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CHARACTERISTIC OF POLYMER COMPOSITES STRENGTHENED WITH CARBON NANOTUBES

Carbon nanotubes because of their high mechanical, optical or electrical properties, have found use as semiconducting materials constituting the reinforcing phase in composite materials. The paper presents the results of studies on the mechanical properties of polymer composites reinforced with carbon nanotubes (CNT). Before introduction to the polymer matrix, the nanotubes were subjected to chemical cleaning. Carbon nanotubes cleaning was carried out in the liquid phase using a mixture of oxidising concentrated nitric and sulphuric acids. Three-point bending tests were carried out on the composites. The density of each obtained composite was determined as well as the surface roughness and the conductance at room temperature. Carbon nanotubes constituting the reinforcement for a polymer composite improve the mechanical properties and conductivity of both the composite and the polymer.

Keywords: carbon nanotubes, composite material, mechanical strength

CHARAKTERYSTYKA KOMPOZYTÓW POLIMEROWYCH WZMACNIANYCH NANORUKAMI WĘGLOWYMI

Nanorurki węglowe z uwagi na wysokie własności mechaniczne, optyczne czy elektryczne znalazły zastosowanie jako materiały półprzewodnikowe stanowiące fazę zbrojącą w materiałach kompozytowych. W pracy przedstawiono wyniki badań właściwości mechanicznych kompozytów polimerowych wzmacnianych nanorurkami węglowymi. Przed wprowadzeniem nanorurek do osnowy polimeru nanorurki zostały poddane chemicznemu procesowi oczyszczania. Oczyszczanie było prowadzone w fazie ciekłej z użyciem mieszaniny utleniających stężonych kwasów azotowego (HNO_3) i siarkowego (H_2SO_4). Na wytworzonych kompozytach przeprowadzono próbę trójpunktowego zginania. Określono gęstość każdego z otrzymanych kompozytów, wyznaczono chropowatość powierzchni oraz przewodność elektryczną w temperaturze pokojowej. Nanorurki węglowe stanowiące zbrojenie dla kompozytów polimerowych poprawiają właściwości mechaniczne oraz przewodność zarówno samego kompozytu, jak i polimeru.

Słowa kluczowe: nanorurki węglowe, kompozyty, wytrzymałość mechaniczna

INTRODUCTION

Carbon nanotubes possess a combination of extraordinary mechanical, electrical and thermal properties. Because of that, they are a promising new class of materials for special applications [1]. Nanotubes are an allotropic form of carbon. Their biaxially ordered structure is built of rolled graphen planes ($d \approx 0.4$ nm), being a set of hexagonal carbon rings [2]. They have extremely high mechanical properties: a tensile strength up to $R_m \cong 500$ GPa, and the modulus of elasticity reaches $E \cong 7\div 8$ TPa. At a small diameter ($1\div 80$ nm) and high aspect ratio (L/D even above 10,000), they are an attractive reinforcing material for polymers, ceramic materials and metals [3].

In numerous areas of life we now observe increasingly broader use of composite materials due to physical-chemical properties better than those of traditional materials. Composite materials, understood as a human product being a combination of two or more components (phases) of different physical-chemical properties, feature properties dissimilar to those of the phases forming them. The components forming them consist of: a binder, referred to as the matrix, and a material improving the mechanical properties of the matrix, referred to as strengthening or the reinforcement [4].

Carbon nanotubes added to polymers cause a substantial change in the material physical properties, even

a small amount gives features of a conducting polymer. To achieve the most desired composite properties, it is important that interaction forces between the dispersed phase and the polymer matrix are as high as possible, the filler distribution in the polymer is homogenous and the filler is well wettable with the polymer [5].

Apart from the physical-mechanical properties of the components, the size of the dispersed phase (filler) contact area and the nature of interactions between the continuous and dispersed phase play a significant role for the properties of polymer composites as structural materials [6].

