



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™) 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 an epoxidation degree of 52% (mol% of epoxidized polybutadiene units) as calculated by ¹H 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 an 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 epoxy-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 Data-physics 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 determine 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.

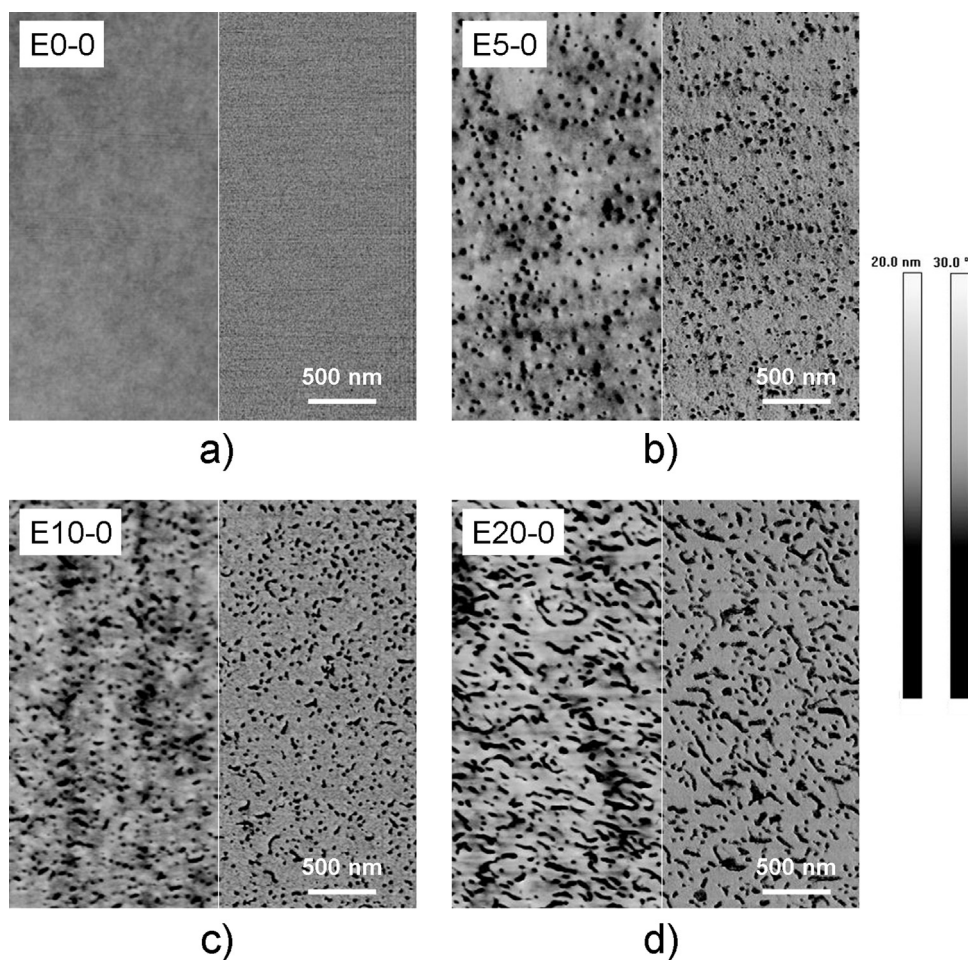


Fig. 1. Cross-sectional TM-AFM height (left) and phase (right) images ($3 \mu\text{m} \times 3 \mu\text{m}$) for epoxy systems containing: (a) 0, (b) 5, (c) 10 and (d) 20 wt% ep52SBS block copolymer.

Images were taken in cross section of coatings. Fig. 1 shows TM-AFM images for thermosetting mixtures containing 0 (Fig. 1a), 5 (Fig. 1b), 10 (Fig. 1c) and 20 (Fig. 1d) wt% of ep52SBS. It should be noted that all cured mixtures containing block copolymer exhibited microphase-separated morphologies.

The segregation of PS block increased with block copolymer content (that is, size of PS domains increased with block copolymer content), displaying different microstructural features: spherical micelles of PS block in the epoxy matrix for the mixture with 5 wt% ep52SBS (E5-0), and worm-like micelles for mixtures with 10 (E10-0) and 20 (E20-0) wt%, being these micelles longer in the case of 20 wt% ep52SBS content. Those coatings made by spraying, showed similar morphologies to those previously found by our group for the same copolymer and epoxy resin using another amine curing agent [15], solvent [13] or procedure to prepare the coatings [13,15].

