

DOI: 10.5604/20830157.1130205

CHEMICALLY-MODIFIED POLYANILINE AS A NEW CONDUCTING FILLER FOR POLYMER COMPOSITES

Ewa Kolasinska, Boleslaw Mazurek

Electrotechnical Institute, Division of Electrotechnology and Materials Science, Wrocław

Abstract. Polyaniline (PANI) is a potential filler in polymer composites with antistatic properties. As an intrinsic conducting polymer, PANI may be an alternative for carbons and metals. It is lighter than metals and shows better chemical affinity to traditional polymers than carbon allotropes. After modification, it may be incorporated into the matrix and thus helps to avoid the accumulation of static electricity in insulating polymers. In this research, insulating epoxy resin was filled with chemically-modified polyaniline and compared with classical fillers. Measurements of resistivity, thermal analysis and SEM observations were also conducted.

Keywords: conducting additives, polymer composites, electrical resistivity

CHEMICZNIE MODYFIKOWANA POLIANILINA JAKO NOWY WYPEŁNIACZ PRZEWODZĄCY W KOMPOZYTACH POLIMEROWYCH

Streszczenie. Polianilina to (PANI) to potencjalny wypełniacz do kompozytów polimerowych o właściwościach elektrostatycznych. PANI, jako samoistnie przewodzący polimer, może stanowić alternatywę dla wypełniaczy węglowych i metalicznych. Jako polimer, polianilina jest lżejsza niż metale i wykazuje lepsze powinowactwo chemiczne do tradycyjnych polimerów niż węglowe. Po odpowiedniej modyfikacji, może być wprowadzona w matrycę w celu zapobiegania akumulacji ładunku w dielektrykach polimerowych. W poniższej pracy, wykorzystano chemicznie modyfikowaną polianilinę jako wypełniacz do żywicy epoksydowej i porównano jej działanie z tradycyjnymi dodatkami. Przedstawiono wyniki pomiarów rezystywności, analizy termicznej i obserwacji SEM.

Słowa kluczowe: dodatki przewodzące, kompozyty polimerowe, rezystywność

Introduction

Over the past decade, engineers and scientists have focused on resolving the issue of how to build up electrostatic discharge channels to avoid the accumulation of static electricity in insulating polymers [6, 10, 20]. Thus, conducting materials, such as carbons [14, 20] and metals [3, 8, 20], were employed as fillers in polymer composites. The most common additives that increase conductivity are carbon black, graphite and carbon nanotubes, as well as silver, nickel and copper powders. The contribution of the filler in the polymer matrix that is necessary to increase the electrical conductivity by a few orders (5-15) depends on the given filler's structure and its tendency to form agglomerates and aggregates. Selection criteria also include the filler's shape, its conductivity, and similar polarity or chemical structure to the target polymer. The most effective method of achieving suitable polarity involves the chemical functionalization of filler surface [1, 2]. Such modification improves the dispersion of a filler in a nanocomposite [5, 7], and antistatic polymer nanocomposites will achieve percolation with lower additive content [11].

Metallic additives show the highest conductivity. However, metals – in pristine form – are not suitable fillers for a polymer matrix because of their different chemical nature, large weight or passivation facility.

Carbon nanotubes (CNTs), due to their smaller weight, were developed to be a better filler than metals, and also as a result of their high aspect ratio and electrical conductivity than other carbon allotropes [20]. It is possible to modify CNTs with an organic agent or to decorate them with silver particles and then they can be employed as conducting filler in epoxy resin [5, 7, 20]. It has been found that the electrical conductivity of such composite is higher than those containing the same content of pristine CNTs [9]. Nanocomposites show a percolated CNT network structure at functionalized CNTs loading 1 vol%, which is twice less than for unfunctionalized SWCNTs [9]. It is well known that carbon nanotubes can be considered to be polymers composed solely of carbon [4, 18, 21].

The magnitude of the room temperature conductivity for conducting polymers and CNTs in comparison to copper, platinum or amorphous metals is shown in Fig. 1, where solid symbols designate metallic samples and open symbols are non-metallic samples, squares designate samples with metallic

sign for temperature dependence ($d\sigma/dT < 0$) at room temperature, circles – non-metallic ones [4].

In this paper, the authors propose using polyaniline, a popular conducting polymer, as a filler in antistatic polymer composites. It might constitute a potential alternative for carbons and metals.