In the case of nanotubes, it is difficult to obtain their homogeneous distribution in the polymer, because Van der Waals forces between individual nanoparticles cause easy formation of aggregates and agglomerates, which substantially reduce the contact area between the nanotubes and polymer. Therefore modification of the nanofiller surface e.g. via the connection of functional groups (-OH, -COOH, -NH₂, etc.), capable of chemical or physical binding with the matrix, seems necessary, which would allow increasing interactions on the interface.

The modification methods are different and they also depend on the type of polymer which is to form the nanocomposite matrix [5, 7].

MATERIALS AND EXPERIMENTAL PROCEDURE

CNT CO. LTD carbon nanotubes, with the commercial name CTUBE 100, obtained using the thermal CVD method, were used as the studied material. According to the producer, the raw nanotubes were 1 to 25 µm long, 10 to 40 nm in diameter, with the density of 0.03÷0.06 g/cm³ and a specific surface area of 150÷250 m²/g.

Carbon nanotubes carboxylated after cleaning were used to reinforce the composites. Carbon nanotubes cleaning was carried out to get rid of the pollution created during their synthesis. It was performed first of all to remove iron and other metals used as the reaction catalysts and amorphous carbon. This process was carried out in the liquid phase using a mixture of oxidising concentrated nitric and sulphuric acids.

During cleaning, the amorphous carbon oxidised and degraded much faster than the undefected CNT structures. The carboxylated nanotubes formed in the process of cleaning (Fig. 1) were introduced to the polymer. The content of the carboxyl groups is 40÷50 wt.%. Polyvinyl alcohol (PVA) with a water acrylate dispersion (Osakryl 1M) was used as the matrix.

The composites were produced using the solvent method, i.e. via mixing in the solution. The first stage consisted in mixing nanotubes with polymer solutions obtained as a result of PVA and acrylate dissolved in water. A small amount of plasticiser was also added for better nanotubes dispersion. The mixture prepared in such a way was poured into a mould, where the solvent was removed through evaporation.

The produced composites featured a different content of nanotubes versus PVA and acrylate (Table 1). In Composite 1, the ratio of carbon nanotubes to PVA and to the water dispersion was: 1:1:1, in Composite 2, this ratio was 1:3:1, in Composite 3 ÷ 1:8:2 and in Composite 4 ÷ 1:7:1, respectively. In addition, for comparison purposes, a fifth composite was produced consisting of the polymer matrix only with a PVA to Osakryl ratio of 4:1.

TABLE 1. Composition of produced composites
TABELA 1. Skład poszczególnych kompozytów

	CTUBE [g]	PVA [g]	Osakryl [g]
Composite 1	50	50	50
Composite 2	50	150	50
Composite 3	50	400	100
Composite 4	50	350	50
Composite 5 (matrix)	-	400	100

The solvent was then removed by evaporation. After spontaneous evaporation of the solvent, the composites were crosslinked at room temperature for 30 days. The structure was examined using an optical microscope Olympus GX41. Then test specimens of 10 mm x 10 mm x 50 mm dimensions were cut for three-point bending. Mechanical strength tests by means of three-point bending were performed on the specimens.

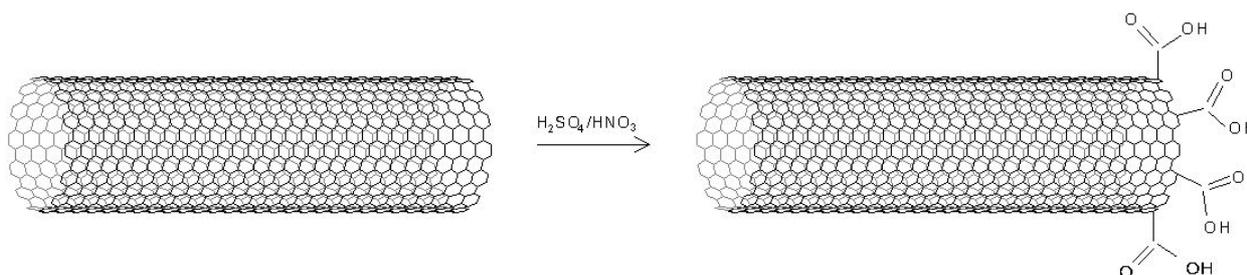


Fig. 1. Functionalisation of carbon nanotubes

Rys. 1. Funkcjonalizacja nanorurek węglowych

The tests were carried out by means of a ZWICK/ROELL Z100 testing machine using a force of 50 kN. Three-point bending is one of the basic methods to determine bending strength. Bending strength presents the highest stress originating in the material at the moment of breakage. The diagram of three-point bending is presented in Figure 2.

