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IMPACT OF CARBON NANOTUBES ON THE MECHANICAL AND ELECTRICAL PROPERTIES OF SILICONE

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Abstract

This paper presents the results of a structure study of a dispersion composite on a silicone matrix with a filler in the form of multi-walled carbon nanotubes (MWCNTs). The study aims to determine the effect of the filler on the composite mechanical properties and electrical conductivity. Materials that are electrically conductive and exhibit high mechanical properties can find applications in high-strain sensors. During the study, the characteristic properties of the susceptible materials, silicone alone and silicone with different filler contents (4%, 6%, and 8% by weight), were determined after curing. Microscopic observations were performed to assess the influence of carbon fillers on the material structure and to determine the level of homogeneity of the material. Examination of mechanical properties facilitated the determination of the Shor A hardness (ShA), stiffness, and Poisson's ratio of the cured composites, depending on the nanotubes' content. In parallel with the study of mechanical properties, the effect of loading, and the associated deformation of the samples, on the conductivity of the composite was investigated. Based on the results obtained, a discussion was carried out on the type of conductivity characteristic of silicone with different filler content as well as depending on the level of deformation of the samples.

Keywords: nanotubes; silicon, mechanical properties, electrical properties
Article Category: research article

1. INTRODUCTION

Research and technology in the area of carbon nanotube materials have grown rapidly in recent years.

Nanotubes are specific carbon structures characterized by different parameters (Borowiak-Palen et al., 2002; Borros et al., 2006; Huczko, 2004; Terranova et al., 2006). However, generally, the division is based on their structure: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs are built from a single graphene shell (Terranova et al., 2006) and MWCNTs are from concentrically co-axial cylinders (cylindrical), polygonal (polygonal) and graphene coil (helical) (Przygocki & Włochowicz, 2001). The outer diameter (OD) of SWCNTs is in the order of several nm and MWCNTs are in the order of several tens of nm (Iijima, 2002). The length of the nanotubes is of the order of 105 μm (Przygocki & Włochowicz, 2001).

According to Borowiak-Palen et al. (2002) SWCNTs can be either conductors or semiconductors. On the other hand, according to Bielanski (1980) MWCNTs have the properties of electrical conductors. Nanotubes are diamagnets (Przygocki & Włochowicz, 2001).

Nanotubes have a high specific surface area (SSA) and a low density at the same time, due to the presence of a hollow core. SWCNTs have a SSA of 100–200 m^2/g and a density of 0.6 g/cm^3 while MWCNTs have a SSA of 10–20 m^2/g and a density of 1–2 g/cm^3. The tensile strength of nanotubes can be up to 100 times greater than that of steel, while their density is 16 times lower. The maximum tensile deformation of nanotubes is up to 40%, which makes them highly elastic and resilient. Therefore, it is possible to bend, torsion and axial compression without compromising their integrity. However, it should be borne in mind that nanotubes have variable chirality and, upon deformation, their electrical properties change. Furthermore, for certain values of deformation, nanotubes lose stability – they bulge or constrict (Bielanski, 1980; Bachmatiuk, 2008).

When nanotubes are used as an additive in various resins, the resulting composite has new interesting properties. Manufacturing of a mixture of nanotubes with a matrix is a scientific issue itself.

In practice, mechanical mixing – using an agitator followed by ultrasonic treatment at frequencies in the range of 40kHz (Mucha et al., 2020), mixing using a calendar (Gojny et al., 2004; Rosca & Hoa, 2009; Gardea & Lagoudas, 2014) or in bead mills – is used. Recently, dispersing devices have appeared in the market, whose operating principle is based on the optimum action of shear forces, flow turbulence and cavitation. In this way, high homogenization of the mixed materials is achieved and the nanotubes are not damaged (Grupa Wolf, 2023). In order to improve the mixing of nanotubes with the polymer, nanotube modifications can be used. However, it should be reckoned that this action degrades the electrical conductivity properties (Królikowski & Rosłaniec, 2004; Bakar Sulong et al., 2009).

Nevertheless, filling polymers with nanotubes raises the problem of achieving adequate homogenization of the mixture because of nanotubes tendency to agglomerate (Ciecierska et al., 2015). The large SSA of the nanotubes makes them capable of entanglement (Pen-Cheng Ma et al., 2010) so that even a small number of nanotubes leads to a very large increase in the viscosity of the fluid in which they are mixed. Latko-Durałek et al. (2020) proved that a mass fraction of 7% MWCNTs in a thermoplastic resin (180°C) results in a 4–5 times increase in viscosity compared to a resin without nanotubes. In contrast, Ciecierska et al. (2015) showed that a mass proportion of 1% MWCNTs in an epoxy resin with a viscosity of 800 mPa·s increased the viscosity of the mixture so much that it prevented the proper removal of air bubbles, resulting in high porosity.

Thanks to the properties described, the use of nanotubes as fillers facilitates modification of the various materials' properties.

From an aeronautical engineering perspective, the material should have high strength and high modulus of elasticity at low weight. By filling epoxy resins with carbon nanotubes, the strength properties of the resulting nanocomposite can be modifieddepending on the resin and nanotubes used. According to Ciecierska et al. (2015), Ganesh et al. (2017), and Liu et al. (2020), the highest strength of the obtained nanocomposite is observed at a content of 0.1%–0.5% by weight of nanotubes, and according to the work (Smoleń et al., 2021) at a content of 1.5%. Increasing the amount of nanofiller added results in a decrease in the strength of the material. Ciecierska et al. (2015) presented the same relationship for impact resistance, and according to Domun et al. (2015) a nanotube content of 0.1%–2.0% by weight had a good effect on fracture resistance. Smoleń et al. (2021) noted that the modulus of elasticity with an increase in nanotube content up to 1.5% does not change significantly, but further increases in content cause a drastic decrease in stiffness. According to Ganesh et al. (2017) the increase in tensile strength of materials for lower filler weight percentages is probably due to improved adhesion between matrix and filler. On the other hand, for higher amounts of nanotubes in the epoxy matrix, the phenomenon of agglomeration of nanofillers and the formation of voids is observed. Agglomeration occurs due to Van der Waals forces. In the case of larger weight fractions of fillers, they are located close to each other and thus attract each other. This phenomenon leads to agglomeration causing stresses to concentrate in this region, which leads to a reduction in the strength of the material. In the case of a silicone matrix, with fillers in the form of metallic powders and in the form of graphene flakes, the strength also increases as the amount of filler increases and decreases beyond a certain value. However, the limiting content is an order of magnitude higher. According to Kumar, Kumar, Song, et al. (2021) the limiting level of silicon matrix nanofillers after which the mechanical properties decrease is about 15 wt.%.