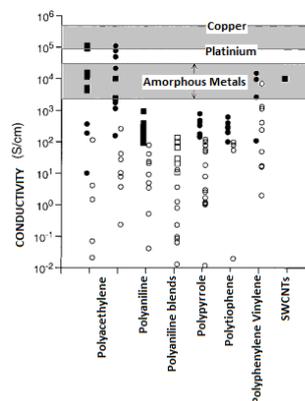


Fig. 1. Magnitude of the room-temperature conductivity of different types of conducting materials [4]

1.1. Polyaniline

Polyaniline (PANI) as a conducting polymer shows an advantageous connection of small weight, good electrical conductivity, and chemical affinity to the traditional polymer matrix (epoxy resin, PMMA, PVC, etc.). PANI is also a cheap material, as it is easy to produce, modify and process. PANI is a very stable conducting polymer with good damping and antistatic properties, resistant to most organic solvents. The conductivity of polyaniline depends on the degree of its oxidation. Conductivity can be improved by choosing an appropriate method and suitable conditions for its synthesis (oxidizing polymerization, electrochemical polymerization, synthesis of the conducting salt PANI-HCl) or by modifying the polymer (doping with sulfonic acid) [15, 22]. The conductivity of polyaniline depends also on processing conditions since the use of too strong cutting forces or too high temperatures may lead to the loss of conducting properties. Therefore, it is better to mix PANI with other polymers, such as dry blends, inter-polymer networks or copolymers, for easier processing or plastics refining [12, 17, 22].

The value of the electrical conductivity of pristine PANI varies within a range of $1 \cdot 10^{-12} (\Omega \cdot m)^{-1}$ to $1 \cdot 10^5 (\Omega \cdot m)^{-1}$. For PANI composites with traditional polymers, the conductivity values are much lower, and the percolation thresholds depend on the polymer matrix: PANI/PVC $\sigma = 1-100 (\Omega \cdot m)^{-1}$ with a percolation threshold of 20 wt.% of PANI and PANI/PU $\sigma = 1000 (\Omega \cdot m)^{-1}$ with a percolation threshold of 10 wt.% [12, 13]. Polyaniline has reactive nitrogen groups in its structure: the amine group in its reduced form and the imine group in its oxidized form. Both groups can react with epoxy resin according to the curing mechanism. This improves the internal compatibility and homogeneity of materials, which influences the mechanical, electrical and barrier properties [13].

The aim of this research is to find such a polyaniline-based material which could be used as a conducting filler in antistatic polymer composites without negative consequences for the other properties of the material. The main problem is to improve the electrical conductivity of PANI by introducing additives, such as protonating acids, carbon or metal additives.

2. Experimental

2.1. Materials

Aniline 99% Sigma-Aldrich, Ammonium Persulfate 98% Sigma-Aldrich, Multi-walled Carbon Nanotubes $d=110-170 \text{ nm} >90\%$ Sigma – Aldrich, Carbon Black Printex XE2 Degussa GmbH, Graphite LZ(-) 100-92 Sinograf SA, Hydrochloric Acid 35-38% Chempur. All materials were used as purchased.

2.2. Synthesis

The chemical modification of polyaniline was performed in two ways. First, polyaniline was synthesized by conducting an oxidating polymerization of aniline in a water solution with ammonium persulfate as the polymerization agent. Powder additives were incorporated into the water solution of polyaniline, always in the amount of 20 wt.%. In this experiment, carbon black (PANI-CB) and graphite (PANI-CG) were chosen as fillers. This method was also used to obtain pristine polyaniline (PANI) as a reference sample.

In the second method of polyaniline modification, a protonating acid was mixed *in situ* with an aniline water solution before the polymerization. The polyaniline-based material prepared in this way was called PANI-HCl.

The polyaniline-based materials were used as fillers for epoxies and compared with traditional carbon-conducting fillers: multi-walled carbon nanotubes (MWCNTs), carbon black (CB) and graphite (CG).

All conducting fillers, in the amount of 2 wt.%, were then mixed with epoxy resin and an anhydride hardener at a temperature of 70°C for 15 minutes by 2000 rpm, after which they were degassed and cured in $70^\circ\text{C} / 18\text{h} + 100^\circ\text{C} / 4\text{h} + 130^\circ\text{C} / 4\text{h}$.

During the research, an additional epoxy composite, filled with 20 wt.% of PANI-HCl, was prepared (EPOXY/PANI-HCl20).

