

## EPOXY COMPOSITES WITH CARBON NANOTUBES

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### Summary

In the work viscosity, curing process of epoxy resins, electrical conductivity and mechanical strength of epoxy composites with carbon nanotubes were investigated. As a component was used Epidian 6 epoxy resin cured with 1-butylimidazole by anionic polymerization. Compositions with nanofillers were prepared by sonification of multiwall carbon nanotubes (BAYTUBES 150 P and BAYTUBES 150 HP) in epoxy resin without any solvent. The morphology of prepared nanocomposites was examined by using SEM. Scanning electron microscopy confirms good dispersion of CNTs, but the presence of agglomerates is also identified. Viscosity of compositions with two kind of carbon nanotubes was established by means of ARES rheometer. Curing process with ARES rheometer and DSC was investigated. Bending strengths and electrical conductivity were performed on composites made of an epoxy resin loaded with 0.1, 0.2, 0.5, 1 and 2 wt.% both types of MWNTs. The incorporation of MWCNT to epoxy resin results in a sharp insulator-to-conductor transition with a percolation threshold ( $\Phi_c$ ) as low as 0.5 wt.% for Baytubes 150 HP and 1.0 wt.% for Baytubes 150 P. An electrical conductivity of  $10^{-4}$  S/cm was achieved for 0.5 wt. % of MWCNT 150 HP. The low percolation threshold for each MWCNTs and relatively high electrical conductivity are attributed to the high aspect ratio, large surface area and uniform dispersion of the carbon nanotubes in epoxy matrix.

**Keywords:** epoxy resin, multiwall carbon nanotubes, morphology, curing process, electrical conductivity, bending strength

### Kompozycje epoksydowe z nanorurkami węglowymi

#### Streszczenie

W pracy ustalono właściwości mechaniczne, przewodnictwo elektryczne, lepkość oraz proces sieciowania kompozycji epoksydowych z nanorurkami węglowymi. Stosowano żywicę epoksydową Epidian 6 sieciowaną 1-butyylimidazolem zgodnie z mechanizmem polimeryzacji anionowej. Kompozycje z nanonapełniaczami przygotowano poprzez sonikację wielościennych nanorurek węglowych (BAYTUBES 150 P oraz BAYTUBES 150 HP) w żywicy epoksydowej bez użycia rozpuszczalnika. Strukturę wytworzonych nanokompozytów określono metodami skaningowej mikroskopii elektronowej (SEM). Nanokompozyty cechuje duża dyspersja CNT z nielicznymi aglomeratami. Określono wpływ zawartości nanorurek na lepkość kompozycji. Kinetykę procesu sieciowania ustalono metodą różnicową kolorimetrii skaningowej (DSC) oraz reometrii, przy zastosowaniu aparatu ARES. Wytrzymałość na zginanie oraz przewodnictwo elektryczne określono dla kompozycji epoksyd/MWCNT o zawartości nanorurek 0.1, 0.2, 0.5, 1 oraz 2% mas. dla obu typów nanorurek węglowych. Wprowadzenie nanorurek węglowych do żywicy epoksydowej powoduje nagłe przejście od izolatora do przewodnika z progiem perkolacji ( $\Phi_c$ ) wynoszącym 0.5% mas. dla Baytubes

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150 HP oraz 1.0% mas. dla Baytubes 150 P. Przewodnictwo elektryczne  $10^{-4}$  S/cm uzyskano przy zawartości 0.5% mas. nanorurek MWCNT 150 HP. Mała wartość perkolacji dla obu użytych typów nanorurek węglowych oraz dobre przewodnictwo elektryczne są spowodowane dużą wartością współczynnika kształtu, dużą powierzchnią właściwą oraz jednolitą dyspersją nanorurek węglowych w żywicy epoksydowej.

**Słowa kluczowe:** żywice epoksydowe, wielościenne nanorurki węglowe, morfologia, proces sieciowania, przewodnictwo elektryczne, wytrzymałość na zginanie

## 1. Introduction

The discovery of carbon nanotubes (CNTs) [1] has led to their use in development of the next generation of composite materials with unique properties. The interest was mostly focused on the improvement of the mechanical, thermal and electrical properties [2-6] of both thermoplastic and thermoset polymers. Multi-wall carbon nanotubes (MWCNT) show unique electrical and chemical properties [7-11], and because of the combination of low density, nanometerscale diameter, high aspect ratio, and more importantly, unique physical properties such as extremely high mechanical strength and modulus [12-16], MWCNTs have emerged as potential reinforcing filler in polymer composites with excellent performance and multifunction [17-21] which led to a variety of applications: energy storage and energy conversion devices, sensors, field emission displays, radiation sources, hydrogen media, nanometer-sized semi-conductor devices, probes, interconnects, coatings, encapsulates, structural materials, and others [17-22]. One of the most intriguing applications of CNTs is the polymer/CNTs composites [21-24].