In addition to being conductors of electricity, carbon nanotubes have a much higher aspect ratio than other powder fillers, such as carbon black, which allows them to form prelocation-percolation networks in the matrix. Percolation networks of carbon nanotubes in a dielectric matrix, turn the resulting nanocomposite into an electrical conductor (Ciecierska et al., 2015). The electrical conductivity of composites has become increasingly significant. Areas of application in this area include the aerospace industry. Here, work is being done to eliminate the heavy copper mesh used as a lightning strike mitigation system and replace it with a resin layer filled with nanotubes (Ganesh et al., 2017; Dydek et al., 2021). Ciecierska et al. (2015) described that epoxy resin-based composites with 0.2 wt% nanotubes achieved conductivity equal to composites with 9 wt% carbon black. The results of a comparative study of two structural solutions for lightning protection performance are presented by Dydek et al. (2021). The first solution is a Tuball paper containing 75% by weight or 90% by weight of carbon nanotubes, applied on top of a carbon fiber reinforced polymer prior to the formation of the aeronautical structure panels. At the same time, reference panels, covered with copper mesh – in accordance with current aviation regulations – were tested. The effectiveness of the lightning protection was assessed using the ultrasonic phased-array technique. It was found that the introduction of Tuball paper with nanotubes on the surface of the laminates improved both surface and volumetric electrical conductivity by 8800% and 300%, respectively. Another area is the wider electronics and electrical systems in both stationary devices and the growing automotive industry using hybrid and electric drives. The idea is to use conductive adhesives that eliminate traditional, heavier lead-tin solder joint (Geipel et al., 2018; Lopes et al., 2019).

An interesting research area related to the use of nanotubes is electrical susceptible materials with applications in medicine, and the textile industry.

Krainoi et al. (2021) presented several attempts to disperse nanotubes in a matrix of natural rubber, trying to avoid agglomeration. To this end, the addition of secondary fillers was introduced into the composites by generating new conductive pathways of hybrid fillers. An improvement in conductivity was achieved by adding carbon black to the polymer nanotube composites. However, the electrical conductivity of the composites was found to increase slightly with carbon black concentration when the nanotube content was below the percolation threshold, which is 1–7 wt% depending on the rubber used. However, there was no significant increase in electrical conductivity above the percolation threshold concentration, with a maximum conductivity of 0.1S/cm. As the authors note, this may be due to the agglomeration of carbon black bonded to the nanotube surfaces, which hinders the conductivity of the hybrid ternary composites. Thus, it can bridge the nanotubes and contribute new electron pathways only with a highly homogeneous distribution of both fillers. Therefore, the extremely high viscosity of the natural rubber is essential to increase conductivity by allowing good dispersion of the fillers during mixing. Another material widely used in industry is silicone (Kumar, Alam, et al., 2021). Silicone consists of a base and a vulcanizing agent of variable hardness (Lee et al., 2004). One of the most advantageous characteristics of silicone, in terms of modification with fillers, is its low viscosity in the uncured state. Other important advantages include ease of processing, high resistance to heat and acid ageing and good flexibility (Kumar, Lee, et al., 2020; Yadav et al., 2021). Hence, silicone as the parent matrix in carbon nanomaterial-reinforced nanocomposites is usedfor various applications, including as strain measurement sensors (Kumar & Lee, 2016; Yang et al., 2018). Due to the previously described properties, nanotubes have become a suitable filler for silicone (Kumar, Lee, et al., 2020; Kumar, Kumar, Han & Park, 2020) and are displacing other fillers used previously, including carbon black (Cardona-Uribe et al., 2021; Plagge & Lang, 2021; Sivaselvi et a;., 2021). As in other matrices, as presented above, nanotubes in the form of silicone positively influence the properties of the new nanocomposite (Hagita & Morita, 2019; Sajith, 2019; Zhang et al., 2021).

In Gogurla et al. (2019), the properties of a susceptible material, a hydrogel, with potential applications in human-machine interactions and personal health monitoring, were presented in detail. Following this path and using the existing knowledge presented in this chapter, the challenge was to test the properties of the developed silicone-based nanocomposite depending on the nanotube content.

2. MATERIALS

2.1. Raw materials

As the matrix for the study RTV-2 (Room Temperature Vulcanization) silicone of the Siliform series from Ag-Bet (Dobrzelin, Poland) was used. This is a two-component, sulfurized silicone rubber. According to the technology sheet enclosed with the product, the Shor A hardness of the material is 25 ShA, and the material integrity is up to 3.8 MPa with deformation up to 400%. The viscosity of the A component is 23Pa·s, and when mixed with the hardener (3% wt.), the viscosity is 19 Pa·s.

The useable time after mixing the silicone and hardener is 20 min and the time to full cure at room temperature after mixing the components is 5 h. The silicone used in this study is a typical material used for moulds used to cast components from gypsum or chemicallycured duroplastic resins. Thanks to its properties, silicone can also be used for gaskets used in low-pressure hydraulics and vacuum systems.

For the nanofiller, industrial-grade multi-walled nanotubes of 90% wt.%, 10 nm OD, manufactured by Bucky USA (Houston, TX, USA), were chosen. The MWCNTs were delivered in the form of powder. The manufacturer specifications were as follows: purity: 90 wt.%, OD: 10–30 nm, inner diameter (ID): 5–10 nm, length: 10–30 m, SSA: >200 m^2/g, bulk density: 0.06 g/cm^3, true density: ~2.1 g/cm^3.

2.2. Samples for tests

Four types of samples were made. The first type of specimen, reference specimens with an s0% designation, was made from pure silicone, without filler. The next three types were:

- s4%–4% wt. nanotubes content,
- s6%–6% wt. nanotubes content,
- s8%–8%wt. nanotubes content.

The content of 8 wt.% of nanotubes in the silicone is the maximum amount that facilitates the components to be mixed with each other in a doughy fluid consistency. A content of 4 wt.% and 6 wt.% of nanotubes was used to estimate the effect of the percentage of nanotubes on the properties of the newly formed composite.

Due to the short useful time after mixing the silicone with the hardener, the measured masses of silicone and filler were mixed first. Samples of 20 g from each mixture were measured for analysis of the uncured materials viscosity testing. Next, curing agents were added to the mixture. After mixing, the materials were molded. The mixing process was performed as follows:

- Mechanical mixing A agent with nanotubes.
- 10-min exposure in a vacuum chamber (–0.8 bar).
- Adding the hardener and mechanical mixing.
- 5-min exposure in a vacuum chamber (–0.8 bar).