A THF/DMF mixture was chosen as solvent for epoxy-based coatings. The a-MWCNT dispersion ability is greater in DMF than in other solvents due to intensive van der Waals interaction between the carboxylic acid groups on MWCNT sidewalls and DMF as compared with methanol or water [30]. THF was added to decrease the evaporation temperature of the casting solvent.

The addition of carbon nanotubes did not modify achieved nanostructured morphologies, being very similar to those of epoxy/block copolymer samples without nanotubes. As Fig. 2 shows for unmodified (E0-02) and Fig. 3 for 10 wt% ep52SBS-modified (E10-02) matrices containing 0.2 wt% of a-MWCNT, the presence of block copolymer improved the dispersion of a-MWCNT in the nanostructured matrix. Due to the high strength of nanotubes to be cut, and to the fact that images show the cross section

of coatings, nanotubes appear as white dots in the height and phase images. Agglomerates, as regions with high concentration of nanotubes and regions with lack of them, present in epoxy/MWCNT mixture composites (Fig. 2) were not observed for the ternary systems (Fig. 3), because the block copolymer acted as dispersing agent [12,31]. The π - π stacking interactions between nanotube walls and aromatic rings into microphase separated PS domains [16], as well as the interactions between the carboxylic acid groups and epoxy matrix [28] seemed to act synergistically to improve dispersion of nanotubes. This improvement can be seen in the height images, in which several bright dots (present in Image 3), corresponding to isolated carbon nanotubes, can be seen dispersed into the matrix.

Fig. 4 shows the cross-sectional AFM images for epoxy composites modified with 20 wt% ep52SBS containing 0.2 (E20-02) and 0.5 (E20-05) wt% a-MWCNT, confirming the dispersion of a-MWCNT into the nanostructured matrix. A comparison between Figs. 1 and 4 shows that nanostructuring was not significantly affected by the addition of a-MWCNT.

In order to analyze the effect of block copolymer and a-MWCNT on the surface properties of composites, both contact angle and wear resistance measurements were carried out for all systems. As indicated by AFM height images [32,33] of coating surfaces (not shown here), Root-Mean-Squared roughness values (RMS) for unfilled systems were very similar to those of filled ones. Therefore, the roughness contribution to contact angle and wear measurements was similar in both cases. For that reason, roughness was not considered when contact angle and wear variations were observed.

Fig. 5 shows images of water drops in the surface of unfilled epoxy coatings modified with different block copolymer

