

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

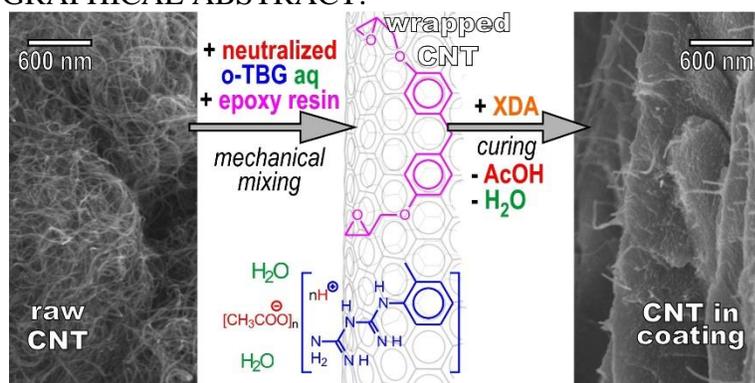
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ABSTRACT: Epoxy thin coatings, containing 0.025-0.5 wt.% of carbon nanotubes (CNT), exhibited outstanding combination of transparent and surface conductive properties, showing transparency up to 83% and electrical surface resistivity decreased by up 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 π - π 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.

GRAPHICAL ABSTRACT:



KEYWORDS: Coatings; Carbon nanotubes non-covalent functionalization; Tolybiguanide;

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.

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.⁻¹ (Epon 862; Hexion, USA); B) o-cresyl glycidyl ether (CGE), viscosity 8 mPa·s (25 °C), EEW 164 g·equiv.⁻¹ (EKG; Ciech, Poland); C) o-tolylbiguanide (TBG), melting point 144 °C, amine hydrogen equivalent weight (AHEW) 32 g·equiv.⁻¹, 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.⁻¹, AHF 4, (Sigma-Aldrich, Germany); F) multi-walled carbon nanotubes, average length 1.5 μm, average diameter 15 nm, average specific surface 275 m²·g⁻¹ (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_s), 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, 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_g), DSC Q100 calorimeter (TA Instruments), hermetic aluminum pan, range -20 – 180 °C, 5 °C·min⁻¹, air atmosphere. I) Thermal stability, TGA Q5000 thermoanalyzer (TA Instruments), platinum pan, range 20–600 °C, 10 °C·min⁻¹, air atmosphere.

3. RESULTS AND DISCUSSION

3.1. Preparation and nanostructure of coatings

Preparation scheme of the coatings is presented in Figure 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 (Figure 2), which show the CNT tangled agglomerate (Figure 2A) and effectively dispersed CNT inside the cured coating (seen at the sample breakthrough, Figure 2B). Moreover, the average diameter of CNT in Figure 2A (14-16 nm) was three times lower than CNT sticking out of coating breakthrough in Figure 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 Figure 1A and 1B present raw CNT and CNT in the cured coating, respectively. CNT in Figure 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 (Figures 1C and 2B, respectively). The n-TBG/epoxy mixture showed significant ability to untangle raw CNT (Figures 2A and 2B) 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 (Figures 1B and 2B).

3.2. Electrical and optical properties of coatings

Prepared CNT-filled coatings exhibited excellent logarithmic reduction of electrical surface resistivity (R_s) from $1 \cdot 10^{15} \Omega$ (sample E-0) to $9 \cdot 10^4 \Omega$ (E-C0.5) with percolation threshold at CNT loading of 0.025-0.05 wt.%, which is shown in Figure 3. A rapid decrease of R_s (7 orders of magnitude) was observed for CNT contents from 0.025 to 0.1 wt.%. For samples containing from

0.1 to 0.5 wt.% of CNT the R_S decrease was smaller (3 orders of magnitude). Unfortunately, there was not possible to obtain coatings with higher CNT content due to growing viscosity of coating compositions, although the decreasing trend of R_S in function of CNT content (presented in Figure 3) allows to estimate the R_S value for hypothetical coating with 1 wt.% of CNT to ca. $5 \cdot 10^2 \Omega$. Preferably, the achieved CNT content at percolation threshold (0.025-0.05 wt.%, Figure 3) is heretofore one of the lowest published results, competing only with UV-cured coatings of unpublished transparency prepared by Sangermano et al. (percolation threshold also at 0.025-0.05 wt.%) [3]. Moreover, the achieved result is considerably more favorable than results of coatings prepared from UV-cured (0.05-0.2 wt.% [1,2,21]), solvent-borne (>1 wt.% [22,23]), water-borne (0.4-0.8 wt.%, [24,25]) or solventless (0.1-0.3 wt.% [26]) coating systems. It is noteworthy, that the lowest CNT contents at percolation thresholds were observed for coating systems containing a component with (i) at least one aromatic ring with an strong electron withdrawing group (EWG), or electron donating group (EDG) and, (ii) an asymmetry of component molecule. An aromatic ring with an EWG or EDG interacts with CNT creating π - π electron interactions, whereas an asymmetry of whole molecule provides steric stabilization of such functionalized nanoparticles in coating composition [26]. Such structure constitutes 1-hydroxycyclohexyl phenyl ketone [21], phenalkamine [26], triphenylsulfonium hexafluoroantimonate [1-3], n-TBG (used in current work), as well as popular sodium dodecylbenzenesulfonate used for preparing stable CNT dispersions in water [27]. Coatings based on aromatic molecules without strong EWG/EDG groups [22,23] or symmetrically constructed [22,23,26] are characterized by considerably higher CNT contents at percolation threshold.