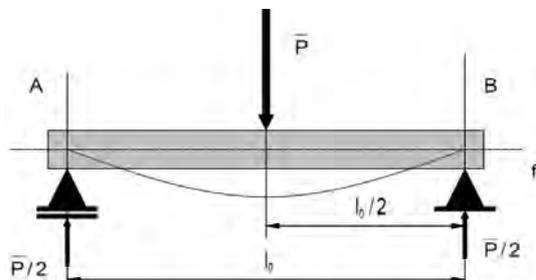


Fig. 2. Diagram of three-point bending test

Rys. 2. Schemat próby trójpunktowego zginania

According to the diagram, the load is executed by force P applied at the beam centre, resulting in reactions o in the supports, equal to $P/2$. The highest bending moment is [8]:

$$M_g = \frac{Pl_o}{4} \quad (1)$$

The bending stress originating from moment M_g is [8]:

$$\sigma_g = \frac{Pl_o}{4W_g} \quad (2)$$

where: W_g is the bending strength index, which for a rectangular cross section b wide and h high is calculated in accordance with formula [8]:

$$W_g = \frac{bh^2}{6} \quad (3)$$

Hence bending strength R_g is [8]:

$$R_g = \frac{M_g}{W_g} \quad (4)$$

Roughness was measured on a T600 HOMMEL TESTER, in which the surface shape is mechanically followed by a system of moving inductive converters. The examination was carried out on the composite surface which was not in contact with the mould to determine the roughness of free surface and hence the porosity influence on the composite density.

The obtained composites conductance was measured at room temperature using a digital Hontek DT-9208A multimeter.

Each composite density was also measured. The basic method of density measurement consists of independent measurement of the specimen mass and volume. The specimens mass was determined by means of an electronic balance ($\Delta \pm 0.01$ g) and the volume

of cuboidal specimens via measuring their dimensions using a vernier calliper ($\Delta \pm 0,01$ mm).

RESULTS OF TESTS

Examples of images of the composites and of the matrix obtained by an optical microscope are presented in Figure 3. Specimen 5 (Fig. 3a) featured a uniform structure, which proves the homogeneous mixing of both polymers, while composites 2 and 4 (Fig. 3b and 3c) featured a homogeneous distribution of reinforcement.

