



Influence of synthetic and bio-based amine curing agents on properties of solventless epoxy varnishes and coatings with carbon nanofillers



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ABSTRACT

Solventless epoxy varnishes and coatings were prepared using carbon nanotubes (CNT) and/or graphene (GNP) dispersions in a Bisphenol F-type epoxy resin, synthetic hardeners [tetraethylenepentamine, poly(oxyethylene) diamine, isophoronediamine, m-xylylenediamine] or bio-based amine hardener (Cardanol-based phenalkamine, abbreviation: PAA). Room temperature cured coatings, containing 0.35 wt.% of CNT pre-dispersed in PAA, showed outstanding combination of optical (i.e. high gloss and transparency, low haze in humid conditions) and electrostatic dissipative properties (surface resistivity ca. $5.5 \times 10^7 \Omega$) in relation to the samples containing carbon nanofiller(s) dispersion in the epoxy resin or a synthetic amine. PAA-based coatings with the carbon nanofillers exhibited increased cupping resistance (+20% for samples with CNT) as well as high hardness and excellent adhesion to a glass substrate. The carbon nanofillers addition influenced on curing process and glass transition temperature (monitored using differential scanning calorimetry technique) of the epoxy varnishes and coatings as well.

1. Introduction

Nanocomposite polymer films and coatings with recently discovered carbon nanoparticles (CN), i.e. carbon nanotubes (CNT) or graphene (GNP) exhibit many improved properties, such as electrical conductivity [1–11], anticorrosion/barrier features [5,12–23], thermal stability [6,10,11,14,19,21,22,24–27], hydrophobicity [11,18,28], adhesion to different substrates [5,13,16,18,20,23,25] as well as mechanical features (i.e. hardness [2,6,10,11,29], tensile strength [4,23,24,30,31], impact strength [14,15,22]). In some cases, higher cupping [15], scratch [7,23,27] and abrasion [13,26] resistance of CN-filled materials are observed as well. Unfortunately, a preparation process of carbon nanofiller-based polymer materials causes several difficulties in practical implementation of these materials, i.e.: (i) obstacles to direct introduction of CN into coating compositions and, (ii) necessity of utilization of toxic/dangerous organic solvents. The former aspect is caused by a lack of chemical affinity between CN and polymeric matrices. The most common way to solve that problem is a surface functionalization of the nanoparticles [32]. Thus, CN for coating applications are modified by covalent [2,3,9,12,14,16,20–22,26,27,29–31] or non-covalent methods using dispersing agents [1,6,9,11,17,19,24]. Unluckily, covalent methods seriously increase CN price and often negatively influence on features (mainly electrical conductivity [2]) of CN/polymer nanocomposites. Although non-covalent treatment

of CN with surfactants [1,19,24,27] or solvents (such as methanol [23], tetrahydrofuran [28] or chloroform [33]) is quite effective and cheap, utilized modifiers (mainly ionic surfactants) may negatively affect on features of nanocomposites and often they are harmful and/or inflammable (solvents). It seems that dispergation of CN in a reactive non-volatile and non-flammable component of a coating system could eliminate the mentioned inconveniences of non-covalent methods. In that situation, commercially available carbon nanofillers could be directly incorporated into a coating system (e.g. two-component epoxy) without their extra functionalization.

It should be noted, that processes of raw carbon nanofillers dispergation in an epoxy resin [25], its solution [5,18,33], or in a whole coating system (based on industrial organic components) [3,4] were utilized and described in the literature. It was revealed that applied epoxy resins (i.e. Bisphenol A/F glycidyl ethers) were indisputable good dispersants for CN [1,2,7,25,29,31], but none of prepared nanocomposite coatings exhibited satisfactory optical properties (while most of unfilled epoxy lacquers create transparent layers). Interestingly, an application of raw CN/amine dispersions as components of epoxy coating systems have not yet been discussed in scientific papers. Thus, in this work series of commercially available synthetic amines with aliphatic, cycloaliphatic and aliphatic-aromatic structures as well as a bio-based long chain aliphatic-aromatic amine (phenalkamine, PAA) were tested as dispersing agents for untreated CNT and GNP. For

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comparison, dispersions of CN in an epoxy resin were also utilized for preparation of two-component solventless varnishes, curable at room temperature. Influence of applied dispersing medium on electrical surface conductivity and transparency of the epoxy coatings (0.35 wt. % of CNT or GNP) were primarily investigated. In the case of PAA-based hardener a few varnishes and coatings with CNT, GNP and CNT/ GNP mixture (0–0.35 wt.%) were examined.

2. Experimental

2.1. Materials

Solventless epoxy varnishes were based on the following components:

A) Epoxy components:

- Bisphenol F diglycidyl ether (BFDE), viscosity ca. 3 500 mPa·s (at 25 °C), epoxy equivalent weight (EEW) 169 g/eqv. (Epon 862; Hexion, USA).
- o-Cresyl glycidyl ether (CGE), viscosity 8 mPa·s (25 °C), EEW 164 g/eqv. (EKG; Organika-Sarzyna, Poland).

B) Plasticizer:

- Non-volatile reactive plasticizer (RP) (glycol ester of omega-6 fatty acid), iodine value 150, viscosity 20 mPa·s (25 °C) (Archer RC; ADM, USA).

