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Reinforcement effect of acid modified nanodiamond in epoxy matrix for enhanced mechanical and electromagnetic properties

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ABSTRACT

We applied acid treatment for the surface modification of detonation nanodiamond (DND) powder by minimizing their surface energy to overcome agglomeration and improve dispersion of DNDs. Different concentrations of acid modified DND in 828 epoxy matrix were fabricated to check their mechanical and electromagnetic properties. Mechanical properties were checked in terms of ultimate tensile strength (UTS), toughness, energy to break, percent strain break and Young's modulus while electromagnetic shielding properties were studied in frequency range of 11–17 GHz. To analyze electrical and magnetic properties of the nanocomposites, relative permittivity and permeability tests were performed. Excellent interactions among acid modified DND and epoxy resin was observed due to carboxyl and hydroxyl functional groups that results in the formation of efficient load transfer interface, which in turn enhance the mechanical and electromagnetic properties of epoxy nanocomposites. During investigation it was observed that mechanical properties and relative permittivity showed enhancements when, 0.2 wt% acid modified DND were used as a nano-filler, while on further increment of modified DND these properties start decreasing. Unlike this, the relative permeability, reflection and transmission loss values were increased with the increase of acid modified DND content.

1. Introduction

Hybrid materials are those composites which are composed of continuous matrix, incorporated and an interface phases. Enhancement in the properties of the composite is known as reinforcement. Composites having one phase (filler) in nanometer range are called nanocomposites [1]. Limitation of the microcomposites has been overcome by nanocomposites. The challenges related to the fabrication of nanocomposites are control of elemental composition and stoichiometry. Significant changes in the properties of materials are observed when the particle size is less than a particular level, known as critical size [2–3].

A lot of work has been done in the last decade to improve the mechanical properties of the nanocomposite by using DND as reinforcement. High concentrations of DND increase the mechanical properties by forming the load transfer interface between matrix and reinforcements phases but high concentration causes heavy composites which is not economical. Further, by reducing the concentrations of DND lightweight composites are obtained but there are certain obstacles which must be tackled down for effective use of DND as reinforcement. Nanocomposites have excellent properties due to large interfacial area between polymer matrix and nano-reinforcement [7]. Different nanomaterials like nanoclays, graphene nanoplatelets, fullerene and carbon nanotubes have already been used as nano-reinforcements [6]. Detonated nanodiamond(DND) has excellent optical, thermal, mechanical and chemical properties as compare to other carbon based materials. The availability of DND in large quantities and high tailorable surface area are the features of DND which make it important as nano-reinforcement. Due to excellent properties DND has a wide range of potential applications such as in bio imaging, tissue engineering, drug delivery, protein and mimics [8]. The extraordinary properties of nanocomposites are due to the characteristics of strong interface between filler and matrix part [7]. Stability of DND particles depends upon the surface atoms and their state of cooperation. DNDs are unstable due to large tendency of agglomeration rather than isolated particles because of large surface to volume ratio [2]. The clusters obtained after the detonation process, having diameter range of 100–200 nm, are tightly packed and difficult to disintegrate. Kruger et al. used stirred media

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milling technique with micron-sized ceramic beads to disintegrate the diamond clusters into isolated nanoparticles [9–10]. Ozawa et al. prepared colloidal solutions of de-agglutinated DNDs in several solvents by applying bead assisted sonic disintegration (BASD) or stirred-media-milling techniques [11]. Aleksenskiy et al. purified commercial DND from metal impurities and appropriate control of its residual amount by electronic spin resonance [12–13]. Surface modification of DND is also necessary for the formation of efficient load transfer interface in nanocomposites [2]. Urmimala et al. synthesized polymer-matrix composite with low DND content upto 0.6 wt% having high mechanical properties. DND content is uniformly distributed within the polymer-matrix with no agglomeration. It was observed that due to strong interaction between DND and poly (vinyl alcohol) (PVA)-matrix, increment in the DND content increased the crystallinity of the polymer [4].