When 4% filler was added to the silicone, it was still liquid. When 6% and 8% filler were added to the silicone, the viscous forces exceeded the bulk forces – it adhered to the surface with no tendency to run off at an observation time of about 1 min.

3. Methods

3.1. Rheological properties

In order to investigate the effect of the addition of MWCNTs on the change of the complex viscosity, storage modulus and loss modulus of the uncured mixture, rheological tests were carried out using an oscillatory ARES rheometer (Rheometric Scientific Inc., TA Instruments, New Castle, DE, USA) in parallel plate geometry mode. Using the appropriate strain (0.10%) from the linear elastic range, a dynamic oscillatory stress-controlled rotational test was performed at room temperature with a frequency sweep from 0.1 Hz to 100 Hz.

3.2. Microscopic observations

To assess the quality of the produced and cross-linked silicone-based nanocomposites after adding MWCNTs, observations of the structure were performed using transmission optical microscopy. Samples were prepared using Ultramicrotome Leica EM UC6 (Leica Microsystems, Wetzlar, Germany) equipped with a chamber for low-temperature cutting, where the materials were cut with a diamond knife at the temperature –100°C into slides with 2 μm thickness. Afterwards, samples were placed on the surface of a microscopic glass and observed through a light transmission microscope PZO Biolar (Biolar, Warsaw, Poland).

3.3. Determination of mechanical properties

Testing of mechanical properties consisted of measurements of Shor A hardness, modulus of elasticity and Poisson's ratio.

For susceptible materials such as rubbers, silicones and polyurethanes, one of the most characteristic strength parameters is the Shor hardness A. Susceptible materials can change their properties due to time or external influences (Frigione et al., 2001). Therefore, the measurement of Shor A hardness has become a convenient and quick method to determine the state and physical changes of a material. According to Rodríguez-Prieto et al. (2021), O-rings used in nuclear power plants are tested using the Shora A method after delivery to the user, before installation and during operation. Thanks to the mean values determined from several measurements taken at different locations, it is possible to assess changes in the hardness of the material. The determined standard deviation and normal distribution, on the other hand, make it possible to become a parameter for assessing the homogeneity of the material (Limpert & Stahel, 2011; Liu et al., 2019).

Accordingly, it was assumed that each sample of cured material would be checked 30 times, manually with the use of the Rubber hardness tester Limit 4000. On this basis, the mean value and the standard deviation were determined. In addition to the information obtained about the effect of the nanotube content on the hardness of the nanocomposite, the standard deviation of the hardness at randomly selected locations was used as one parameter to assess the level of homogenization.

In the introduction, a number of publications on the effect of nanotubes on the tensile properties of nanocomposites in a matrix of different polymers were cited. In the present study, the strength properties were also investigated.

Flat panels of 3 mm thickness were made from each nanocomposite and silicone. After curing, three samples were cut from each panel according to the scheme illustrated in Figure 1.

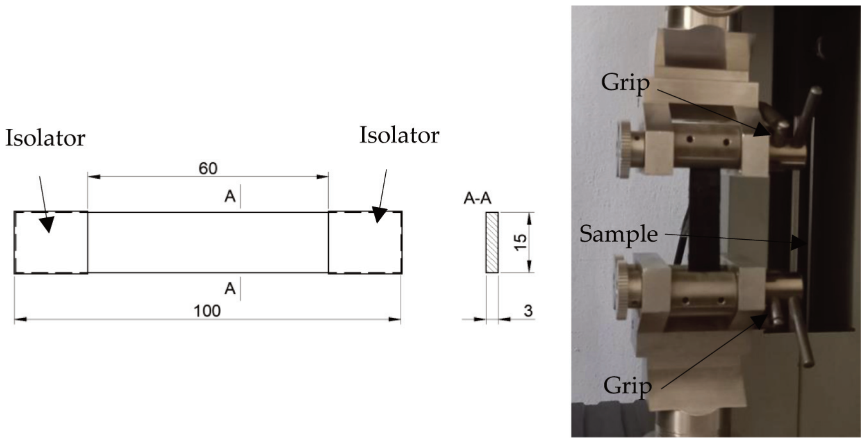


Figure 1. Mechanical and electrical test specimen: **(a)** Schematic of the specimen; **(b)** Sample on the test bench.

The tests were performed on an Adamel 2M testing machine from MTS (Eden Prairie, MN, USA) with a sensor type ISA 3125 No. 2066 with a range up to 500N. At four fixed loads F: 5N, 10N, 15N and 20N, the tension was stopped and the cross-sectional area of the specimens was measured using an electronic caliper with a measurement accuracy of 0.02 mm. The change in specimen length ΔL was recorded using the testing machine software. From the measurements, strains Eq. (1), stresses Eq. (2) and Poisson's ratios Eq. (3) were determined.

$$\varepsilon = \frac{\Delta L}{L}, \tag{1}$$

$$\sigma = \frac{F}{a \cdot b}, \tag{2}$$

$$v = \frac{\Delta b}{b} \cdot \frac{L}{\Delta L}, \tag{3}$$

ε – strain,
L –sample initial length [mm],
ΔL – change in sample length [mm],
σ – stress [MPa],
F – tensile force [N],
a – sample initial thickness [mm],
b – sample initial width [mm],
Δb – change in sample width [mm],
v – Poisson's ratio.

A change in the Poisson's ratio Eq. (3) affects the change in value and the reciprocal of the moduli: the bulk elasticity K – Helmholtz modulus for the three-dimensional case Eq. (4) and the form deformability G – Kirchhoff modulus Eq. (5).

$$K = \frac{E}{3 \cdot (1 - 2 \cdot v)}, \tag{4}$$

$$G = \frac{E}{2 \cdot (1 + v)}. \tag{5}$$

For example, a decrease in the Poisson's ratio results in a decrease in the bulk modulus K and an increase in the modulus of elasticity G. The modulus quotient Eq. (6) also decreases, which can be interpreted as a decrease in the material's susceptibility to bulk deformation. This in turn makes the material more susceptible to volumetric deformation – it becomes more compressible (Baughman et al., 1998; Hall et al., 2008; Yeganeh-Haeri et al., 1992; Lakes, 1987):

$$\frac{3 \cdot K}{2 \cdot G} = \frac{1 + v}{1 - v}. \tag{6}$$

Given the above, it was assumed that Poisson's ratios of the materials obtained would be determined. On this basis, the compressibility will be calculated according to the definition for solids Eq. (7):

$$B = \frac{1}{K}. \tag{7}$$

3.4. Determination of electrical properties as a function of sample elongation

In the publications cited in the Introduction, the properties of the nanocomposites were characterized by the specific conductivity, expressed in (s/m). In the present study, the current density was determined as a function of voltage Eq. (8). From the current-voltage characteristics, it is possible to determine the level of percolation depending on the percentage of nanotubes in the matrix and the applied load/extension of the nanocomposite sample. Furthermore, this characterization makes it possible to determine whether the material satisfies Ohm's law.

$$J = \frac{I}{S(F,x)}, \tag{8}$$

J – current density $\left[\frac{A}{mm^2}\right]$

I – measured current intensity [A],

$S(F, x)$ – cross-sectional area of the specimen [mm^2] depending on the applied load F and displacement x.