C) Solvent-free amine curing agents (Fig. 1):

- Tetraethylenepentamine (TEPA), amine hydrogen equivalent weight (AHEW) 27 g/eqv., amine hydrogen functionality (AHF) 7 eqv./mole, viscosity 80 mPa·s (20 °C) (Sigma-Aldrich, Germany).
- Poly(oxyethylene)diamine (JA), AHEW 37 g/eqv., AHF 4 eqv./mole, viscosity 798 mPa·s (25 °C) (Jeffamine EDR-148; Huntsman, USA).
- Isophoronediamine (IPDA), AHEW 43 g/eqv., AHF 4 eqv./mole, viscosity 20 mPa·s (23 °C) (Baxxodur EC201; BASF, Germany).

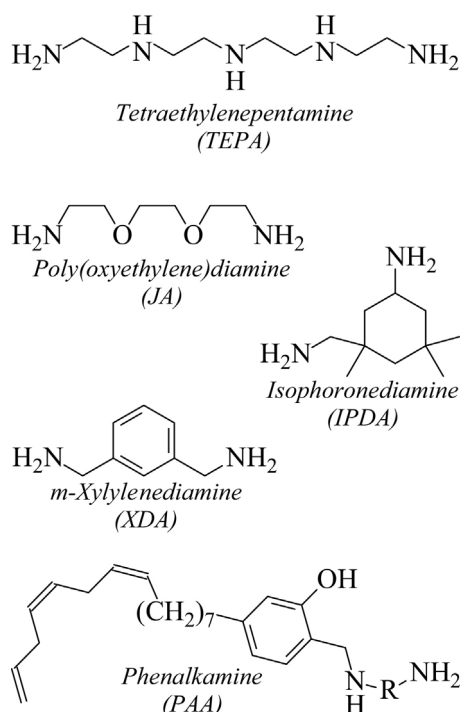


Fig. 1. Chemical structures of tested amines.

- m-Xylylenediamine (XDA), AHEW 34 g/eqv., AHF 4 eqv./mole, viscosity 7 mPa·s (23 °C) (Sigma-Aldrich, Germany).
- Cardanol-based phenalkamine (PAA), AHEW 104 g/eqv., AHF 3 eqv./mole, iodine value 214, viscosity 650 mPa·s (25 °C) (Lite 2002LP; Cardolite, Belgium).

D) Carbon nanofillers:

- Multi-walled carbon nanotubes (CNT), specific surface ca. 275 m²/g, average length 1.5 μm, average diameter 9.5 nm (NC7000; Nanocyl, Belgium).
- Graphene (GNP), specific surface > 750 m²/g, particle diameter < 0.1 μm and less than 3 carbon layers in a particle (GrapheneX; Graphene Technologies, USA).

2.2. Sample preparation

Epoxy varnishes with CNT and/or GNP were prepared as follows. The carbon nanofiller was introduced to the resinous (“R”) component (i.e. BFDE/CGE mixture, 75/25 m/m) or to the hardener (“H”) component (amine/RP mixture; 75/25 m/m); system was homogenized for 20 min using ultrasonic homogenizer equipped with ø3 mm sonotrode (UP 200S; Hielscher Ultrasonics, Germany). Coating composition was prepared by mixing (in stoichiometric ratio) of R and H components (unfilled or filled with a carbon nanofiller) for 5 min using a mechanical stirrer. Then, the composition was applied onto glass or steel substrates using a gap applicator and cured for 2 days at room temperature (RT). All samples were additionally kept for 12 days at RT to eliminate potential differences in their crosslinking degree resulting from use of various hardeners. Composition of the prepared coatings (thickness 30 μm) is presented in Table 1.

2.3. Methods

Viscosity of liquid compositions was evaluated using high shear viscometer (I.C.I. cone-plate system, Research Equipment Ltd, UK). Electrical surface resistivity (ESR) of the prepared coatings (glass substrate, 20 °C, 50% RH, 10 V) was determined by means of 6487 electrometer with electrode set 8009 (Keithley, USA). Their transparency (at 700 nm wavelength) was measured using UV-vis spectrophotometer (V-630; Jasco, USA). Gloss at 20° and haze were determined using Rhopoint IQ206085 device (Rhopoint Instruments, UK) in compliance with the ISO 2813 standard (five measurements of each sample were performed). The surface roughness of coatings (R_a parameter) was assessed using laser scanning microscope VK-9700 (Keyence, USA).

The pendulum hardness of coatings (glass substrate, PN-EN ISO 1522 standard) was tested using König pendulum (AWS-5; Dozafil, Poland). Adhesion to glass substrate was evaluated according to PN-EN ISO 2409 (cross-cut method). Cupping resistance (ISO 1520) of coatings on steel was determined using Model 200 cupping tester (Erichsen, Germany).

Curing process of an epoxy composition was monitored at 25 °C (air atmosphere) by means of Differential Scanning Calorimetry (DSC) (Q100 calorimeter; TA Instruments, USA). Glass transition temperatures (T_g) of cured samples were evaluated by DSC as well (20–180 °C, heating rate of 5 °C/min). Thermogravimetric analysis (TGA) was carried out using Q5000 thermoanalyzer (TA Instruments); temperature range was 20–600 °C with heating rate of 10 °C/min (air atmosphere). Humidity resistance of selected coatings were tested using KBK-100W climate chamber (Wamed, Poland); cured samples were stored for 5 days at 50, 60, 70, 80 or 95% RH (23 °C) before tests.

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