Thus the presence of only 0.025 wt.% (250 ppm) of CNT gave static dissipative feature to the coating according to ANSI/ESD S541 standard ($R_S=8 \cdot 10^9 \Omega$ for E-C0.025). It must be underlined, that static dissipative coatings with 0.025-0.05 wt.% of CNT exhibited top transparency (81-83%) which is presented in Figure 3. As can be seen, this parameter decreased proportionally to the CNT content. To discuss the real importance of the achieved results of transparency, they should be correlated with R_S , because CNT always partially reduce transparency of coating materials [21-25]. Figure 4 presents transparency and R_S of prepared coatings in comparison with materials whose both R_S and transparency was previously described in the literature [21-25]. This comparison includes only coatings prepared by application of a CNT-filled varnish onto a substrate. It does not include composite films with carbon layers applied in a separate process, e.g. [28]. The comparison is presented as a R_S reduction in correlation with a relative transparency. These two parameters were introduced for easier evaluation of conductive and transparent properties of various coating systems with CNT, characterized by different layer thickness, CNT contents, CNT concentration units, CNT types, and R_S or transparency values of reference samples, as well. The dimensionless R_S reduction expresses how many times lower is R_S of a CNT modified sample compared to an unfilled coating, whereas the relative transparency shows how much smaller is transparency of the sample compared to the unfilled coating. Successfully, prepared coatings exhibited the most advantageous R_S reduction depending on the relative transparency in comparison with literature results (Figure 4). Especially samples E-C0.025 and E-C0.05, showed R_S reduced by 5-7 orders of magnitude at practically unchanged transparency (relative transparency 98-96%). The higher transparency of prepared CNT-modified coatings in comparison with previous studies can result from better CNT dispersion in polymer matrix. It is worth noting, that figures 1C and 2B show more uniform CNT dispersion than SEM/TEM images presented in previous works [1,3,4,21,22,24,25]. Furthermore, samples containing up to 0.25 wt.% of CNT showed gloss over 120 G.U. and zero haze (Figure 5), so they can be classified as high-glossy according to ISO 2813. Only sample E-C0.5 exhibited medium gloss and nonzero haze. Observed

changes of gloss and haze in function of CNT content can be caused by growing amount of CNT which increased coatings roughness and reduced light reflection.

Innovative aspect resulting from optical/electrical features of prepared coatings can be described as follows: (i) to the best of our knowledge, prepared coatings are characterized by the most advantageous combination of antistatic/conductive and transparent properties of all the analogical CNT-modified coating materials described by others [1-25]; (ii) these properties were achieved by using commercially available CNT; (iii) the CNT were dispersed in liquid coating compositions using industrially-scalable mechanical mixer, which is a smaller version of dissolvers widely used in coating industry (unlike ultrasonic mixers and pearl/ball mills used by others [1,2,4,7-9,12-18,20-25]). Mechanical mixer generates much less shearing forces than ultrasonic devices, therefore a medium exhibiting much better CNT dispersing properties is essential to prepare a good nanofiller dispersion, such as epoxy/n-TBG dispersing medium used in this work. Because dispersing of CNT in neat epoxy resin does not apparently give satisfactory optical properties to coatings [1-16], a component exhibiting stronger affinity for CNT (such as n-TBG) can play a key role in formulation of coatings showing better optical/conductive properties.