Electrical measurements were made for unloaded specimens and for four load levels. The tensile test was carried out analogously to the strength tests. For the electrical measurements, a Keithley 2614B Source Meter (Keithley Instruments, Cleveland, OH, USA) with Keithley KickStart Base software was used (Figure 2).

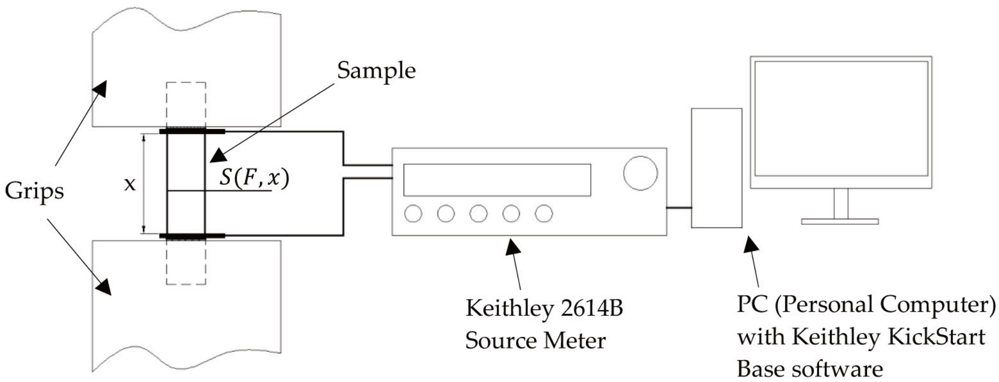


Figure 2. Schematic diagram of an electrical test bench.

4. RESULTS

4.1. Measurement of the viscosity of unfixed mixtures

The effect of the addition of MWCNTs on complex viscosity, storage and loss moduli is presented in Figure 3. Due to the high aspect ratio, MWCNTs are known as nanofillers that strongly influence the viscosity of thermoplastic thermosets nanocomposites (Nobile, 2011). From analyzing the results of complex viscosity (Figure 3a), it is concluded that the viscosity changes as a function of frequency for all materials. This means that there is a shear-thinning behavior with decreasing viscosity, even neat silicone does not behave like a Newtonian liquid. No significant change in complex viscosity was observed between the increase in MWCNTs content from 4 wt.% to 6 wt.% compared to pure silicone. Only for the content of 8 wt% of MWCNTs, the increase was notable. Similar to complex viscosity, storage and loss modulus increase with increasing content of MWCNTs. From analyzing the storage and loss modulus curves (Figure 3b and c), it is observed that nanocomposites with 6 wt.% and 8 wt.% of MWCNTs show elastic behavior due to higher storage modulus values. At lower concentrations of MWCNTs, a more viscous behavior of the material is observed.

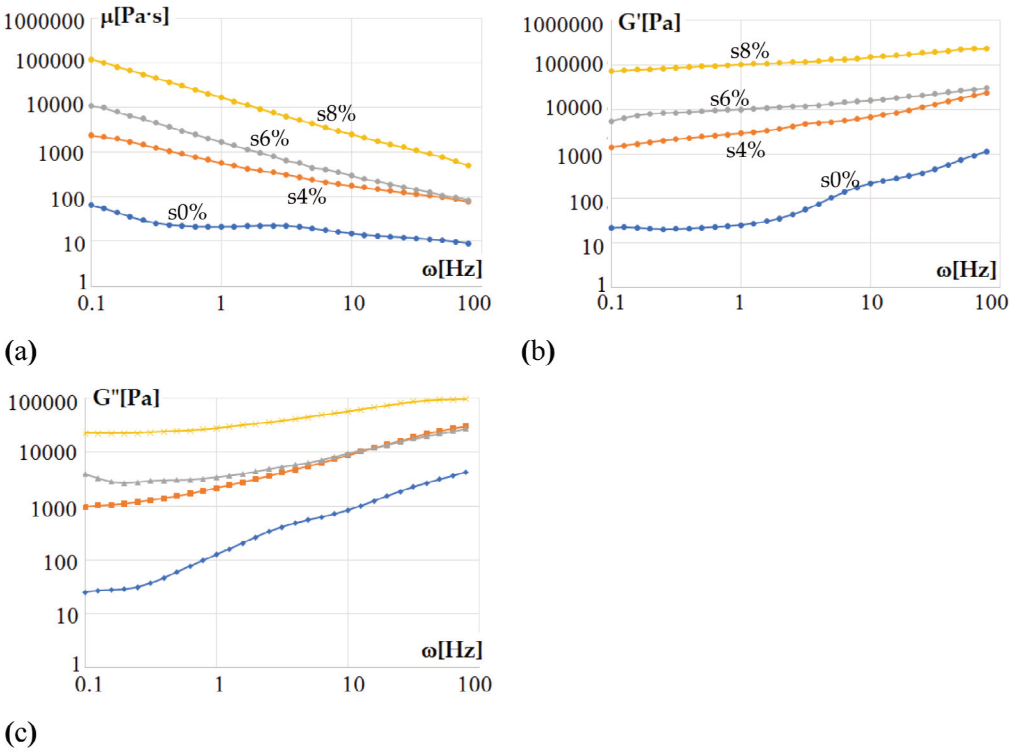


Figure 3. Rheological properties of silicone/MWCNTs nanocomposites: (a) Complex viscosity as a function of frequency; (b) Storage modulus as a function of frequency; (c) Loss modulus as a function of frequency. MWCNTs, multi-walled carbon nanotubes.

4.2. Scanning microscopy

The optical observations of uncured silicone/MWCNT nanocomposites are presented in Figure 4a–d. Due to the significant content of MWCNTs in the produced materials (from 4 wt.% to 8 wt.%), numerous agglomerates of the nanofiller used were observed, which are represented by black areas in Figure 4b–d. The uniformity of observed agglomerates was not noticed, which is the result of a large number of MWCNTs, increased viscosity and strong interactions between the filler and the polymer.

