Contents lists available at ScienceDirect

Progress in Organic Coatings

Dispersion of carbon nanotubes in nanostructured epoxy systems for coating application

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ABSTRACT

This study about the dispersion of carbon nanotubes into an epoxy matrix can be considered as a first approach to investigate a potential industrial coating. In order to well disperse carboxylic acid-modified multiwalled carbon nanotubes (a-MWCNT) in a commercial epoxy-based resin, its nanostructuring with an amphiphilic epoxidized styrene-*b*-butadiene-*b*-styrene triblock copolymer that also acts as surfactant was carried out. In order to determine if coating performance is suitable for industrial applications, morphologies generated for copolymer-modified coating and the dispersion of a-MWCNT was characterized by atomic force microscopy. Contact angle measurements, Taber abrasion testing and thermogravimetric analysis were also performed. A tailor-made coating was developed with improved a-MWCNT dispersion and hydrophobicity due to the effect of block copolymer. System modified with 5 wt% of block copolymer and filled with 1 wt% a-MWCNT present the lowest value in weight loss in the wear test, while systems filled with 0.2 wt% of a-MWCNT showed increased thermal stability. Coating properties analyzed depend largely on the amount of components and a-MWCNT dispersion level, thus adding new application possibilities to the coatings, while most of the conventional epoxy-coating advantages are retained.

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1. Introduction

Carbon nanotubes (CNT) have attracted considerable attention since their first discovery in 1991 [1] due to their remarkable mechanical and geometrical properties [2–12] (extremely high Young's modulus and strength, high aspect ratio, nanometer-range diameter). Polymer-based composites filled with CNT present a better performance when homogeneous dispersions of CNT are achieved [3–5]. For this purpose, different ways have been investigated for increasing compatibility among CNT and polymeric matrices, such as mechanical stirring [3], sonication [4,5], centrifugal mixing [6], oxidation/filtration protocol [7], chemical modification of CNT surface [8–10], and the use of dispersants [2,11] and block copolymers as surfactants [12]. In addition, several works have been reported on the modification of epoxy resins with block copolymers, obtaining long-range order structures in both uncured and cured systems that enhance properties such as toughness [13–15].

Poly(styrene-*b*-butadiene-*b*-styrene) (SBS) is one of the most commercial block copolymers. It can be epoxidized through polybutadiene double bonds in order to increase the compatibility of the block with epoxy resin [14], leading to nanostructured epoxy matrices with long-range order, especially for high epoxidation degrees. This nanostructuring is due to reaction-induced phase separation of polystyrene (PS) block. Moreover, aromatic rings of PS block may interact with CNT walls [16], which could emphasize CNT dispersion. Therefore, nanostructured epoxy matrices could be potential matrices for well dispersed CNT-based composites.

Thermosetting polymeric coatings, especially epoxy based ones, are used on protective components which are subjected to wear processes during use. These coatings are typically applied by spraying with a thickness less than 50 μm. CNT could improve mechanical properties of an epoxy coating in order to minimize problems related to wear processes in industrial pieces, allowing a life extension and a reduction on cost of maintenance of components [17–21].

Thermal resistance [22] and wettability are also important properties of coatings. Contact angle of nanostructured epoxy systems gives some evidences about the ability of surfaces to repel water or mud [23–26].

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For all these reasons, block copolymers have been mainly used as surfactants for the dispersion of carboxylic acid-modified multi-walled carbon nanotubes (a-MWCNT) into epoxy systems, reducing their viscosity and helping the resin to penetrate into nanotube agglomerates [27,28]. The effect of block copolymer addition on the dispersion of a-MWCNT into a nanostructured epoxy matrix, as well as contact angle, wear resistance and thermal stability of nanocomposite coatings have been evaluated, considering several variables such as a-MWCNT and epoxidized SBS content. The aim of this work has been the development and characterization of an air spray coating, based on a commercial epoxy-based one, nanostructured with SBS block copolymer and filled with a-MWCNT.