Epoxy resin is a cross-linked polymer widely used as a matrix for advanced composites given its good stiffness, specific strength, dimensional stability and chemical resistance. The main drawback of epoxy resin for structural applications may be its inherent brittleness. Thus, several research works have recently been devoted to reinforcement of epoxy matrices with CNTs [25-29].

Nanocomposites are defined as composites, where one of the components has at least one dimension in nanometer. The most popular nanofillers are nanosilicas, montmorillonites, fullerenes, and carbon nanotubes. The rationale behind using nanofillers is to improve mechanical, thermal, electrical properties of nanomaterials. Nanocomposites can be obtained in three different ways: (i) by *in situ* method, where they are used to obtain thermosetting composites; (ii) by means of a solvent; in this case nanofiller is dispersed in a solvent and later mixed with monomer; (iii) by dispersing directly in polymer matrix (for thermoplastic polymers) [30-34]. The research paper describes epoxy compositions with imidazole as curing agent (anionic initiator) and carbon nanotubes as nanofillers. The modifications of epoxy resin with nanofiller, especially with carbon nanotubes ought to improve the mechanical strength and electrical conductivity of composites.

## 2. Experimental section

### 2.1. Materials

The epoxy resin Epidian 6 the product of Chemical Works (“Organika Sarzyna” in Nowa Sarzyna) and as a curing agent there 1-buthylimidazole (Sigma-Aldrich) were used. Their chemical structures are shown in Fig. 1, where for epoxy resin the n-parameter value is  $0 \div 0.1$ . The MWCNTs were purchased from Bayer Material Science and used as received. The MWCNTs BAYTUBES C 150 P were produced in a high-yield catalytic process based on chemical vapor deposition with an outer mean diameter of 13-16 nm and inner mean diameter of 4nm and approximately  $1\mu\text{m}$  length. The MWCNTs BAYTUBES C 150 HP were synthesized the same as MWCNT C 150 P using CCVD. The purity of as-received MWCNT P 150 was greater than 95% and the purity of as-received MWCNT HP 150 was greater than 99%. Multiwall carbon nanotubes (P and HP) obtained by Catalytic Chemical Vapour Deposition (CCVD) were introduced to epoxy resin

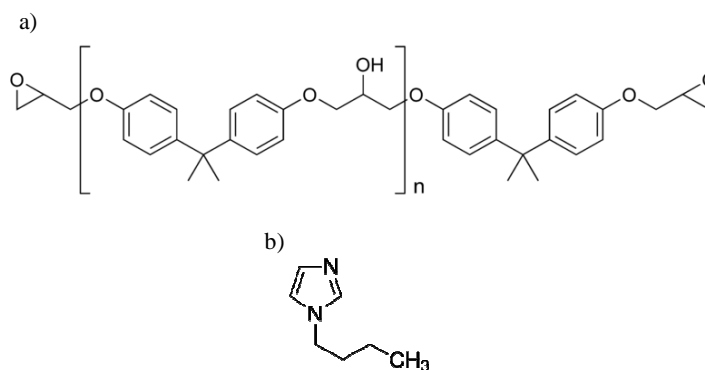


Fig. 1. Chemical structure of (A) Epidian 6 and (B) 1-butylimidazole

### 2.2. Preparation of nanocomposites

Carbon nanotubes (BAYTUBES C 150 P and BAYTUBES C 150 HP) in the amount of 0.1, 0.2, 0.5, 1.0 and 2.0 wt.% using Sonificator UP 200S, Hielscher GmbH (dispersion time 2 hours, amplitude  $70\mu\text{m}$ , frequency 50 Hz) in epoxy resin were dispersed.

Epoxy compositions were hardened in  $120^\circ\text{C}$  for 2 hours.

### 2.3. Methods of characterization

The curing process of the epoxy composition was characterized by using a differential scanning calorimeter DSC Q-100 by TA Instruments (USA), at a heating rate of 10°C/min in the temperature range of 0-300°C and an ARES Rheometer (from Rheometrics Scientific) at a heating rate of 10°C/min in the temperature range of 30-300°C, in 40 mm parallel-plate configuration with a gap of 1 mm.