2.3. Measurement of electrical resistivity

The measurement of bulk material resistivity was conducted in the measuring cell (Fig. 2.) with a cross-section of 1 cm^2 . After being filled up with the powder filler, the cell was closed with a punch. The punch was loaded with a mass of 0.65 kg for 60 seconds and resistivity was measured at a voltage of 12V DC with a HP 34301A multimeter. The value of the resistivity was calculated using the following equation (1) [13].

$$\rho = R \cdot \frac{s}{l} \quad [\Omega \cdot \text{cm}] \quad (1)$$

where: $s = g \cdot l$ because $l = 1 \text{ cm}$, g – height of a filler [cm].

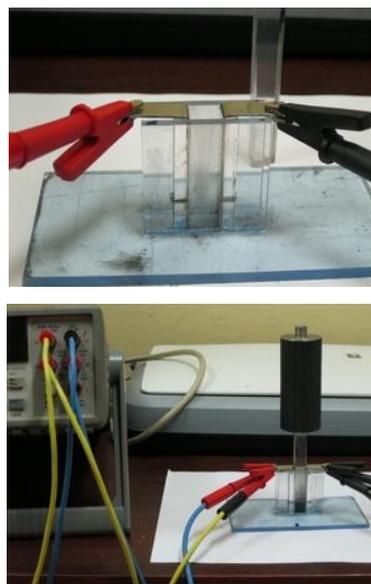


Fig. 2. The system for resistivity measurement of bulk fillers

This method was employed for powder fillers: multi-walled carbon nanotubes, carbon black, graphite and all polyaniline-based materials. The results of these measurements are presented in Tab. 1.

Resistivity of cured epoxy composites was determined from the resistance measurement for samples with the dimensions $10 \times 10 \times 4 \text{ mm}$. Resistance was measured in a four-wire system (Fig. 3), at a voltage of 12V DC, using a HP34401A multimeter.



Fig. 3. Resistance measurement system for hardened epoxy composites

All conducting fillers were incorporated into the epoxy matrix in the amount of 2 wt.%. Conducting carbon black gives a resistivity change of up to $10^5 \Omega \cdot \text{cm}$, and MWCNT even up to 10^4 . This is far too much for antistatic composites, while additionally carbon nanotubes are expensive. Graphite does not change the resistivity of epoxy resin.

For the experiment, PANI-HCl was chosen as a conducting polyaniline-based filler for epoxy resin due to its lowest resistivity. As can be observed in Tab. 1. 2 wt.% is not enough to decrease the resistivity of epoxy resin to $10^9 \Omega \cdot \text{cm}$, which would be a suitable result for an antistatic composite [16]. Therefore, it was necessary to change the content of this filler to 20 wt.% and to

optimize the composition of the epoxy material. The improved material EPOXY/PANI-HCl20 meets the antistatic requirement.

Table 1. The resistivity of conducting fillers and composites

	MATERIAL	ρ [$\Omega \cdot \text{cm}$]
1.	CARBON BLACK	6,8
2.	GRAPHITE	6,3
3.	MWCNTs	2,1
4.	PANI-HCl	$2,7 \cdot 10^2$
5.	PANI-CB	$9,0 \cdot 10^4$
6.	PANI-CG	$4,3 \cdot 10^{10}$
7.	PANI	$5 \cdot 10^{12}$
8.	EPOXY RESIN	$3,7 \cdot 10^{13}$
9.	EPOXY/PANI-HCl	$3,9 \cdot 10^{12}$
10.	EPOXY/PANI-HCl20	$5,0 \cdot 10^9$
11.	EPOXY/CB	$1,5 \cdot 10^5$
12.	EPOXY/CG	$1,5 \cdot 10^{13}$
13.	EPOXY/MWCNTs	$3,2 \cdot 10^4$

2.4. Thermal analysis

Thermoanalytical investigations provide information on mass alterations (TG) and energy variation during processes (DSC)

taking place while heating up the sample. The results are particularly helpful for the improvement of the technology of composite fabrication, showing the real proportion of components and degree of contamination. They also provide data about thermal resistivity.

The measurements were prepared with the use of the Mettler Toledo DCS/TGA1 thermoanalyzer in the following conditions: an air flow of $50 \text{ cm}^3/\text{min}$ and an increase in the temperature rate by $10^\circ\text{C}/\text{min}$.

Fig. 4 presents an example of TG/DSC curves for three selected polyaniline-based materials: PANI, PANI-CG, PANI-CB. Results for all polyaniline-based materials are presented in Tab. 2.

