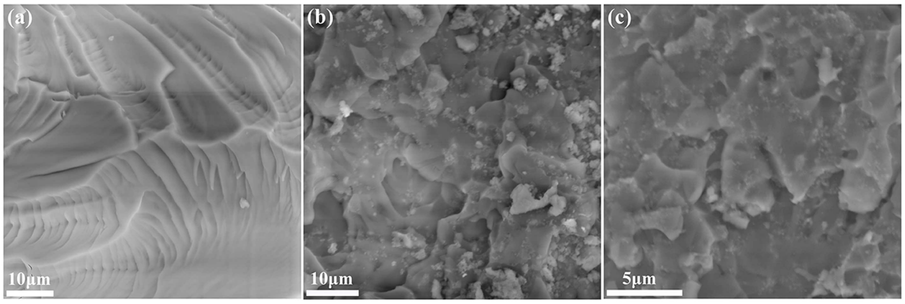

(a)
~315nm
100nm
(b)
~6nm
5nm
(c)
~100nm
100nm
(d)
~3.5nm
5nm


(a)
Pristine
Functionalized
Transmittance (%)
1785
1626
1275
3429
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})
(b)
284.8
Pristine
Functionalized
Intensity (a.u.)
399
530
250
300
350
400
450
500
550
Binding Energy (eV)


Pristine
Functionalized
290
292.9
287.4
285.6
Intensity (a.u.)
Energy (eV)
270
280
290
300
310
320


(a)
🟦 Pristine
🟥 Functionalized
Young's Modulus (MPa)
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
0
1
10
20
30
DND Content (wt. % of epoxy)
(b)
🟦 Pristine
🟥 Functionalized
Ultimate Tensile Strength (MPa)
100
90
80
70
60
50
40
30
20
10
0
1
10
20
30
DND Content (wt. % of epoxy)


(a)
300 µm
(b)
300 µm
(c)
300 µm


(a)
10μm
(b)
10μm
(c)
5μm