2. Experimental

2.1. Materials

A coating formulated from commercially available components for aeronautic applications was used as matrix: diglycidyl ether of bisphenol A (DGEBA) epoxy resin, Epikote 828, provided by Momentive (formerly Hexion), and Ancamine 2500 amine curing agent 1-(2-aminoethyl)piperazine:1,3-bis(aminomethyl)benzene; 2:1 mol/mol, provided by Air Products. Multiwalled carbon nanotubes (GRAPHISTRENGTH^{TM}) supplied by Arkema (diameter between 10 and 15 nm and length between 1 and 10 μm) were used. MWCNT were functionalized with carboxylic acid groups by chemical oxidation in order to improve their dispersion in the solvent. Pristine MWCNT were oxidized with a 1:3 (volume ratio) mixture of concentrated nitric and sulfuric acid (0.125 mg MWCNT/mL acid). This mixture was sonicated at 40 °C for 3 h in an ultrasonication bath (Selecta Ultrasons-H model, which has a nominal frequency of 40 kHz with 200 W power). The acid suspension of oxidized MWCNT was directly filtered through a hydrophilic polypropylene membrane disk filter (Waters Corporation, 0.45 μm pore size) with the help of a vacuum pump. MWCNT were washed several times with deionized water during filtration to remove the acid residue, until the filtrate reached the pH of deionized water. Collected a-MWCNT were then redispersed in ethanol and dried in a vacuum oven at 120 °C overnight. This oxidation method generated mainly carboxylic acid groups on their surface, achieving approximately 1.5 mequiv. COOH/g CNT, as obtained by titration [29]. SBS block copolymer C540, with 60 wt% of PB and a number-average molar mass of 75,000 g mol^{-1} was kindly supplied by Repsol-YPF. The epoxidation procedure of the copolymer was described elsewhere [14]. The copolymer used in this work (ep52SBS) had a epoxidation degree of 52% (mol% of epoxidized polybutadiene units) as calculated by ^{1}H NMR [14]. Tetrahydrofuran (THF) and dimethylformamide (DMF) solvents from Aldrich were used without further purification.

2.2. Sample preparation

Appropriate amounts of ep52SBS, DGEBA and a-MWCNT were dispersed in a solvent mixture (THF/DMF, 1:1, v/v). Solution was sonicated for 4 h (Selecta Ultrasons-H, 950 W, 50/60 Hz) to obtain homogeneous mixtures, further ultrasonicated for 1 h to ensure proper dispersion (high energy ultrasonication, Vibracell 75043, 750 W). Curing agent was then added into the mixture at a epoxy/amine weight ratio of 100/58.

Coatings for further surface characterization were prepared by spraying onto stainless steel plates (100 mm × 100 mm), previously cleaned with ethanol and dried at room temperature for 10 min, with an Airbrush AB300 aerograph (air pressure of 1 atm) to simulate real application. Samples were cured for 1 h at 70 °C and post-cured for 1 h at 135 °C. Uniform coatings (thickness

Table 1
Composition (wt%) and nomenclature of nanocomposite samples prepared.

Sample	Epoxy	SBS	CNT
E0-0	100	0	0
E0-02	99.8	0	0.2
E0-05	99.5	0	0.5
E0-1	99	0	1
E5-0	95	5	0
E5-02	94.8	5	0.2
E5-05	94.5	5	0.5
E5-1	94	5	1
E10-0	90	10	0
E10-02	89.8	10	0.2
E10-05	89.5	10	0.5
E10-1	89	10	1
E20-0	80	20	0
E20-02	79.8	20	0.2
E20-05	79.5	20	0.5
E20-1	79	20	1

40–70 μm) with different amounts of ep52SBS (0, 5, 10 and 20 wt%) and a-MWCNT (0, 0.2, 0.5 and 1 wt%) were prepared. Table 1 shows a resume of samples prepared by this methodology together with the nomenclature of nanocomposites, where Ei-j denotes epoxi-based composite, being i the amount of block copolymer and j the amount of nanotubes.

2.3. Characterization techniques

Morphology of samples and MWCNT dispersion were studied by atomic force microscopy (AFM). Topography and phase images of the cross section of samples were recorded in tapping mode (TM-AFM), under air and room temperature conditions, by using a scanning probe microscope (Nanoscope IV, Dimension 3100 from Digital Instruments). Phosphorus-doped (n-type) silicon probes and a single-beam cantilever (125 μm length) having a tip nominal radius of curvature of 5–10 nm were used. Typical scan rates during recording were 1 line per second. Samples were cut in their transversal section using an ultramicrotome (Leica Ultracut R) equipped with a diamond knife.

Contact angle measurements were carried out using a Dataphysics OCA 20 contact angle system. Measurements were made in air at room temperature by sessile drop technique with water as wetting liquid. A drop volume of 1 μL was used. To determine the uniformity of surfaces, measurements were repeated 5–10 times on different specimens of the same sample. Before measurements, droplets were maintained in contact with the surface for 60 s.

Abrasion tests were performed using a Taber Industries 5135 abraser, with two CS10 wheels of elastomeric and aluminum oxide particles working at 70 rpm. Weight loss of coatings was measured after 500 cycles. Each test was repeated at least three times.

Thermogravimetric analysis (TGA) was carried out using Mettler Toledo TGA/SDTA 851 thermal analyzer equipment at heating rates of 10 °C/min, in the range from 25 to 700 °C (to determinate char amount at 700 °C). Tests were performed in dynamic mode to cover a wide range of thermal conditions under nitrogen atmosphere (flow rate 20 mL/min). TGA tests were performed in alumina crucibles. The average weight of tested samples was approximately 3 mg.

3. Results and discussion

Nanostructures generated on thermosetting systems after curing were analyzed by TM-AFM. Firstly, morphologies achieved for cured epoxy/ep52SBS systems with different copolymer contents using a mixture of THF/DMF as casting solvent are shown, followed by the analysis of a-MWCNT addition on the morphologies.