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Influence of Carbon Nanoparticles Morphology on Physical Properties of Polymer Composites

G. Wróblewski[a,*], M. Słoma[a,b], D. Janczak[a], A. Młożniak[b] and M. Jakubowska[a,b]

[a]Institute of Metrology and Bioengineering, Warsaw University of Technology, A. Boboli 8, 05-525 Warszawa, Poland

[b]Institute of Electronic Materials Technology, Wólczyńska 133, 01-919 Warszawa, Poland

The paper presents influence of diverse shapes and dimensions of carbon nanostructures on physical properties of polymer composites. Graphene nanoplatelets, carbon nanotubes, graphite nanofibers, and graphite microflakes have been investigated as fillers in polymethacrylate resin. Layers were deposited with printing techniques used in printed electronics technology such as screen printing and spray coating, both elaborated in our earlier works. Different sets of measurements have been performed for obtained layers with particular carbon nanofillers. Thickness and topography have been examined using optical profilometer. Morphology of nanostructures has been observed with scanning electron microscope. Moreover, sheet resistivity and optical transmission in visible wavelength have been measured. Also mechanical properties have been characterized for each polymer composite by conducting fatigue test which consisted of multiple bending cycles.

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1. Introduction

Carbon is one of the few elements known since antiquity, widely present in nature, and easy to acquire [1]. It was identified as a chemical element more than 200 years ago by Lavoisier as a elementary component of diamond and graphite [2] which are one of many known nowadays allotropes i.e. graphene, nanotubes, fullerenes, or lonsdaleit. Since the discovery of fullerenes, carbon nanotubes and graphene, researchers from many science disciplines have investigated carbon vastly. Fullerenes, nanotubes and graphite can be considered as different structures made with the same hexagonal array of sp^2 bonded carbon atoms named graphene [3].

Relatively easy access to carbon, interesting mechanical, electrical, and optical properties, especially of nanotubes [4] and graphene [3], resulted in investigations in carbon based electronics as an alternative to existing materials or innovative solutions, i.e. flexible electronics.

Diverse applications of carbon nanotubes, graphene or graphite are described in literature. Carbon nanotubes and graphene are often used as transparent and flexible electrodes [5, 6] in photovoltaics [7–9], displays [10–12], or diverse sensing applications [13–15]. In our earlier works pressure sensors based on graphene nanoplatelets and carbon nanotubes were elaborated, then higher resolution on graphene based devices was observed [16].

In this paper, double-walled carbon nanotubes (DWCNT), graphene nanoplatelets (GNP), graphite microplatelets (GMP) and graphite platelet nanofibers (GNF) were investigated as electronic materials for printed electronics. Investigated layers were prepared using screen printing and spray coating methods.

*corresponding author; e-mail: g.t.wroblewski@gmail.com

2. Experiment

Two sets of samples were prepared, one with screen printing, second with spray coating method. Each set was prepared using DWCNT, GNP, GMP, and GNF fillers in polymethyl methacrylate (PMMA) resin and butyl carbitol acetate (OKB) solvent. Coatings were made on polyethylene terephthalate (PET) foil which is an elastic and transparent substrate. Scanning electron microscopy (SEM) pictures of fillers used in experiment were taken and are presented in Figs. 1a,b and 2a,b. Geometrical properties of investigated material are shown in Table I.

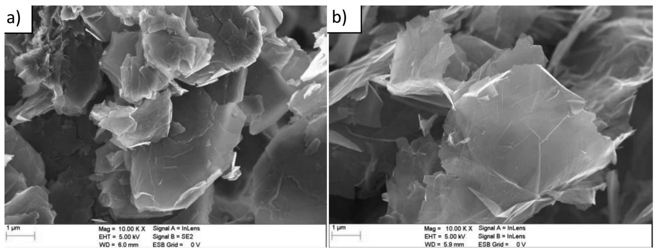

Fig. 1. Scanning electron microscopy pictures of: (a) GMP and (b) GNP.

TABLE I

Geometrical properties of investigated carbon nanostructures.