As can be observed in Tab. 2, all modifiers are incorporated into the polyaniline matrix with a similar yield and close to the primary 20 wt.%. It can also be noted that carbons increase the thermal resistance of polyaniline and hydrochloric acid does not change it.

Table 2. Results of thermal analysis for PANI-based materials

MATERIAL	FILLER CONTENT [wt.%]	THERMAL RESISTANCE [°C]
PANI-CB	16	270
PANI-CG	20	270
PANI-HCl	20	250
PANI	0	250

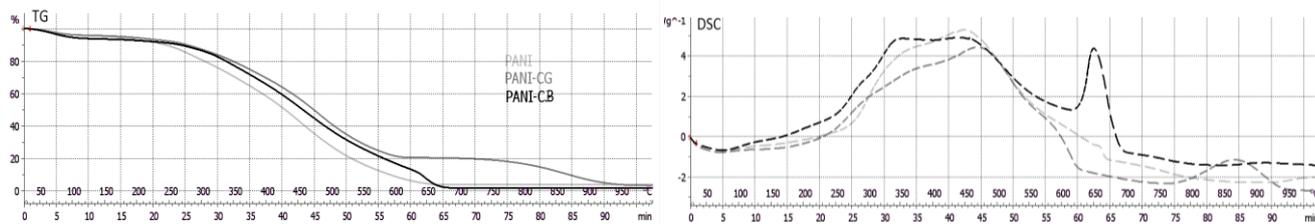


Fig. 4. Thermograms of polyaniline filled with carbons: CB-carbon black, CG-graphite and pristine PANI

