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ABSTRACTS

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(SURFACE-3-3) CHEMICAL SPRAY PYROLYSIS PATH TO SYNTHESIS OF ZNO MICROSAUSAGES FROM AGGREGATION OF ELONGATED DOUBLE TIPPED NANOPARTICLES

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The versatile chemical spray pyrolysis was used to prepare elongated double tipped ZnO nanoparticles and microsausages on glass substrates. X-ray diffraction studies revealed several crystallographic plane orientations with the most predominant along the (002) direction. Scanning electron microscope (SEM) observations indicated double tipped nanoparticles with an aspect ratio of 4.5-8.6 which coalesced in regular patterns to form microsized sausages of width ranging up to 1.2 μm. The absorption mechanism was through direct transitions with an absorption edge corresponding to a band gap of 3.18 eV.

(SURFACE-3-4) A STUDY ON THE SCRATCH BEHAVIOUR OF ACRYLIC/DETONATION NANODIAMOND NANOCOMPOSITE

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The addition of hard particles to polymers in order to promote their mechanical properties is very common. Detonation nanodiamond is one of the new members of carbon nanofamily and has very interesting properties such as high hardness and specific surface structure. It is capable of a variety of surface modifications to insure good dispersion of particles in any media. In recent years it has been used as reinforcement phase in polymeric matrix and some thermal and mechanical properties of the produced nanocomposite is being studied. But based on the author's knowledge the scratch behaviour of nanocomposite coatings based on detonation nanodiamond in polymers is missing.

The main aim of the current study is to elucidate the role of nanodiamonds on scratch behaviour of acrylic resin. For this purpose we used detonation nanodiamond (DND) with average particle diameter 4-6nm. To improve dispersion of as-received (AR) DNDs in acrylic, surfaces of AR-DNDs were modified by heat treatment (oxidation) in air and by oxidation in air followed by carboxylation in concentrated acids mixture. Acrylic nanocomposites containing of about 0.5 and 1.5 wt% of AR-, HT-, and AT-DNDs were produced by 1.5h sonication in Branson 3510 sonicator bath. The produced nanocomposite sprayed on the pre-electro-deposited steel samples. All samples were scratched under constant loads, i.e. 3.5, and 5 N. The scratching speed was kept constant during the test. The results indicated that the presence of DNDs promotes scratch resistance of neat acrylic because of an increase in surface hardness.

A Study on the Scratch Behaviour of Acrylic/Detonation Nanodiamond Nanocomposite

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Abstract. The addition of hard particles to polymers in order to promote their mechanical properties is very common. Detonation nanodiamond is one of the new members of carbon nanofamily and has very interesting properties such as high hardness and specific surface structure. It is capable of a variety of surface modifications to insure good dispersion of particles in any media. In recent years it has been used as reinforcement phase in polymeric matrix and some thermal and mechanical properties of the produced nanocomposite is being studied. The main aim of the current study is to elucidate the role of nanodiamonds on scratch behaviour of acrylic resin. For this purpose detonation nanodiamond (DND) with average particle diameter 4-6nm was used. To improve dispersion of as-received (AR) DNDs in acrylic, surfaces of AR-DNDs were modified by heat treatment (oxidation) in air (HT) and by oxidation in air followed by carboxylation in concentrated acids mixture (AR-AT and HT-AT). Acrylic nanocomposites containing of about 0.5 and 1.5 wt% of AR-, HT-, and AT-DNDs were produced by 1.5h sonication. The produced nanocomposite sprayed on the pre-electro-deposited steel samples. All samples were scratched under constant loads, i.e. 3.5N. The scratching speed was kept constant during the test. The results indicated that the presence of DNDs promotes scratch resistance of neat acrylic because of an increase in surface hardness.

Introduction

Incorporating hard particles into soft polymeric matrixes to alter their properties is very common. These particles are generally ceramic particles such as Al_2O_3 and SiO_2 [1,2]. Nowadays carbon is one of the main nanotechnology branches [3-6]. Nanodiamond is one of the new members of carbon nanofamily and because of its exceptional properties such as very high hardness, finds more applications everyday. Among different nanodiamond types, nanodiamond produced by detonation synthesis called detonation nanodiamond (DND) or ultradispersed diamond (UDD) has been especially noticed because of very small particle size (4-6nm) and capability to be functionalized with a variety of routes. These functionalization methods include heat treatment in gaseous atmospheres [7,8], chemical methods [9], and polymer grafting [10]. DNDs are commercially produced in large scales that result in very low cost in contrast with other carbon nanomaterials such as carbon nanotubes.