Morimune et al. used a simple casting method from aqueous medium and prepared PVA and DND composite. The prepared composites have high mechanical properties due to good dispersion of DND content in a PVA matrix [15–16–17]. Liu et al. reacted mixture of hydrogen/fluorine at temperatures varying from 150 to 470 °C with DND powder which resulted in the formation of fluoro-nanodiamond [18–26]. Salvadori et al. bombarded the surface of polycrystalline diamond films with the ions of hydrogen, oxygen and fluorine by using small, simple and novel plasma gun to produce their surface terminations [19–20]. Krueger et al. used bead-assisted sonic disintegration (BASD) for the production of primary particles from strong clusters of DND. They also demonstrated that amino acids and small peptides can be grafted on the surface of primary particles after reduction with borane [22]. Numerous recent research is focused on the incorporation of DND into thermoplastic polymers, but usually DND are less studied with epoxy (thermo setting polymers) [19]. Yu-Jun Zhai, et al., reported on the improved mechanical properties of epoxy/DND nanocomposites by using low loading of DND particles for better results [38]. Similarly improvement of ~60% in Young's modulus for 3.5% DND loading and of ~700% for high DND loading (up to 25 vol%) were also reported in literature [37]. Sobia et al., investigated about the comparison of mechanical properties of the acid and UV/Ozone functionalized epoxy/DND nanocomposites [36]. Epoxy polymer shows tremendous chemical and physical behaviors that are mostly in favor of polymeric resin. However there are some properties which still need to be improved like thermal and electrical conductivity as well its brittleness. To make these properties ideal, DND particles were incorporating into epoxy resin and this way performances of epoxy polymer were improved up to greater extent. Neitzel and co-workers studied the effect of DND content on the thermo-mechanical behavior of DND/epoxy composite [21]. Monteiro and colleagues reported on mechanical properties of DND/epoxy composite by using high concentration of DND [33]. Ayesha Kausar reported on the preparation of novel blend of epoxy/polyurethane and nanodiamond composite. Various content of functionalized DND (0.1–5 wt%) was used as reinforcement to check its effect on the mechanical properties. Results showed that an increase in the tensile strength from 43.5 to 52.6 occurred when the content of DND is increased from 0.1 to 0.5 wt% [34]. M. R. Ayatollahi et al., reports on the mechanical behavior of nanodiamond/epoxy nanocomposites. They observed that mostly mechanical performances of the epoxy nanocomposites were increases with the increase of nanodiamond amount. They observed maximum increment in the properties like flexural strength, tensile strength, young's modulus and fracture toughness at 0.1 wt% addition of nanodiamond content [25]. Vadym and coworkers reported on the mechanical properties of epoxy nanocomposites containing various amount of aminated and carboxylated DNDs. Based on his results, it was concluded that aminated DND performed good than carboxylated DNDs in term of different mechanical properties [5]. Khan et al., reported on the functionalization and deaggregation of DND particles by using ball milling technique. They observed the effect of functionalization in terms of dispersion of DNDs in liquid media as well as in epoxy polymer. Their study shows the improvement of mechanical performances with the increase of DND content in epoxy matrix [35]. The electromagnetic shielding (EM) properties of DNDs are very rarely studied; in this study we make an effort to highlight this scope of DND particles. Polina P. Kuzhir, et al. [39], reported on the (EM) shielding properties of OLC based polymer composite (based on the annealing of detonation nanodiamond under vacuum conditions).

In this work epoxy/DND nanocomposites having excellent mechanical and electromagnetic attenuation properties were prepared by the direct treatment of nanoparticles with polymer matrix. Different amount of acid modified DND particles was dispersed in epoxy matrix and their aspects were studied on the properties of nanocomposites.

2. Experimental

2.1. Materials used

Gray color of DNDs having 99% purity was provided by Hengqiu Nanotechnology incorporation China. The average DND particle size was 5 nm. Araldite (828) epoxy resin and hardener was purchased from Huntsman Advanced Materials, woodlands USA. H_2SO_4 and HNO_3 (98.07%) from AnalR BDH Laboratory supplies Poole, BH_{15} ITD England while ethanol (98.8%) from Merk Germany was used in this work.

2.2. Purification treatment

As received DND was placed in a crucible and oxidized in a furnace at 440 °C for 5 h to remove the impurities like traces of metal and non-carbon content present in the powder [13–28]. Metal oxides are burnt even at less temperature while the burning temperature of diamond is about 600 °C which is above 440 °C. Therefore, during oxidation process only impurities are burnt while DND content remains unaffected.

2.3. Wet chemical method

After heat treatment process, the oxidized DND was refluxed with mixture of H_2SO_4 and HNO_3 having (9:1) at 280 °C for 24 h in a round bottom flask to attach carboxyl and hydroxyl functional groups on the DND surface [4]. The orange color vapors were produced during the heating which were condensed back to the flask by the condenser. After the reflux period, acidic DND solution was washed with deionized water until neutral pH. The wet DND having neutral pH is then dried to get DND powder and characterized for functionalization and composites formation.

2.4. Nanocomposites fabrication

Various samples were prepared by using different concentrations of functionalized DND powder in epoxy matrix. The epoxy matrix used is Di-glycidyl Ether of Bisphenol-A (DGEBA) which is commercially known as Epon-828 and hardener used for curing of Epon-828 is triethylene-tetramine (TETA) [20]. 0.1, 0.2 and 0.4 wt% of acid modified DNDs were used for the preparation of samples. 10 pph of TETA into Epon-828 were used [30]. In a typical Procedure, known quantity of acid modified DND was dispersed in ethanol and sonicate for 90 min. Then this dispersed DND in ethanol was mixed with Epon-828 and further sonicate for 90 min as well as degassed for 30 min. 10 pph of hardener or curing agent was mixed with the mixture of DND/ethanol/Epon-828 through mechanical mixing by using glass rod for 2 min. Now the whole mixture was poured into the dumb-bell and square shape moulds which was used for the measurement of mechanical and electrical properties. Before casting the surface of the moulds was greased by using silicon grease for easy separation. All the samples were left over night at room temperature for the evaporation of ethanol.