The electrical conductivity of the MWCNT/Epoxy composites was evaluated by means of a dielectric analyzer (Novocontrol, Germany) in the frequency range of 10<sup>-1</sup>–10<sup>6</sup> Hz. The specimens used for the conductivity measurement were gold-sputtered to minimize the contact resistance between the composites and the electrodes.

Bending strengths were measured in accordance with appropriate standards by means of Instron 4026 testing machine from Instron Corporation (speed rate of 1 mm/min.)

The structure of nanoparticles and nanocomposites were observed by scanning electron microscopy (SEM) of Company JEOL JSM 6100 SEM. The samples were cryofractured in liquid nitrogen, and then vacuum coated with a thin gold film before being analyzed using SEM.

The rheological experiments were conducted on an ARES rheometer using a parallel plate geometry, a gap of 1 mm and frequency of 1 Hz.

### 2.4. Results and discussion

The effects of carbon nanotubes on rheological and mechanical properties and electrical conductivity of epoxy resin, cross-linked by anionic polymerization was investigated. Previously, nanocomposites cross-linked with amines or acid anhydrides, formed an uniform network, have been studied. Anionic crosslinking occurs according to the different mechanism. Therefore, it was interesting to determine the effect of nanotubes on the structure and properties of the resin. We proposed a schematic of the general curing reaction for the anionic polymerization of epoxide groups with 1 – substituted imidazoles, such as 1-butylimidazole, in which initiating species was 1:1 adduct (produced via the attack of the pyridine-type nitrogen) as illustrated in Fig. 2.

The prepared nanocomposites of Epidian 6/P and Epidian 6/HP contained respectively 0.1, 0.2, 0.5, 1.0 and 2.0 mas. % of multiwall carbon nanotubes by means of Baytubes 150 P and Baytubes 150 HP (Fig. 3). Additionally, in order to compare, unmodified epoxy resin, obtained in the same way as nanocomposites are characterized. It is not possible to break up all the entanglements of the supplied catalytically-grown carbon nanotube material by the dispersion process used (Fig. 4c), although the exposure to ultrasound of the resin leads to a dramatic improvement in the dispersion of the nanotubes in the

epoxy. Scanning electron microscopy of 2.0 mas. % MWNT-HP nanocomposite revealed that thin MWNT bundles were dispersed uniformly throughout the whole polymer matrix (Fig. 5c). The inset of Fig. 5a shows fine features of MWNT bundles at high magnification.

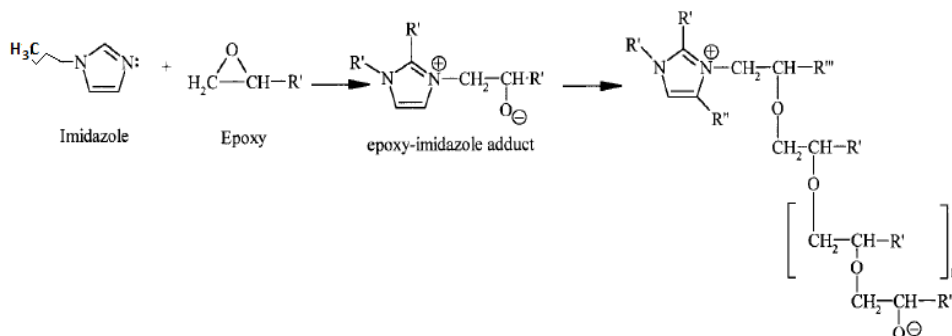


Fig. 2. Reaction mechanisms for polymerization process of epoxy groups using 1-butylimidazole as anionic initiator