The aim of the current study is to elucidate effects of nanodiamond content and type of surface functionalization on the scratch behavior of polyacrylic/DND nanocoating used in automotive industry. For this purpose polyacrylic/DND nanocomposites containing 0.5, 1.5, and 3wt.% DND, each with different surface modification is produced by sonication and scratched with constant load. The scratch behavior of the samples is compared with each other and with a reference blank sample.

Experimental Procedure

Rough materials. The detonation nanodiamond purchased from NaBond technology Co. Ltd., China, as reinforcement phase and polyacrylic as matrix were used. The AR-DNDs were studied by TEM (LEO 912 AB), TGA (Shimadzu TGA-50), and FTIR (Shimadzu 4300) to determine particle size and shape, initiation temperature of oxidation and purity, and surface functional groups, respectively.

Functionalization. To insure good dispersion of AR-DNDs in polyacrylic, the AR-DNDs were functionalized by three methods. In the first method the AR-DNDs were heat treated in 450°C for 2h in air atmosphere. In the second route some HT-DNDs were sonicated in concentrated sulfuric (98%) and nitric (74%) acids mixture (Volume percent of $H_2SO_4/HNO_3=3/1$) in a Branson 3510 sonication bath for 3h. Then the DNDs and acids mixture were poured in 80°C DI water and stirred for 10h. After finishing, the DNDs were rinsed via repetitive centrifugation and sonication until the pH reached about 4.5. In this stage the DND particle could not be settled down by centrifugation anymore and the rinsing process were disrupted. After rinsing, the resultant slurry were dried at 80°C for 4h in a vacuum oven. The process eliminates metallic impurities and turns the majority of surface functional groups to carboxylic group. These DNDs will call HT-AT-DNDs in the following text. In the third method the AR-DND were directly carboxylated with the same method of HT-DNDs. These DNDs will call AR-AT-DNDs hereafter.

Coatings production. To produce 0.5 1.5, and 3wt.% DND containing acrylic/ nanodiamond nanocomposites, pre-weighted masses were mixed by 1.5h sonication with Branson 3510 sonication bath. The coding of samples along with their production parameters and scratch characteristics are provided in Table 1. The produced nanocomposite then sprayed on pre electro-deposited steel plates with 12×3.5×0.8mm dimensions. The resultant coatings were cured at 140°C for 20min.

Table 1: samples codes, production parameters and scratch characteristics

Sample code	DND content [wt.%]	DND type	Coating thickness [μm]	Scratch width [μm]	H_W [N/mm^2]
Blank	-	-	30.3	176	288
AR5	0.5	AR	47.0	164	331
AR15	1.5	AR	43.6	206	211
AR30	3	AR	-*	182	269
HT5	0.5	HT	52.1	204	214
HT15	1.5	HT	74.8	184	262
HT30	30	HT	-*	164	331
AR-AT	1.5	AR-AT	58.9	181	272
HT-AT	1.5	HT-AT	23.1	183	267

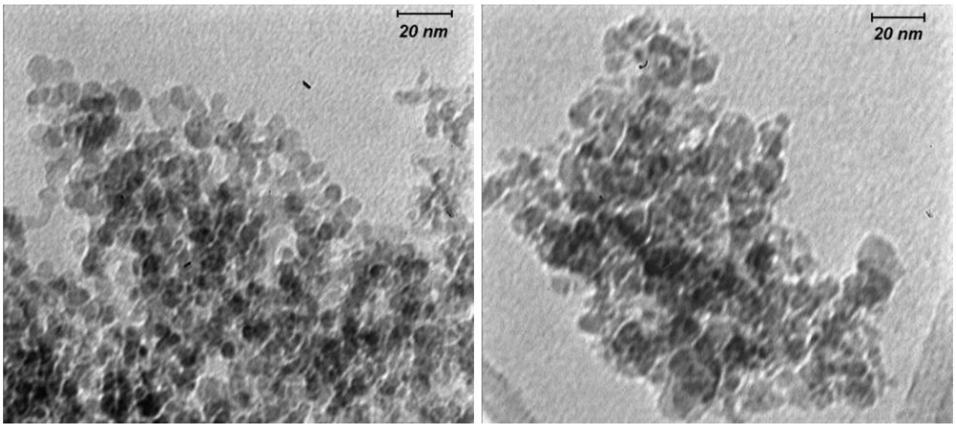
* Was not measured

Scratch test. The samples were allowed to rest for minimum of 24h and then the scratch test were performed on them according to ASTM-G171 standard. Scratch load was 350g and kept constant during the test. Scratching speed was also kept constant for all samples. A scratch of length 8cm is produced during test. Immediately after scratching, 5 pictures were taken by an Olympus BX60M optical microscope in 50× magnification. Scratch width was measured from these images and converted to hardness by using Eq. 1.