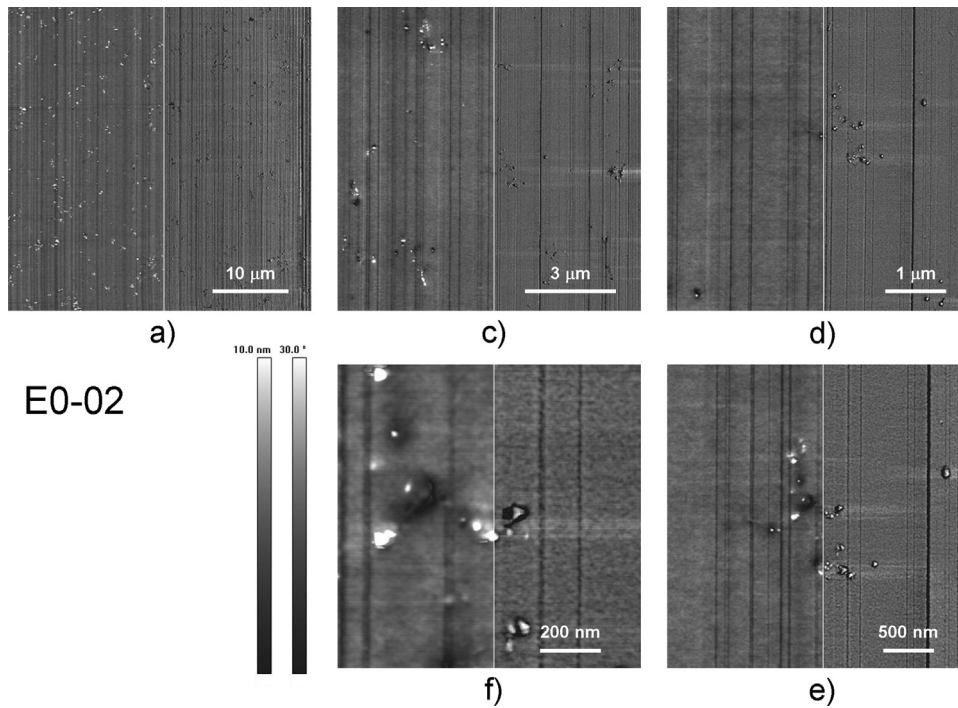


Fig. 2. Cross-sectional TM-AFM height (left) and phase (right) images of epoxy systems containing 0.2 wt% a-MWCNT at different scan sizes: (a) $40\ \mu\text{m} \times 40\ \mu\text{m}$, (b) $10\ \mu\text{m} \times 10\ \mu\text{m}$, (c) $5\ \mu\text{m} \times 5\ \mu\text{m}$, (d) $3\ \mu\text{m} \times 3\ \mu\text{m}$, and (e) $1\ \mu\text{m} \times 1\ \mu\text{m}$.

contents. Fig. 6 represents the variation of contact angle for epoxy matrix composites containing several ep52SBS and a-MWCNT contents (Fig. 6a), and the variation of contact angle with the increase of ep52SBS content in both epoxy/0.5 wt% a-MWCNT and epoxy/0.5 wt% non-functionalized MWCNT composite coatings (Fig. 6b). It is worth noting that the contact angle for unmodified epoxy matrix was around 86° . From Fig. 6a, it can be seen that independently of a-MWCNT content, contact angle values

increased significantly with the addition of ep52SBS. The increase was observed mainly for 5 wt% block copolymer content (E5-j) and then remained constant. This increase is due to the lower surface energy of PB block respect to the rest of components [23,24], the hydrophobic nature of block copolymer [25,26] and the morphology generated in each modified epoxy-based system. Exceptionally, the system containing 5 wt% ep52SBS block copolymer (E5-j) exhibited higher contact angle, probably due to microphase separation

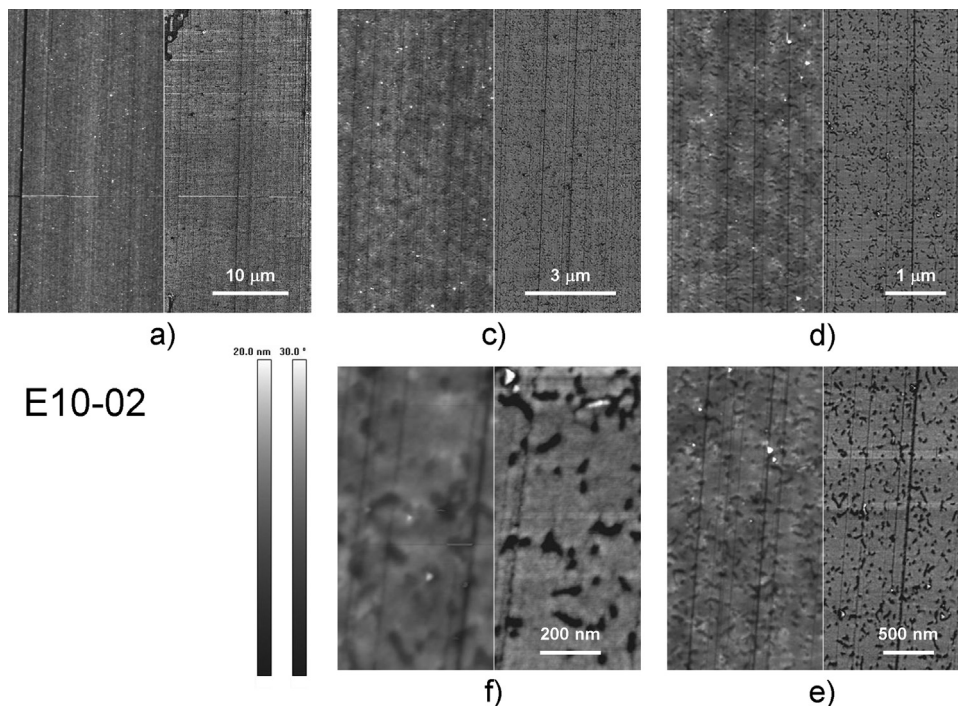


Fig. 3. Cross-sectional TM-AFM height (left) and phase (right) images of epoxy systems containing 10 wt% ep52SBS and 0.2 wt% a-MWCNT at different scan sizes: (a) $40\ \mu\text{m} \times 40\ \mu\text{m}$, (b) $10\ \mu\text{m} \times 10\ \mu\text{m}$, (c) $5\ \mu\text{m} \times 5\ \mu\text{m}$, (d) $3\ \mu\text{m} \times 3\ \mu\text{m}$, and (e) $1\ \mu\text{m} \times 1\ \mu\text{m}$.