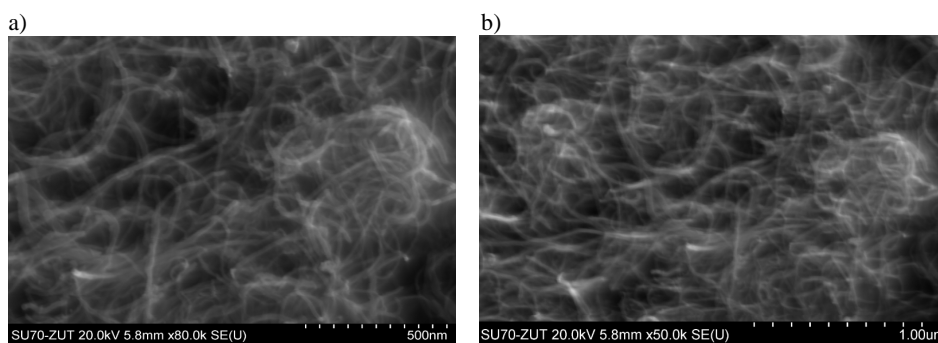


Fig. 3. SEM image of MWCNTs: a) BAYTUBES C 150 HP, b) BAYTUBES 150 P as received

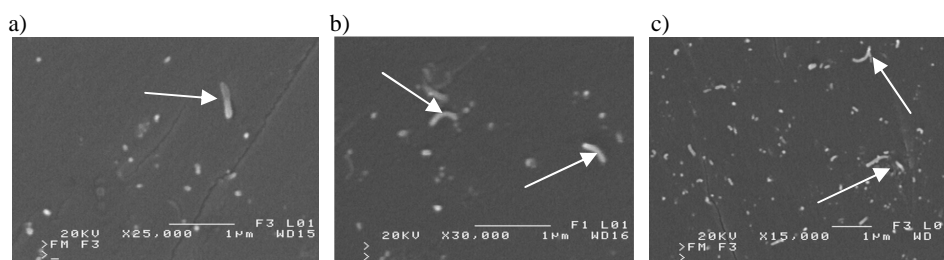


Fig. 4. Scanning electron microscopy (SEM) of Epidian 6/HP CNTs nanocomposites with MWCNTs content of: a) 0.2 mas. %, b) 0.5 mas. %, c) 2 mas. %

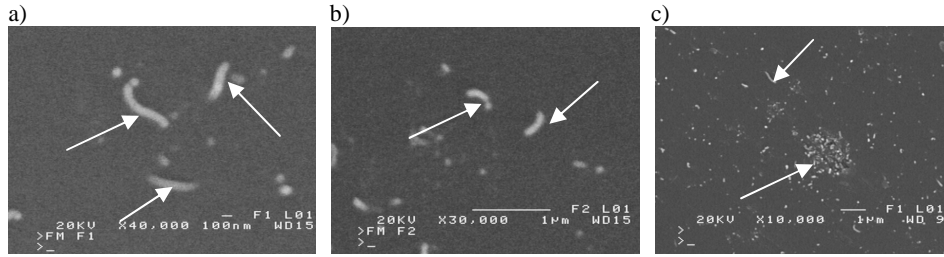


Fig. 5. Scanning electron microscopy (SEM) of Epidian 6/P CNTs nanocomposites with MWCNTs content of: a) 0.2 mas. %, b) 0.5 mas. %, c) 2 mas. %

The epoxy composites filled with the well dispersed CNTs exhibit non-Newtonian behavior, close to the power law fluid, than ones with the well dispersed CNTs and the viscosity of the former specimen increases more rapidly with increase in the CNT loading. As the filler loading increases, interaction between the CNTs and the polymer resin becomes larger due to the high aspect ratio of the CNTs.

Viscosity of epoxy composition increases with the greater content of carbon nanotubes. The highest change can be observed for 1.0 and 2.0 mas. % contents of nanofiller. Introduction of higher-purity carbon nanotubes (HP) more influence the viscosity of epoxy compositions than nanofiller type P. In Table 1 viscosity of epoxy compositions with carbon nanotubes is presented. The viscosity changes depending on the temperature during the curing process of epoxy compositions were also observed (Fig. 6 and 7).

Table 1. Viscosity of epoxy composition with different contents of carbon nanotubes

Carbon nanotubes	Viscosity, Pa·s					
	Content of nanofillers, mas. %					
	0	0.1	0.2	0.5	1.0	2.0
BAYTUBES 150 P	18.04± 0.28	19.57± 0.32	21.59± 0.32	24.22± 0.33	31.48± 0.47	48.02± 0.74
BAYTUBES 150 C HP	18.04± 0.28	21.84± 0.28	23.96± 0.37	29.95± 0.57	37.60± 0.57	51.39± 4.24

The dependence of viscosity on the temperature during the curing process of epoxy compositions with nanotubes (irrespective of filler type) can be divided into several ranges: (i) from 40°C to about 100°C which, depending on the content of nanotubes there are observed more or less visible changes in viscosity initially by a slight decrease in viscosity, then the increase and subsequent reduction in viscosity of the mixture – described changes have not yet been