$$H_W = \frac{8F}{\pi\left(S_W\right)^2}\,. \tag{1}$$

Results and Discussion

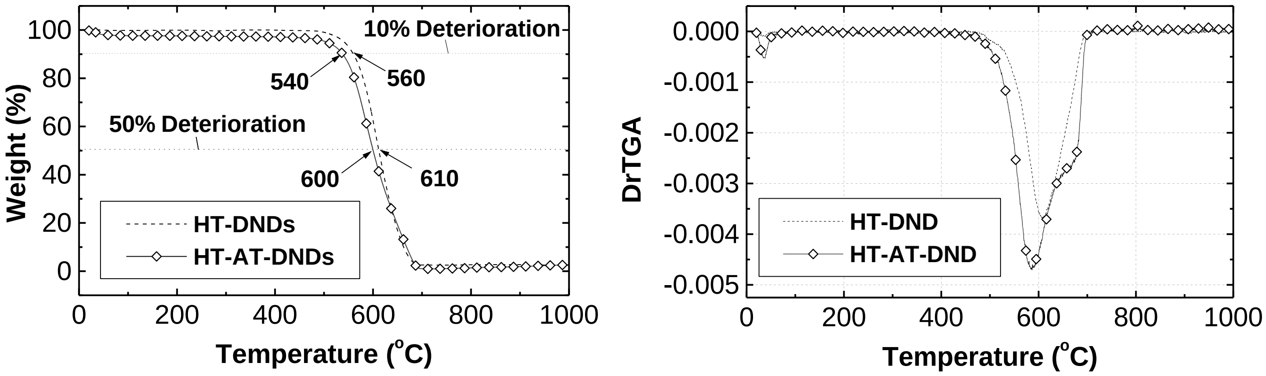
The TEM micrographs of AR- and HT-AT-DNDs are shown in Fig. 1. As the figure shows, the DND particles are spherical in shape and have diameter ranging from about 4 to 10nm. It can also be seen from the figure that the DND particles are *agglomerated,* especially HT-AT-DNDs.



(a) **(b)**

Figure 1: TEM micrographs of (a) AR-DNDs and (b) HT-AT-DNDs. The HT-AT-DNDs were milled in dry condition after production and before using.

The TGA curves of HT- and HT-AT-DNDs are shown in Fig. 2 (TGA curves of AR- and AR-AT-DNDs are the same as HT and HT-AT-DNDs, respectively and were not provided here). In the case of HT-DNDs, it can be seen from the derivation curve that there are two peaks. First peak is at about 50°C and the second peak is at around 600°C. The first peak is at very low temperature and its origin is not yet fully known to authors but probably it is due to the peripheral volatile materials that are along with the DND. The second peak is due to oxidation of nanodiamonds. Based on the curve, initiation temperature for HT-DNDs is about 530°C. The TGA curve of HT-AT-DNDs is so different from that of HT-DNDs. It shows two-stage weight lost (deterioration) between 600-700°C.



(a) **(b)**

Figure 2: (a) TGA curves and (b) their derivatives (DrTGA) of , HT-DNDs and HT-AT-DNDs.

FTIR spectra of AR, HT, and HT-AT-DNDs are shown in Fig. 3 (FTIR spectrum of AR-AT is very similar to that of HT-AT-DNDs and was not provided here). For AR-DNDs, from left to right, peaks are O-H tension at 3440, C-H at 2920, C=O (in CO_2) at 2380, O-H bending at 1630, C-N at 1380, C-O at 1143, and O-H (in water) at 620cm^{-1}. Because the O-H (in water) and C=O (in CO_2) are not functional groups therefore, the functional groups of AR-DNDs are O-H, C-H, C-N, and C-O. After surface functionalization some changes were seen in spectra. The changes were the same for both surface functionalizations (i.e. heat treatment and carboxylation) except for peaks intensities. In functionalized DNDs spectra, C-N peak is vanished and instead a peak at 1780cm^{-1}

(for C=O in carboxylic group) and a peak at 1265cm^{-1} are appeared. Accordingly the surface functional groups of functionalized DNDs are majorly carboxylic (-COOH) and C-H groups. The main aim of heat treatment in air is to eliminate non-diamond carbon allotropes (such as amorphous carbon or graphite) from nanodiamond surface by oxidation. Elimination of other carbon allotropes seems to strongly decrease agglomeration tendency of particles [7]. This process also produces some functional groups such as carbonyl that promotes agglomeration of particles, but the effect of non-diamond elimination is dominant and heat treatment could be beneficial in deagglomeration of particles. Treating of HT-DNDs in concentrated acids mixture, further oxidize their surfaces and turn most of functional groups to carboxylic group. Carboxylic group is shown to result in stability of DNDs in polar media in the pH range 2-12 [9].