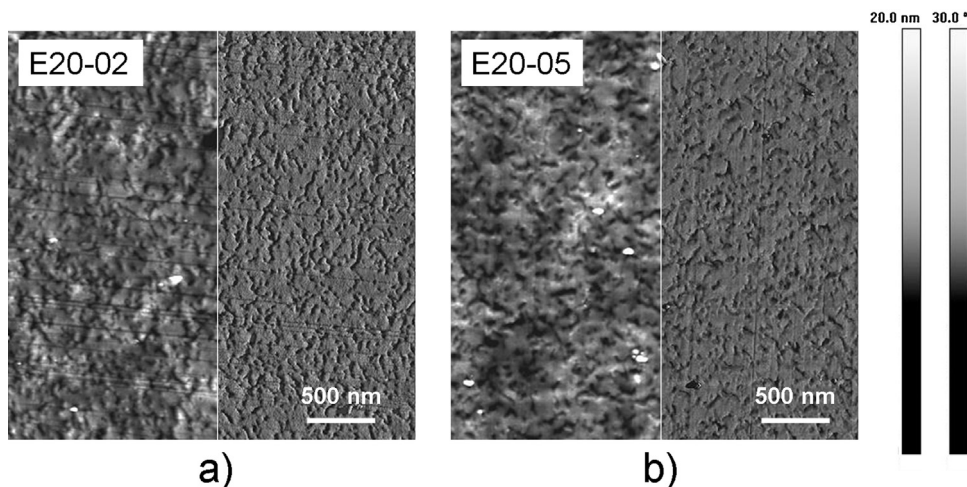


Fig. 4. Cross-sectional TM-AFM height (left) and phase (right) images ($3 \mu\text{m} \times 3 \mu\text{m}$) of epoxy systems containing 20 wt% ep52SBS with: (a) 0.2 wt% and (b) 0.5 wt% a-MWCNT.

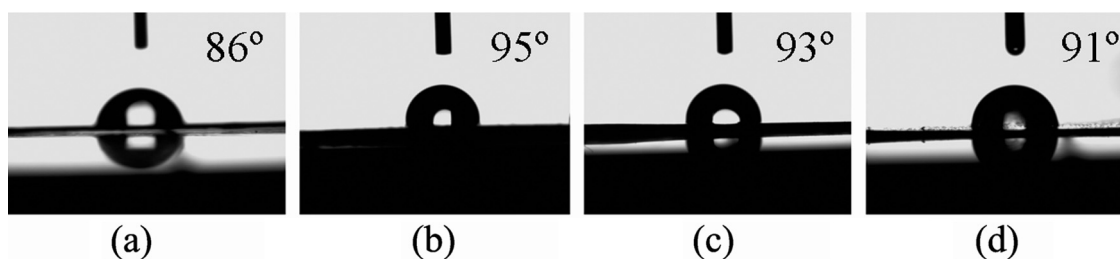


Fig. 5. Images of a water drop in the surface of epoxy systems modified with different amounts of ep52SBS: (a) 0, (b) 5, (c) 10, and (d) 20 wt%.

of PS block into small and regular spherical micelles [34,35]. On the other hand, the presence of a-MWCNT showed the opposite effect on surface hydrophobicity. For a particular block copolymer content, a decrease in contact angle measurement with the increase of a-MWCNT content was observed. This decrease was probably due to the change of surface charge or polarity produced by the addition of a-MWCNT [36].

From Fig. 6b it can be seen that for each ep52SBS content (Ei-05), systems containing non-functionalized MWCNT showed higher hydrophobicity than those with a-MWCNT. The increase in interfacial wettability in systems with a-MWCNT can be attributed to a change of charge or polarity of the composite surface produced by the nanotubes [36].

Regarding the wear behavior of epoxy coatings, a uniform dispersion of MWCNT in polymer composites would contribute to

increase their wear resistance [37,38]. Jacobs et al. showed that epoxy composites reinforced with nanoparticles mostly exhibited a wear minimum of 1–2 wt% of that of nanofillers, for most nanoparticle types [28].