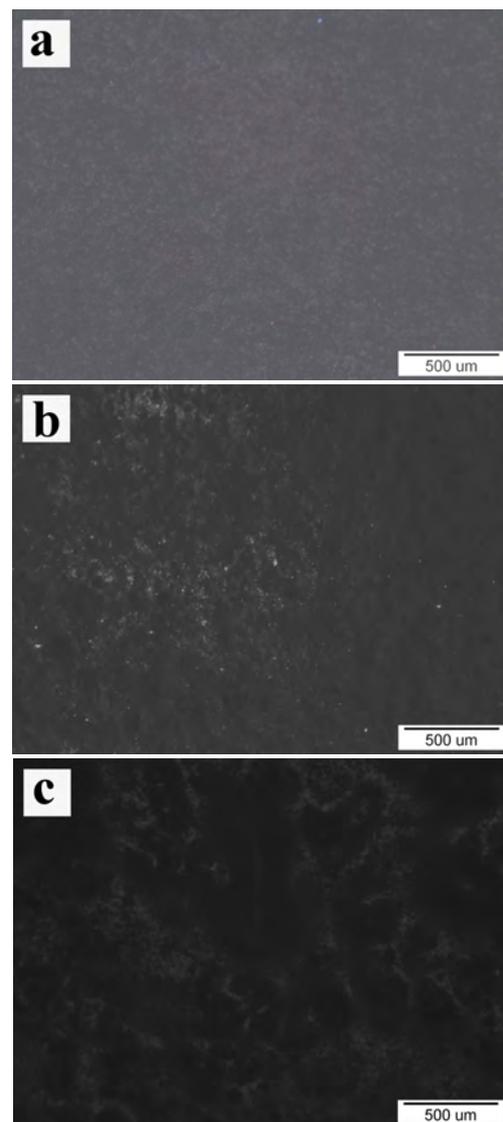


Fig. 3. Microstructure: a) composite 5 (matrix), b) composite 2, c) composite 4

Rys. 3. Obraz mikrostruktury, a) kompozyt 5 (osnowa), b) kompozyt 2, c) kompozyt 4; pow. 50x

Figure 4 presents graphically the force versus deformation relationship for the three-point bending test.

From the graph (Fig. 4), the maximum force was read and individual composites bending strength was calculated based on formula (4). The results of the

bending strength, densities and conductance for individual composites are presented in Table 2.

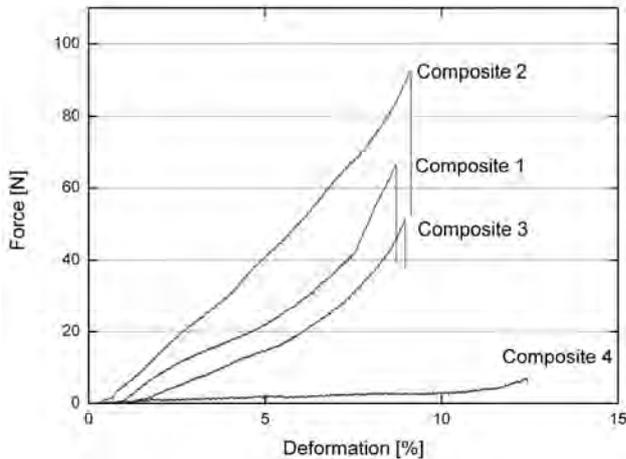


Fig. 4. Force vs. deformation for three-point bending test

Rys. 4. Zależność siły od odkształcenia dla próby trójpunktowego zginania

The strength of Composite 4 is the highest and equal to 8.2 MPa, while the lowest bending strength of 2.052 MPa was shown by Composite 3. The bending strength was not determined for the matrix, because the material was too elastic and during testing the specimen only bent.

With an increasing PVA content, the composites density grew, which is visible in Figure 5. Differences in the composite densities are caused by their diversified porosity, which converts to the result of roughness measurement. However, the matrix has the highest density (1.22 g/cm³).

TABLE 2. Results of bending strength, density and electrical conductivity for individual composites

TABELA 2. Wyniki pomiarów wytrzymałości na zginanie, gęstość oraz przewodność poszczególnych kompozytów

Designations of samples	Bending strength R_g [MPa]	Density d [g/cm ³]	Electrical conductivity σ [S/m]
Composite 1	3.315	0.38	3.9
Composite 2	2.47	0.43	0.4
Composite 3	2.052	0.60	0.007
Composite 4	8.2	0.63	0.09
Composite 5 (matrix)	-	1.22	0.00000004

The composite roughness measurements were performed on area $LT = 4.80$ mm long with the precision of $LC = 0.80$ mm. The tests resulted in obtaining graphs for the studied composites, where voltage changes were recorded in the form of peaks, evaluated by means of instrument head electronics, which are converted into a signal proportional to the position changes of the

diamond tip, by means of which appropriate surface parameters are displayed and documented. The basic parameters of the studied material surface roughness include:

- R_a - arithmetical mean roughness deviation
- R_{max} - maximum roughness height
- R_t - maximum elevation - cavity height
- R_z - average roughness height
- R_p - maximum height of elevation