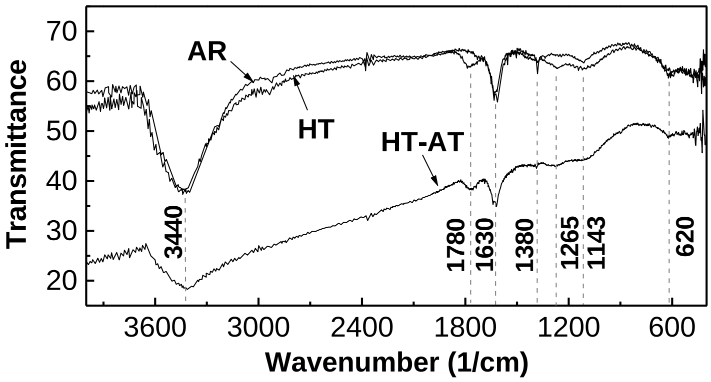


Figure 3: FTIR spectra of AR-, HT-, and HT-AT-DNDs (indicated as AT).

Results of scratch tests are shown in Figs. 4 and 5. Based on the Fig. 4, the trends of scratch resistance variation for AR- and HT-DNDs are different. Regardless of Blank sample, for AR-DNDs there is a minimum at 1.5wt.% DNDs while for HT-DNDs the scratch resistance is uniformly increases as DND content increases from 0.5 to 3 wt.%. Most of samples show scratch resistance less than the Blank sample. Except for 0.5wt.% containing samples, HT-DNDs show better results than AR-DNDs. It can be seen from Fig. 5 that all 1.5wt.% containing samples have scratch resistance less than Blank sample. Among DND containing samples, AR-AT-DND containing sample is the best. HT-AT and HT-DNDs containing samples have similar scratch resistance to AR-AT-DND containing sample (less than 4% decreases in scratch resistance) but AR-DND containing sample shows noticeable drop in scratch resistance (about 22.5%).

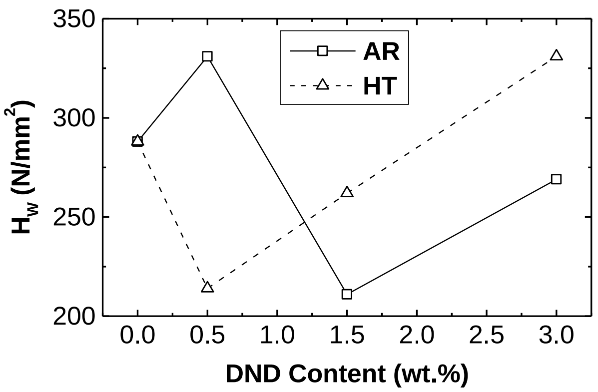


Figure 4: Coating hardness (based on the scratch width as calculated by Eq. 1) versus DND content for AR and HT particles. 0wt.% sample is Blank (reference) sample according to Table 1.

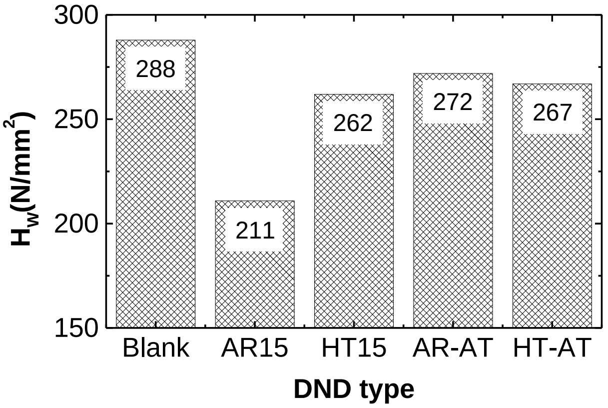


Figure 5: Coating hardness (based on the scratch width as calculated by Eq. 1) versus type of surface functionalization for samples containing 1.5wt.% DNDs.

Summary

Effects of the method of surface modification and DND content on the scratch behaviour of detonation nanodiamond/polyacrylic nanocomposite clear coats were investigated in this study and the main conclusions are as below:

1. Addition of DNDs almost deteriorates the scratch resistance of neat polyacrylic.
2. With increasing DNDs content there is no general rule that describes the scratch resistance trend.
3. Surface functionalization methods used have profound effect on increasing scratch resistance of DND containing samples (nanocomposite coats).

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