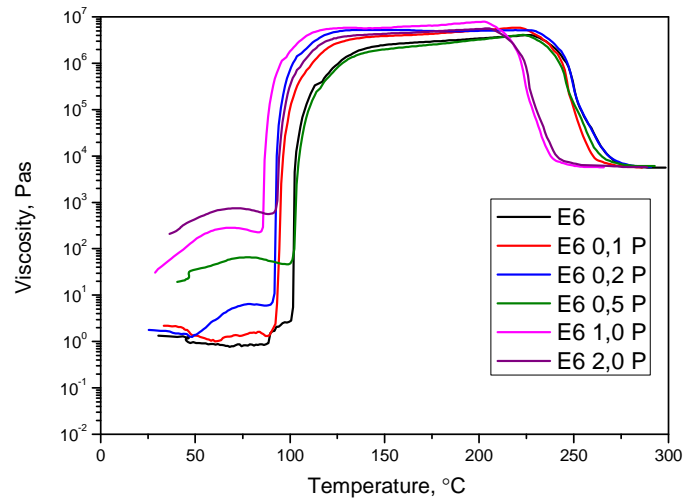


Fig. 6. Curing process of epoxy composition with different contents of carbon nanotubes BAYTUBES 150 P

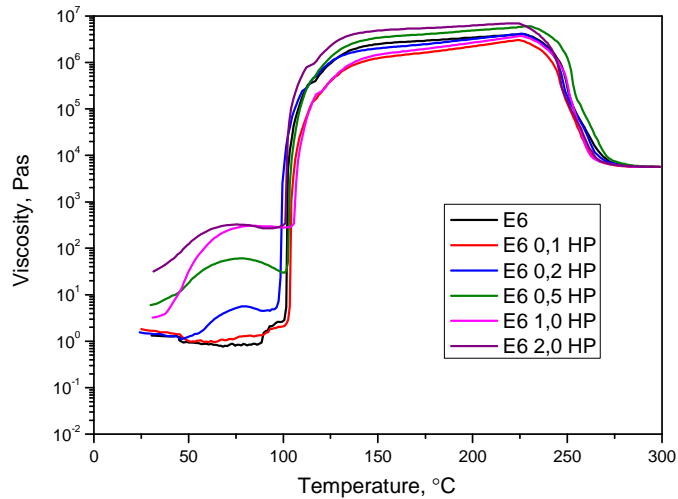


Fig. 7. Curing process of epoxy composition with different contents of carbon nanotubes BAYTUBES 150 C HP

observed during the curing of epoxy resins with nanofillers, fillers or unmodified compositions; (ii) 100°C to 125°C followed by a high increase in viscosity due to the crosslinking process; (iii) the range of 125 to 230°C, which is observed a slight increase in viscosity is observed; (iv) range from 230 to 300° C, in

which the viscosity of the material decreases. In Table 2 the results of DSC investigations are presented.

Table 2. Results of DSC tests for epoxy composition with carbon nanotubes

Content of nanotubes, mas. %	Temperature $T_p$ , °C		Enthalpy, J/g	
	CNT P	CNT HP	CNT P	CNT HP
0	120.4		302.0	
0.1	120.1	120.7	206.7	245.3
0.2	115.5	120.5	422.0	230.0
0.5	118.0	120.9	255.5	309.8
1.0	120.1	122.9	249.2	211.6
2.0	118.5	121.7	330.3	338.1

In the case of the composition with the lower purity nanotubes a peak temperature ( $T_p$ ) – the temperature at which the maximum energetic effect is observed during curing process of epoxy compositions are similar and are in a range from 115 to 120°C. Enthalpy values of crosslinking process are in the range from about 200 to 420 J/g, while the highest value of this parameter is observed for the composition of 0.1 mas. % content of nanotube type P.

In the case of the composition with the nanotubes of greater purity, enthalpy values of crosslinking process are in the range from about 210 to 340 J/g, in contrast to the values obtained for mixtures with a lower purity nanotubes, when major differences are not observed. Similar trends can be seen for temperatures of maximum exothermic effect, which are in the range from about 120 to 122°C. The values of this parameter increase with increasing content of nanofiller.

Incorporation of nanotubes into epoxy resins can potentially provide structural materials with dramatically increased modulus and strength. The critical challenges lie in uniformly dispersing nanotubes, achieving nanotube-matrix adhesion that provides effective stress transfer, and avoiding intratube sliding between concentric tubes within MWNTs.