Filler material	GMP	GNP	GNF	DWCNT
platelet thickness	12–16	10 nm	–	–
diameter	2–10 μm	2–25 μm	50–250 nm	2–4 nm
surface area [m^2/g]	–	100	80	350
length [μm]	–	–	0.5–5	10–50

Screen printing pastes were sonicated for 30 min at room temperature to achieve the uniformity of the filler

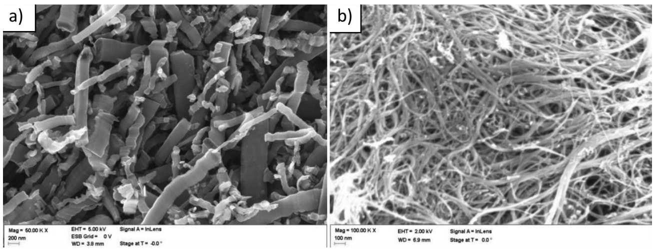

Fig. 2. Scanning electron microscopy pictures of: (a) GNF and (b) DWCNT.

TABLE II

Inks and pastes compositions.

Method of deposition	Screen printing				Spray coating			
Filler material	GNP	DWCNT	GPM	GNF	GNP	DWCNT	GPM	GNF
filler content [wt%]	1.50	0.25	22.00	21.00	1.96	0.35	4.15	3.25
PMMA content [wt%]	8.00	8.00	8.00	8.00	0.09	0.09	2.99	0.98
OKB content [wt%]	90.50	91.75	82.00	71.00	97.95	99.56	92.87	95.77

in the PMMA matrix. Then they were rolled twice on three-roll mill with silicon carbide (SiC) roller. The printing process of the final mixtures was done using screen printer AMI Presco type 242. Spray coating inks are thinner than screen printing pastes. Their content of PMMA resin is much smaller, which can sometimes cause problems with adhesion but in general brings beneficial effects i.e. smaller sheet resistance, slimmer layers, and better light transmission, especially in visible wavelength. Inks and pastes compositions are presented in Table II. Spray coating inks were sonicated for 30 min at room temperature to achieve the uniformity, then they were coated using our spray coating equipment. The air pressure was set on 0.3 MPa, the nozzle diameter was 0.5 mm and the distance between the nozzle and the substrate was 200 mm. Layers after deposition with screen printing and spray coating have been thermally cured in a dryer in 120 °C for 30 min.

3. Results and discussion

3.1. Transmission, thickness and sheet resistivity

Measurements of optical properties were performed for wavelengths from 350 nm to 1100 nm. Transmission was measured with Perkin Elmer Lambda 40 spectrometer. Transmission values in Table III are measured for wavelength $\lambda = 550$ nm. DWCNT layers showed the best transmission for all investigated wavelengths for both deposition methods. GNF and GMP screen printed layers were not transparent at all, but the same material while spray coated showed transmission around 20% for wavelength $\lambda = 550$ nm due to their openwork structure. GNP for both methods was transparent and showed the most flat characteristic in measured wavelength range, which can be beneficial for example in photovoltaic or display applications, however the transmission has to be improved. Overall spray coated layers showed better transmission than those made with screen printing irrespective to the carbon filler which can be seen from Fig. 3.

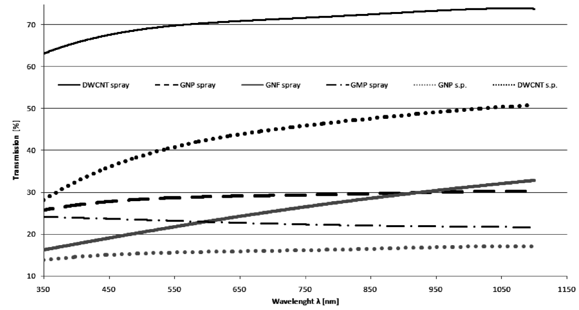

Fig. 3. Carbon layers transmission in wavelengths range between 350 and 1100 nm.

TABLE III

Properties of carbon based screen printed and spray coated layers.

