



# Transparent epoxy coatings with improved electrical, barrier and thermal features made of mechanically dispersed carbon nanotubes



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## ABSTRACT

Epoxy thin coatings, containing 0.025–0.5 wt.% of carbon nanotubes (CNT), exhibited outstanding combination of transparent and surface conductive properties, showing transparency up to 83% and electrical surface resistivity decreased by up to 10 orders of magnitude, accompanied by the highest chemical resistance to methyl-ethyl ketone, improved thermal stability up to 20 °C, perfect adhesion and considerable hardness. Such significant improvement of numerous properties of coatings was possible thanks to the use of neutralized o-tolylbiguanide/epoxy resin dispersing medium characterized by low viscosity and strong tendency to create  $\pi$ - $\pi$  electron interactions with CNT. This enabled non-covalent functionalization and dispersion of CNT in varnish via common, industrially applicable one-step process, driven by mechanical mixing.

## 1. Introduction

The presence of dispersed carbon nanotubes (CNT) in epoxy coatings in amount of below 0.5 wt.% significantly improves many of their properties, i.e. electrical conductivity [1–7], electric heating behavior [4], corrosion resistance [6–16], barrier [10], galvanic protection [10], glass transition temperature [1–3], thermal stability [6,16–18], hardness [2,19], storage modulus [1–3], Young modulus [17], tensile strength [20], elongation at break [20], adhesion [7,12–15,17], flexibility [15], hydrophobicity [14] as well as resistances to environmental degradation [5], abrasion [12,18], impact [8,16], bending [8], cupping [8], scratch [1] and wear [17,19].

Unluckily, there are some substantial problems with CNT-modified epoxy coatings which makes them unattractive for implementation. Although raw CNT are getting cheaper, they need complicated procedures to be effectively dispersed in epoxy matrices which hinders their implementation in industrial practice. Mentioned procedures include covalent functionalization [9–11,13,15,16,18,20], and dispersion by certain relatively expensive and complicated techniques, i.e. sonication [1,2,4,12,15–18,21–25] and pearl/ball milling [7–9,13,14,20]. Nowadays the coating industry resigns from fillers which cannot be dispersed by mechanical mixing using standard solvents and, moreover, it is not interested in irrationally expensive additives, like covalently

functionalized carbon nanostructures. So far, there are no available reports on efficient dispersion of raw CNT as primary nanofiller in liquid epoxy paints via mechanical mixing using industrially-scalable stirrers.

Furthermore, epoxy layers with CNT do not show significant visual properties [1–16], i.e. transparency and gloss, despite commonly known excellent transparent and glossy features of unmodified epoxy coatings. It can be caused by low compatibility between CNT and popular amine curing agents, as well as some non-aromatic epoxy resins, resulting in unsatisfactory CNT dispersion efficiency. Although there are more transparent carbon nanofillers, i.e. graphene and its derivatives, they do not give sufficient electrical properties to coatings when they are in powder form [4,24].

In current study we used o-tolylbiguanide in neutralized aqueous solution in triple role of amine hardener, CNT dispersing agent, and coating composition viscosity depressant. In result, commercially available CNT were successfully dispersed in water-thinnable epoxy compositions via common mechanical mixing. Subsequently, we prepared epoxy coatings and investigated their nanostructure as well as electrical, visual, functional and thermal properties.

**Abbreviations:** AA, acetic acid; AHEW, amine hydrogen equivalent weight; AHF, amine hydrogen functionality; a.u., auxiliary unit; CGE, o-cresyl glycidyl ether; CNT, carbon nanotubes; DGEBF, bisphenol F diglycidyl ether; DSC, differential scanning calorimetry; EDG, electron donating group; EDX, energy dispersive X-ray spectrometry; EEW, epoxy equivalent weight; EWG, electron withdrawing group; f-CNT, functionalized carbon nanotubes; G.U., gloss unit; MEK, methyl-ethyl ketone; n-TBG, aqueous solution of o-tolylbiguanide neutralized by acetic acid;  $R_s$ , electrical surface resistivity (sheet resistance); TBG, o-tolylbiguanide; TEM, transmission electron microscopy;  $T_g$ , glass transition temperature; TGA, thermogravimetric analysis; wt.%, weight (mass) percent; XDA, m-xylylenediamine