The well dispersed CNTs are more efficient than the aggregated CNTs in the transferring applied load. Enhancement of mechanical properties is a general tendency for nanocomposites, because the nanomaterials act as reinforcement and the degree of reinforcement is dependent on the dispersion state of nanomaterials. Bending strengths of nanocomposites are generally higher than this value obtained for hardened epoxy materials without nanofillers. There exists a definite optimum of carbon nanotubes content, in which there can be observed maximum bending strength (for the content of 0.5 mas. % of nanofiller). The deterioration of mechanical properties at the highest concentrations (1.0 and 2.0 mas. %) of nanotubes may be due to the counteraction of forming polymer chains during anionic polymerization. Addition of carbon nanotubes causes

changes in intermolecular interaction mechanism. Good mechanical properties of nanocomposites are caused by cohesion forces between chains in polymer matrix. Furthermore, all impurities in carbon nanotubes (Baytubes 150P) cause even greater disturbances in creating polymer network. Composites with purer carbon nanotubes BAYTUBES 150 HP were characterized by higher mechanical strength than epoxy materials with BAYTUBES 150 P. In Tables 3-5 the results of bending strengths for epoxy composites with carbon nanotubes are presented.

Table 3. Bending strength of epoxy composites with carbon nanotubes

Content of nanotubes, mas. %	Bending strength, MPa	
	BAYTUBES 150 P	BAYTUBES 150 C HP
0	50.35 ± 8.74	
0.1	53.34 ± 8.74	58.02 ± 13.78
0.2	56.00 ± 9.80	67.04 ± 9.57
0.5	54.26 ± 4.32	67.69 ± 11.60
1.0	56.27 ± 6.52	68.16 ± 5.21
2.0	56.00 ± 7.29	63.52 ± 1.31

Table 4. Modulus of elasticity for epoxy composites with carbon nanotubes

Content of nanotubes, mas. %	Modulus of elasticity, MPa	
	BAYTUBES 150 P	BAYTUBES 150 C HP
0	2952 ± 119	
0.1	2600 ± 171	2779 ± 149
0.2	2677 ± 406	2733 ± 272
0.5	2498 ± 244	2997 ± 298
1.0	2140 ± 53	2651 ± 78
2.0	2375 ± 177	2286 ± 244

The analysis of modulus of elasticity demonstrates that the composite obtained from Epidian 6 epoxy resin was characterized by the highest value modulus of elasticity. Nanocomposites proved to have insignificantly smaller modulus of elasticity than epoxy materials without nanofiller. The values of these parameters were higher for composites with purer BAYTUBES 150 HP carbon nanotubes than with second nanofiller (BAYTUBES 150 P). In the case of filled composites there can be observed the maximum value for 0.5 mas. % of nanofillers for two kinds of carbon nanotubes.

Deflection of nanocomposites is generally better than epoxy materials obtained from Epidian 6. The highest values of this parameter have materials with the content of 0.1 and 0.2 mas. % carbon nanotubes regardless of the type of nanofillers used.

Table 5. Deflection of epoxy composites with carbon nanotubes

Content of nanotubes, mas. %	Deflection, mm	
	BAYTUBES 150 P	BAYTUBES 150 C HP
0	2.19 ± 0.37	
0.1	2.48 ± 0.37	2.55 ± 0.49
0.2	2.52 ± 0.17	3.36 ± 0.25
0.5	2.82 ± 0.46	2.58 ± 0.40
1.0	1.87 ± 0.34	2.97 ± 0.37
2.0	2.70 ± 0.53	2.75 ± 0.54

Carbon nanotubes are very attractive due to their potential in the increase of the electrical conductivity of insulating polymers at the very low concentration. In general, the electrical conductivity of a material should follow a law:  $\sigma(F) = \sigma_{dc} + A \cdot F^s$  where the presence of a frequency independent component,  $\sigma_{dc}$ , is characteristic of a conducting behavior with a significant direct current (dc) conductivity. Epoxy composites with purer MWCNT (HP 150) higher than 0.2 mas. % exhibit an absence of frequency dependence indicating the presence of a  $\sigma_{dc}$  contribution significantly higher than that of the polymer matrix. While MWCNT 150 P/Epoxy nanocomposites exhibit the insulator-to-conductor transition with nanofillers concentration of 1.0 mas. % (Table 6).