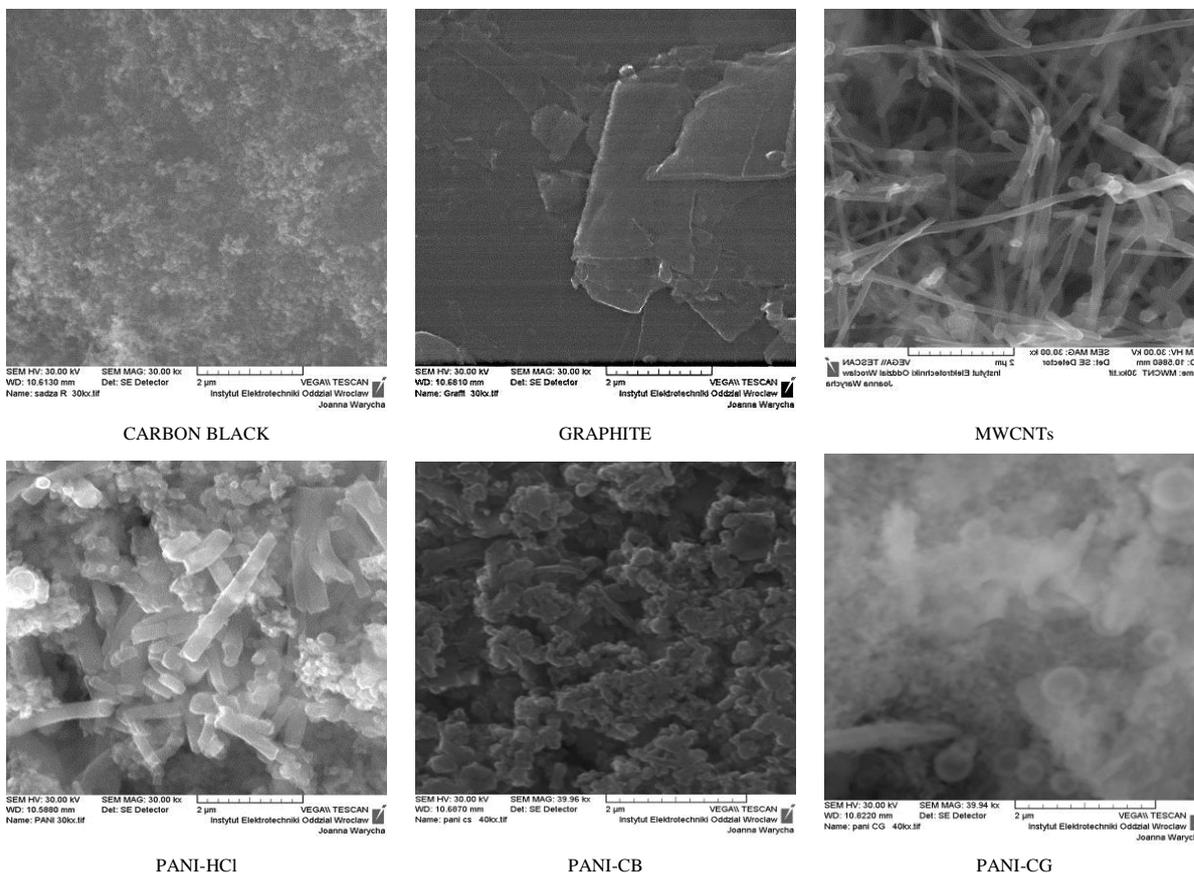


Fig. 5. SEM pictures of bulk materials (magnitude 30,000)

2.5. Scanning Electron Microscope

Structure observations of the conducting fillers were conducted using a Tescan VEGA II Scanning Electron Microscope.

SEM images (Fig. 5) of the conductive fillers at the same magnification of 30,000 show clear differences in the shape of grains of these additives. Carbon black is a powder in the form of spheres of a diameter of approximately 50 nm. Graphite grains possess plates much larger than carbon black, up to 2.5 microns. The cylindrical structure of nanotubes does not exhibit branches. The average particle size (0.15 x 5 µm), as well as the fact that the primary particles are spindle-shaped constitute very desirable features in the formation of conductive paths in the composite. The geometric structure of polyaniline modified by hydrochloric acid connects these three primary particles, but it is most similar to carbon nanotubes. Such a structure may be significant in the application of PANI-HCl as a conductive filler in polymer composites. Polyaniline filled with graphite and carbon black exhibits an amorphous structure. Such a difference may be the reason behind the much lower electrical conductivity of PANI-CB and PANI-CG.

3. Summary

During this research, polyaniline protonated with hydrochloric acid was synthesized. Carbon black and graphite were also used for polyaniline modification. Each additive was introduced into a polyaniline matrix in the amount of *ca.* 20 wt.%. These materials were used as conducting fillers for epoxies in the amount of 2 wt.%.

It is possible to replace traditional conducting materials (carbons or metals) with chemically-modified polyaniline (PANI-HCl). However, it is necessary to enlarge its content to 20 wt.%.

Polyaniline-based materials are lighter than metallic fillers and their chemical nature is similar to that of classic polymers. Even if the additive content is higher than 2 wt.%, the epoxy composite may be more homogeneous.

Such a combination of a small weight, good compatibility with the epoxy matrix and appropriate electrical properties is a strong argument for further work to be conducted on polyaniline-based materials in antistatic applications. On the other hand (and for further research projects), polyaniline may also play the role of a compatibilizer between the epoxy matrix and inorganic fillers – for example metals.

Literature

- [1] Bekyarova E., Thostenson E.T., Yu A., Itkis M.E., Fakhruddinov D., Chou T.-W., Haddon R.C.: Functionalized Single-Walled Carbon Nanotubes for Carbon Fiber-Epoxy Composites. *Journal of Physical Chemistry C* 111/2007, 17865-17871.
- [2] Chen J., Chen Q., Ma Q.: Influence of surface functionalization via chemical oxidation on the properties of carbon nanotubes. *Journal of Colloid and Interface Science* 370/2012, 32-38.
- [3] Jiang H., Moon K.S., Li Y., Wong C.P.: Surface functionalized silver nanoparticles for ultrahigh conductive polymer composites. *Chemistry of Materials* 18/2006, 2969-2973.
- [4] Kaiser A. B.: Systematic Conductivity Behavior in Conducting Polymers: Effect of Heterogeneous Disorder. *Adv. Mater.* 13/12-13/2001, 927-941.
- [5] Kim S.W., Kim T., Kim Y.S., Choi H.S., Lim H.J., Yang S.J., Park C.R.: Surface modifications for the effective dispersion of carbon nanotubes in solvents and polymers. *Carbon* 50/2012, 3-33.
- [6] Koul S., Chandra R., Dhawan S.K.: Conducting polyaniline composite for ESD and EMI at 101 GHz. *Polymer* 41/2000, 9305-9310.
- [7] Leon V., Parret R., Almairac R., Alvarez L., Babaa M.R., Doyle B.P., Jenny P., Parent P., Zahab A., Bantignies J.L.: Spectroscopic study of double-walled carbon nanotube functionalization for preparation of carbon nanotube/epoxy composites. *Carbon* 50/2012, 4987-4994.