3.3. Functional and thermal properties of coatings

The excellent optical/electrical features of prepared epoxy coatings were accompanied by top functional properties, i.e. chemical resistance to MEK, cross-cut adhesion and pendulum hardness. As can be seen in Figure 6, the addition of CNT in amounts of 0.025-0.5 wt.% increased chemical resistance of reference sample to the highest measurable level according to EN 13523-11 standard (over 400 double rubs in rubbing test). Moreover, all prepared coatings showed the highest adhesion to glass substrate according to ISO 2409 (0 ° with no delamination, Figure 6). Furthermore, the coatings were characterized by significant hardness (201-209 a.u.) with the value of 205 a.u. being within measurement uncertainty of all samples (Figure 6). CNT had no monotonic influence on this parameter. It is noteworthy, that trial coatings composed and cured without XDA exhibited noticeably worse functional properties compared to discussed samples. These results indicated that the high functional performance of the coatings depended on aromatic-structure-rich, strongly cross-linked by TBG and XDA polymer matrix, rather than CNT presence. Only some improvement of chemical resistance of CNT-modified coatings was observed.

On the other hand, CNT distinctly improved thermal stability of prepared coatings, expressed as temperature at 5, 10 or 20% mass loss, up to 20 °C for E-C0.5 sample (Figure 7). These results are consistent with former studies [17,18]. This improvement can be explained by mechanical reinforcing effect of the CNT on polymer coating, widely discussed in our previous work [24]. Such strong influence of CNT on T_g of cured coatings was not observed. T_g values did not differ by more than 2 °C (Figure 7). Such thermal properties of the coatings are suitable for protective applications.

4. CONCLUSIONS

In summary, commercially available raw CNT were successfully dispersed in epoxy coating compositions via mechanical mixing using industrially-designed stirrer. It was possible thanks to the use aqueous solution of neutralized TBG in triple role of CNT dispersing agent, amine epoxy hardener and viscosity depressant. CNT non-covalent functionalization by TBG and epoxy was confirmed by TEM and SEM observations and also EDX spectrum. Prepared coatings were characterized by the most advantageous combination of antistatic/conductive and transparent properties of all the analogical CNT-modified coating materials described by others. Only 250 ppm of CNT in coating significantly reduced its R_s , practically without compromising transparency. In comparison with reported materials, utilizing relatively more complicated solutions which could increase their electrical/visual performance, such as ultrasonic dispergation [1,2,4,12,15-18,21-25],

single-walled CNT [1] or UV curing [1-3,21], prepared coatings offered the most satisfactory reduction of R_s keeping excellent visual features, i.e. high transparency and gloss as well as zero haze. Because previously obtained CNT-modified epoxy coatings did not show noteworthy visual properties [1-16] the addition of a component exhibiting strong affinity for CNT (such as n-TBG) can be a crucial factor in formulation of coatings showing better optical/conductive properties. Valuably, prepared coatings cured by two independent hardeners, i.e. TBG and XDA, exhibited also perfect chemical resistance to MEK, adhesion, significant hardness and improved thermal stability. The top properties and processing simplicity of prepared materials allow to apply them as lampshades or sight-glasses used in explosive atmosphere in mines and chemical installations, as well as in other technical solutions, where transparent and semiconductive properties play a key role.

ACKNOWLEDGMENTS

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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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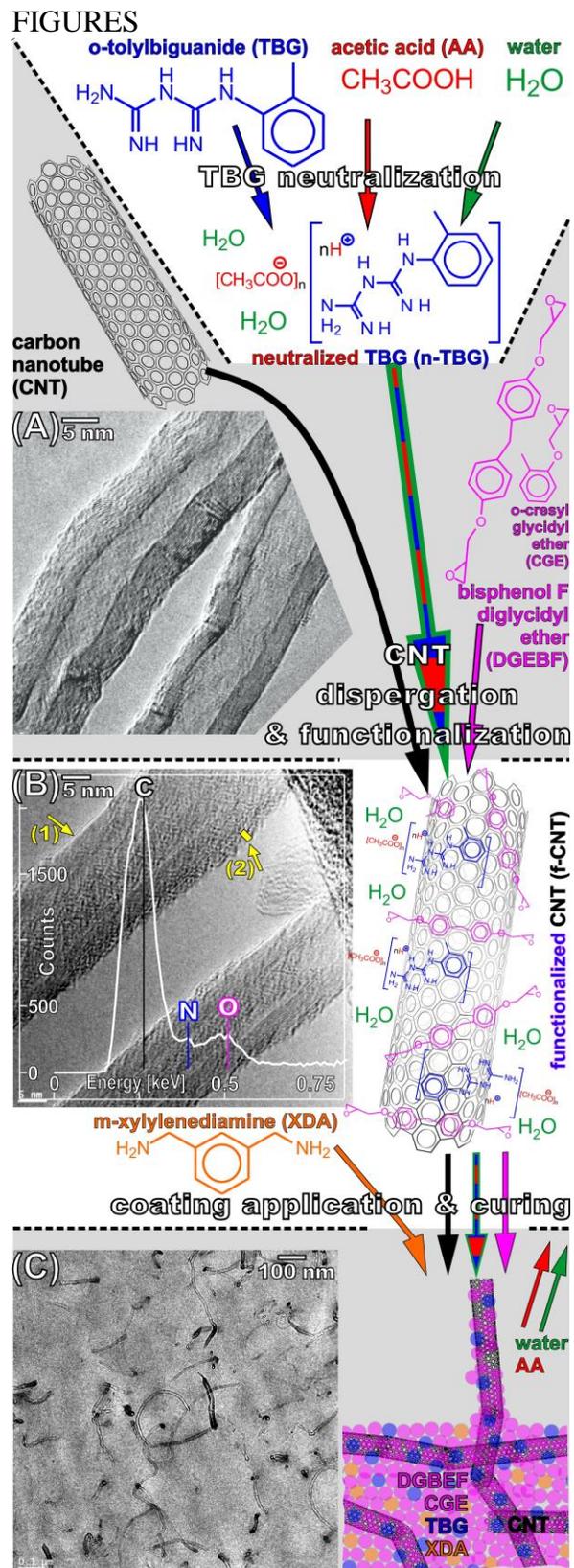


