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Effect of nanodiamond surface functionalization using oleylamine on the scratch behavior of polyacrylic/nanodiamond nanocomposite

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ABSTRACT

Addition of hard particles such as nanodiamonds to polymers to improve their physical and mechanical properties is very common. However, nanodiamonds are usually hydrophilic so their tendency to form agglomerates in a polymeric matrix is quite strong. In this study, the effect of nanodiamond surface modification on its uniform dispersion in a polymeric matrix such as polyacrylic-base polymer clear coat was investigated. For this purpose, detonation nanodiamond (DND) with an average particle diameter of 4–6 nm was used. To improve dispersion of as-received DND (AR-DND) in the polymeric matrix, the surfaces of the particles were modified by heat treatment (oxidation) in air and followed by functionalization using oleylamine (OLA) as surfactant. So, nanocomposites with different contents of AR-DND, HT-DND and OLA treated HT- DND (OLA-HT-DND) particles were produced. Their characterizations were investigated by employing many analytical methods such as: Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and thermo-gravimetry analysis (TGA). Scratch resistance test and study of coating surfaces, using scanning tunneling microscopy (STM), were carried out on the polymeric nanocomposites. The results showed that the surface-functionalized nanodiamonds are highly dispersive and stable in the polymeric matrix. In addition, scratch resistance was increased with the addition of nanoparticles.

1. Introduction

Nanodiamonds are diamond-structured particles measuring less than 10 nm in diameter, which are the resultant of residue from a TNT or hexogen explosion in a contained space. They are now being studied in a variety of science, technology and health applications [1,2]. Nanodiamonds possess a unique combination of qualities, such as remarkable hardness, fracture strength, environmental inertness, nanotribology [3], thermal expansion, thermal conductivity, electrical insulation [4], chemical corrosiveness [5] and biocompatibility [6,7]. These characteristics and the fact that nanodiamonds are non-toxic, make the particles ideal candidates for a variety of tasks including biological systems [8,9], composites [10–12] and electronic applications [13].

Due to the high surface energy of nanoparticles their tendency to form agglomerates is quite strong [14]. But the existence of agglomerates affects its characteristics as nano-scale materials. Nanodiamond, as received from vendors, exhibit inadequate colloidal stability [15]. Colloidal particles collide with each other due to the Brownian motion, convection, gravity and other forces. Collisions may result in coagulation of the particles and destabilization of the colloid. If a colloidal particle is brought to a short distance to another particle, they are attracted to each other by the van der Waals force. To achieve stability, sufficient repulsive forces must exist between the particles while in a suspension [15].

Therefore, to obtain a stable suspension from commercial DNDs and to increase repulsive forces between nanoparticles, surface modification must take place. The energy barrier resulting from the repulsive force prevents two particles from approaching one another and adhering together.

In order to fully benefit from nanoparticle properties, a uniform dispersion in the suspension is essential [7,16]. To achieve this goal, two ways can be investigated, either chemical or mechanical treatments. Nanodiamonds possess chemically inert cores, very high exohedral surface areas (300–400 m^2/g for DND), a wide variety of surface groups, and facile surface functionalization. So far, several studies for the surface modification and deagglomeration have been done such as heat treatment in gaseous atmospheres [17–19] mechano-chemical methods, using surfactants, acidic oxidation [20], beads milling [21], sonication and fractionation using centrifugation [22] and polymer grafting.

Usually nanodiamond powder is chemically functionalized so that it can be dispersed in water or hydrophilic solvents such as alcohols. However, often a hydrophobic material is required because typical polymer processing solvents, as well as many industrial polymers themselves, are hydrophobic [23].

In the current study, the colloidal stability of DNDs with amine-surface modifications has been analyzed. In this regard, a process is described by which strongly hydrophobic nanodiamond powder is created

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via the chemical reaction of carboxylic groups on the surface of purified nanodiamond particles with amino groups of oleylamine (OLA).

2. Experimental procedures

2.1. Materials

The detonation nanodiamond (DND) used in this study was received from NaBond technology Co. Ltd., China. Their specifications are as: purity 99%, size 4–6 nm, density 3.05–3.3 g/mm^3 and specific surface area 282.83 m^2/g. Oleylamine (OLA) (70%, Sigma–Aldrich) was used as surfactant in this investigation. The as-received powder (AR-DND) was studied by LEO 920 AB TEM to determine particle size and shape. All nanoparticle powders used in this study were studied by Shimadzu 4300 FTIR spectroscope to characterize particle surfaces and by Shimadzu TGA-50 to define initiation temperature of oxidation and purity. TGA was carried out under air conditions with a heating rate of 10 k/min. Particle size was measured using Cordouan device model VASCO3 in thinner media.

2.2. Thermal oxidation of nanodiamonds

To apply homogenous functional groups on particle surfaces, thermal oxidation was carried out on AR-DND by treating the powder in a furnace at 420 °C under air condition for 2 h to eliminate non-diamond carbons and producing oxide containing functional groups (such as ether and carboxyl) on their surfaces. Hereafter, the oxidized detonation nanodiamond is denoted as HT-DND.