- [8] Lilei Y., Zonghe L., Johan L., Tholen A.: Effect of Ag particle size on electrical conductivity of isotropically conductive adhesives. *IEEE Transactions on Electronics Packaging Manufacturing* 22/1999, 299-302.
- [9] Ma P.C., Tang B.Z., Kim J.-K.: Effect of CNT decoration with silver nanoparticles on electrical conductivity of CNT-polymer composites. *Carbon* 46/2008, 1497-1505.
- [10] Mai T.T., Schultze J.W., Staikov G.: Microstructured metallization of insulating polymers. *Electrochimica Acta* 48/2003, 3021-3027.
- [11] Maiti S., Suin S., Shrivastava N.K., Khatua B.: Low Percolation Threshold in Melt-Blended PC/MWCNT Nanocomposites in the Presence of Styrene Acrylonitrile (SAN) Copolymer: Preparation and Characterizations. *Synthetic Metals* 165/2013, 40-50.
- [12] Morgan H. Foot S., Brooks N.W.: The effects of composition and processing variables on the properties of thermoplastic polyaniline blends and composites. *Journal of Material Science* 36/2001, 5369-5377.
- [13] Moron L., Zawadzka E., Zych B.: Opracowanie założeń technologii wytwarzania półprzewodzących kompozytów polimerowych wypełnionych nanowypełniaczami węglowymi. Technical Documentation Nr 500/9390/26, IEL OTIME, Wrocław 2010.
- [14] Narkis M., Ram A., Flashner F.: Electrical properties of carbon black filled polyethylene. *Polymer Engineering & Science* 18/1978, 649-653.
- [15] Nishio K., Fujimoto M., Yoshinaga N.: Electrochemical characteristics of polyaniline synthesized by various methods. *Journal of Power Sources* 56/1995, 189-192.
- [16] Paściak G.: Opracowanie zmodyfikowanej technologii wytwarzania nanokompozytów epoksydowych z wykorzystaniem specjalistycznych urządzeń technologicznych i badawczych. Quarterly Report Wykorzystanie nanotechnologii w nowoczesnych materiałach, POIG 01.01.02-02-002/08, Wrocław 2014.
- [17] Ryabenko A., Fokeeva L., Dorofeeva V.: Spectroscopic study of suspensions of single-wall carbon nanotubes in polyaniline solutions in N-methylpyrrolidone in UV-Vis-NIR regions. *Russian Chem. Bull, Int. Ed.* 53/2004, 2695-2699.
- [18] Saito R., Dresselhaus G., Dresselhaus M. S.: *Physical Properties of Carbon Nanotubes*. Imperial College Press, London 1998.
- [19] Velasco-Santos C., Martínez-Hernández A.L., Fisher F.T., Ruoff R., Castano V.M.: Improvement of thermal and mechanical properties of carbon nanotube composites through chemical functionalization. *Chemistry of Materials* 15/2003, 4470-4475.
- [20] Wang Y., Zhang Ch., Du Z., Li H., Zou W.: Synthesis of silver nanoparticles decorated MWCNTs and their application in antistatic polyetherimide matrix nanocomposite. *Synthetic Metals* 182/2013, 49-55.
- [21] Yakobson B. I., Smalley R. E.: Fullerene nanotubes: C-1000000 and beyond. *Am. Sci.* 85/1997, 324.
- [22] Zawadzka E., Kulinski R., Szubzda B., Mazurek B.: Polyaniline–multi-walled carbon nanotube shell-core composite as an electrode material in supercapacitors. *Materials Science-Poland* 27/4/2/2009, 1271-1278.

M.Sc. Ewa Kolasinska

e-mail: kolasinska@iel.wroc.pl

Graduate of the Faculty of Chemistry, Wrocław University of Technology with a specialization in the Chemistry and Technology of Polymers (2007). Since 2007, she has been an employee of the Electrotechnical Institute. The main subjects of her research include: nanotechnology, polymer nanocomposites, conducting and dielectric fillers, thermal analysis.



Prof. Bolesław Mazurek

e-mail: mazurek@iel.wroc.pl

Is a specialist in the field of electrical engineering materials and technology of high voltage. Since 1961, he worked at the Department of Electrical Engineering at the Wrocław University of Technology. He currently works at the Electrotechnical Institute Division of Electrotechnology and Materials Science in Wrocław.



otrzymano/received: 2014.09.29

przyjęto do druku/accepted: 2014.10.20