Figure 1. Epoxy coatings preparation scheme including TEM images of: raw CNT (A), CNT in coating with its EDX spectrum (B), cross sections of E-C0.25 coating surface (C).

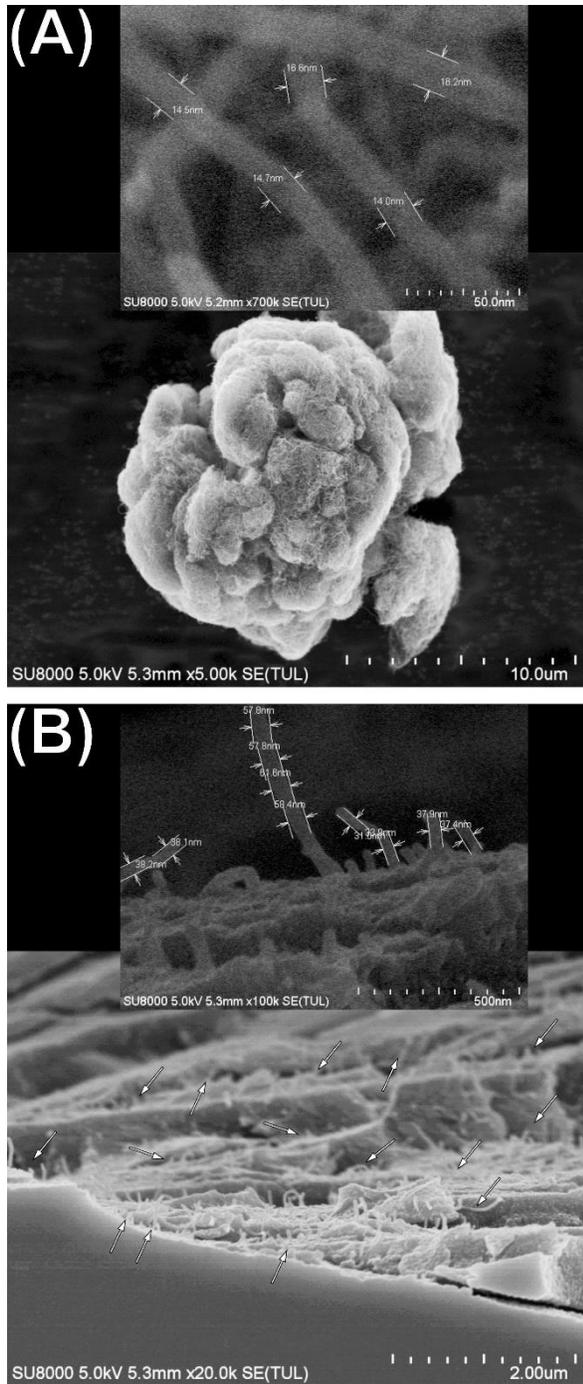


Figure 2. SEM images with CNT diameter measurements of raw CNT bundle (A) and f-CNT dispersed in E-C0.5 coating (B). Some of f-CNT in the coating are indicated by arrows.

