Progress in Organic Coatings 76 (2013) 1258–1264

Contents lists available at SciVerse ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Effect of heat treatment of nanodiamonds on the scratch behavior of polyacrylic/nanodiamond nanocomposite clear coats

M.H. Avazkonandeh-Gharavol[a], S.A. Sajjadi[a,*], S.M. Zebarjad[a], M. Mohammadtaheri[a], M. Abbasi[a], M. Alimardani[b], K. Mossaddegh[c]

[a] Department of Materials science and Engineering, Ferdowsi University of Mashhad, Mashhad, Iran
[b] Department of Chemistry, Ferdowsi University of Mashhad, Mashhad, Iran
[c] Central laboratory, Iran-Khodro Khorasan Company, Binalood, Khorasan Razavi, Iran

ARTICLE INFO

Article history:
Received 13 October 2011
Received in revised form 17 February 2013
Accepted 27 March 2013
Available online 13 April 2013

Keywords:
Heat Treatment
Detonation Nanodiamond
Scratch Behavior
Polyacrylic
Nanocomposite Coatings

ABSTRACT

In the current paper, effects of heat treatment of nanodiamond particles on the scratch behavior of polyacrylic/diamond nanocomposite coatings were studied. Two types of nanodiamond, i.e. one produced by detonation synthesis (DND) and the other produced by nondetonation synthesis (NDND) were used as reinforcement phase to increase scratch resistance of polyacrylic base polymeric clear coat. Heat treatment was used as the surface modification route. Coatings containing both types of particles in two surface conditions (as-received and heat treated) were compared to each other and also to the neat polyacrylic coating. The results showed strong effect of heat treatment on scratch resistance of coatings based on the scratch width criterion. The effect of heat treatment was more pronounced on DND particles than on NDNDs. However the pendulum hardness showed a reverse trend.

1. Introduction

The addition of hard particles into polymers to improve their physical and mechanical properties is very common. The reinforcements are generally ceramic particles [1–6]. Currently, a great portion of nano science and technology is focused on nanocarbon family [7]. One of the major members of nanocarbon family is nanodiamond which is finding more applications these days [8,9]. Detonation nanodiamond (DND) is one of the most important members of the nanodiamond family because of its unique properties especially, ultimate small particle size and commercial production capability. One of the primary fields of application of DNDs is as reinforcement phase in polymeric nanocomposites [10–15]. Maitra et al. [11] produced dilute nanocomposites of polyvinyl alcohol reinforced with 0.6 wt.% DND particles and studied hardness and module changes. They observed that addition of the particles severely improves hardness, about 180% of the neat polymer.

To insure good dispersion of the reinforcement particles in any media they need proper surface modification or functionalization. The treatment includes heat treatment in gaseous atmospheres [16–22], chemical methods [23–30], mechano-chemical methods [31–34], using surfactants [35,36] and polymer grafting [37–41]. Some of these methods are so difficult and time consuming to apply on DNDs which makes them uneconomical especially in industrial applications. Heat treatment in air (as one of the easiest methods) has been used as a purification method of DNDs in recent years. It eliminates non-diamond carbon allotropes (such as graphite or amorphous carbon) from the nanodiamond particle surfaces which is beneficial to its dispersion capability. However, it produces oxide functional groups, such as: ether, carbonyl, and carboxyl groups, on ND surface which some of them are bridge-forming groups and hence detrimental to their dispersion capability. Elimination of non-diamond carbon from ND surface and formation of some beneficial functional groups such as carboxyl groups, however, is dominant and heat treatment could be beneficial to dispersion capability of ND, especially in polar media [21].

Behler et al. [10] studied the effect of DND addition to polyacrylonitrile and polyamide 11 on their module and hardness by nanoindentation test. By using electro-spinning method to produce nanocomposite films they could introduce high portion of DNDs as much as 80 and 40 wt.% in polyacrylonitrile and polyamide 11, respectively. They heated and then acid treated the DNDs to obtain better dispersion in polymeric matrix. They indicated that addition of NDs to polymeric matrix could severely increase its hardness (around 2 times) [10].

The aim of this research is to study the effects of heat treatment of nanodiamond particles on scratch behavior of

* Corresponding author. Tel.: +98 5118763305.
E-mail address: sajjadi@um.ac.ir (S.A. Sajjadi).

0300-9440/$ – see front matter
http://dx.doi.org/10.1016/j.porgcoat.2013.03.016

polyacrylic-based clear coats. Hence, nanodiamonds produced by detonation and nondetonation processes were used as reinforcement phase and microstructural, physical and mechanical properties of these nanocomposite coatings were compared to those of neat polyacrylic coating.

2. Experimental procedures

2.1. Materials

Both DND and NDND powders were obtained from NaBond Technologies Co. Ltd, China. Based on the supplier data some powder characteristics for DNDs are: purity: 98–99%, average particle size: 4–6 nm, density: 3.05–3.3 g/mm^3, and specific surface area: 282.83m^2/g. For NDNDs the characteristics are: purity: higher than 99.95% and average particle size: 50–60 nm. The as-received (AR) DND and NDND powders were studied by LEO 912 AB TEM, and Shimadzu 4300 FTIR spectroscope to determine shape and size of particles and surface functional groups, respectively. A commercially available polyacrylic-base polymer used as clear refinish in automotive industries, was used as matrix.