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## 2. Experimental

### 2.1. Materials

A) Bisphenol F diglycidyl ether (DGEBF), characterized by viscosity 3 500 mPa·s (at 25 °C), epoxy equivalent weight (EEW) 169 g·equiv.<sup>-1</sup> (Epon 862; Hexion, USA); B) o-cresyl glycidyl ether (CGE), viscosity 8 mPa·s (25 °C), EEW 164 g·equiv.<sup>-1</sup> (EKG; Ciech, Poland); C) o-tolylbiguanide (TBG), melting point 144 °C, amine hydrogen equivalent weight (AHEW) 32 g·equiv.<sup>-1</sup>, amine hydrogen functionality (AHF) 6 (Sigma-Aldrich, Germany); D) acetic acid (AA) aqueous solution (71%, Chempur, Poland); E) m-xylylenediamine (XDA), viscosity 7 mPa·s (23 °C), AHEW 34 g·equiv.<sup>-1</sup>, AHF 4, (Sigma-Aldrich, Germany); F) multi-walled carbon nanotubes, average length 1.5 μm, average diameter 15 nm, average specific surface 275 m<sup>2</sup>·g<sup>-1</sup> (Nanocyl, Belgium).

### 2.2. CNT dispersion and preparation of coatings

TBG was dissolved/neutralized in acetic acid aqueous solution. Then DGEBF/CGE epoxy resin (80/20 m/m) was added and the mixture was kept in ambient conditions, shaken periodically, to obtain a solution. CNT were added to the solution in amounts of 0.025–0.5 wt.% of dry mass of coating and dispersed using Dispermat LC30 mechanical mixer (VMA, Germany) equipped with ø40 mm disc for ¾ h at 5800 rpm. In order to prepare a coating composition, a CNT epoxy/TBG dispersion was mixed with XDA in epoxy/XDA weight ratio of 10:1. Then, such varnish was applied onto glass (4 mm-thick, 88% transparency at 700 nm wavelength) or silicone substrate using 30 μm gap applicator and cured in air atmosphere for ½ h at 200 °C to obtain coatings with a thickness of 24 ± 1 μm. The detailed composition of all prepared dispersions and varnishes is presented in Table 1; numbers in acronyms mean CNT content (wt.%) in dry coatings.

### 2.3. Performed cured coatings investigations

A) Nanostructure, (i) transmission electron microscope (TEM) with energy dispersive X-ray spectrometer (EDX) Tecnai F30 (FEI Corp.), samples delaminated from silicone, embedded in resin and cut crosswise into thin slices using microtome; (ii) scanning electron microscope (SEM) SU8020 (Hitachi) samples delaminated from silicone. B) Electrical surface resistivity/sheet resistance (R<sub>s</sub>), 6487 electrometer with electrode set 8009 (Keithley), glass substrate, 10 V, 20 °C, 50% of relative humidity (RH), 10 measurements of each sample. C) Transparency at 700 nm wavelength, UV-vis spectrophotometer V-630 (Jasco), glass substrate, 5 measurements of each sample. D) Gloss at 20° and haze, IQ20/60/85 device (Rhopoint Instruments), in compliance with the ISO 2813 standard, 5 measurements. E) Chemical resistance to methyl-ethyl ketone (MEK), rubbing test, according to EN 13523-11 standard, 3 measurements. F) Adhesion to glass, cross-cut test,

**Table 1**  
Composition of epoxy varnishes with CNT.

Sample acronym	Coating composition components (wt. part)					
	CNT <sup>a</sup>	DGEBF/CGE	TBG	H <sub>2</sub> O	AA	XDA
E-0	0	64/16	12	9 <sup>b</sup>	22 <sup>b</sup>	8
E-C0.025	0.025					
E-C0.05	0.05					
E-C0.1	0.1					
E-C0.15	0.15					
E-C0.2	0.2					
E-C0.25	0.25					
E-C0.5	0.5					

<sup>a</sup> CNT content in wt.% of dry coating.