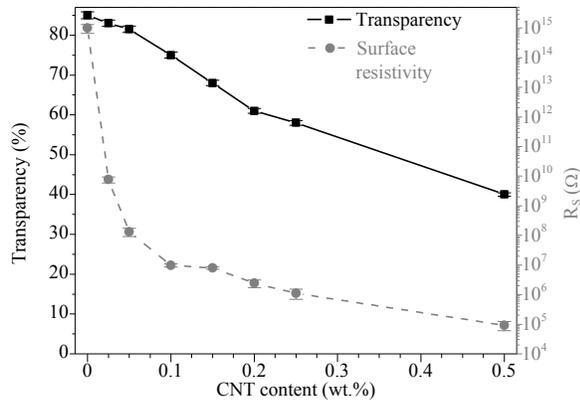


Figure 3. Transparency and electrical surface resistivity of epoxy coatings with CNT.

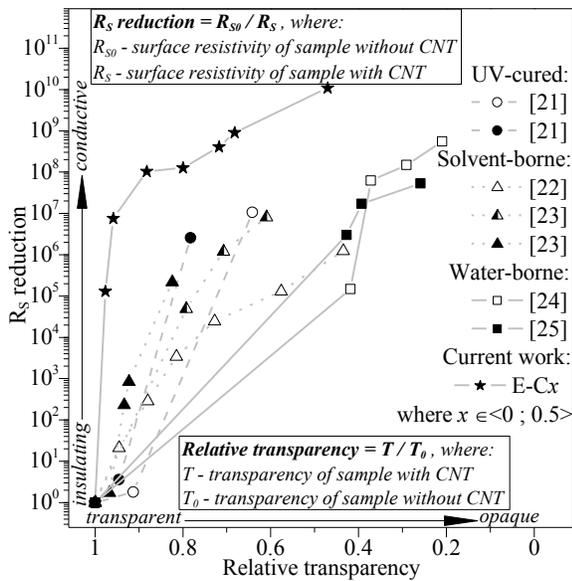


Figure 4. Increment of electrical surface conductivity (i.e. surface resistivity reduction) in relation to the transparency reduction of prepared epoxy coatings compared to literature results [21-25].

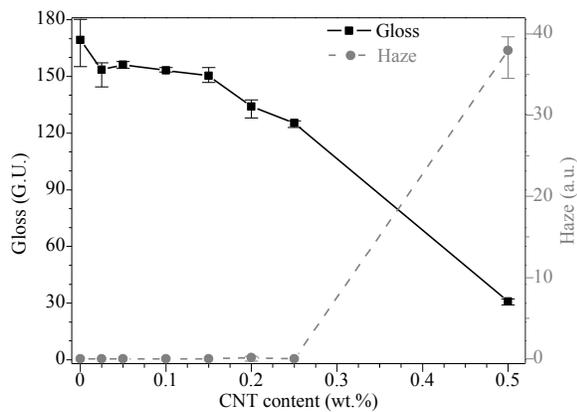


Figure 5. Gloss and haze of epoxy coatings with CNT.

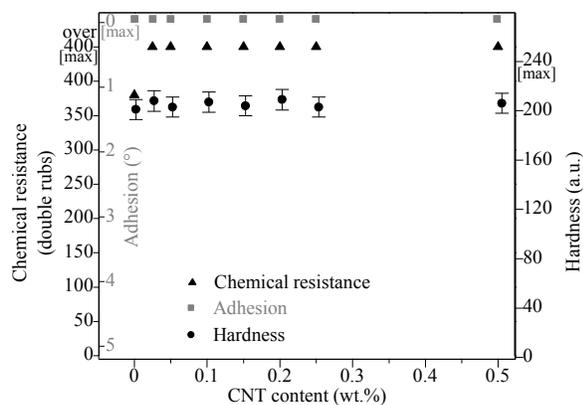


Figure 6. Functional properties of epoxy coatings with CNT.

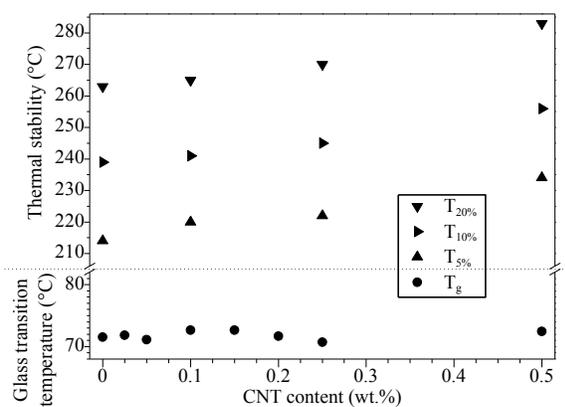


Figure 7. Thermal properties of epoxy coatings with CNT.

TABLES

Table 1. Composition of epoxy varnishes with CNT

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

a – CNT content in wt.% of dry coating; b – component evaporates during curing;