In addition, voids were observed in the structure of the nanocomposite with a content of 8 wt.% of MWCNTs, which was marked in yellow in Figure 4d. This is the effect of a significant increase in viscosity, which was confirmed in rheological tests (Figure 3a). In this case, for the obtained mixture's viscosity, the applied vacuum was too low to get rid of air bubbles during the material manufacturing process.

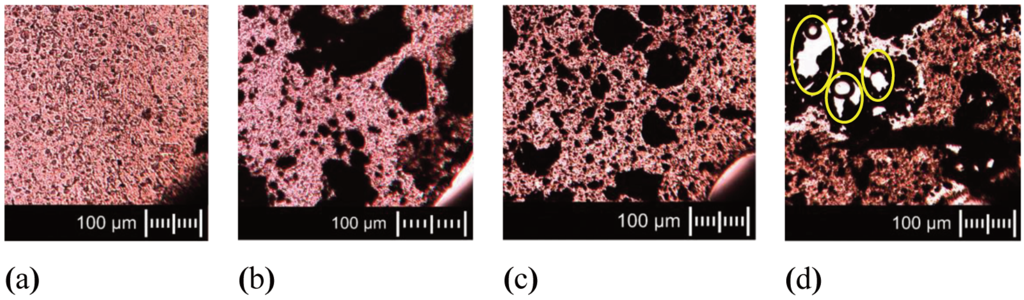


Figure 4. Optical micrographs of produced materials:
(a) neat silicone, (b) silicone with 4 wt.% of MWCNTs, (c) silicone with 6 wt.% of MWCNTs, (d) silicone with 8 wt.% of MWCNTs.
MWCNTs, multi-walled carbon nanotubes.

4.3 Mechanical properties

The tests were carried out and as expected they showed an increase in hardness with increasing nanotube content. According to the graph (Figure 5), it can be assumed that the increase in Shor A hardness is linear as a function of the nanotube content. The average increase in hardness per one per cent of no nanotube content is approximately 2.7 ShA.

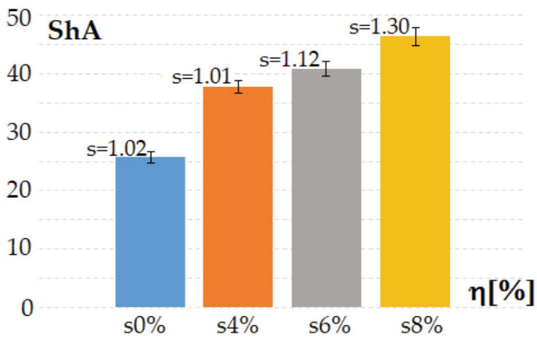


Figure 5. Effect of nanotube content on Shor hardness factor A,
s – standard deviation.

The standard deviation with 30 hardness measurements on each sample, was less than 5% of the mean value which was within 1.02–1.30ShA. Taking the scatter measure as a means of measuring material homogenization, the measurement result can be considered satisfactory. The gaskets used in radioactive storage elements are characterized by similar homogenization as determined by the spread measure of the Shor A hardness measurement (Rodríguez-Prieto et al., 2021).

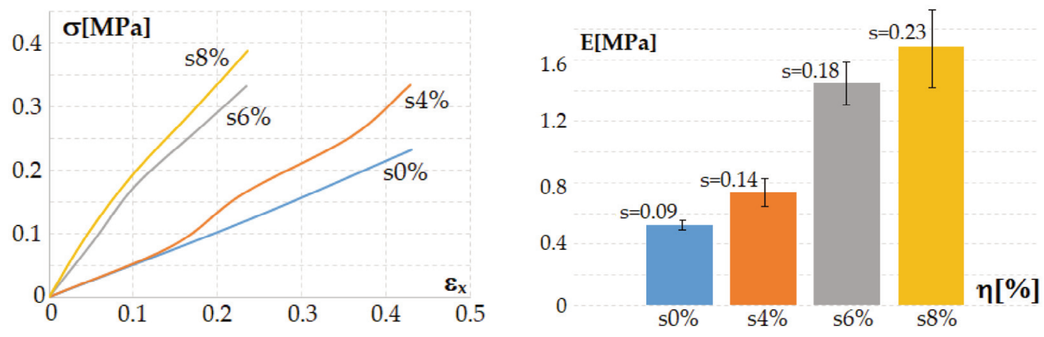
Strength tests were limited to the determination of two parameters: elastic modulus and Poisson's ratio.

From Figure 6a it can be assumed that the stresses as a function of strain have a linear course. Consequently, the moduli of elasticity (Figure 6b) for the nanocomposites were determined from the relationship (9).

$$E = \frac{\sigma}{\varepsilon}, \quad (9)$$

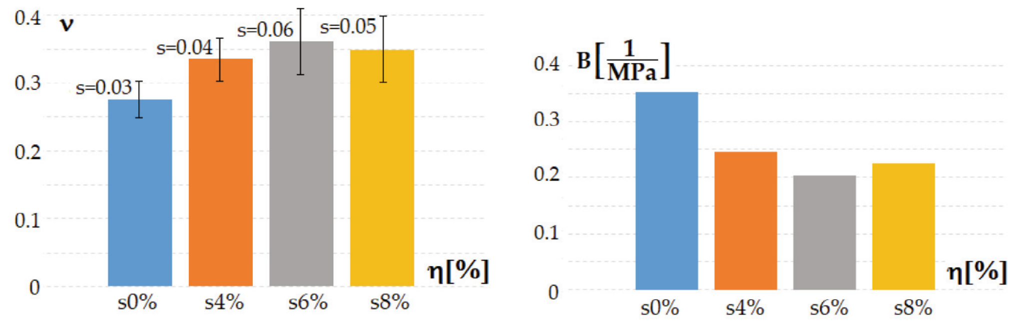
σ – stress [MPa], ε – strain.

As the nanotube content in the silicone increased, the elastic modulus of the nanocomposite increased. Between 4 wt% and 6 wt% nanotube content in the nanocomposite, there was a step increase in the elastic modulus. The standard deviation also increased as a function of the nanotube content in the nanocomposite (Nicolau-Kuklińska et al., 2017).



(a) (b)

Figure 6. Effect of nanotube content on the stiffness of silicone,
(a) stresses as a function of strain – mean values from three measurements for one material; (b) elastic moduli. s – standard deviation.



(a) (b)

Figure 7. Effect of nanotube content on: (a) Poisson's ratio of the silicone; (b) compressibility. s – standard deviation.