Fig. 7 shows the weight loss of block copolymer-modified epoxy matrices containing 1 wt% a-MWCNT (Ei-1) compared with that of unfilled one (Ei-0) after 500 abrasion cycles at 70 rpm. For each ep52SBS content, samples filled with 1 wt% a-MWCNT showed a slightly lower weight loss value (in terms of arithmetic mean values) than the corresponding unfilled matrices. For nanocomposites filled with 1 wt% a-MWCNT (Ei-1), abrasive particles generated at initial wear cycles should have a high weight percentage of a-MWCNT. The presence of a-MWCNT on air/polymer interface was confirmed by AFM and contact angle measurements. These particles with high percentage of a-MWCNT could be dispersed on the

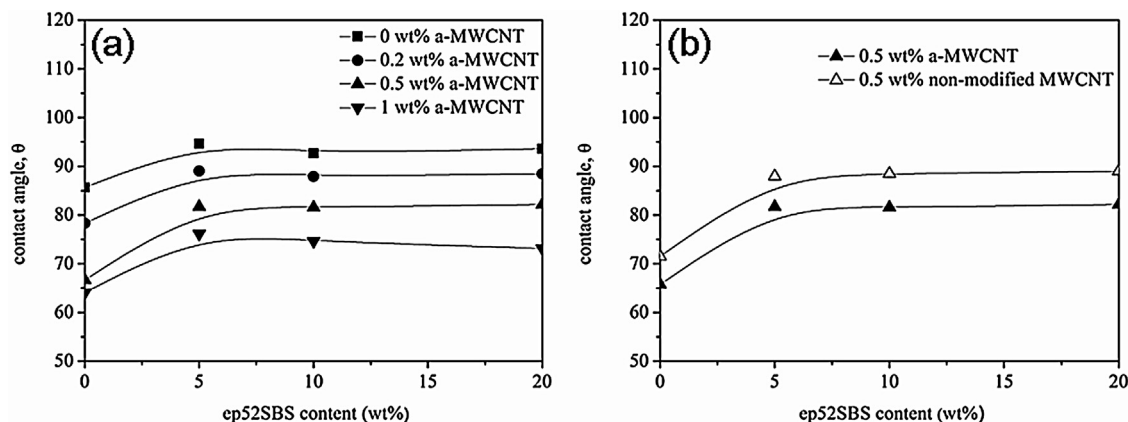


Fig. 6. Variation of contact angle with ep52SBS for: (a) several a-MWCNT contents; (b) acid-modified and non-modified 0.5 wt% MWCNT (lines used as guide for visualization).

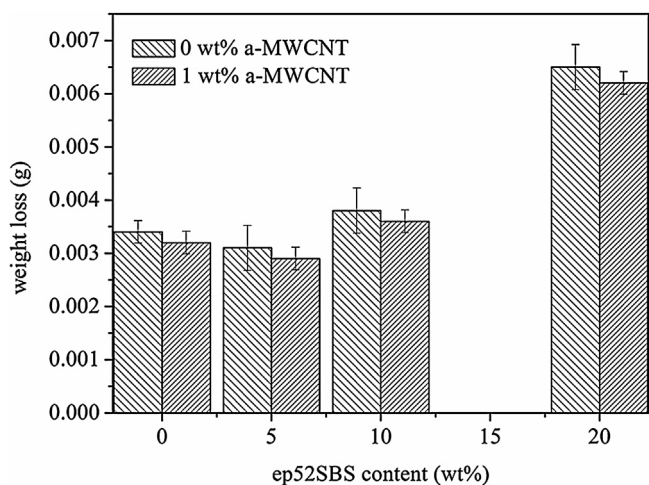


Fig. 7. Evolution of weight loss after 500 abrasion cycles for all systems.

worn surface and over the abrasive wheel surface during wear test. If so, this could serve as solid lubricant, covering the worn surface and preventing the direct contact between nanostructured coating and abrasive wheel, thereby reducing the weight loss [37,38].

Thermal stability of epoxy composites modified with block copolymer was analyzed by determining the temperature of 5% of weight loss (T_5) related with the beginning of degradation, the temperature of the maximum rate weight loss (T_{max}) calculated from the peak at the derivative weight loss curve, and the relative residual weight remaining at 700 °C (R_{700}), composed by polymeric char and non-degraded carbon nanotubes.