Table 6. Electrical conductivity of epoxy composites with carbon nanotubes

Nanotubes	Electrical conductivity, S/cm					
	Content of nanofillers, mas. %					
	0	0.1	0.2	0.5	1.0	2.0
BAYTUBES 150 P	$10^{-12}$	$10^{-12}$	$10^{-12}$	$10^{-11}$	$10^{-3}$	$10^{-2}$
BAYTUBES 150 C HP	$10^{-12}$	$10^{-12}$	$10^{-12}$	$10^{-4}$	$10^{-3}$	$10^{-2}$

The fitting of the percolation equation to the experimental data could be only prepared for nanocomposites with Baytubes 150 HP, where three points above percolation threshold were obtained. The results are represented in Fig. 8 by the continuous lines. This analysis provides  $t$  values of around 1.21 and  $\phi_c = 0.19$ . Theoretical calculations, supported by a great amount of experimental observations propose values of  $t$  between 1.6 and 2 for three-dimensional systems. In this framework a homogeneous distribution of isotropic distribution is considered and  $t$  values indicate that the three-dimensional conductive network was obtained.

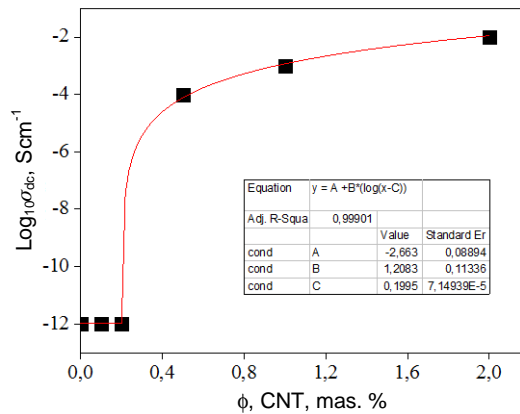


Fig. 8. Logarithm of the dc electrical conductivity versus nanoadditive weight concentration for CNT/epoxy nanocomposites. The continuous lines are the predictions of percolation theory

## Conclusion

This study has demonstrated the influence of multiwall carbon nanotubes Baytubes 150 P and Baytubes 150 HP as a nanofillers on the properties of anionic cross-linked epoxy resin. The dispersion of carbon nanotubes in a polymer matrix was relatively good despite the dispersion methods. The investigation of the CNT/epoxy-nanocomposites via SEM gives evidences for improved interfacial interaction between the high purified nanotubes and the matrix. Introducing carbon nanotubes to epoxy resin increases the viscosity of uncured compositions. The results obtained from using two kinds of epoxy nanocomposites lead to conclusion that introducing carbon nanotubes increases mechanical strength, especially by using purer BAYTUBES 150 HP as nanofiller. The optimum content of nanotubes is 0.5 mas. %, nanocomposites with this content have the highest mechanical strength and proper viscosity. The deterioration of mechanical properties at the highest concentrations (1.0 and 2.0 mas. %) of nanotubes is due to the counteraction of forming polymer chains during anionic polymerization. The incorporation of MWCNT to epoxy resin results in a sharp insulator-to-conductor transition with percolation threshold ( $\Phi_c$ ) as low as 0.2-0.3 mas. % for Baytubes 150 HP, is smaller than the critical content of nanotubes (0.5 mas. %), accomplishing of which the mechanical properties decrease. An electrical conductivity of  $10^{-4}$  S/cm was achieved for 0.5 mas. % of MWCNT 150 HP. The low percolation threshold for each MWCNTs and relatively high electrical conductivity are attributed to the high aspect ratio, large surface area and uniform dispersion of the carbon nanotubes in epoxy matrix.