Method of deposition	Screen printing				Spray coating			
Filler material	GNP	DWCNT	GPM	GNF	GNP	DWCNT	GPM	GNF
filler content [wt%]	1.50	0.25	10.00	21.00	1.96	0.34	4.15	3.25
thickness [μm]	11.81	10.23	14.92	7.34	3.51	1.17	3.84	2.91
transmis--sion [%]	15	37.21	–	–	28.75	69.59	23.24	21.68
sheet resistivity [kΩ/□]	56.2	35.21	87.40	26.70	10.92	10.56	292.13	715.51

DWCNT layers showed the lowest sheet resistivity both for screen printing and spray coating methods. Spray coated GPM and GNF layers had higher sheet resistance which can be caused by lower layer thickness and lower filler content in inks in comparison to the screen printing pastes. Spray coated DWCNT and GNP layers had lower sheet resistance than those made with screen printing despite the smaller coating thickness, which can be caused by higher filler content.

3.2. Optical profilometry

The topography of prepared layers was measured with optical profilometer Veeco NT2000. Measured roughness parameters are shown in Table IV.

Spray coated DWCNT layers had the smallest *Rp* parameter, which in many applications is beneficial as regard the susceptibility for electrical breakdowns. In other applications high *Rp* parameter (i.e. screen printed GPM) can be advantageous for example when there is a need of point charge congregation. Spray coated GNF has the smallest average *Ra* and root mean squared *Rq* roughness in contrast to screen printed GPM coating.

TABLE IV

Roughness parameters with standard deviation errors.

Method of deposition	Screen printing				Spray coating			
Filler material	GNP	DWCNT	GPM	GNF	GNP	DWCNT	GPM	GNF
root mean squared *Rq*	2.21±0.25	2.07±0.19	3.95±0.39	1.21±0.14	0.47±0.16	0.18±0.05	0.61±0.09	0.14±0.12
arithmetic average *Ra*	1.83±0.16	1.60±0.13	3.46±0.23	0.97±0.09	0.35±0.07	0.13±0.08	0.39±0.11	0.09±0.05
maximum height *Rt*	11.61±0.47	10.03±0.53	14.70±0.44	6.46±0.39	3.15±0.32	0.98±0.13	3.66±0.27	1.43±0.17
maximum peak height *Rp*	4.77±0.41	6.62±0.47	11.52±0.58	3.15±0.38	2.08±0.31	0.53±0.19	2.23±0.28	0.67±0.21
maximum valley depth *Rv*	−6.83±0.48	−3.41±0.41	−3.17±0.37	−3.32±0.44	−1.07±0.22	−0.45±0.07	−1.43±0.24	−0.76±0.18

3.3. Fatigue tests

Figure 4 presents fatigue tests results for two sets of samples — screen printed and spray coated. All samples in both sets showed high mechanical stability as regards the almost constant sheet resistance irrespectively of the number of bending cycles. Those results consider carbon based layers as an interesting material for flexible applications.

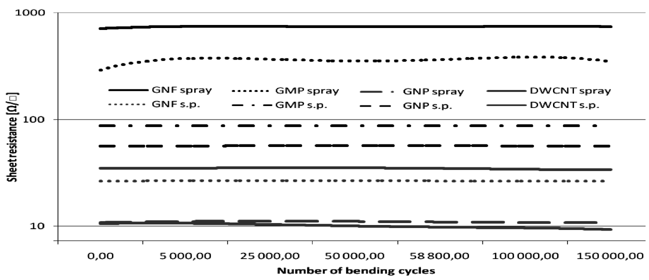

Fig. 4. Fatigue tests results for carbon fillers based layers.

4. Conclusions

All carbon based fillers showed excellent mechanical stability under several bending cycles in fatigue test. Transparency was related to the thickness of the layer therefore to the deposition technique — spray coated layers were much more transparent. Even layers made with opaque materials, while spray coated showed the transparency due to the openwork coating structure. Spray coated layers had also smaller sheet resistance for the same filler load, which was caused by smaller amount of polymer resin. Moreover spray coated layers had smaller differences in transmission for particular wavelengths. DWCNT spray coated layers showed high transmission between 65% and 75% with sheet resistance near 10 kΩ/□ and perfect mechanical stability which makes this coatings an excellent material for flexible and transparent electrodes that can be used in displays or photovoltaics. Furthermore, spray coated DWCNT layers are made in non-rigorous laboratory environment, without harmful substances and in low temperature processes which makes them cheap and easy in industrial implementation.

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