2.3. Amine functionalization

In experiments involving dispersion, 1 g HT-DND powder was dispersed into an organic solvent (paint thinner) containing 2 cm^3 OLA as surfactant and stabilizer. The mixture was then deagglomerated by a high-energy ultrasonic horn (Branson 3510) for 30 min. Then, OLA treated HT-DND were washed and filtered via repeated centrifugation and sonication. The resultant slurry was dried at 80 °C for 4 h in a vacuum oven.

2.4. Production of nanocomposites

The nanoparticles were dispersed into a polyacrylic-base polymer, known as clear, after surface modification. Clear coat is a polyacrylic melamine layer of paint or resin which is applied on top of a vehicle's colored layer of paint without pigment or coloration. The clear was first diluted by a commercial paint thinner with the ratio of clear to thinner: 4/1 to reach the suitable viscosity. Then, 0.5, 1 and 1.5 wt.% AR-DND, HT-DND and OLA-HT-DND, respectively, were mixed with 200 ml of diluted clear by sonicator for 90 min. The resultant suspension was then sprayed on pre-electrodeposited (ED) steel plates with dimensions of 120 × 70 × 0.8 mm. The produced samples then were cured at 140 °C for 20 min in a vacuum oven. An unfilled sample (blank) was also produced. The characteristics of the produced samples are listed in Table 1.

2.5. Microscopy study using STM

In this study to examine the surface topography of the produced coatings scanning tunneling microscope was used. The microscope utilized in this study was a product of NANO SYSYTEM company model STM SSI.

2.6. Scratch resistance test

The coated ED steel plates were allowed to rest for a minimum of 24 h and then scratch tests were performed on their surfaces. The scratch test was carried out according to ASTM-G171 standard by a Parsa Polymer Sharif scratch device. Scratch load was 750 g and kept constant during the test. Scratching speed was also kept constant for all samples. A scratch of length 8 cm is produced during test. Immediately after scratching, some pictures were taken by OM in 50× magnification. Scratch width was measured from these images using MIP image processing software then converted to hardness by Eq. (1).

$$HS_P = \frac{KP}{W^2} \quad (1)$$

where, HS_P is hardness based on the scratch width measure (MPa), P is applied load (g), and W is scratch width (μm).

Table 1
Characteristics of the produced samples.

Sample code	Filler condition	Filler content (wt.%)
AR-5	As received	0.5
AR-10	As received	1
AR-15	As received	1.5
HT-5	Heat treated	0.5
HT-10	Heat treated	1
HT-15	Heat treated	1.5
OLA-5	Oleylamine	0.5
OLA-10	Oleylamine	1
OLA-15	Oleylamine	1.5

3. Results and discussion

The AR-DND in this experiment was initially a black to dark-grey powder. The color turned light-grey when particles were heat treated at 420 °C for 2 h in air atmosphere. The TEM micrograph of the as-received DND nanoparticles used in this study is shown in Fig. 1. Based on the figure, DND particles are spherical in shape and mostly have single digit diameter. The surface chemistries of the as-received nanodiamond, thermal treated nanodiamonds, and amino functionalized nanodiamonds with OLA were determined by Fourier transform infrared (FTIR) spectra.

As presented in Fig. 2, (a), (b), and (c) indicate the FTIR spectra of the AR-DND, HT-DND, and OLA-HT-DND, respectively. For the AR-DND powder, the main features in the spectrum are related to C–H vibration at 2973.27 cm^{-1}, O–H and N–H bending vibration at 1632.28 cm^{-1}, C–O–C vibration at 1288.45 cm^{-1}, C═O stretching vibration at 1793.31 cm^{-1} and O–H vibration at 3448.13 cm^{-1}. They have been assigned to surface functional groups such as: alkanes, ketones, aldehydes, esters, alcohols, ethers and acids [24,25]. For the HT-DND powder, it has almost the same IR adsorptions as those of AR-DND, C═O

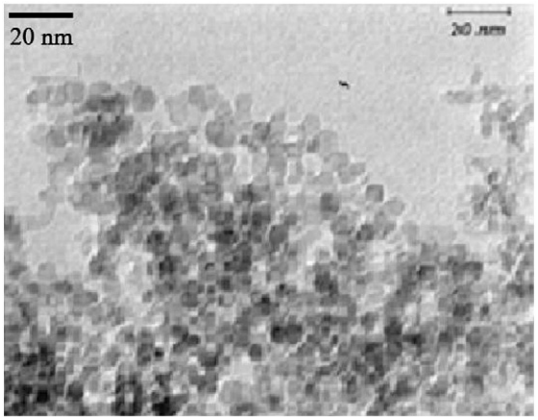

Fig. 1. TEM micrograph of DND nano-particles.