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### References

- [1] S. IJIMA: Helical microtubules of graphitic carbon. *Nature*, **354**(1991), 56-58.
- [2] R.H. BAUGHMAN et al.: Carbon nanotubes-the route toward applications. *Science*, **297**(2002), 787-792.
- [3] P. MELISSA et al.: Carbon nanotubes-production and industrial applications. *Mater Des*, 282007;28:1477-89.
- [4] G. PHILIP et al.: Current saturation and electrical breakdown in multiwalled carbon nanotubes. *Phys Rev. Lett.*, **86**(2001), 3128-31.
- [5] K.T. LAU et al.: The revolutionary creation of new advanced materials-carbon nanotube composites. *Composites: Part B*, **33**(2002), 263-77.
- [6] M.F. YU et al.: Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. *Science*, **287**(2000), 637-40.
- [7] J.P. LU: Elastic properties of carbon nanotubes and nanoropes. *Phys Rev. Lett.*, **79**(1997), 1297-300.
- [8] J.P. SALVETAT et al.: Elastic and shear moduli of single-walled carbon nanotube ropes. *Phys Rev. Lett.*, **82**(1999), 944-7.
- [9] D. SRIVASTAVA et al.: Nanomechanics of carbon nanotubes and composites. *Appl. Mech. Rev.*, **56**(2003), 215-30.
- [10] V.A. BURYACHENKO et al.: Multi-scale mechanics of nanocomposites including interface: experimental and numerical investigation. *Comp. Science Technology*, **65**(2005), 2435-65.
- [11] E.T. THOSTENSON et al.: Advances in the science and technology of carbon nanotubes and their composites: a review. *Comp. Science Technology*, **61**(2001), 1899-912.
- [12] M. ALEKSANDER: Design and identification methods of effective mechanical properties for carbon nanotubes. *Mater. Des.*, **31**(2010), 1671-5.
- [13] A.B. DALTON et al.: Super-tough carbon-nanotube fibres-these extraordinary composite fibres can be woven into electronic textiles. *Nature*, **423**(2003), 703.
- [14] D. QIAN et al.: Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites. *Appl. Phys. Lett.*, **76**(2000), 2868-70.
- [15] R. ANDREWS et al.: Fabrication of carbon multiwall nanotube/ polymer composites by shear mixing. *Macromol. Mater. Eng.*, **287**(2002), 395-403.
- [16] S. BARRAU et al.: DC and AC conductivity of carbon nanotubes-polyepoxy composites. *Macromolecules*, **36**(2003), 5187-94.
- [17] E. CAMPONESCHI et al.: Uniform directional alignment of single-walled carbon nanotubes in viscous polymer flow. *Langmuir*, **22**(2006)4, 1858-62.
- [18] Y-H. LIAO et al.: Investigation of the dispersion process of SWNTs/SC-15 epoxy resin nanocomposites. *Mater Sci. Eng. A*, **385**(2004)1-2, 175-81.
- [19] A. EITAN et al.: Surface modification of multiwalled carbon nanotubes: toward the tailoring of the interface in polymer composites. *Chem. Mater.*, **15**(2003)16, 3198-201.

- [20] H.D. WAGNER et al.: Stress-induced fragmentation of multiwall carbon nanotubes in a polymer matrix. *Appl. Phys. Lett.*, **72**(1998), 188-90.
- [21] P. PÖTSCHKE et al.: Rheological behavior of multiwalled carbon nanotube/polycarbonate composites. *Polymer*, **43**(2002), 3247-55.
- [22] J.A. ROBERTS et al.: Electromagnetic wave properties of polymer blends of single wall carbon nanotubes using a resonant microwave cavity as a probe. *J. Appl. Phys.*, **95**(2004), 4352-6.
- [23] A.M.K. ESAWI et al.: Carbon nanotube reinforced composites: potential and current challenges. *Mater. Des.*, **28**(2007), 2394-401.
- [24] T. KASHIWAGI et al.: Relationship between dispersion metric and properties of PMMA/SWNT nanocomposites. *Polymer*, **48**(2007), 4855-66.
- [25] F.H. GOJNY et al.: Functionalization effect on the thermomechanical behaviour of multi-wall carbon nanotube/epoxy-composites. *Comp. Science Technology*, **64**(2004), 2303-8.
- [26] F.H. GOJNY et al.: Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content. *Comp. Science Technology*, **64**(2004), 2363-71.
- [27] L. LIU et al.: Rubbery and glassy epoxy resins reinforced with carbon nanotubes. *Comp. Science Technology*, **65**(2005), 1861-8.
- [28] J.D FIDELUS et al.: Thermomechanical properties of randomly oriented carbon/epoxy nanocomposites. *Composites: Part A*, **36**(2005), 1555-61.
- [29] Y. ZHUO et al.: Experimental study on the thermal and mechanical properties of multi-walled carbon nanotube reinforced epoxy. *Mater. Science Eng. A*, **452-453**(2007), 657-64.
- [30] M. KACPERSKI: Polymer nanocomposites, part I. *Polimery*, **11-12**(2002), 49-55.
- [31] M. KACPERSKI: Polymer nanocomposites, part II. *Polimery*, **2**(2002), 12-17.
- [32] M.R. LOOS et al.: Effect of carbon nanotubes addition on the mechanical and thermal properties of epoxy matrices. *Mat. Res.*, **11**(2008).
- [33] Ch. ZHEN-KUN et al.: Reinforcement of epoxy resins with multi-walled carbon nanotubes for enhancing cryogenic mechanical properties. *Polymer*, **50**(2009), 4753-4759.
- [34] F.H. GOJNY et al.: Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites – A comparative study. *Comp. Science Technology*, **65**(2005).

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