Measurements of the specimens, taken during the tensile test, allowed to determine the Poisson's ratio for the composites and silicone (Figure 7) and then determine the compressibility (Figure 7). From the calculation results, it can be seen that as the nanotube content increases to a level of 6 wt.%, the Poisson's ratio increases and thus the compressibility decreases. At a nanotube content of 8 wt.%, the Poisson's ratio decreases slightly, and with it the compressibility increases.

In publication (Li et al., 2004) the authors presented a new formula for the dependence of porosity on rock compressibility. According to this formula, rock compressibility increases as porosity increases, while the conventional empirical formula displays the reversal. Based on this approach, the compressibility of the 8% composite can be assumed to be due to porosity, as illustrated in Figure 4d.

4.4 Electrical properties

A weak electrical conductivity is observed for the manufactured nanocomposites with a content of MWCNT of 4 wt.% and 6 wt.% (see Figures 8 and 9). The current density of these composites places them in the group of dielectrics. Moreover, after applying tensile loading to these specimens, vanishing of electrical conductivity is observed. In contrast to the above-discussed cases, the composite with a content of MWCNT of 8 wt% manifested significantly improved electrical conductivity at the level of semiconductors (see Figure 10). What is interesting, conductivity drops insignificantly when the specimen is subjected to tensile loading and the conductivity remains strong. This phenomenon can be interpreted as exceeding the electrical percolation threshold, resulting in the formation of a critical percolation cluster, enabling the conductivity of an electrical current. This fact is confirmed by the micrographs presented in Figure 4, where for the highest considered content of MWCNT, the agglomerates of the MWCNT nanofiller reveal a tendency of formation of such a critical percolation cluster. Also for previous cases, it can be concluded that there is aformation of percolation clusters, i.e. when the content of MWCNT was 4 wt.% and 6 wt.%, respectively, however, the applied tensile loading successfully interfered with the electrical conduction. In the case of 8 wt.% MWCNT composites, such loading slightly decreases the measured current density values, however, the conductivity of the composite was retained. This confirms the formation of a critical percolation threshold for a content of MWCNT between 6 wt.% and 8 wt% in the analyzed silicone/MWCNT nanocomposite.

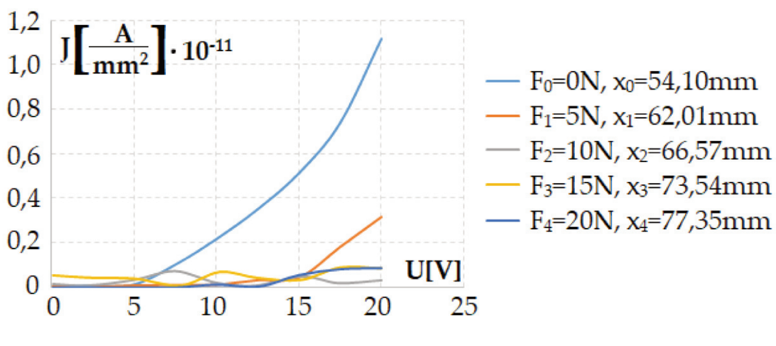


Figure 8. Current density as a function of voltage for silicone-filled with 4% nanotubes.

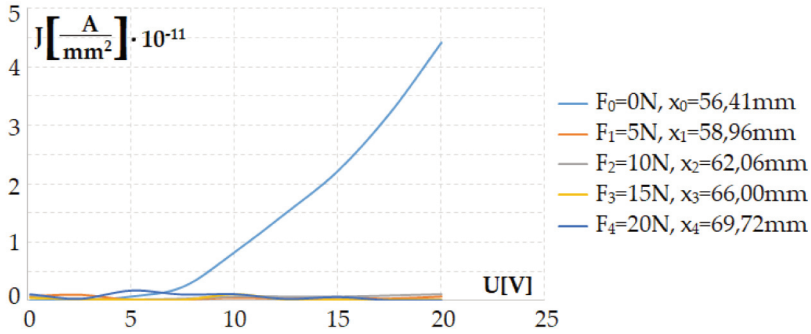


Figure 9. Current density as a function of voltage for silicone-filled with 6% nanotubes.

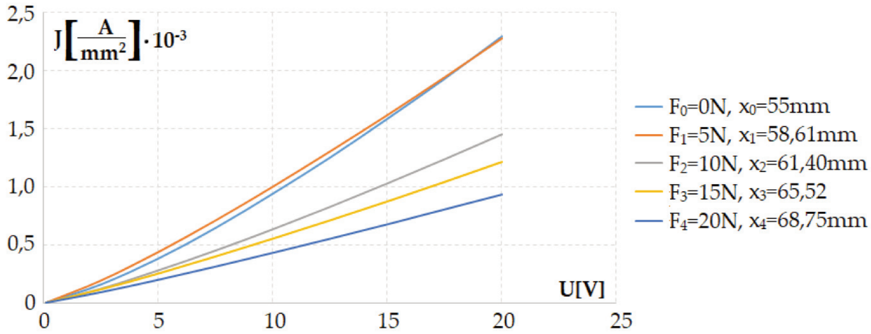


Figure 10. Current density as a function of voltage for silicone-filled with 8% nanotubes.

CONCLUSIONS

This paper presents the results of a structure study of a silicone matrix dispersion composite with a filler in the form of MWCNTs to determine the effect of the filler on mechanical properties and electrical conductivity. To this end, comparative studies were carried out on pure silicone and composites containing 4 wt.%, 6 wt.% and 8 wt.% MWCNTs. The studies consisted of determining characteristic properties for uncured materials and cured materials. The uncured materials were subjected to viscosity analysis. The cured materials, on the other hand, were subjected to SEM observation, strength tests and the characteristic electrical properties of the materials were determined. Mechanical property tests involved the determination of Shor A hardness, modulus of elasticity and measurement of Poisson's ratio and compressibility. The electrical properties were tested by measuring the current density as a function of voltage.

Based on the tests conducted, it can be concluded that the addition of MWCNTs to silicone causes changes in all the properties tested. However, only an 8 wt.% concentration significantly alters the properties.

At 8 wt.% MWCNTs in the unagglomerated state result in a significant increase in the conservative modulus. SEM observation showed that the high MWCNTs content facilitates the formation of conglomerates, and the composite is the most porous.

The stiffness and hardness of this material is also the highest. Special attention should be paid to the results of Poisson's ratio and compressibility studies. It was observed that as the nanotube content increases to a level of 6 wt.%, the Poisson's ratio increases and thus the compressibility decreases. At a nanotube content of 8 wt.%, the Poisson's ratio decreases slightly and with it the compressibility increases. It was assumed that the increase in compressibility is due to the high porosity of the composite with 8% wt. MWCNTs content.