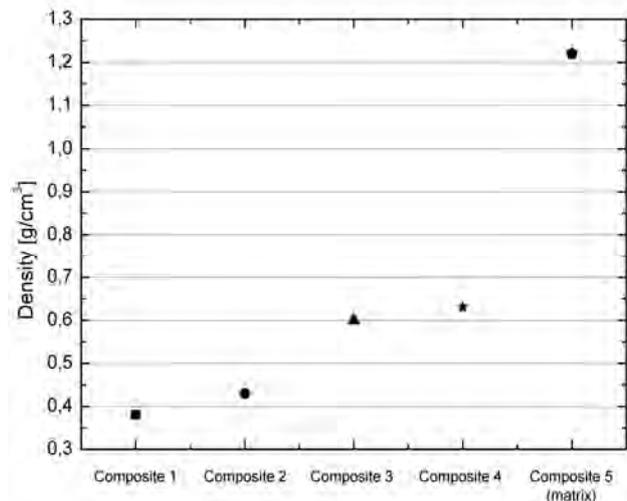


Fig. 5. Density changes in relation to change in individual composite components content

Rys 5. Wykres zmian gęstości wraz ze zmianą zawartości poszczególnych składników kompozytów

The obtained roughness results (Table 3) have shown that the composite which contained the highest PVA amount featured the highest roughness, whereas composites with a low PVA content (composite 1 and composite 2) feature the lowest roughness.

TABLE 3. Basic roughness parameters of studied composites surface

TABELA 3. Podstawowe parametry chropowatości powierzchni badanych kompozytów

	Composite 1	Composite 2	Composite 3	Composite 4
R_a [μ m]	3.88	2.07	4.16	4.31
R_{max} [μ m]	3.61	13.12	32.80	46.54
R_t [μ m]	44.00	13.45	32.80	46.54
R_z [μ m]	22.36	11.16	22.87	20.56
R_p [μ m]	26.62	7.24	16.73	26.28

On the obtained graphs (Fig. 6) it is possible to notice the appearance of high peaks, which prove the high porosity of the composite surface. Composites 3 and 4 featured the highest roughness.