DTG (differential thermogravimetric) representations are shown in Fig. 8 while results are summarized in Table 2. For block copolymer-modified epoxy matrices (epoxy/ep52SBS) (Ei-0), T_5 was around 375 °C under nitrogen atmosphere. The addition of block copolymer did not cause a significant reduction of thermal stability because the high concentrations of aromatic rings

and epoxy groups in the repeating units of block copolymer could improve thermal stability of matrices [39]. On the other hand, the incorporation of 0.2 wt% a-MWCNT (Ei-02) provided a slight shift of thermal stability to higher values (around 2%) with respect to unfilled nanostructured matrices (Ei-0). This improvement could be attributed to the thermal stability of a-MWCNT and the possible interactions between the a-MWCNT and ether or amide linkages of epoxy matrix, from which the epoxy degradation is known to occur. Thus, a slight delaying in the degradation process was observed. This shift of thermal stability can be also observed by the increase in solid residue (R_{700}) [40]. However, for high weight percent of a-MWCNT (E5-1), T_5 was lower than that of E5-0.2, probably due to the increase of thermal conductivity of the polymer [40,41].

4. Conclusions

Coatings based on a commercial epoxy resin nanostructured with an epoxidized SBS triblock copolymer and filled with several amounts of carboxylic acid-functionalized multiwalled carbon nanotubes were prepared. The dispersion of nanotubes was improved as compared with MWCNT-filled epoxy systems without block copolymer, while the morphology of modified epoxy matrix did not seem to be affected by the presence of carboxylic acid functionalized MWCNT.

Hydrophobicity of coatings increased with the addition of block copolymer. However, MWCNT functionalized with carboxylic acid groups decreased the contact angle probably due to a change in the polarity or charge of the coating surface.

Tribological property and thermal stability results of coatings depend on the block copolymer and carbon nanotubes content. Despite the fact that wear resistance values of composites with nanotubes are within the error bars of the corresponding systems without nanotubes, it should be pointed out that the main decrease of around 6% of the mean value was observed for the system with 5 wt% ep52SBS and 1 wt% a-MWCNT (E5-1), with respect to that of neat epoxy (E5-0). Meanwhile, in the case of systems with

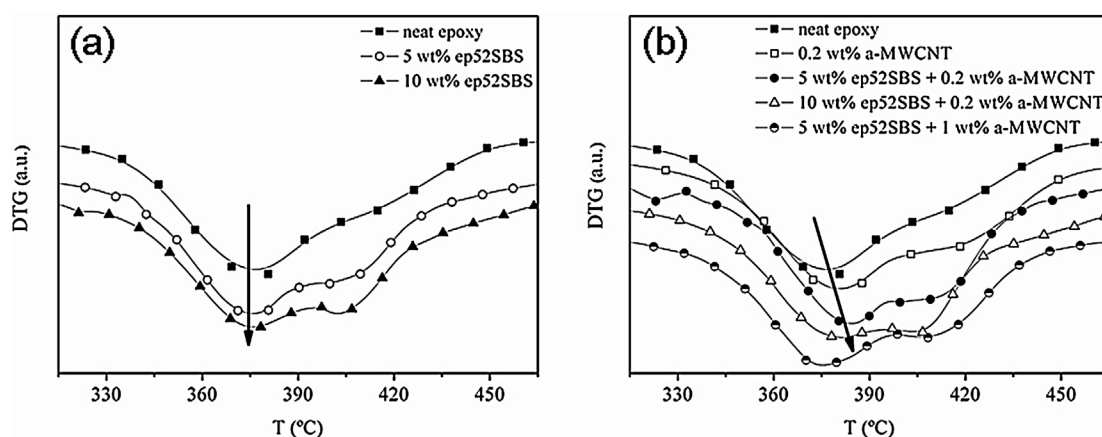


Fig. 8. Differential thermogravimetric (DTG) curves of cured epoxy modified with 5 and 10 wt% ep52SBS: (a) without wt% a-MWCNT, (b) with several a-MWCNT contents.

Table 2

TGA results for thermal degradation of epoxy/ep52SBS/a-MWCNT nanocomposites.

SBS	CNT								
	Ei-0			Ei-02			Ei-1		
	T_5	T_{max}	R_{700}	T_5	T_{max}	R_{700}	T_5	T_{max}	R_{700}
E0-j	332	374	16	334	380	20	–	–	–
E5-j	336	375	16	348	384	19	343	377	20
E10-j	337	375	16	345	383	18	–	–	–

0.2 wt% a-MWCNT (Ei-0.2) a 2% increase of thermal performance was shown.

According to the behavior of the designed coatings and the requirements to further improvement of superficial properties, nanostructured epoxy coatings filled with a-MWCNT could be an interesting alternative for industrial coatings.

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