By measuring the current density as a function of voltage, it was possible to indicate the percolation threshold for MWCNTs content is between 6 wt.% and 8 wt.% in the analysed nanocomposite. It should be assumed that only a content of 8 wt.% and more than that guarantees the electrical conductivity of the composite under load.

In the conclusion, further studies should consider the use of other methods of mixing silicone with MWCNTs to reduce the level of porosity and the number of agglomerates. This will increase the quality of the composite, but, according to the conclusions in Latko-Durałek et al. (2020) it is expected that this will also contribute to improved electrical properties.

REFERENCES

Bachmatiuk, A. (2008). *Badania nad technologią otrzymywania i właściwościami nanorurek węglowych* [Unpublished doctoral dissertation]. Politechnika Szczecińska, Wydział technologii i Inżynierii Chemicznej.

Bakar Sulong, A., Muhamad, N., Sahari, J., Ramli, R., Md Deros, B., & Park, J. (2009). Electrical Conductivity Behaviour of Chemical Functionalized MWCNTs Epoxy Nanocomposites. *European Journal of Scientific Research*, *29*(1), 13–21.

Barros, E. B., Jorio, A., Samsonidze, G. G., Capaz, R. B., Souza Filho, A. G., Mendes Filho, J., Dresselhaus, G., & Dresselhaus, M. S. (2006). Review on the symmetry-related properties of carbon nanotubes. *Physics Reports*, *431*(6), 261–302.

Baughman, R. H., Shacklette, J. M., Zakhidov, A. A., & Stafström, S. (1998). Negative Poisson's ratios as a common feature of cubic metals. *Nature*, *392*(6674), 362–365.

Bielanski, A. (1980). *Chemia Fizyczna*. Państwowe Wydawnictwo Naukowe PWN.

Borowiak-Palen, E., Pichler, T., Liu, X., Knupfer, M., Graff, A., Jost, O., Pompe, W., Kalenczuk, R. J., & Fink, J. (2002). Reduced diameter distribution of single-wall carbon nanotubes by selective oxidation. *Chemical Physics Letters*, *363*(5-6), 567–572.

Cardona-Uribe, N., Betancur, M., & Martínez, J. D. (2021). Towards the chemical upgrading of the recovered carbon black derived from pyrolysis of end-of-life tires. *Sustainable Materials and Technologies*, *28*, Article e00287.

Ciecierska, E., Boczkowska, A., Chabera, P., Wiśniewski, T., & Kubiś, M. (2015). Epoxy composites with carbon fillers. Structure and properties Kompozyty żywicy epoksydowej z napełniaczami węglowymi. Struktura i właściwości. *Przemysł Chemiczny*, *1*(11), 159–163.

Domun, N., Hadavinia, H., Zhang, T., Sainsbury, T., Liaghat, G. H., & Vahid, S. (2015). Improving the fracture toughness and the strength of epoxy using nanomaterials – a review of the current status. *Nanoscale*, *7*(23), 10294–10329.

Dydek, K., Boczkowska, A., Kozera, R., Durałek, P., Sarniak, Ł., Wilk, M., & Łogin, W. (2021). Effect of SWCNT-Tuball Paper on the Lightning Strike Protection of CFRPs and Their Selected Mechanical Properties. *Materials*, *14*(11), 3140.

Frigione, M., Naddeo, C., & Acierno, D. (2001). Cold-Curing Epoxy Resins: Aging and Environmental Effects. I - Thermal Properties. *Journal of Polymer Engineering*, *21*(1).

Ganesh, M., Lavenya, K., Kirubashini, K., Ajeesh, G., Bhowmik, S., Epaarachchi, J., & Yuan, X. (2017). Electrically conductive nano adhesive bonding: Futuristic approach for satellites and electromagnetic interference shielding. *Advances in Aircraft and Spacecraft Science*, *4*(6), 729–744.

Gardea, F., & Lagoudas, D. C. (2014). Characterization of electrical and thermal properties of carbon nanotube/epoxy composites. *Composites Part B: Engineering*, *56*, 611–620.

Geipel, T., Meinert, M., Kraft, A., & Eitner, U. (2018). Optimization of Electrically Conductive Adhesive Bonds in Photovoltaic Modules. *IEEE Journal of Photovoltaics*, *8*(4), 1074–1081.

Gogurla, N., Roy, B., Park, J.-Y., & Kim, S. (2019). Skin-contact actuated single-electrode protein triboelectric nanogenerator and strain sensor for biomechanical energy harvesting and motion sensing. *Nano Energy*, *62*, 674–681.

Gojny, F. H., Wichmann, M. H. G., Köpke, U., Fiedler, B., & Schulte, K. (2004). Carbon nanotube-reinforced epoxy-composites: Enhanced stiffness and fracture toughness at low nanotube content. *Composites Science and Technology*, *64*(15), 2363–2371.

Hagita, K., & Morita, H. (2019). Effects of polymer/filler interactions on glass transition temperatures of filler-filled polymer nanocomposites. *Polymer*, *178*, 121615.

Hall, L. J., Coluci, V. R., Galvao, D. S., Kozlov, M. E., Zhang, M., Dantas, S. O., & Baughman, R. H. (2008). Sign Change of Poisson's Ratio for Carbon Nanotube Sheets. *Science*, *320*(5875), 504–507.

Huczko, A. (2004). *Nanorurki Weglowe. Czarne diamenty XXI wieku*. BEL STUDIO.

Iijima, S. (2002). Carbon nanotubes: past, present, and future. *Physica B: Condensed Matter*, *323*(1-4), 1–5.

Krainoi, A., Johns, J., Kalkornsurapranee, E., & Nakaramontri, Y. (2021). Carbon Nanotubes Reinforced Natural Rubber Composites. In P. Ghosh, K. Datta, & A. Rushi (Eds.), *Carbon Nanotubes - Redefining the World of Electronics*. IntechOpen.

Królikowski, W., & Rosłaniec, Z. (2004). Nanokompozyty polimerowe. *Kompozyty*, *4*(9), 3–15.

Kumar, V., Alam, M. N., Manikkavel, A., Song, M., Lee, D.-J., & Park, S.-S. (2021). Silicone Rubber Composites Reinforced by Carbon Nanofillers and Their Hybrids for Various Applications: A Review. *Polymers*, *13*(14), 2322.

Kumar, V., Kumar, A., Han, S. S., & Park, S.-S. (2020). RTV silicone rubber composites reinforced with carbon nanotubes, titanium-di-oxide and their hybrid: Mechanical and piezoelectric actuation performance. *Nano Materials Science*.