<sup>b</sup> component evaporates during curing.

according to EN ISO 2409 standard, 3 measurements. G) Hardness, AWS-5 König pendulum (Dozafil), 20 °C, 50% of RH, 5 measurements. H) Glass transition temperature (T<sub>g</sub>), DSC Q100 calorimeter (TA Instruments), hermetic aluminum pan, range -20–180 °C, 5 °C min<sup>-1</sup>, air atmosphere. I) Thermal stability, TGA Q5000 thermoanalyzer (TA Instruments), platinum pan, range 20–600 °C, 10 °C min<sup>-1</sup>, air atmosphere.

## 3. Results and discussion

### 3.1. Preparation and nanostructure of coatings

Preparation scheme of the coatings is presented in Fig. 1. TBG is solid, so it was neutralized using an aqueous solution of AA to apply it in a liquid dispersing medium. Next, the neutralized TBG (*n*-TBG) was mixed with epoxy resin containing DGEBF and CGE to prepare a dispersing medium for CNT. The medium exhibited viscosity of ca. 70 mPa·s, which was considerably lower than bisphenol A-based epoxy resin usually used for CNT dispersion [1,2,4,6,17]. The medium remains liquid in a hermetic vessel, because AA prevents reaction of TBG amino groups with epoxy. The CNT were added and dispersed in the medium via common mechanical mixing. All prepared dispersions were stable for at least 3 months. In order to make a coating, a CNT dispersion was mixed with XDA as a secondary hardener to prepare a varnish. The varnish was applied as a thin layer onto a substrate and cured at elevated temperature. At this stage volatile components, i.e. water and AA, evaporated, unblocking TBG reactive groups. The efficiency of the nanofiller dispersion is depicted in SEM micrographs (Fig. 2), which show the CNT tangled agglomerate (Fig. 2A) and effectively dispersed CNT inside the cured coating (seen at the sample breakthrough, Fig. 2B). Moreover, the average diameter of CNT in Fig. 2A (14–16 nm) was three times lower than CNT sticking out of coating breakthrough in Fig. 2B (31–62 nm). This shows, that the nanofiller in cured sample was coated by 8–16 nm layer of a material from polymer matrix, and the adhesion of the material to CNT was stronger than cohesion with cured epoxy sample. Transmission electron microscopy (TEM) images in Fig. 1A and B present raw CNT and CNT in the cured coating, respectively. CNT in Fig. 1B were effectively coated by thin layer of a material; places on the CNT uncoated and coated by the material are marked by arrows (1) and (2), respectively. Energy dispersive X-ray spectrum (EDX) of this area contains major peak corresponding to carbon and smaller peaks corresponding to oxygen (present in epoxy), and nitrogen (represented mainly by TBG, because XDA and its AA neutralized derivative showed unsatisfactory dispersing properties to the CNT in preliminary tests).

These results showed that CNT were non-covalently functionalized by *n*-TBG and epoxy during mechanical mixing. This can occur due to the π-π electron interactions of CNT aromatic structure with aromatic rings of *n*-TBG or epoxy components. It is noteworthy, that electron poor aromatic rings of *n*-TBG, which are under electron-withdrawing inductive effect of protonated ammonium groups create stronger π-π electron interactions than DGEBF and CGE, whose aromatic rings are under two opposing effects, i.e. inductive and mesomeric. Such functionalized CNT (f-CNT) formed well dispersed nanostructure inside the cured coatings, confirmed by TEM and SEM observations (Fig. 1C and B, respectively). The *n*-TBG/epoxy mixture showed significant ability to untangle raw CNT (Fig. 2A and B) using relatively low shear forces in mechanical mixing process and, moreover, chemical affinity enabling efficient CNT wetting and the formation of thin polymer layers on CNT surface (Figs. 1 B and 2 B).

### 3.2. Electrical and optical properties of coatings

Prepared CNT-filled coatings exhibited excellent logarithmic reduction of electrical surface resistivity (R<sub>s</sub>) from 1 × 10<sup>15</sup> Ω (sample E-0) to 9 × 10<sup>4</sup> Ω (E-C0.5) with percolation threshold at CNT loading of

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