2.2. Heat Treatment

DND and NDND particles were heat treated at 450 °C for 2 h in air to eliminate nondiamond carbons and produce oxide containing (such as ether and carboxyl) functional groups on their surfaces. The modified particles were analyzed by FTIR. The particles are called HT-DND and HT-NDND, hereafter.

2.3. Coating production

A mixture of aromatic and aliphatic hydrocarbons, with the chemical name of Solvesso 150 was used as thinner for clear coat. The polyacrylic-base polymer was first diluted by a commercial paint thinner (with the ratio of polyacrylic to thinner: 4/1) to reach the satisfactory viscosity. The pre-weighted nanoparticles were then mixed with proper quantity (200 ml) of diluted polyacrylic by sonication in a Branson 3510 sonicator bath for 1.5 h. Three samples containing 0.5, 1.5, and 3 wt.% AR and HT-DNDs nanodiamond were produced. In addition, from each AR and HT-NDNDs only one sample containing 1.5 wt.% filler was produced. Since the purpose of this research was to study the effects of heat treatment of nanodiamond particles on the scratch behavior of polyacrylic/diamond nanocomposite coatings, the tests were started from 0.5 wt.% nanodiamond and then 1.5 wt.% and finally 3 wt.%. On the one hand, for samples bellow 0.5 wt.% nano particle no considerable improvement in coating properties was observed. On the other hand, after the addition of 3 wt.% nano diamond, because of particle agglomeration, the gloss and scratch resistance of the coatings reduced. The resultant liquid nanocomposites were then sprayed on 120 × 70 × 0.8 mm pre (epoxy) electrodeposited (ED) steel plates and 75 × 25 × 1 mm glassy slides. The samples were then cured at 140 °C for 20 min in a vacuum oven. An unfilled sample (neat or blank) was also produced as reference guide. The characteristics of the samples are listed in Table 1.

2.4. Coating characterization

The thickness of the coating on ED steel plates was measured according to PSA D265316 standard by an Elcometer Coating Thickness Gauge apparatus. Microstructure of coatings was studied by a BX60M Olympus (metallurgical) optical microscope (OM). The microstructure of glassy slides was examined by transmission optical microscopes (TOM). The gloss of coated ED steel plates were measured according to PSA D251413 standard by a Sheen Tri-Glossmaster device. A beam of visible light was radiated on to the coating surface and its reflection was detected and measured.

Table 1
Samples specification and their gloss.

Sample code	Filler type	Surface condition	Filler content (wt.%)
DND-AR-5	DND	As-received	0.5
DND-AR-15	DND	As-received	1.5
DND-AR-30	DND	As-received	3
DND-HT-5	DND	Heat treated	0.5
DND-HT-15	DND	Heat treated	1.5
DND-HT-30	DND	Heat treated	3
NDND-AR-15	NDND	As-received	1.5
NDND-HT-15	NDND	Heat treated	1.5
Blank	–	–	–

All coatings have thickness in the range 110 ± 10 μm.

2.5. Scratch test

The coated ED steel plates were allowed to rest for minimum of 24 h before performing mechanical tests on their surface. The scratch test was carried out according to ASTM-G171 standard by a Parsa Polymer Sharif scratch device. Scratch load was 500 g which was kept constant during the test. Scratching speed was also kept constant for all samples. A scratch of length 8 cm was produced during each test. Immediately after scratching, 5 pictures were taken by OM in 50× magnification. Scratch width was measured from these images and converted to hardness using Eq. (1).

$$H_W = \frac{8F}{\pi(S_W)^2} \quad (1)$$

where, H_W is hardness based on the scratch width measure (N/mm^2), F is applied load (N), and S_W is scratch width (mm).

2.6. Industrial tests

Some industrial tests were also carried out on the coated ED steel plates. These were pencil and pendulum (or Persoz) hardness tests indicating scratch resistance.

Pencil hardness which is a criterion of scratch resistance was evaluated by Sheen 720N device based on JIS K 5400 standard. Different kinds of pencil from the softest (9B) to the hardest one (9H) were used in order to find out the softest pencil which can scratch the surface of the coated plates. For this purpose a pencil was held at an angel 45° to the test plate, under a weight of 1 ± 0.05 kg, and moved forward on the coated surface. The first pencil which could scratch the coating was reported as pencil hardness.

The pendulum hardness of the coated plates was measured by Elcometer K.3034M001 Persoz Tester according to PSA D251298 standard. The pendulum rod equipped with two balls was inclined at 12° and released to move on the surface of the plates and then allowed to oscillate. The number of oscillations of the pendulum before stopping was counted and reported as hardness of the sample.

3. Results and discussion

The TEM micrographs of both DND-AR and NDND-AR are shown in Fig. 1. Based on this figure, DND particles are spherical in shape and mostly have single digit diameter in nanometer. However, NDND particles are irregular in shape and have a wide range of size.

Figs. 2 and 3 show FTIR spectra of DNDs and NDNDs in both AR and HT conditions. 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