Kumar, V., Kumar, A., Song, M., Lee, D.-J., Han, S.-S., & Park, S.-S. (2021). Properties of Silicone Rubber-Based Composites Reinforced with Few-Layer Graphene and Iron Oxide or Titanium Dioxide. *Polymers*, *13*(10), 1550.

Kumar, V., & Lee, D.-J. (2016). Studies of nanocomposites based on carbon nanomaterials and RTV silicone rubber. *Journal of Applied Polymer Science*, *134*(4).

Kumar, V., Lee, G., Monika, Choi, J., & Lee, D.-J. (2020). Studies on composites based on HTV and RTV silicone rubber and carbon nanotubes for sensors and actuators. *Polymer*, *190*, 122221.

Lakes, R. (1987). Foam Structures with a Negative Poisson's Ratio. *Science*, *235*(4792), 1038–1040.

Latko-Durałek, P., Kozera, R., Macutkevič, J., Dydek, K., & Boczkowska, A. (2020). Relationship between Viscosity, Microstructure and Electrical Conductivity in Copolyamide Hot Melt Adhesives Containing Carbon Nanotubes. *Materials*, *13*(20), 4469.

Lee, J.-Y., Kumar, V., Tang, X.-W., & Lee, D.-J. (2017). Mechanical and electrical behavior of rubber nanocomposites under static and cyclic strain. *Composites Science and Technology*, *142*, 1–9.

Li, C., Chen, X., & Zhimin, D. (2004). *A New Relationship of Rock Compressibility with Porosity*. Paper presented at the SPE Asia Pacific Oil and Gas Conference and Exhibition, Perth, Australia, October 2004.

Limpert, E., & Stahel, W. A. (2011). Problems with Using the Normal Distribution – and Ways to Improve Quality and Efficiency of Data Analysis. *PLoS ONE*, *6*(7), Article e21403.

Liu, Q., Lomov, S. V., & Gorbatikh, L. (2020). Enhancing Strength and Toughness of Hierarchical Composites through Optimization of Position and Orientation of Nanotubes: A Computational Study. *Journal of Composites Science*, *4*(2), 34.

Liu, Q., Shi, W., Chen, Z., Li, K., Liu, H., & Li, S. (2019). Rubber accelerated ageing life prediction by Peck model considering initial hardness influence. *Polymer Testing*, *80*, 106132.

Lopes, P., Moura, D., Freitas, D., Proença, M., Figueiredo, R., Alves, H., & Paiva, M. (2019). Advanced electrically conductive adhesives for high complexity PCB assembly. *AIP Conf. Proc. 22 January 2019*, *2055*(1), 090009.

Ma, P.-C., Mo, S.-Y., Tang, B.-Z., & Kim, J.-K. (2010). Dispersion, interfacial interaction and re-agglomeration of functionalized carbon nanotubes in epoxy composites. *Carbon*, *48*(6), 1824–1834.

Mucha, M., Krzyzak, A., Kosicka, E., Coy, E., Kościński, M., Sterzyński, T., & Sałaciński, M. (2020). Effect of MWCNTs on Wear Behavior of Epoxy Resin for Aircraft Applications. *Materials*, *13*(12), 2696.

(n.d.). GRUPA WOLFF.

Nicolau-Kuklińska, A., Latko-Durałek, P., Nakonieczna, P., Dydek, K., Boczkowska, A., & Grygorczuk, J. (2017). A new electroactive polymer based on carbon nanotubes and carbon grease as compliant electrodes for electroactive actuators. *Journal of Intelligent Material Systems and Structures*, *29*(7), 1520–1530.

Nobile, M. R. (2011). Rheology of polymer–carbon nanotube composites melts. In T. McNally & P. Pötschke (Eds.), *Polymer–Carbon Nanotube Composites* (pp. 428–481). Woodhead Publishing.

Plagge, J., & Lang, A. (2021). Filler-polymer interaction investigated using graphitized carbon blacks: Another attempt to explain reinforcement. *Polymer*, *218*, 123513.

Przygocki, W., & Włochowicz, A. (2001). *Fulereny i nanorurki – Właściwosci i zastosowanie*. Wydawnictwo Naukowo – Techniczne.

Rodríguez-Prieto, A., Primera, E., Frigione, M., & Camacho, A. M. (2021). Reliability Prediction of Acrylonitrile O-Ring for Nuclear Power Applications Based on Shore Hardness Measurements. *Polymers*, *13*(6), 943.

Rosca, I. D., & Hoa, S. V. (2009). Highly conductive multiwall carbon nanotube and epoxy composites produced by three-roll milling. *Carbon*, *47*(8), 1958–1968.

Sajith, S. (2019). Investigation on effect of chemical composition of bio-fillers on filler/matrix interaction and properties of particle reinforced composites using FTIR. *Composites Part B: Engineering*, *166*, 21–30.

Sivaselvi, K., Varma, V. S., Harikumar, A., Jayaprakash, A., Sankar, S., Krishna, C. Y., & Gopal, K. (2021). Improving the mechanical properties of natural rubber composite with carbon black (N220) as filler. *Materials Today: Proceedings*, *42*, 921–925.

Smoleń, P., Czujko, T., Komorek, Z., Grochala, D., Rutkowska, A., & Osiewicz-Powęzka, M. (2021). Mechanical and Electrical Properties of Epoxy Composites Modified by Functionalized Multiwalled Carbon Nanotubes. *Materials*, *14*(12), 3325.

Terranova, M. L., Sessa, V., & Rossi, M. (2006). The World of Carbon Nanotubes: An Overview of CVD Growth Methodologies. *Chemical Vapor Deposition*, *12*(6), 315–325.

Yadav, S. G., Guntur, N. P. R., N., R., & Gopalan, S. (2021). Effect of titanium carbide powder as a filler on the mechanical properties of silicone rubber. *Materials Today: Proceedings*, *46*, 665–671.

Yang, H., Yao, X., Zheng, Z., Gong, L., Yuan, L., Yuan, Y., & Liu, Y. (2018). Highly sensitive and stretchable graphene-silicone rubber composites for strain sensing. *Composites Science and Technology*, *167*, 371–378.

Yeganeh-Haeri, A., Weidner, D. J., & Parise, J. B. (1992). Elasticity of agr-Cristobalite: A Silicon Dioxide with a Negative Poisson's Ratio. *Science*, *257*(5070), 650–652.

Zhang, X., Cai, L., He, A., Ma, H., Li, Y., Hu, Y., Zhang, X., & Liu, L. (2021). Facile strategies for green tire tread with enhanced filler-matrix interfacial interactions and dynamic mechanical properties. *Composites Science and Technology*, *203*, 108601.