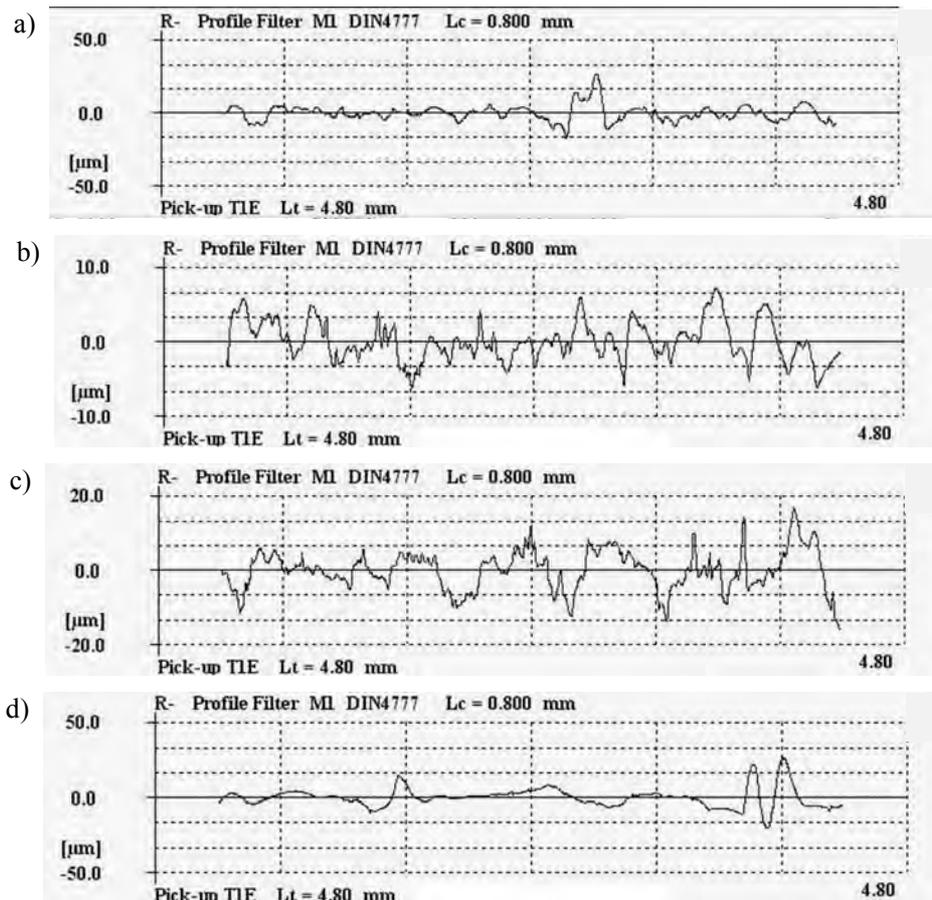


Fig. 6. Roughness measurement graphs for individual composites

Rys. 6. Wykresy pomiaru chropowości dla poszczególnych kompozytów

The conductance measurements are presented in Table 2. As nanotubes are good conductors, the composites feature good conductance. The highest conductance is shown by Composite 1 in which the ratio of nanotubes content to PVA and to water dispersion is 1:1:1. Such a composite conductance is 3.9 S/m, and the lowest conductance is shown by Composite 3, whose ratio of nanotubes content to PVA and to water dispersion is 1:8:2. Its conductance is 0.007 S/m. For the composite in which the ratio of nanotubes content to PVA and to water dispersion is 1:3:1, the conductance is 0.4 S/m, while for the composite in which the ratio of nanotubes content to PVA and to water dispersion is 1:7:1, the conductance is 0.09 S/m. The addition of carbon nanotubes to the matrix causes it to become conductive.

SUMMARY AND CONCLUSIONS

It has been noticed during the nanocomposites mechanical strength tests that the highest bending strength is shown by the composite of nanotubes content ratio to PVA and to water dispersion equal to 1:7:1. For such a composite the bending strength is 8.2 MPa. The bending strength for the composite with the nanotubes content ratio to PVA and to water dispersion of 1:1:1 is 3.315 MPa, and with the nanotubes content ratio to PVA and to water dispersion of 1:3:1 it is

2.47 MPa. The lowest bending strength is shown by the composite of nanotubes content ratio to PVA and to water dispersion equal to 1:8:2. Its strength amounts to 2.052 MPa. It results from the tests that the higher the acrylates content in the composite, the lower the bending strength, caused by substantial brittleness of the given composite.

The density of the obtained composites ranges from 0.3 to 0.6 g/cm³ and may be considered promising, because such solutions are sought as to obtain as high as possible mechanical strength at as low as possible density. The best composite may be considered the one in which the ratio of nanotubes content to PVA and to water dispersion is 1:1:1, because its density is 0.38 g/cm³ and the bending strength is 3.315 MPa. Nanotubes added to the matrix reduced the density of the composites.

The highest roughness was featured by the composite with the ratio of nanotubes content to PVA and to water dispersion of 1:7:1. Its maximum roughness is 46.54 µm, and the lowest roughness is featured by the composite with the ratio of nanotubes content to PVA and to water dispersion of 1:3:1. The maximum roughness for it amounts to 13.12 µm. The other parameters, such as R_a , R_t , R_p , R_z are also higher for composites of higher PVA content. The differences in specific composite roughness result from diversified porosity.

The highest conductance is shown by Composite 4, in which the ratio of nanotubes content to PVA and to water dispersion is 1:1:1. Such a composite conductance is 3.9 S/m, and the lowest conductance is shown by composite 3, whose ratio of nanotubes content to PVA and to water dispersion is 1:8:2. Its conductance is 0.007 S/m. The higher the nanotubes content in the composite, the better its conductance is. Nanotubes added to a non-conductive matrix make the composite become conductive.

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